PERMEABILITY DEGRADATION AND WEAR

OF DENTAL COMPOSITES

BY

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ABSTRACT

Permeability, Degradation and Wear of Dental Composites

By L. H. Mair

When early dental composites were used in posterior restorations their wear rate was unacceptable. Many devices were developed to study wear in the laboratory; but the results failed to correlate with clinical experience. One explanation for this was that degradation in the oral environment predisposed to wear. Degradation is partially determined by the permeability of composites to oral fluids. The aim of this thesis was to investigate the wear of three posterior composites together with a study of sub-surface permeability and degradation.

Wu & Cobb claimed to have used silver nitrate to stain a layer of subsurface degradation in restorations which had been removed for replacement [J Biomed Mat Res (1981), 15: 343-348]. Many features reported in the latter publication were found to be artefacts which were eliminated by modifying the staining technique and optical system of the microscope. With this revised method subsurface porosity was less extensive than previously reported. SEM of the stained areas revealed little or no evidence of degradation indicating that the technique of silver staining was more sensitive to increased permeability and degradation.

During these studies a "Silver Sorption Layer [SSL]" was discovered in composites that had been immersed in silver nitrate. The increase in depth of the layer was diffusion controlled. Its colour has been attributed to the scattering of light by small silver particles as predicted by Mie theory. A comparison of silver nitrate and water sorption indicated that the SSL may mark the extent of fluid penetration into the material. This would signify that fluids accumulate closer to surface than previously postulated. The sorption experiments did not support the mathematical criteria for Case II sorption.

In the laboratory both thermal and mechanical cycling caused considerable degradation whilst ethanol increased the depth of penetration of the silver nitrate stain. However, the appearance of the clinical specimens indicated that these processes have limited effects in the mouth.

In a clinical trial of three posterior composites, the two processes of abrasion and attrition occurred at different rates in the materials. The data indicated that local factors had a significant influence on abrasion. The subsurface analysis of failed restorations from the clinical trial indicated that permeability and degradation was highly material specific. There was considerable degradation of the proximal surface of a three year old P-30 restoration; but very little evidence in Occlusin or Clearfil. In all the materials occlusal wear occurred faster than the establishment of degradation layers. Therefore it is concluded that the wear resistance of the material was more important than degradation in determining surface loss.

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OVERVIEW

INTRODUCTION

Dental composites were first used in the late 1960's and proved a good restorative material for anterior teeth. There was a natural tendency to use them for posterior restorations but early investigations indicated that wear resistance was inadequate in these situations. In the early 1980's modified systems were developed to improve wear resistance and these materials were advocated for use as "posterior composites". Clinical investigations of both anterior and posterior composites indicated different wear rates between materials and this put pressure on dental material scientists to develop testing systems that would predict clinical rates of wear. Although many test machines and procedures were devised there was a lack of correlation between clinical results and in vitro tests.

Early in the 1980's researchers were beginning to investigate the surface degradation of composites which had occurred in the mouth. One team (Wu & Cobb 1981, Wu et al 1984) claimed to have demonstrated a layer of sub-surface porosity in composites that had been removed from the mouth, but which was absent in recently prepared composites. This finding, together with the work of Soderholm et al (1981, 1983, 1984) on hydrolytic degeneration, Asmussen (1984) on acidic degeneration and Mc Kinney & Wu (1982,1985) on solvent degeneration, suggested that a valid line of research would be to investigate surface permeability and degradation together with their relationship with wear.

EXPERIMENTS

The starting point of this investigation was to establish a clinical programme which would indicate the clinical performance of some of the materials to be studied in the laboratory. An evaluation of three posterior composites had been commissioned by the Department of Health. This allowed not only personal placement and investigation of ninety composite restorations; but also made available data from another two hundred and seventy restorations placed by two general practitioners using the same protocol. Although the trial was to evaluate all aspects of clinical performance only factors related to wear are reported in this thesis.

A number of failed anterior restorations were collected from patients undergoing treatment at the dental hospital. At the beginning of the laboratory stage these "biopsies" were used to investigate the silver staining technique of Wu et al (1981). Many of the reported findings were seen to be artefacts; but the technique was developed to enable the correct interpretation of results.

During early attempts to stain microcracks with silver nitrate an entirely new observation of a "Silver Sorption Layer" was noticed. This layer was the first direct observation of the location of a penetrant in dental composites and warranted further investigation. Of special importance was the relationship between the depth of stain and water sorption as the latter is associated with many time related changes in dental composites. Another property of the layer was that its colour varied between materials and coloured layers could be observed after laboratory degradation of the specimens. A tentative hypothesis for the colours was postulated: namely that the colour depends on the size of silver particles precipitated within microcavities in the composite. Investigations with transmission electron microscopy supported this hypothesis.

The results of the permeability experiments and related scanning electron microscopy indicated that physical and chemical preconditioning caused considerable surface degradation. A three body wear test was used to determine the relationship between degradation and wear.

Towards the end of the experimental stage the knowledge of silver nitrate staining and electron microscopy gained during the previous three years was used to investigate sub-surface degradation in restorations which had failed during the clinical evaluation.

CHAPTER 1

THE DEVELOPMENT OF DENTAL COMPOSITES

Degradation and wear are functions of both the structure of the material and the environment to which it is exposed. Clinical problems associated with surface degeneration have been a major consideration in the development of new composite systems. This chapter describes the concepts underlying the development of modern composites and the next chapter discusses the processes of permeability, degradation and wear.

COMPOSITE MATERIALS

Dental composites are two phase materials consisting of fillers embedded in a polymer matrix. Polymerisation is induced in the resin phase by a process in which the double carbon bond of a suitable monomer is broken by free radicals. Free radicals may be generated in a number of ways including both chemically and light activated processes (Cook & Standish 1983).

Although composites replaced silicate cements as the most widely used anterior filling material some twenty years ago, they were developed from unfilled resins used in the 1940's and 50's. The major disadvantages of the latter materials were their low abrasion resistance, lack of viscosity, high polymerisation shrinkage, high coefficient of thermal expansion and relatively low elastic modulus which allowed flow under stress (Coy 1953). The earliest "composite" had 60% (by wt) silicate glass powder distributed throughout an acrylic matrix (McLean and Short 1969). Magnification of exposed surfaces revealed missing fillers and an early development was to pre-coat the fillers with a polymer layer via an intermediary silane coupling (Carter & Smith 1967). This improved the wear resistance of the acrylic but other limitations remained unchanged.

With these problems in mind Bowen, in the early 1950's, recognised the potential in epoxy resins that were being developed for other non-dental applications. These had longer monomer units, set at low temperatures and were adhesive to many materials thereby enabling bonding to filler particles. The first composite with the potential for dental use was therefore an epoxy resin matrix with fused quartz fillers (Bowen 1956). Both these developments decreased polymerisation shrinkage and the filler particles gave increased wear resistance. However the setting time was too long for direct placement and the materials had to be used as an indirect technique. Replacing the epoxy groups with methacrylate groups, Bowen developed a monomer that would set in the mouth and yet maintain a relatively low polymerisation shrinkage. This was 2,2-bis[2(2-hydroxy -3- methacryloxypropoxy) phenyl]propane commonly known as BIS-GMA. (Bowen 1962). It really marked the advent of dental composites and is still a major component of modern materials. In all the early composites the free radicals were formed chemically by a redox reaction between an initiator and activator (Ruyter 1985).

The addition of fillers has two important effects. By acting as an inert material, that does not take part in the polymerisation reaction, they reduce polymerisation shrinkage. Secondly, they improve many mechanical properties compared with the unfilled resin, especially the hardness and wear resistance (Vanherle et al 1985). There was however a reduction in fracture toughness because the interface of the two phases was a site for crack initiation and promotion (Craig 1981). Nonetheless the fracture toughness of early composites was considerably improved over silicates (Lloyd & Mitchell 1984).

The next major development was the use of radiation to form free radicals. Initially ultra-violet (UV) radiation was used to cleave "photoinitiators" leaving two free radicals. The great clinical advantage of this system was that the working time was not limited by the reaction time of the chemical systems hence the term "command set" composites. Another advantage of this system was that it eliminated the necessity of chairside mixing thereby reducing the number of air bubbles in the set material (Bassiouny and Grant 1980).

Associated with the introduction of UV systems was the development of the "acid etching" whereby the resin was able to physically adhere to enamel via tags of resin penetrating the etched surface. This system was developed from a concept that had first been advocated for use with acrylic resins (Buonocore 1955). With UV light it was initially used for fissure sealing (Buonocore 1970); but its potential for bonding small amounts of composite directly onto enamel was soon realised (Jorden et al 1977, Gwinnett et al 1981). This adjunct to the composite concept also had the advantage of minimising the marginal gap around restorations. In retrospect the development of composites together with enamel bonding has revolutionised the treatment of small enamel defects in both dentitions which had previously involved destructive tooth preparations. As an alternative to acid etching Smith and Cartz (1973) developed a system for growing gypsum enamel crystals on the tooth surface. However, the bond strengths with this technique are less than with acid-etching (Artun & Bergland 1984, Read et al 1986).

All of the early composites had comparatively large filler particles (Lutz et al 1983). Finishing techniques (Hannah & Smith 1973) and surface degradation (Bowen 1979) caused preferential depletion of the resin phase resulting in exposure and eventual loss of the fillers. This resulted in a rough surface that caused absorption and scattering of light. In clinical trials the colour performance was inferior to unfilled resins (Leinfelder et al 1980): the surface appeared dull and was prone to staining by foodstuffs or nicotine (Gross & Moser 1977, Hayashi et al 1974, Raptis et al 1982). The protruding particles intensified occlusal stress resulting in microcracking and consequently accelerated wear. Although the latter problem was partially resolved by bonding the particles to the resin with silane coupling agents (Craig 1981), the problem of surface projecting particles remained.

A potential solution to this problem was the development of microfilled composites in the mid 1970's. The fillers were pyrolytic silica of diameter 0.007-0.06 microns (mean= 0.04) (Craig 1981). The great advantage of this system was that even if wear occurred the resulting surface irregularities would be less than the wavelength of visible light and remain reflective (Phillips 1981, Lui & Low 1982). Microfillers greatly reduced surface roughness, minimised surface stress intensification and reduced the coefficient of friction (Wilson et al 1981). However the major problem with microfillers was their large surface area. The largest particle that would satisfy the requirement of being less than the wavelength of light was 0.02 microns (these would be 0.04 after silane coating). The highest filler loading for particles of this size was 40% before the mixture became too viscous for use or there was insufficient wetting of the fillers (Lutz et al 1983). Reducing the filler content to this extent conflicted with the original purpose of fillers. The polymerisation shrinkage and thermal expansion of these early homogeneous microfilled composites was greater than the conventional systems (Bowen et al 1982).

The filler loading problem was partially solved by including high filler loadings in factory polymerised composites which were then ground to form "pre-polymerised particles" in the clinical systems. These systems were termed "Inhomogeneous microfilled composites" and this concept has been the basis of microfilled technology to the present day. There is conflicting evidence about these materials. An initial trial of the material in denture teeth indicated improved wear resistance with respect to conventional composites (Jorgensen & Asmussen 1978). After eighteen months clinical trial Ameye et al (1981) concluded that the colour stability of these materials was superior to conventional composites. The results of another study indicated that although the surface smoothness and wear of a microfilled composite (Isocap) was better than a conventional composite (Adaptic), there was no difference in the rating for colour (Christensen & Christensen 1982). The explanation for this finding is likely to be that reflectivity is only one factor determining colour; of greater importance is hue and chroma which can deteriorate as a result of oxidation of the chemical components of the composite (Bowen & Argentar 1967).

Although the extent of polymerisation shrinkage has been improved, Lambrechts et al (1982) noticed substantially more chip fractures in these materials. One reason for this is that during curing in the mouth there are insufficient double carbon bonds available in the prepolymerised particles to enable optimal bonding to the resin. In the process of wear the pre-polymerised particles could be displaced "on block" from the surface and were therefore behaving like conventional fillers (Craig 1981, Lambrechts et al 1985). Recent clinical trials have indicated that the microfilled composites maintain a better surface texture than conventionally filled composites; but that their wear resistance and colour match was inferior (Crumpler et al 1988).

The next logical development was the "hybrid" composite having conventional fillers with the matrix phase reinforced by colloidal silica. The wear and associated surface roughness was improved, but in areas of occlusal contact there was still loss of anatomical form (Lutz et al 1984, Lambrechts et al 1984). Nonetheless the concept was correct and even so-called "conventional" composites have some colloidal silica dispersed in the matrix phase (Vankerckhoven et al 1981).

Although the use of UV lights was common in dental schools and the community health service, they did not become popular in general dental practice, certainly in the United Kingdom. As well as the safety problems associated with UV radiation, penetration in enamel was limited. It was recognised that visible light would be safer and probably more efficient. Photoinitiators were prepared which would yield free radicals in the visible spectrum; the main example being camphoroquinone. Early in-vitro studies indicated that the light activated composite "Fotofil" had good abrasion and attrition resistance (Swartz et al 1982). Onose et al (1985) demonstrated that the depth of cure for three light activated systems was considerably better with light rather than UV initiated systems. However for a limited depth UV is a more efficient initiator possibly because there are less stages involved in the formation of free radicles (Ruyter 1985). The conversion of light cured composites is dependant not only on the power of the light; but also on the wavelength of the light (Watts et al 1984, Blankenau et al 1983). Although the intra-oral cure causes sufficient immediate conversion for clinical use, the process continues for up to one month (Hansen 1983, Watts et al 1986, 1987a). A recent clinical development is the composite inlay which after an initial intra-oral cure is placed in a heat and light "oven" to promote further conversion (Levy 1988). The ability of the latter system to improve the dynamic properties of the material has been demonstrated by Watts (1989 a&b).

The obvious goal in the process of development was a composite that could be used in the posterior quadrants. All the formulations so far described were tried but, as will be discussed in the literature review on wear, failed to provide adequate wear resistance. Researchers and manufacturers differ as to which group of materials really represented the advent of "posterior composites". Certainly Profile (Chemical-Cure) was advocated for use in posterior restorations but the term is best reserved for those material designed solely for posterior restorations. Representative materials are P10 & P30 (3M Company), Occlusin (ICI), Ful-Fill (Caulk), Clearfil Posterior (Kuraray) and Estilux Posterior (Kulzer). The two concepts of "hybrid" filler loading and "command set" curing were two important preludes to the present posterior composite systems. The major developments were ultrastructural involving properties of the fillers and chemistry of the polymerisation.

FILLERS

In the laboratory Draughn & Harrison (1978) found that composites with the largest and hardest fillers had the greatest wear resistance; but electron microscopy indicated that in vivo these fillers caused crack nucleation in the polymer matrix as a result of stress transmitted by the filler particles (O'Brien & Yee 1980). Softer particles either fracture or wear rather than transmit the load, therefore the first material specifically advocated for posterior use [Profile (Chemical-Cure)] had friable fillers of strontium glass. Early results indicated increased wear resistance (Moffa and Jenkins 1978); but these results have been contradicted by recent studies using more discriminating methods of measurement (Leinfelder et al 1982, Derkson et al 1984). Most of the recent posterior composites have involved a shift away from quartz fillers to the use of various glasses (Mc.Lundie et al 1985). The percentage loading of fillers was also extremely important. Jorgensen & Asmussen (1978) had recognised the importance of inter-particle spacing, indicating that a spacing of <0.1 microns was necessary to protect the matrix. Manufacturers incorporated ranges of varying size filler particles to achieve the highest possible loadings. However this situation is often confused because filler percentage by weight is given in the manufacturers literature whereas inter-particle spacing depends upon filler volume.

POLYMERS AND POLYMERISATION

Regardless of the system of initiation, the polymerisation of dental composites is by no means complete and a substantial population of residual double carbon bonds remain (Vankerckhoven at al 1982, Asmussen 1982). The majority of these double bonds are thought to be methacrylate groups in pendant side chains rather than being as residual monomer (Ruyter 1985, Cook 1985, Fan 1985). Evidence for the latter was found by Fan et al (1985) who found that very little monomer was leached out during the first 30 days in water after polymerisation. The percentage of double bonds utilised is characterised by the "degree of conversion" although the term "degree of polymerisation" is often used erroneously in the literature (Ruyter 1985). Although there is some clinical advantage to residual double bonds in that additional material can be added to the surface, low conversion makes the materials susceptible to chemical degradation (Asmussen & Hansen 1986, Ruyter 1985). The degree of conversion also correlates with the hardness of the material (Asmussen 1982), although Ferracane (1985) has indicated that hardness should not be used as an indirect measure of conversion. Although there is no direct relationship between hardness and wear (Harrison and Draughn 1976), it is generally accepted that high degrees of conversion are desirable (Cook 1985).

Conversion is affected by all the components of the composite and in the case of "command set" systems by the characteristic of the curing light. Four light cured composites (Silux, Durafil, Estilux, Prisma-fil) were found to have higher degrees of conversion when cured with a light that produced a small amount of UV radiation rather than with a light output entirely limited to the visible spectrum (Ruyter 1985). However the power of the light source was not stated and Watts et al (1984) found that the light with highest luminous intensity (at 470 nm) gave the best cure as measured by hardness.

The constituent monomers are extremely important in the determination of conversion influencing the movement available to the growing chains and also the diffusion of radicals and monomers. BIS-GMA is a very viscous monomer and methyl methacrylate was added to the early systems to achieve a clinically workable mix (Cook 1985, Vankerckhoven et al 1981). Modern systems utilise the aliphatic ethylene glycol dimethacrylates (EGDMA, DEGDMA, TEGDMA, Te-EDGMA) as viscosity controllers (Craig 1981). The flexibility of the copolymers formed between these and BIS-GMA allow greater movement of the forming chains and subsequently greater conversion. Ruyter (1985) states that the higher the n-EDGMA to BIS-GMA ratio the greater the degree of conversion. He also found that two materials with similar ratios (P-10 & P-30), but cured by different systems (chemical & light respectively), had the same degree of conversion. Of course if there is too much flexibility in the chains the resultant polymer will be too soft. Recently modified urethane dimethacrylate monomers have been synthesised with similar strength to BIS-GMA but slightly more flexible.

In the case of chemical initiation both the initiators and inhibitors influence conversion. With unfilled resins it has been that shown that more efficient initiating complexes cause greater conversion. The importance of the inhibitor was shown by Cook and Standish (1983): a highly reactive inhibitor like Tetramethyl piperidinyl-1-oxide rapidly scavenges the forming radicals and is quickly exhausted allowing a rapid gelation of the polymer (snap-set); whereas a less reactive inhibitor continues to scavenge free radicals during the gelation period. Although a snap-set is an advantage clinically as it prevents manipulation of the filling during polymerisation, too fast a set may limit the migration of radicals resulting in short polymer chains.

Of greater importance is the "oxygen inhibition effect" which forms at the surface of the polymerised composite because the radicals have a greater affinity to oxygen than to double carbon bonds. This results in a sparcity of radicals and poor polymerisation of the surface (Ruyter 1981). The layer may be from 5-100 microns in depth and may manifest clinically as stickiness of the surface. Oxygen inhibition layers are thinner in "radiation" cured systems because of the greater rate at which the free radical are formed (Cook 1985). Provided the resulting surface is not too sticky the degree of conversion may be improved by polishing (Vankerckhoven et al 1982), possibly because of the increase in surface temperature (Cook 1985).

In summary it can be seen that the present generation posterior composites have been developed by modifying and improving the shortcomings of earlier systems. Although the wear resistance, degree of conversion and coefficient of expansion has been improved, the colour of the posterior composites would (in many instances) not be appropriate at the front of the mouth. Also the materials are more expensive than "anterior" composites. Consequently the two "species" presently exist side by side. In the laboratory experiments reported in this thesis both groups have been used including a representative of the microfilled category from each. It was hoped that the laboratory data could be compared with the clinical performance that had been reported in the literature.

CHAPTER 2

PERMEABILITY, DEGRADATION AND WEAR -TERMS AND PRINCIPLES

INTRODUCTION

Permeability is a term used to indicate that fluid or gas can move into a material from it's immediate environment. It is determined by the molecular activity of both the penetrant and the material. In a homogeneous material permeability is the product of two factors: solubility which determines the number of penetrant molecules entering the material and diffusion which relates to the mobility of the molecules (Perera and Selier 1973). Degradation implies that there has been some breakdown of the material and the term is usually reserved for breakdown that is irreversible. It may result from local swelling stresses caused by the diffusing penetrant, superimposed upon which may be chemical degradation of the material. These processes are summarised in Fig. 2-1 and will be discussed in this chapter. It is important to note that diffusion may occur in the absence of degradation. It is the molecular interaction that takes place whenever two or more materials are in contact and will even occur between two solids.

PERMEABILITY

Mathematically the Permeability Coefficient (P) is the product of the Solubility Coefficient (S) and the Diffusion

Coefficient (D) (Crank 1968). The Solubility Coefficient describes the relationship (S=C/p) between the penetrant concentration (C) in the immediate subsurface of the material and the vapour pressure of the penetrant surrounding the material (p). It is therefore important in determining the penetration of gases into materials. However, with liquids there is fluid rather than vapour pressure and, as this remains relatively constant, solubility and concentration are considered as equivalent. Consequently permeability (P=SD) is determined by the concentration of the penetrant and the diffusion coefficient of the system. In some materials such as polyvinyl alcohol there is a strong dependence on the concentration of the penetrant, whereas other materials (polyvinyl acetate) are apparently independent of surface concentration (Brewis et al 1980, Spencer & Honeycutt 1973, Barrie 1968, Gillespie & Williams 1966)

Whilst these terms are useful for a theoretical consideration of permeability in homogeneous polymers, they need to be considered alongside the microstructure of the material and the interaction between penetrants and materials. In particular the presence of voids, microcavities and other spatial defects have a great influence on permeability (Rodgers 1985). Larger defects "fill up" far more rapidly than the penetrant diffuses around them. Gross surface defects such as cracks allow penetration deep into the material and further diffusion is then established at the crack margins (Fig 2-1). However, the accumulation of penetrant in small microvoids can have a more subtle effect depending upon the interaction between the penetrant and the inner surface of the void.

The penetrant may polarise and form associations with the material via hydrogen bonds. As this necessarily reduces the number of hydrogen bonds available for inter-chain bonding of the polymer, there is a potential for segmental motion of the polymer chains in the material which facilitates diffusion (Perera and Selier 1973). Conversely if the cohesive bonds of the penetrant are greater than the penetrant-polymer interaction then the penetrant forms clusters in the microvoids (Rodgers 1985, Perera and Heertjes 1971, Barrie 1968). These are relatively immobile compared with the diffusion of the penetrant in the surrounding material and the net result is decreased diffusion. Water has been shown to have both types of behaviour in polymers. In hydrophilic polymers there is increased diffusion as a result of attraction and segmental mobility (Spencer & Honeycutt 1973, Barrie 1968), whereas in hydrophobic polymers there is clustering and decreased diffusion (Moy & Karasz 1980, Spencer & Honeycutt 1973, Barrie & Machin 1971). The three conditions, bound, clustered and free may be present simultaneously (Barrie, 1968). Diffusion in some modern polymers may be apparently independent of the void distribution (Grayson & Wolf 1987).

The latter interactions are important when considering the permeability of composites because microvoids are commonly present at the filler-matrix interface (Marom 1985). In dental composites occlusion causes microcracking (Abell et al 1983) and this will therefore influence the penetration of oral fluids into the material. Another factor which influences the penetration of fluids is the relaxation of stress, either present as a result of the fabrication process or generated during the penetration process. The relaxation and swelling at the advancing diffusion front determines the kinetics of the advancing diffusion front which are discussed later when considering Case II sorption.

From the preceeding discussion it is apparent that permeability is a complex phenomena. The term sorption is frequently used to express permeability in dental composites. Water sorption is one of the tests required on new materials (Council on Dental Materials and Devices 1977, ADA Spec.27) and is a figure often quoted in manufacturers literature. Sorption is a generalised term used to express the overall penetration and dispersal of penetrant molecules in a material (Rodgers 1985). In dental composites this includes water accumulation in voids and interfacial defects together with molecular clusters in the free volume.

DIFFUSION

Diffusion is caused by the kinetic energy of molecules.

It results from successive jumps of penetrant molecules through the material. For a jump to take place it is necessary for there to be free volume available for movement. It is not necessary for a "hole" to be formed in the polymer between two successive penetrant positions, however there must be a rearrangement of van der Waals and other bonds to allow rearrangement of local structure (Rogers 1985). There are many theories to explain the formation and behaviour of free volume (Kumins and Kwei 1968).

Fig. 2-2 shows the model for free volume in diffusion postulated by DiBenedetto (1963). The polymer is considered as an array of segments enclosing cells of free volume. Normal molecular vibration causes movement of the segments and this changes the volume of the cells. When adjacent segments move outwards in relation to one another, a cylindrical void is formed and the kinetic energy of gas or fluid molecules trapped in the cells causes them to move through the void. Further movement of segments again entraps the diffusing molecules. For the "activated" state to occur there must be rupture of the van der Waals bond between adjacent segments. Although this is only one of many theories it is a useful pictorial aid to help understand a complex phenomenon. As the model is based on an amorphous polymer it may be applied to BIS-GMA and other "dental" polymers which have this morphology (Sawyer and Grubb 1987a).

The importance of segmental mobility in the process of diffusion was demonstrated by Davydov et al (1981) by comparing the change in the infra spectrum caused by deuteroexchange in polyurethane films. Deuterium diffusing into the material reacted with active hydrogen trapped during polymerisation shifting the IR spectrum for active hydrogen. Diffusion was much faster and greater in the polyurethane with the most flexible chains.

Mathematically diffusion can be considered in two ways. The classical "Fickian" approach was derived by Fick who considered the flux of the penetrant into the material (Cussler 1984, Crank 1975a). A second approach is that of "Random Walk" which considers overall molecular movement by statistical analysis of random molecular collisions (Marshall 1978). Whilst the latter approach is excellent for a theoretical discussion of pure diffusion in flawless homogeneous polymers, it is not useful to consider sorption which is dependent on so many structural properties. Much of the work on "anomalies" from classical diffusion has been performed by considering how experimental data deviates from the classical "Fickian" model. This is the approach which has been adopted in this thesis. It is important to restate that the objective of this work was to investigate the relationship between permeability, degradation and wear. The determination of absolute diffusion equations and coefficients for dental composites was not the concern of this work and "Fickian" mathematics are presented only as a tool to understand underlying principles.

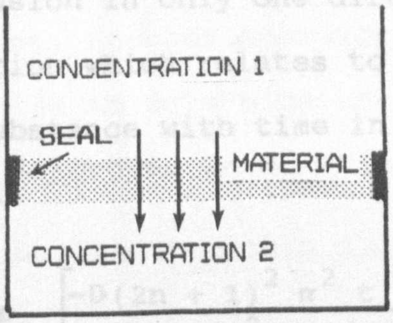
Fick's Laws of Diffusion

The first law states that the rate of transfer (flux) of the diffusing substance through unit area is proportional to the concentration gradient measured normal to the section.

$$F = - D \frac{\partial C}{\partial x} \qquad (1)$$

Where F = Flux C = concentration of diffusant and
x = penetration distance in the direction of the flux

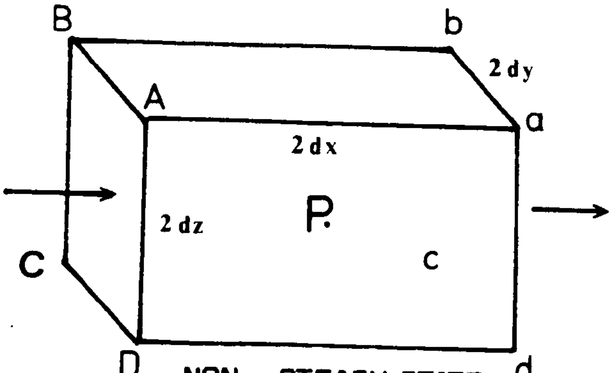
The first law applies only to steady state diffusion as indicated .



STEADY STATE DIFFUSION FROM CONC 1 - CONC 2

This law is impractical for determining the penetration of a fluid into a material (eg. water sorption in dental composites). Fick's second law was derived for this situation by considering the various fluxes acting on a slab of the material under consideration (Comyn 1985, Crank 1975b)

By considering the fluxes at the six faces of the slab it is possible to derive the following equation for the rate of change of concentration with time.



NON - STEADY STATE DIFFUSION FROM ABCD ->P-> abcd

$$\frac{\partial C}{\partial t} = D\left[\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2}\right] \qquad (2)$$

Normally this is simplified to

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad (3)$$

which is an expression for diffusion in only one direction (x). The solution for this equation which relates to the increase in mass of diffusing substance with time in a slab has been given by Crank (1975b).

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left[\frac{-D(2n+1)^2\pi^2 t}{1^2}\right] \qquad (4)$$

where

M_t = Mass of diffusant gained at time t
M_∞ = Mass of diffusant gained at equilibrium
t = Time
21 = Thickness of slab.

This equation takes into consideration the complex situation which exists when the two diffusion fronts overlap in the middle of the slab. Before this situation is reached at values of $M_t/M_\infty < 0.5$ the equation can be simplified to:

$$\frac{M_t}{M_\infty} = \frac{2}{l} \left[\frac{D\,t}{\pi} \right]^{\frac{1}{2}} \qquad (5)$$

It is important to understand the significance of D, the diffusion coefficient. This is not a physical constant of the material like melting point or molecular weight, but it is specific to the material-diffusant system under consideration. If the same diffusant is used in a number of different composites then it is possible to compare the diffusion coefficients attained. However, to say that a material has a diffusion coefficient of value x is meaningless unless the diffusant is stated.

Besides the diffusion coefficient, another approach adopted in the study of diffusion is to determine the pattern of diffusion with time. According to equation 5 the graph of M_t/M_∞ v $t^{0.5}$ should be linear with a slope of $2/1\ (D/\pi)^{0.5}$. In the 1940s diffusion systems were observed in which there was a sharp front of diffusant at the edge of the material with the remaining material unaffected (Hartley 1946). It became apparent that in these systems the graph of M_t/M_∞ was linear with time rather than $\text{time}^{0.5}$. In 1965 this type of behaviour was christened Case II sorption, characterised by a sharply defined front, uniform concentration of diffusant behind the front and a linear relationship with time (Alfrey 1965). It is important to note the name, Case II sorption not Case II diffusion. As already discussed sorption includes the overall penetration of the penetrant including its distribution in micropores and flaws.

At present the two situations of "Fickian" and Case II sorption are seen as extremes with the majority of observed diffusion patterns lying between. Therefore if, in any diffusion experiment, Log(M_t) is plotted against Log(time) then the slope n will be between n=0.5 (characteristic of "Fickian" diffusion) and n=1 (Case II sorption). However, these are not limiting values and n may be <0.5 (pseudo-fickian) or >1 (Super Case II) (Rodgers 1985, Jacques et al 1974). It is important to realise that various n numbers are not purely of academic significance, but may give an insight as to the microstructure of the material and its sorption behaviour. To understand the latter statement, consider two materials with water sorption values of 1 mg/cm^2 and 2 mg/cm^2 respectively. If the water in material 1 is confined to a narrow subsurface band, whilst that of material 2 is distributed over a wider area, then the effects of water may be more pronounced in the first material even though it has the lower water sorption value.

DEGRADATION

Chemical degeneration

In pure diffusion the penetrant may pass into the material without chemically reacting with the polymer. All materials exhibit solubility which is the molecular equilibrium established between the surface and the solution in which it is immersed. If the solution is constantly being renewed (as in the flow of fluids over the teeth) then the surface will be constantly going into solution to maintain the equilibrium. The rate at which solution occurs is determined by the solubility product of the system (ie the material and the solution). If the solubility product is high then the solution is termed a solvent and the process becomes dissolution. Four layers can be determined on the surface of a dissolving polymer (Fig 2-3) and these describe the process (Ueberreiter 1968). The outer layer is termed the "liquid layer" because the dissolved polymer molecules are now in the liquid state. The liquid layer represents the boundary layer that occurs with any solid in a streaming fluid. Its depth is related to the flow rate of the solvent around the material. This is important because the rate of flow influences the degree of dissolution (Ueberreiter & Kirchner, 1965).

The next layer is the gel layer where the macromolecules of the polymer are still entangled and maintain their position to each other. This layer can be considered as the swollen layer because it has swelled away from the bulk polymer; however a swollen layer can occur in the absence of dissolution through relaxation of polymer chains at the diffusion front (Rodgers 1985). In the latter case the dimensional change (expansion) of the surface is far less than when a gel layer occurs through dissolution. Deep to the swollen layer is the bulk polymer within which there are two layers. Firstly the solid swollen layer, in which the solvent is building up to sufficient concentration for plasticisation and secondly, the infiltration layer which is where the penetrant has entered microcavities in the material. The latter layer marks the limit of penetration. The main factors determining the velocity of dissolution (s) are the thickness of the gel layer and the diffusion coefficient.

Physical degeneration

Stress applied to the surface of a material may cause cracks, microcracks or crazes (Kambour 1973). Swelling and polymer relaxation cause stress at the diffusion front because the natural tendency of the material to swell in all dimensions is constrained by the unaffected polymer beneath. This effect is shown as relaxation strain at the diffusion front in Fig 2-1. Another process causing degeneration in composites is osmotic forces. Fedors (1981a) has shown that solute particles in microcavities within the composite can cause osmotic forces leading to the formation of discoid cracks. Sucrose has been demonstrated to have this potential (Fedors 1981b). Osmotic forces are thought to develop in the interface between fillers and the resin in dental composites (Soderholm et al 1984).

Interelationship of permeability and degradation.

It is apparent from Fig 2-1 that all the processes so far discusssed are interrelated. If solvents can penetrate into a polymer and accumulate in voids or flaws then plasticisation and the initial stages of dissolution may occur. However the process cannot continue unless the reaction products are able to diffuse away. Any physical processes such as cracking that will facilitate the transport of these products may allow the pre-dissolution foci to become active leading to subsurface dissolution. Gross cracks, of sufficient size to allow capillary transport of the diffusant, will modify the shape of the diffusion front and allow the related processes to initiate deeper in the material.

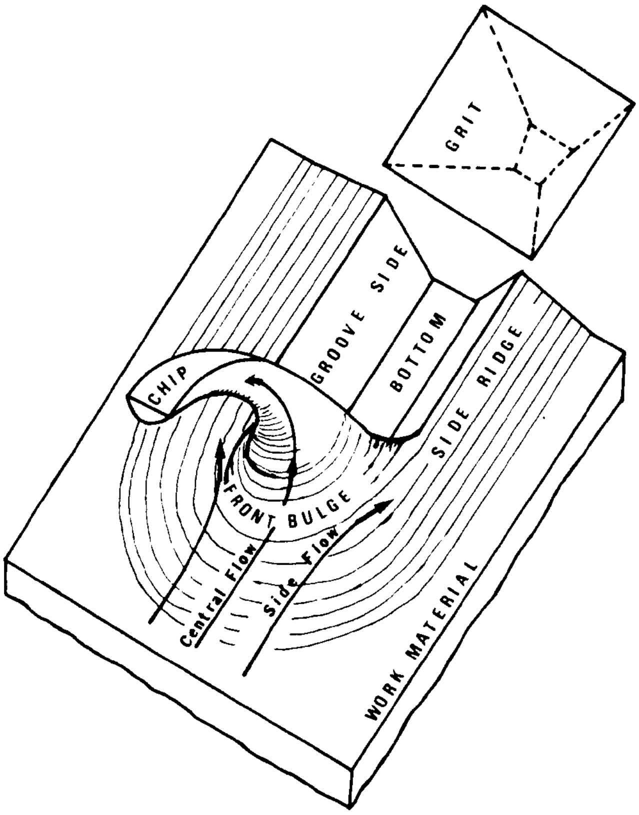
WEAR

There is a tremendous amount of confusion in the dental literature concerning the processes of wear which are often considered as a single phenomenon although they involve several mechanisms. Some terms used have an entirely different meaning than their use in engineering. As the latter discipline has far more experience and understanding of the basic principles underlying wear, it seems prudent that we should adopt its terms and meanings. The following definition of wear is generally accepted "the progressive loss of substance from the operating surface of a body occuring as a result of relative motion at the surface" (Pugh 1973). The same author continues "the usual classification of types of wear is abrasive wear, adhesive wear, wear due to fatigue, fretting wear, erosive wear and that due primarily to chemical action, each being seldom met in isolation; most examples in practice are a combination of two or more of these."

Two major processes are recognised in dental restorations; attrition at the mating areas of sliding cuspal contacts and abrasion across the whole surface of the restoration exposed to abrasive particles. Attrition is not a wear type in its own right, but is the combined result of two body abrasion, adhesive and fatigue wear. Abrasion has a contribution from the abrasive particles in food (which will subsequently be referred to as the "masticatory slurry") and from toothbrushing. It can occur without direct contact of the opposing teeth (Lambrechts et al 1984). However, with the possible exception of fretting wear (which occurs as a result of slipping of two surfaces in constant contact), all types of wear contribute to the loss of surface from a restoration and a brief explanation of these processes follows. An underlying principle in wear is that no surface is entirely or perfectly smooth. Consequently when surfaces are in contact it is by the meeting of asperities on either surface. It follows that real contact stress is not load per area of surface, but load per area of asperity contact. This is of course of extreme importance with filled composites as the whole of the occlusal load may initially fall on only a small number of protruding particles. In dental composites it has been shown that the exposed particles of a conventional composite can act as a highly efficient two body abrader (Wilson et al 1981) and that the displaced particles may act as third body (Embong et al 1987).

Abrasion.

This literally means cutting and occurs as a result of particles cutting into the surface. It is subdivided into two types: two body when the particles are fixed to one surface (eg sandpaper) and three body when there is a slurry of abrasive particles between the surfaces. The submerging surface of dental composites (Kusy and Leinfelder 1977) is caused by three body abrasion whereas facets in occlusal contact areas (Lutz et al 1984) have a contribution from two body abrasion as a result of asperities on the opposing tooth. The particles result in "cutting" and "ploughing" of the surface (Abebe & Appl 1988). If there are many sharp projecting asperities then these are cut by the grit. If the surface is smoother the particles plough into it. If the surface is relatively plastic then initially a "chip" is lifted in front of the furrow and then, as a result of plastic flow, side ridges are formed. Both chips and ridges are new asperities that may be cut by the following particles.



The chip, side-ridge
and "furrow" formed by
a ploughing particle.
(From (Abebe & Appl 1988))

The overall abrasion is influenced by the hardness and ductility of the surface, work hardening of the surface caused by the ploughing, the "rake angle" of the impinging particle, its size and velocity.

Adhesive Wear.

This is caused by adhesive forces between the surfaces that result in local cold welding of asperities. Friction forces arise because of the need to produce shear failure within these welded asperites, although the line of separation is not necessarily coincident with the original weld (Pugh 1973). The overall result can be the transfer of material from one surface to another. Adhesive wear is important in the process of attrition: Vaziri et al (1988) have shown that sliding between two surfaces of PMMA or between PMMA and a steel counterface results in the tranfer of material to the harder surface. As a result of this transfer, plates of material build up on one surface which may subsequently break away and contribute to the abrasive slurry. Adhesive wear may contribute to surface loss in occlusal contact areas.

Fatigue wear.

This occurs when two surfaces move under dynamic load and is usually associated with gears and bearings where there is rolling rather than sliding of the surfaces (DiBenedetto 1967). Although there is no rolling in mastication, the contacting surfaces do not just come together and slide but are controlled by a delicate series of relays. This allows them to come gently together before slipping in and out of cuspal contact as successive teeth guide the translocation of the mandible (Matthews 1975). Considering the very large number of times this occurs, even during one meal, it seems reasonable to assume that there will be a contribution from fatigue in the areas of cuspal contact.

Associated with fatigue is the theory of "delamination wear" which describes the effects of fatigue namely, the loss of small increments from the surface after a period of time (Suh 1973). According to this theory, when two surfaces contact, asperities on the softer surface are either fractured or bent over each other. The surface traction exerted by the harder surface causes plastic shear deformation energy to accumulate in the softer surface, increasing with repeated loading. As a result of this stored energy, cracks are nucleated below the surface which eventually spread laterally to the surface resulting in displacement of the increment. Although most of the evidence for this theory has been accumulated from the analysis of metals, it is applicable to thermoplastics with inclusions (Suh 1977). In the latter case an important consideration is the ability of an inclusion to nucleate a void beneath the surface. This was considered by Jahanmir & Suh (1977) using the model of cylindrical inclusions in metals. They concluded that void formation could occur either by fracture of the inclusion or separation of the interface, the predominant mechanism being determined by the alignment of the particle with the stress. The processes of delamination may well be important in the occlusal contact areas of dental restorations and contributory to the stages of wear given by O'Brien & Yee (1980).

Erosive Wear.

This is similar to three body abrasion but results from impact of particles or fluid under pressure (Pugh 1973). Sandblasting and the wear of rocks under waterfalls are examples. In the mouth it is hard to draw a distinction between erosion from the masticatory slurry that is constantly squashed between the teeth and three body abrasion. A recent finding is that the "air-powder" device used for periodontal cleaning may cause significant erosion of composite restorations (Cooley et al 1986).

Wear of Dental Restorations.

From the preceeding discussion it can be seen that wear is a very complicated phenomenon. Early composites were assessed for clinical performance according to the criteria of Ryge et al read at the FDI conference in 1963. In a modified form the criteria were adopted by the United States Public Health Service for the clinical assessment of anterior restorations (Cvar and Ryge 1971, Ryge & Snyder 1973, Ryge 1981). Although this system of assessment has some advantage, in that it corresponds to what clinicians actually recognise in a restoration, it has caused many misconceptions about wear, particularly the tendency to regard wear as a single process manifesting as exposure of the cavity margins. In-vivo studies of the first composites called this type of wear abrasion and the attrition of the palatal contact areas reported by Liatukas (1972) was also called abrasion. This is correct in so far as they represent three and two body abrasion respectively. However in the context of this thesis it is necessary to define three terms to differentiate the processes that contribute to and cause clinical manifestations.

ABRASION is defined here as wear caused by free abrasive particles suspended in a slurry. This includes particles in food, toothpaste and any contribution from the flow of fluid over the surface. ATTRITION will describe the wear resulting from contact between the restoration and the opposing tooth; it includes contributions from two-body abrasion of surface asperities and wear resulting from adhesion, delamination and fatigue. Both abrasion and attrition may be potentiated by chemical DEGRADATION of the surface.

CHAPTER 3

LITERATURE REVIEW - WEAR AND DEGRADATION OF DENTAL COMPOSITES.

WEAR OF DENTAL COMPOSITES

Composites replaced silicates and unfilled resins as anterior restorative materials. Early trials concentrated on marginal wear and surface degradation which were considered shortcomings of the latter materials. After a seven year clinical trial of the experimental acrylic composite (TB71) the surface had worn with exposure of the enamel margins (McLean & Short 1969). Although enamel was exposed, the adaption of the material at its submerged depth was good with little marginal discoloration. The composites with polymer coated fillers (Addent 35 & TD 71) had improved abrasion resistance and could be finished without displacement of the fillers (Peterson et al 1966). In restorations involving the incisal edge,abrasion was noted after six months (Liatukas 1972) and Scott & Roydhouse (1968) estimated the life expectancy of these early systems to be limited to two years .

The advent of the first quartz filled BIS-GMA resins was welcomed enthusiastically by the dental profession. Wibblesman (1969) placed over 2000 (Adaptic) restorations in all types of cavity and remained thoroughly satisfied with their six month performance. However by 1972 the inadequate wear resistance of composites in posterior quadrants was apparent (Phillips et al 1971, 1972). Using the USPHS system of assessment, 49 out of 92 restorations were rated Bravo after 2 years indicating a clinically identifiable catch at the margin. This finding was substantiated by Leinfelder et al (1975) who found that with four composites, between 53 and 90 per cent showed considerable wear. Nuckles & Fingar (1975) and Eames et al (1974) also found inadequate wear resistance in the posterior quadrants. The use of Scanning Electron Microscopy (SEM), with replica models of restorations under clinical investigation, was a major advance in the study of wear (Tay et al 1974). Initial studies on anterior restorations again concentrated on marginal features, although it was noted that considerable wear occured if the margin was in the area of palatal contact. After three years considerable surface wear had occurred regardless of whether the original restoration had been overfilled (Tay et al 1979, Flynn 1978). In addition to marginal exposure, the SEM demonstrated preferential wear of the resin with exposure of fillers. These two features were quickly accepted as the characteristics of wear in posterior composites (Kusy & Leinfelder 1977, Leinfelder et al 1980).

Possibly the combined influence of the latter papers and the USPHS system for clinical evaluation detracted from the importance of attrition. Meier and his co-workers recognised this and their ideas (published in German) led to the design of a modified profilometer for the measurement of surface wear (Lutz et al 1979). This report noted the different effect of abrasion and attrition at various locations on the surface. These locations were later christened the "Occlusal Contact Area" (OCA) and the "Contact Free Area" (CFA) which are self explanatory in terms of location (Lutz et al 1984). The CFA is a site of abrasion whereas the OCA has contributions from both abrasion and attrition.

The merits of the systems of measurement were a subject of discussion at a major conference on posterior composites at Chapel Hill, N. Carolina, USA in 1982. Ryge defended the USPHS system in that the three grades of wear represented criteria that were well understood stages of clinical deterioration, whereas a value "x-microns" was meaningless to most practitioners (Ryge 1982). Although the latter is certainly true, the major drawback of the system is that it is insensitive to facetting and other scars caused by attrition. For this reason research was directed at establishing techniques that would quantitatively measure the change in profile across the whole surface. These methods included "directly measured" profiles such as the profilometer of Lutz and measurement using optical contours on the surface (Howell and Boyde 1980, Atkinson et al 1982, Adams et al 1989). An alternative technique was surface analysis by backscattered Beta particles (Harrison et al 1984, Glentworth et al 1984). The major problem associated with all these methods was accurate repositioning of the models at successive time intervals. The problem was partially resolved by Lambrechts et al (1984) using computer aided alignment for the final superimposition of successive images. Both the latter paper and that of Lutz (1984) really differentiated between the effects of abrasion and attrition, the latter often being 2.5x greater than the former. More recently Roulet (1987 a,b) developed a device, similar in concept to that of Lambrechts, which measured the wear at up to 5000 points on the surface. This was achieved by the use of computer controlled step motors to move the stage of the measuring device. The reference points were mounted on modified orthodontic brackets bonded onto the buccal and lingual surfaces of the restored teeth. The concept of the latter device has recently been refined such that the mechanical switch which determined the z coordinate in Roulet's apparatus has been replaced with a "laser stylus" switch (DeLong et al 1989). The "z-step motor" is inactivated when the laser stylus is exactly focused on the restoration surface. As with the laser contouring technique, no physical contact with the model is necessary and there is less scope for distortion. Interfacing with commercially available softwear has enabled the three dimensional coordinate data to be converted to three dimensional graphic images which allow sites of attrition to be accurately defined (DeLong et al 1985, McDowell et al 1988, Lambrechts et al 1989).

A great problem with all the preceeding methods was that they required expensive equipment which was not easily available at all centers of research. In 1979 Jorgensen used a stereo microscope to measure enamel exposure and this idea was modified by Goldberg et al (1981 & 1984). In the latter method five replica models were selected which had increasing enamel margin exposure ranging from 100 - 500 microns. All of the models from the clinical trial were then compared with these standards and categorised accordingly. It was considered legitimate to regard this as ratio rather than categorical data in the statistical analysis (Leinfelder et al 1986a). An alternative system was devised by Moffa-Lugassy and is known as the M-L system (Lugassy and Moffa 1985). In this system the standards are cylinder shaped models with a machined offset in the center (Leinfelder 1987).

Although the "Goldberg" method has become very popular, it must be remembered that it is not sensitive to attrition. A simple method that is sensitive to overall wear, but that does not discriminate between causes involves the use of closely adapted "special trays" to take impressions of the restorations at successive recall intervals; the weight of the impression layer is used to evaluate surface loss (Vrijhoef et al 1985). When the results of investigations using the preceeding methods were compared with the USPHS data for the same restorations it was noted that the latter system is not sensitive to marginal exposure of less than 100 microns and often 200 microns (Lutz et al 1984, Leinfelder et al 1986a, Boksman et al 1986, Heymann et al 1986).

This inherent problem with the USPHS system caused the erroneous concept that the prototype posterior composite Profile (Chemical-cure) did not wear during the first years service (Moffa & Jenkins 1978). However clinical studies using replica models indicated that wear was continuous but lower than the sensitivity of the USPHS criteria (Horsted & Borup 1984). A further problem with the USPHS system is that the result is influenced by the cavo-surface angle of the cavity. A clinical catch may be less evident with a bevelled margin (Davidson 1987). Although the original defense of the system by Ryge still stands, it was the general feeling at a major conference on posterior composites at St. Maarten (Netherlands) in 1985, that indirect measurement is preferable in properly controlled scientific trials (Leinfelder 1985, McComb 1985, Roulet 1985). However at the same conference Eick (1985) restated that the USPHS system gives the best overall appraisal of clinical performance. Recently the ADA Council on Dental Materials have revised their directive to manufacturers, the major revision being the necessity to include indirect evaluation of wear (cited by Sturdevant et al (1988)).

The majority of clinical trials on the present generation posterior composite have used the USPHS system to evaluate clinical performance; but have supplemented the results with wear measurement with indirect evaluation using the "Goldberg" technique (Wilson et al 1988, Robinson et al 1988, Boksman et al 1986). Although some authors have acknowledged that this method is insensitive to attrition (Sturdevant et al 1988), there is still a tendency to regard wear as synonymous with enamel exposure.

Not withstanding these controversies over the methods of measurement, the present generation posterior composites appear to have much improved abrasion resistance compared with the early materials. The results of three and five year trials are rapidly appearing in the literature and these indicate that the materials will satisfy the ADA specification of <250 microns of wear over five years.

THE RELATION BETWEEN CLINICAL AND LABORATORY STUDIES OF WEAR

As the clinical signs of inadequate wear resistance are not apparent until months or years after placement; it was obviously necessary to develop laboratory testing procedures that would be predictive of clinical wear. The multitude of tests varied in degree of complexity and ingenuity (Craig & Powers 1976). There were "almost as many wear testing devices as there were scientists who are interested in such wear" (Roulet 1987a). It became apparent that tests failed to correlate with clinical findings or even with each other. Lutz (1979) indicated that comparative measurements of composites and amalgams do not match clinical experience because they are strongly influenced by experimental design. Gettleman (1980) reviewed the situation in 1980 pointing out that the wear of composites measured against the wear of amalgam varied between 0.8 and 22.4 times in various reports. Lambrechts et al (1984) described the correlation as "at best - inconclusive" and other authors draw attention to the inconsistencies (Harrison & Moores 1985, Harrison 1985). However this does not mean that laboratory tests have no place in the wear testing of dental materials; but that more thought needs to be given to the basic processes that underly each test and the factors which will affect them.

The classification used for clinical wear is not entirely appropriate for in-vitro tests which should be divided according to three predominant processes: (1) **Three body abrasion** with the abrasive particles in an abrasive slurry. (2)**Two body abrasion** where the particles are fixed as in the silicon carbide paper used in the device developed by Harrison & Lewis (1975), (3) **Two body sliding tests** where the slider has a "smooth" counterface as in the use of enamel or hydroxyapatite pins (Meuller et al 1985, Rice et al 1984, Mc Kinney & Wu 1982, Bailey & Rice 1981). The first group correspond to the processes causing clinical abrasion wear whereas the latter two are related to attrition wear.

Although some researchers have drawn the distinction between the various processes (Bream et al 1986, Sakaguchi et al 1986, Ehrnford et al 1980, Derand & Ehrnford 1980, McCabe & Smith 1981, Wilson et al 1981) [1]; the distinction has frequently been missed and often clinical trials measuring three body abrasion have been compared with laboratory results from two body tests (Powers et al 1983). Many of the laboratory tests have found a greater wear rate for amalgam than for composite which is the reverse of clinical experience. Ehrnford et al (1980) developed a test that combined two and three body abrasion and gave the correct ranking order for amalgam and composites. McCabe & Smith (1981) developed a test that involved vibrating the composite in a capsule with abrasive paper. This was thought to cause two and three body abrasion simultaneously and the test ranked the wear of an unfilled resin, a composite and an amalgam in the correct order. A similar device was used by Pilliar et al (1984) who found much greater wear in the materials with conventional fillers. Although these combination tests may be useful for screening materials they do not help determine the relative contributions of the processes. When comparisons have been made between similar types of wear in vitro and clinically there has been a degree of correlation. An artificial mouth (as described and used by DeLong & Douglas (1983)) was used to study wear in posterior composites (Sakaguchi

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1. this list is by no means complete

et al 1986). No free abrasive particles were used in the latter devices and the authors correctly confined their discussion to the formation of facets by two body processes noting a correlation between their results and clinical facet wear. Jorgensen (1980) reported the correlation between a three body abrasion test and the clinical abrasion of a material measured as exposure of the enamel margin (Jorgensen et al 1979).

Recent developments have included a three body abrasion device utilising poppy or millet seed as the abrasive medium (De Gee et al 1986, Fingar & Thieman 1987, Palav et al 1988). The use of seeds was advocated by Davidson (1985) who thought that enzymes in the seeds may be important in the process of degradation: this latter idea doesn't appear to have been substantiated. Another device utilises a thin sheet of PTFE between two abrading bodies to dissipate the load over a wider area (Leinfelder et al 1989). Although the authors claim that it is a three body device, this is doubtful because there is no free abrasive slurry.

One reason for the difficulties in comparing data from different tests is the number of factors that interact in a test. Using a wear machine specifically designed to simulate human masticatory movements (Harrison and Lewis 1975) an interaction was noted between the grit size of the abrasive plate and the size of the composite filler particles. (Harrison & Moores 1985). This gave unpredictable results when relating the grit size with the rate of two body abrasion. The latter authors also reported the importance of the contact stress, finding that stresses over 1.3 MPa increased the wear rate of one material but had the reverse effect on another three. In an earlier paper Harrison and Draughn (1976) showed that there was no relationship between two body abrasion, tensile stress and hardness. Another factor that is frequently overlooked in the assessment of wear is the presence of the resin rich surface. Wilson et al (1981) found a significant difference in the rate of wear between surfaces "as set" and after removing the layer.

At present, although laboratory tests have become more sophisticated, a consensus view is that they are not predictive of clinical performance. It appears that the only way to test performance is with a clinical trial using indirect techniques to determine wear. A recent report on the long term clinical performance of anterior composites has indicated that the ranking of some materials at three years was reversed by six years (van Dijken 1986). This illustrates the great problem of predicting wear in composite materials. The experiments described in this thesis were instigated in 1984 to study permeability and degradation as factors that may contribute to clinical wear and help to clarify the poor correlation between clinical and laboratory results.

PERMEABILITY AND DEGRADATION

Composites are subject to degradation by their environment especially the combined effects of water and heat - "hygrothermal aging" (Marom 1985). Hygrothermal aging may affect the fillers (Soderholm et al 1981), the resin (Kaelble & Dynes 1977), the interface (Kaelble & Dynes 1976) and combinations of these three sites. The experimental conditions used in the latter investigations on non-dental composites (100 ^{o}C for 60 hours) are obviously not comparable to the clinical situation. The effects of water at room (body) temperature may be temporary; for example, an increase in fracture toughness (as a result of plasticisation), or permanent such as the decrease in elastic modulus (Kaelble et al 1974). The importance of water sorption with dental composites was demonstrated by Wilson et al (1981). They showed increased two body abrasion of a microfilled and unfilled resin after 24 hours storage in water, but no significant effect with conventionally filled materials. As a result of plasticisation water may increase the strength or fracture resistance of a composite (Lloyd 1982, Kaelble et al 1974. On the other hand hydrolysis of intermolecular bonds may cause these parameters to decrease (Pilliar et al 1986).

An early investigation of water sorption in dental composites was included in the study of Peterson et al (1966). The data showed a linear weight gain as a function of $(\text{time})^{0.5}$ rather than time. The latter is indicative of "Fickian" diffusion. Although three materials (testpiece thickness = 2.5 mm) had reached equilibrium within 90 days, one (Addent) failed to achieve this in 200 days. More recently water sorption in conventional dental composites was studied by Braden et al (1976) who reported that the process was diffusion controlled and that 0.8-1.3 mm thick testpieces took three months to attain equilibrium. It was noted that the process was slower in the cross linked BIS-GMA systems. Pearson (1979) found that diffusion and solubility were fairly uniform in four conventional composites regardless of their constituent monomers. Braden and Clarke (1984) found that some microfilled materials had higher diffusion coefficients than conventional materials and correspondingly high solubilities. Using experimental composites, Braden (1984) found that the diffusion coefficients for experimental composites which were based on the TEGMA monomer, were almost double those of materials based on a mixture of urethane dimethacrylate and TEGMA. In both materials diffusion was independent of filler loading, indicating that the resin was the determining factor. This was noted by Fan et al (1985) who indicated that both sorption and solubility should be expressed in terms of wt per gram(resin) rather than wt per gram(material). Germain et al (1985) noted that although sorption was independent of filler loading, with silica particles there was a significant difference if the silica was agglommerated into pre-polymerised particles. The overall finding is that equilibrium is reached in months rather than days. It is therefore surprising that the standard water sorption test required of manufacturers involves immersion for only seven days (Council on Dental Materials ADA Spec 27 1977).

Soderholm (1981) investigated the effect of storage in water on soda lime fillers in BIS-GMA and PMMA resins. In the experimental systems, without silane coating, there was evidence of degeneration of the glass fillers after 180 days. The pH of the storing water increased regardless of the type of resin indicating dissolution of the silica network. The leaching of silica from commercial composites was confirmed by Soderholm (1983) who found that strontium and barium were leached more than other ions. Investigating the long term leaching of ions, Soderholm et al (1984) found that leaching increased in amount up to four months after immersion indicating that it was occuring from subsurface fillers as well as those exposed at the surface. The latter paper and the work of of O'Brien & Yee (1980) noted cracks at the surface which Soderholm attributed to microcrack growth as a result of osmotic pressure developing in the zones of leaching. This theory is supported by the work of Fedors (1981a&b) on crack growth through osmotic forces. Using infrared spectroscopy, Braden and Pearson (1981) found evidence that composites leached monomer into the surrounding water; but Fan et al (1985) considered that this was minimal after the first thirty days.

In 1981 Wu & Cobb reported to have demonstrated a zone of subsurface porosity in fillings that had been removed after a few years service. Any such zone would potentiate the effect of osmosis and also influence the laminar process of wear. Evidence for the latter statement was obtained by Mc Kinney and Wu (1982) who demonstrated the damaged layer under the wear scar of a two body wear scar in vitro.

The effect of "Food Simulating" solvents on wear was investigated by Wu & McKinney (1982) who examined the effect of cyclohexanone and ethanol on the hardness and two body wear of Adaptic. All solvents decreased hardness and increased the rate of wear. However at the International Symposium on posterior composites (Chapel Hill, USA 1982), Wu et al indicated that the loss of hardness caused by ethanol was entirely reversible by subsequent immersion in water or evaporation in air. The relationship between solvents, hardness and wear was confirmed by Wu and Debelius (1984), Mc Kinney & Wu (1985) and more recently by Kao (1989).

Acetic and proprionic acid, which are present in dental plaque, also cause softening of dental composite especially in those formulations with a low percentage of the diluting monomer TEGDMA (Asmussen 1984). This was attributed to the relatively low degree of conversion in these materials (Asmussen 1982). Subsequently it was demonstrated that, in materials with low degrees of conversion, there was increased staining of restorations in patients with poor oral hygiene. This attributed to the softening of the matrix by plaque acids (Asmussen & Hansen 1986).

The effect of degradation in vivo was investigated by Roulet and Walti (1984) who placed samples of composite (Adaptic) and glass ionomers on the undersurface of pontics aiming to determine dissolution in an area protected form occlusal trauma. They found that both materials showed evidence of initial swelling and then degradation of the material resulting in the exposure of filler particles. This resulted in an increase in surface roughness of the materials. The surface roughness of the glass ionomer was easily distinguishable at two months whereas the same degradation in the composites took up to sixteen months. In a similar experiment van Groenigen et al (1986) placed composites into the buccal flanges of lower dentures and reported surface loss.

The findings reported in this thesis complement many of the findings that have been reported since 1984 when the work was commenced. It is now apparent that any laboratory study of wear must consider the effect of both physical and chemical degradation likely to occur in the oral environment.

CHAPTER 4

DEVELOPMENT OF A MODIFIED TECHNIQUE TO IDENTIFY SURFACE DEGRADATION IN FAILED RESTORATIONS.

INTRODUCTION

In 1981 Wu and Cobb reported a method to stain subsurface porosity using silver nitrate. Alternatively the technique could be used to stain marginal defects (Wu et al 1983). The technique was used by Wu et al (1984) to examine eighteen composite "biopsies". The theory of the technique was that silver nitrate penetrated into the subsurface porosity. Subsequently the specimens were exposed to UV radiation thereby reducing silver ions to metallic silver which was subsequently developed into larger silver particles with photodeveloper. The presence of silver in the subsurface, after staining, corresponded to regions of microporosity which had been present in composite. As the silver did not appear to stain freshly made laboratory testpieces, it was concluded that the presence of silver indicated subsurface porosity caused by degradation in the oral environment.

The stained layer was uniform in thickness ranging between 50 and 200 microns in various specimens. Additional information showed that the layer was more clearly defined when viewing thin sections by transmitted light; but that the relationship between the silver and fillers was more obvious by incident light microscopy. A flow diagram of the original method is showing in Fig. 4-1.

In the work described in this chapter the original technique of Wu and Cobb was used to stain a number of failed restorations which were collected from the conservation clinic at the dental hospital. A number of artefacts were recognised and the technique was modified to allow the correct interpretation of the results.

DEVELOPMENT OF TECHNIQUE

Wu and Cobb described two methods of specimen preparation in their original publication. Firstly, "block mounted" specimens, where the restorations were embedded in another composite and polished prior to staining and examination by incident light microscopy. Secondly, thin sections were cut from the restorations and viewed by transmitted light. With the block mounted specimens the stain appeared on examination with **Differential Interference Contrast microscopy** (DIC). The modifications to both techniques are described.

USE OF BLOCK MOUNTED SPECIMENS.

At the start of the present investigation, the original method of Wu and Cobb was used to stain four composite restorations collected from the clinic. The only difference was that "Concise" was used as the embedding material because "Exact" (used by Wu and Cobb) is no longer available. Initial results were disappointing typified by Plate 1. Although there is some evidence of the interface between specimen and embedding resin, it is impossible to distinguish a silver layer. An early modification was to use a microfilled composite (Silar) as the embedding resin as this gave better contrast with the specimen. Plate 2 shows a specimen embedded in Silar: there are obvious deposits of silver but no uniform layer. It is apparent from the scratches on Plate 1 and 2 that the polishing process was inadequate and therefore a polishing regime of 2 hours ultrasonic polish (Vibromet, Beuhler UK Coventry England) with 1 micron aluminium oxide was adopted. The original 4 specimens were repolished using this process. Resolution was improved and at this stage an interesting observation was made which would have important consequences. Plate 3 shows the interface between the specimen (unidentified) and the embedding resin (Concise). It was noticed that when the Normaski (DIC) lens was rotated to an extreme position, black crystals of silver could be seen in the subsurface of both the specimen and embedding resin (Plate 4). At first the significance was not appreciated and the effect would only occur with the x8 Normaski objective. After many hours "experimenting" with various configurations of lenses, reflectors and filters the cause of this appearance was recognised. In an extreme position of rotation the Normaski prism was not causing phase separation of the reflected light and was therefore behaving purely as a sheet of plain glass. The optical effect was produced by the polarizing plates which have to be used simultaneously with differential interference microscopy. A new lens adapter ring was purchased to enable the Normaski prism to be excluded from the optical system. The resulting images were much clearer. Plate 5 is a magnified view of Plate 4 using only crossed polarizers.

MICROSCOPE OPTICAL SYSTEMS.

At this stage it is necessary to explain the optical systems used with incident light microscopy. When a specimen is examined by bright field incident light microscopy it is the reflectivity of the surface which causes contrast of the image (Rose 1982). Therefore, in Plate 3 the filler particles are seen because they are more reflective than the resin. Differential interference contrast (DIC) uses a Normaski (or Wollaston) prism to phase separate the illuminating beam. This system enhances the appearance of filler boundaries because it increases or decreases the phase separation of the light waves at the boundary. If the separated rays summate at the image plane, the boundary appears bright; if they cancel it appears dark (Rose 1982, Zeiss 1979). The overall effect of DIC is that there is an apparent three dimensional effect with well defined boundaries between components of varying refractive index (eg fillers and resin: Plate 6).

When the Normaski lens is removed the only optically active glass in the light path are the two polarizing plates. The first, the "polarizer", is in the incident beam and the second, the "analyser", is in the reflected beam. When polarized light reflects at the specimen surface the majority of the light is directly reflected and this light is polarized in one plane. However, a smaller portion of the light is scattered. If the analyser is rotated to selectively "filter out" the directly reflected rays, then only the scattered rays are available to form the image. The result is that the colour rather than the reflectivity of the surface is seen. Culling (1974) gives an excellent example to explain this: if one stands in front of a mirror on which is a spider's web and shines a torch straight at the mirror, then the web cannot be seen because it is "drowned" by the bright reflected ray. If on the other hand a colleague shines the torch at 45 degrees to the mirror, then the observer sees the web glowing on the glass. This is because the beam is scattered by the web, the main beam having been reflected away. Another optical system which enables the surface colour to be observed is dark field microscopy which uses oblique rays to illuminate the object similar to the example above. All of the effects reported in this thesis, that were observed with scattered light microscopy could be seen with dark field incident light microscopy. However, the technique using crossed polarizers had the advantage that scattered light (showing colour) could be interchanged with directly reflected light (showing reflectivity) simply by rotating the analyser. The effect of this can be seen in Plates 3 and 4 which are exactly the same field viewed by reflected light and scattered light respectively. It is important to state that the silver grains appear because of their colour and not as result of birefringence with the polarized light (Sawyer & Grubb 1987b).

No claim is made to the originality of the optical system. It has previously been used for examining polymer surfaces, usually whilst looking for birefringent effects such as the Maltese Cross pattern (Fridman et al 1980). Although these effects were seen in various specimens (see Plates 47 & 49) they were a side effect caused by circular polarisation at voids on the composite surface.

SUB SURFACE POROSITY (continued)

The location of the silver grains in Plate 5 was very different from the result reported by Wu & Cobb (1981) because there was obviously silver in the embedding resin as well as the specimen. Also the distribution of silver on either side of the interface was apparently equal. It appeared as if the silver grains were located in the "valleys" which form between the fillers during polishing.

As silver was equally distributed on either side of the interface, clearly sub-surface degradation in-vivo could not account for its presence. It seemed obvious that if such a layer of porosity existed then it should have been possible for the silver to penetrate the specimen before embedding. Therefore, another three specimens were collected, cleaned in the ultrasonic bath, allowed to dry and immersed in silver nitrate (3 mole/litre). After sixty hours they were removed, allowed to dry, embedded and polished with 1 micron alumina. The results of this modified process are shown in Plates 7 and 8. There appeared to be a uniform layer but it was difficult to determine the interface with the embedding resin or the depth of silver penetration. The V shaped accumulation seen in Plate 8 was a common finding and caused by the staining of calculus in a surface void.

The problem of identifying the interface is illustrated in Plate 9. It is not clear if the thin brown line (arrowed) is an interfacial gap, a surface layer, or staining of the embedding resin. It had been noticed that traces of the nail varnish (used to stick the specimens onto the embedding moulds) showed up clearly on some specimens. Therefore the next specimens to be prepared were painted with a layer of varnish prior to embedding. The result of this modification is shown in Plate 10. Dark silver deposits are visible in the subsurface and the interface is clearly demarcated. Although this layer of nail varnish was useful to define the interface, if the specimen was very rounded and translucent, then the back reflection of scattered light caused the edge to appear red (Fig 4-2 & Plate 11) Nonetheless, it was felt that the advantage of clear demarcation outweighed this problem. At this stage no uniform layer corresponding to that reported by Wu and Cobb was seen. The silver deposits appeared in discrete areas and its appearance in Plates 10 and 11 indicated that it may be located in surface defects rather than a zone of subsurface porosity.

The next development was fortuitous. One of the original specimens had become badly scratched and it was decided to regrind and polish it. The ultrasonic polisher required at least five specimens to balance the vibrating platten; so this specimen was polished on a Minimet polisher (Buehler, UK). The polishing base available with this machine was nylon and the polishing agent was 0.05 micron aluminium. The result seen in Plate 12. A uniform zone of black "stain" is seen around the periphery. Other specimens were polished by this regime and evidence of the uniform zone was seen. The layer was clearly visible using DIC (Plate 13). However, when cross-polarizers were used there was no evidence of black silver (Plate 14). In another specimen (Plate 15) there was evidence of the black layer with bright field (directly reflected light), whilst with crossed polarizers there was brown and black stain at the palatal subsurface; but no stain proximally (Plate 16). A similar situation was seen in other specimens (Plate 17 and 18).

At this stage it was necessary to determine, which if any, of the layers were caused by silver and what was the significance of the brown rather than the black stain. It must be remembered that the uniform black layer which was seen with bright field (or DIC), occurred only after a specific polishing regime. If the specimens were reground and polished with 1 micron alumina the layer disappeared.

The specimens which had been polished on nylon with 0.05 micron alumina were thoroughly examined to determine any differences. It was noticed that the whole specimen appeared to be the proud of the embedding plastic. It was thought that the appearance may have been due to the reflection of light at the rounded edge of the specimen. To investigate this hypothesis unstained bars of composite (2.5mm x 3.0mm x 12mm) were embedded in PMMA embedding plastic (Austenal Dental, Harrow Middlesex) and polished for 2 hours with 0·05 micron alumina on nylon. The result is seen in Plate 19. The edge had a uniform black "stain" under bright field (or DIC) illumination, whilst with crossed polarized no stain was present (Plate 20). As there was no silver in the specimen it was apparent that the black "stain" was an optical artefact. To confirm that silver would be seen under cross-polarizers and not bright field a specimen of the cermet "Ketac-Silver" was viewed by both systems. This material has silver particles dispersed with the glass fillers. The small black particles of silver are clearly visible under cross polarizers (Plate 22); but not with bright field illumination (Plate 21).

To confirm that the false "stain" was a result of light reflecting from the rounded edge of the specimens, laboratory testpieces (2.5 mm x 2.5 mm x 12 mm) of four composites (Occlusin, P30, Clearfil, Silux) were polished for various lengths of time using different grades of alumina on various polishing cloths. The profiles across the specimen edge were recorded with a profilometer (Planer Products Model SF 101). The horizontal length of the steep part of the slope was measured (Fig 4-3) and compared with the depth of apparent stain measured using a calibrated eyepiece graticule. It was found that the width of apparent stain always corresponded with the length of the slope.

The reasons for the black edge can be seen in Fig 4-4. The incident light reflects normally from the flat surface of the sample and the embedding plastic. However, at the rounded edge it is reflected away from the objective leaving a dark "space" in the image corresponding to the edge of the specimen. An important effect noted in later experiments was that the slope was longer on solvent treated testpieces because the softened material was more easily rounded. This may explain the observation by Wu and Cobb that the "stain" appeared deeper on the oral surface than on the fitting surface if this layer had been softened by the oral environment.

From these experiments it was concluded that with incident light microscopy silver particles present in the specimen would be seen with crossed-polarizers and not bright field or DIC.

As it was not possible to determine the exact nature of the stained layer from the journal photograph, copies of Plates 15 and 23 was sent to Professor Wu asking if this was the layer he had reported. The reply confirmed that the uniform black layer was the one he had attributed to silver staining. The experiments reported here indicate that the black layer is an optical artefact.

It can be seen in Plates 7,8,9,10,11,16 and 18 that staining of the subsurface is ill-defined and difficult to interpret. A second important feature was that often the stain appeared brown rather than black. Chronologically this stage of the experiments corresponds with the discovery of the "brown diffusion layer" reported in the next chapter.

The theory for the brown colour of silver will be discussed more extensively in Chapter 5. At this stage it can be summarised as being a light scattering effect dependant on the size of the silver particles that had developed in the composite. Small particles appear brown as a result of selective scattering, large particles absorb all the wavelengths and appear black. It is important at this stage to re-emphasise that the cause is scattering, as this accounts for many of the effects discussed in the next part. As the different colours represent different sizes of silver particle, then they also represent different sizes of microcavity in the specimen, as it is these that determine the size to which the silver particles can grow.

THIN SECTION INVESTIGATIONS

A second paper (Wu et al 1984) indicated that the black subsurface had better resolution when viewed on a thin section with transmitted light. To investigate this thin sections of composite biopsies, which had been soaked in $AgNO_3$ for 60 hours and developed under UV with developer, were cut into 200 micron sections with a diamond wafering blade (Beuhler UK, Coventry). These were then mounted on the anvils of a precision thinning attachment and wet ground to 80 micron sections. The thin sections were floated off the anvil with acetone and immediately washed and dried. An early result is seen in Plate 25 showing black silver deposits around some filler particles. With the thin section lying freely on a microscope slide it was hoped to be able to alternate between transmitted and incident light. However with incident light the image was distorted because of light reflected back through the specimen from the slide (Fig 4-5 A). To overcome this problem the slide was replaced with a sheet of polarising glass. By crossing the polarisation plane of the incident light with the stage polarizer it was possible to eliminate back reflection (Fig 4-5 B). The advantage of this system was that the specimen could be alternatively observed by transmitted or incident light simply by rotating the lamp source mirror from XL (transmitted) to ZL (incident) (Fig. 4-6). The difference between the two systems can be appreciated from Plates 25 and 26 which are exactly the same field of section viewed by transmitted and incident light respectively.

The colour of silver with transmitted and incident light is caused by different processes. With transmitted light the black colour results from absorption of light, whereas with incident light the brown colour appears because of scattering (See Chapter 5). The difference is extremely important because the appearance of the silver by incident light indicates the density distribution of the silver particles whereas with transmitted light all detail is lost. This is illustrated in Plates 27/28 and Plates 29/30 which show the distribution of silver in calculus that had formed in surface defects. In Plate 27 the silver is seen to be predominantly brown with a few areas of black particles. This indicates a more finely dispersed silver than in Plate 29 where the silver is predominantly black. In the corresponding Plates 28 and 30 viewed with transmitted light there is no resolution of the colour which appears black as a result of absorption. The cause of the different colours is illustrated in Fig 4-7. The situation in A caused the black colour in Plates 29 and 30. The situation in B caused the appearances in Plates 25 and 26 and in Plates 27 and 28. The situation in C caused the thin brown stain in the composite by transmitted light (Plate 30 (arrowed). The appearance of calculus was an incidental finding which has been used solely to illustrate the effect of the optical systems. The relationship between calculus and composites is not a concern of the thesis.

It is important to note that in Plates 27/28 and Plates 29/30 there is small amount of staining in the composite itself. By using incident and transmitted light alternatively it was possible to gain a clearer understanding of both the location and density distribution of the silver in the stained composites. Fig 4-7 D illustrates an extremely important difference between the two optical systems. If the edge of the specimen is angled then, by transmitted light, the apparent depth is greater than the real depth of the silver stained layer. This is seen in Plates 31 and 32 where the stained layer is apparently deeper by transmitted light. The black colour of the silver in these plates corresponds to the situation illustrated in Fig 4-7 A.

The uniform layer of stain seen in Plates 31 and 32 was not common. The patient was a male aged 20 who indicated that the restoration was at least 6 years old. The restoration in-vivo is shown in Plate 33 and after staining in silver nitrate in Plate 34. The surface defects that had filled up with calculus (Plate 27) are obvious macroscopically.

To compare the resolution of thin sections with that of block mounted specimens, a stained specimen was coated with nail varnish. Next a thin section was cut and the "stub" was block mounted (Fig. 4-8). By grinding the thin section from its "offside" face and minimising the polishing of the block, it was estimated that the separation between the two samples was 400 microns (300 microns - thickness of wafering blade, 100 microns - polished away). The result is seen in Plates 35 and 36. It is clear that there is far more detail on the thin section. The same specimen viewed by transmitted light is seen in Plate 37. The apparent depth of the layer is increased because of the effect described in Fig. 4-7 D. The clinical photo of this specimen is shown in Plate 38.

There was concern about the preparation technique because the final stage involved floating off the 80 micron sections with acetone. Although this stage could be accomplished in four minutes, acetone is a powerful organic solvent and could have accentuated the dissolution of the composite. The problem was resolved by the purchase of a reciprocating diamond wire saw (Bennet & Co, Leicester, UK). With this it was possible to directly cut 80 micron sections thus eliminating the necessity for precision grinding.

It will be recalled that in the early experiments the sections were placed in photodeveloper under UV light. From the experiments to be reported in Chapter 5 and the work in this chapter, it became apparent that this stage was unnecessary and that metallic silver would precipitate if the sections were left exposed to daylight. Hammesfahr et al (1987) also realised this and eliminated the stage when using silver nitrate to study microleakage.

The modified technique so far described is summarised in the flow diagram (Fig 4-9).

DETERMINATION OF THE EXTENT OF SUBSURFACE POROSITY IN RESTORATIONS WHICH HAD BEEN REMOVED FOR REPLACEMENT

At this stage thirty four out of fifty one specimens which had been collected were processed by the revised method. The remaining specimens were too small to section. All of the restorations had required replacement for clinical reasons. Tooth number, age/sex of the patient and wherever possible an approximate age of the restoration were recorded. Clinical photos were taken of the restorations before removal. As with all data presented in this thesis, data was stored and handled with a computer database (DBase III, Ashton Tate UK, Maidenhead, UK). The specimens were analysed to determine the location of stain, its average depth, maximum depth and colour of the stained layer.

Stain was seen on the majority of specimens but the appearance of a few specimens was puzzling. Plate 39 shows a specimen viewed by incident light with crossed polarizers and Plate 40 shows the same specimen viewed the other way up. There appears to be crystals of calculus on one side but not the other. It was this discrepancy that prompted the next development which was to use a stereomicroscope to look at the edge of the specimen. The result is seen in Plate 41. The cause of the stained layer in this specimen was not absorbed silver but a thin layer of adsorbed silver on the surface. There is a limit to the magnification for photography with the stereomicroscope but direct viewing indicated that there was no silver in the subsurface. The importance of this discovery can be assessed from Plate 42 which is the same view as Plates 39 & 40; but with transmitted light. The apparent sub-surface stain is entirely an artefact resulting from optical absorption by the surface silver. The cause of the "stained layer" is illustrated in Fig. 4-10. At first it was thought that all of the silver staining may have been caused by this artefact, but on some thin sections subsurface silver could be seen distinct from the edge (Plate 43).

At this stage the following criterion was defined which must be fulfilled to confirm the presence of sub-surface silver: The absorbed silver layer must be seen on a thin section to be entirely distinct from surface adsorbed silver.

Once the shape of the edge had been established with a stereomicroscope it was possible to determine the real depth of subsurface stain by subtracting the fringe caused by adsorbed silver (Fig 4-11). On Plate 44 it is just possible to discriminate the real edge of the specimen and hence determine the real depth of stain.

The thirty four original specimens were re-evaluated to see if they fulfilled the above criterion. The importance of the re-evaluation is seen in Fig. 4-12 which is a high-low graph of the real v the apparent depth of stain. The difference was highly significant ($Z = 3.17$ $p < 0.001$).

DISCUSSION

The frequency distribution of the real depth of stain is shown in Fig. 4-13 distinguishing between the number of specimens with predominantly brown or black stain. Unfortunately the majority of the patients had been unable to estimate the age of their restoration. A detailed statistical analysis of the results was therefore inappropriate as the latter parameter would have been the major variable. Also in the majority of cases it proved impossible to identify the individual composites. Identification was attempted using an "EDX Fingerprint" (see Chapter 8 - Electron microscopy). However the components of the early quartz filled composites were very similar and it was impossible to distinguish between them. A disadvantage of using thin sections was that it was impossible to determine the filler particle distribution seen with block mounted specimens (eg Plates 6,12,13,15,17). Where possible the fragments remaining after sectioning were block mounted and polished, but it was still not possible to accurately identify the materials. It is unfortunate that dentists generally record their work as "amalgam, resin, glass ionomer, cermet" etc without stating the brand name. This should become a common practice because of the significant information that may be aquired from retrospective analysis.

The objective of this part of study was to develop the method for the analysis of "composite biopsies". It was felt that this had been achieved and that subsequent analysis of specimens generated by the clinical trial would be possible now that the major artefacts had been identified.

It is important to discuss some of the features that had be established by this phase of the investigation. From Fig. 4-13 it is apparent that no stain was obvious on almost half of the restorations. This conflicts with the finding of Wu et al (1984) who had found the uniform layer on all eighteen of their biopsies. This was undoubtedly because of the confusion caused by the artefacts. A true uniform layer of stain was seen on only five specimens; in the majority, staining was limited to specific areas. As noted in Plates 8 & 27 staining was common in surface defects but this is obviously not subsurface porosity. A common location for local staining was in association with attrition scars. An example is shown in Plates 45 & 46 where the profile of the lower incisor in the palatal surface of the upper central can be seen. The colors by incident and transmitted light correspond to Fig 4-7 B showing a fairly high density of smaller silver particles in the subsurface especially under the point of contact of the incisal edge (arrowed). There is also evidence of staining at the gingival surface (right of field). The former supports the concept of microcracking and mechanical degradation whilst the latter corresponds to chemical degeneration by plaque acid (Asmussen 1984). Four specimens had surface stain in excess of 900 microns thickness. Two of these were identified as glass ionomers which are completely permeable and stain throughout; however the other two were definitely composites (Plates 47 & 48). With both of these specimens there was fairly uniform permeability all surfaces indicating that degradation at the surface exposed in the mouth was not responsible. Specimen V26 (Plate 47/49/50) had conventional fillers while V9 (Plate 48/51/52) was a microfilled composite. At the base of the stained layer silver particles could be seen between filler particles (pre-polymerised particles in the microfilled composite) (Plates 50 & 52). None of the data recorded for each case indicated why these two had this "excess" permeability. A possible explanation is poor bonding of the filler to the polymer resulting in permeability through interfacial gaps. With the conventional material in V26, this could have resulted from poor silanization of the fillers, whereas in the microfilled material, it could have been the result of an inadequate population of C=C bonds in the pre-polymerised particles. In relating this appearance to that described in the next chapter it must be remembered that these specimens had been immersed in silver nitrate for only 10 days, whereas in the laboratory studies this depth of permeability was not seen even after one year.

SUMMARY

This chapter has described the development of a system to identify sub-surface porosity by staining with silver nitrate. Although many of the features originally reported were identified as artefacts, subsurface degeneration was demonstrated in a number of cases. After elimination of artefacts almost half of thirty four cases had no stained layer indicating that it was not a universal feature as reported by Wu et al (1984). Although stain was present in some cases, associated with occlusal trauma, it was absent in other such restorations. The absence of stain in many restorations suggest that the porosity was either material specific or dependant upon the oral environment to which it had been exposed. When wear has been measured in clinical trials there has been a high variance (Sturdevant et al 1988, Boksman et al 1986, Leinfelder et al 1986b). Patient factors giving rise to surface degradation, such as the chemical nature of the diet, may account for part of the variance. Some of the experiments to be reported in later chapters have determined physical and chemical factors which make composites susceptible to staining. The methods explained in this chapter were used to examine degradation in restorations which failed on the clinical trial (Chap. 10).

CHAPTER 5

THE SILVER SORPTION LAYER IN VITRO

RECOGNISING THE LAYER

Chronologically the first experiments undertaken for this thesis were the fracture toughness experiments described in the paper by Mair & Vowles (1989) [Appendix 3]. The interest in fracture toughness derived from its association with cracking which is implicated in the process of wear. Prior to cracking a material may undergo crazing (Comyn 1985, Kambour 1973, Kambour 1964). Crazes are precursors to microcracks caused by local yielding resulting in sheets of molecular orientation within the material (Sawyer and Grubb 1987c). As the polymer molecules line up, voids appear between the oriented sheets (Farrar & Kramer 1981, Kambour 1973). In a clear polymer optical reflection at these voids appears as crazes, but they cannot be seen in a composite because of the optical heterogenicity of the material. Kambour (1964) stained the voids with silver nitrate prior to electronmicroscopy to determine their diameter. As a complementary experiment to fracture toughness, it was decided to attempt to stain crazes and microcracks with silver nitrate and observe them by light microscopy. A simple testpiece was devised with a "crack" formed by moulding the composite around a scalpel blade as described by Lloyd & Iannetta (1982) (Fig 5-1). Having established the fracture load for each material, new testpieces were loaded to 80% of this load, removed from the tensile tester and stained with silver nitrate (3 mole/litre) for 10 days. Finally they were embedded, polished and viewed by incident light microscopy as described in Chapter 4. A result from this experiment is shown in Plate 53 which shows a stained "craze" at the crack tip. However this was not a frequent finding and in the majority of testpieces there was no evidence of crazing or cracking. Of far more consequence was the observation that a stained layer was developing along the whole length of the crack surface (Plate 54). As this layer appeared to represent a permeability layer it was decided that further investigation was warranted.

Pilot Studies

Pilot experiments were undertaken to see whether the stained layer occurred in all the composite materials selected for in-vitro study (Appendix 1), and to determine its progression with time. Rectangular bars (3.0mm x 2.5mm x 12mm) of the seven materials were prepared with a split stainless steel mould. One face of the bars had the resin rich layer removed with 240 grit silicon carbide paper. The bars were immersed in silver nitrate (3 mole/litre) for 10, 21 and 42 days, embedded and processed. The latter two stages are shown in Fig. 5-2 and were used for all future in-vitro experiments on silver permeability. The results indicated that a stained layer occurred in all materials, the depth and colour was similar within specimens of the same material; but varied between materials. For all materials the stain depth increased with time. Plate 55 and 56 show the stained layer in Profile and Concise respectively after 42 days in $AgNO_3$. It was decided to establish an experiment to determine the long term behaviour of the stained layer. Initially the reason for the stain was not known especially as it appeared brown rather than the black colour usually associated with silver. Energy dispersive analysis by X-ray (EDX) was used to identify the presence of silver in the layer. These experiments are reported in this chapter.

Determination of the progression of stain with time.

METHOD

Two identical experiments (Expts 1 & 2) were initiated in order to study the stain, its progression with time and reproducibility. The testpiece for the experiments is shown in Fig. 5-3. 20mm bars of each material were made in three part stainless steel moulds with a glass slide forming one face of the mould. Where appropriate the material was light cured at 3mm intervals along the long axis with a Luxor Light (ICI, Macclesfield, UK). After moulding, the testpieces were light cured along the opposite face to ensure optimal conversion of the material (Abdalla et al 1985). One face of the bar had an identification groove cut along the long axis and a face at right angles to this was ground with wet silicon carbide paper to remove the resin-rich layer. A bevel was cut to aid identification of the resin rich face under the microscope. The bars were then cut at 2.5 mm intervals to give final dimensions of 3.0 mm x 2.5 mm x 2.5 mm. Finally the testpieces were washed in an ultrasonic bath for 2 minutes to remove the cutting debris and allowed to dry. Samples were stored in $AgNO_3$ (3 mole/litre) for 1,6,10,21,42,90,135,180 and 360 days. At each interval three samples of each material were removed and processed as shown in Fig. 5-2. The embedded specimens were examined with incident cross polarized light and the depth of stain measured with a calibrated eyepiece graticule.

RESULTS

Experiment 1

The depth of stain increased with time. Plate 57 shows the depth of silver stain for Profile at 360 days and can be compared with its depth at 42 days (Plate 55). Plates 58, 59, 60 show the depth of stain for Heliomolar, P30 and Occlusin respectively at 360 days. The rate of stain depth increase was investigated using simple regression analysis to determine the slope (B_i) of the equation

$$\text{Depth} = B_i(\text{Time})^{0.5} + B_o$$

where
B_o = origin

Although the mean values are shown in Figs 5-4 and 5-5 the regression analysis used all data points. Table 5-1 shows the mean depth of stain at 360 days (+ Standard Deviation) and the slope (B_i) of the regression together with the Coefficient of Determination (r^2). The latter value (x 100) indicates the percentage of the relationship between the variables which may be regarded as linear. High values of r^2 indicate a strong linear relationship with low standard deviations at each time interval. The mean depths of stain for the resin rich surfaces were greater than those of the ground surfaces. The slope values need to be interpreted. The higher slopes for the ground surface of Clearfil, Heliomolar and Profile indicates a higher initial depth of stain for the resin rich surface as illustrated in Fig 5-6 A. For the other materials the initial rates were similar and the increases were steady with time (Fig 5-6 B). As the long term behaviour of a restoration is more important than its initial performance, the difference between materials at 360 days is more important than the slopes. This difference at 360 days was analysed by one-way analysis of variance with the Scheffe multiple comparison test (Level =0.05) set to determine homogeneous subsets (see Appendix 2). The result of this analysis is shown in Table 5-2.

Qualitatively the stain varied in colour between materials. Profile (Plate 57) had by far the greatest depth of stain which appeared as a uniform brown layer with

Mean Depth of Stain at 360 + Slopes of Regression (Experiment 1)

Resin Rich Surface

	N	Mean at 360 Days	STD	Slope	R^2
Clearfil	9	113	5	2.98	.83
Concise	9	87	7	3.13	.72
Heliomolar	9	101	3	4.20	.91
Occlusin	9	30	1	0.62	.34
P-30	9	99	6	5.08	.92
Profile TLC	9	290	30	14.10	.95
Silux	9	183	5	8.75	.97

Ground Surface

	N	Mean at 360 Days	STD	Slope	R^2
Clearfil	9	75	5	3.78	.74
Concise	9	58	8	2.60	.78
Heliomolar	9	71	6	4.40	.87
Occlusin	9	20	1	0.51	.22
P-30	9	60	1	3.58	.84
Profile TLC	9	270	1	14.22	.99
Silux	9	150	1	8.23	.97

N = No. of samples. STD = Standard Deviation.
R^2 = Coefficient of Determination.
Slope = Slope (B_1) of Regression of Stain v Depth.

Table 5-1

Experiment 1 ANOVA & SCHEFFE MULTIPLE COMPARISON TESTS

RESIN RICH SURFACE

ANOVA	ONE-WAY	F=409.83	P = .0000				
Subset							
1	Occlusin (30)						
2		Concise (87)	P-30 (99)	Heliomolar (101)			
3					Clearfill (113)		
4						Silux (183)	
5							Profile (290)

GROUND SURFACE

ANOVA	ONE-WAY	F=1406.91	P = .0000				
Subset							
1	Occlusin (20)						
2		Concise (58)	P-30 (60)				
3				Heliomolar (71)	Clearfil (75)		
4						Silux (150)	
5							Profile (270)

Figures in parenthsis = Mean Depth of Stain (μm) at 360 days

Table 5-2

no evidence of layering. Occlusin had a uniform black layer with no layering; but the least depth of all (Plate 60). The stain in the microfilled Heliomolar and Silux was a lighter brown with the deeper part lighter than the surface colour (Plate 58). The chemically cured materials had a more irregular border and after 360 days the outlines of the larger filler particles were visible in Clearfil (Plates 61, 62).

Experiment 2

The progressive increase in the depth of stain for the two surfaces is shown in Fig 5-7. The one-way ANOVA and homogeneous subsets are given in Table 5-3. The appearance of the layers was similar to that described previously. To determine reproducibility, the results of both experiments for each surface were analysed using multiple regression (Appendix 2). The two conditions: Experiment 1 and Experiment 2 were ascribed the dummy values 0 and 1 respectively. The regression equation:

$$\text{Depth} = B_{it}(\text{Time})^{0.5} + B_{ic}(\text{condition}) + B_{ii}(\text{interaction}) + B_{o}$$

was analysed using the statistical package SPSS^{X}.

A significant T value for the interaction (Time$^{0.5}$ x Condition) indicated a significant difference in the slopes of the regression lines for Experiments 1 and 2. The results are given in Table 5-4.

Experiment 2. ANOVA & SCHEFFE MULTIPLE COMPARISON TESTS

RESIN RICH SURFACE

ANOVA ONE-WAY F = 208.42 P=.0000

Subset							
1	Occlusin (37)						
2		Helio (99)	Clearfil (100)	Concise (103)	P-30 (104)		
3						Silux (165)	
4							Profile (280)

GROUND SURFACE

ANOVA ONE-WAY F = 812.22 P=.0000

Subset							
1	Occlusin (22)						
2		Clearfil (68)	P-30 (70)	Helio (73)	Concise (75)		
3						Silux (156)	
4							Profile (263)

Figures in Parenthesis = Mean Depth of Stain at 360 Days

Table 5-3

COMPARISON OF EXPERIMENTS 1 & 2

	RESIN RICH SURFACE		GROUND SURFACE	
	T interaction	P_T	T interaction	P_T
Clearfil	5.76	.000 ***	0.74	.461
Concise	1.34	.184	0.94	.350
Heliomolar	1.61	.120	1.32	.188
Occlusin	5.74	.000 ***	2.26	.026 ***
P-30	0.91	.367	2.83	.005 ***
Profile TLC	1.30	.196	1.47	.144
Silux	0.88	.379	1.48	.141

*** Significant Difference

T interaction = T value for interaction

P_T Significance of T.

Table 5-4

DISCUSSION

With the exception of Occlusin, the R^2 values for both surfaces was high, indicating a linear relation between the depth of stain and $time^{0.5}$. As discussed in Chapter 2 this relationship suggests that the process governing the stain depth was diffusion. In both experiments the depth of stain of the resin rich surface was greater than in the ground surface. Although this appears to indicate greater diffusion in the resin rich layer, this discussion is best delayed until these results can be compared with the sorption experiments (Chapter 6) which relate stain depth with weight gain of diffusant.

It is apparent from Tables 5-2 & 5-3 that there was a considerable difference between materials, but with no obvious common features between materials in the same subset. Concise and P-30, both manufactured by the same company (3M), were in the same subset suggesting that the polymer structure may have been a controlling factor. The percentage compositions of BIS-GMA and TEGDMA in these two materials are different (Appendix 1), but manufactures tend to use polymers with the same ultra-structure. Although the literature quotes the percentage of BIS-GMA in a material, there are many forms of this polymer which influence conversion (Ruyter 1985). The influence of conversion on diffusion was noted by Watts et al (1986).

The multiple regression analysis (Table 5-4) indicated that with the exception of 4 (out of 14) surfaces there was no significant difference between the two experiments. The significant difference for the resin rich surface of Clearfil occurred because in Experiment 1 there was an early rapid increase (Fig. 5-4 A) whereas in the second experiment the rate of increase was steady (Fig 5-7). The difference may have arisen because of the varying thickness of the resin rich layer formed during fabrication of the testpieces. This depends upon the force used to pack the material into the mould and was not controlled during the formation of the samples. The significant difference for the two surfaces of Occlusin is almost certainly accounted for by inaccurate measurement of the layer due to low discrimination of the measuring technique. This would also account for the low R^2 values for this material. As all the directly reflected light had been filtered out, there was a limit to the magnification possible without the specimen being too dark for measurement. The smallest unit of measurement was 5 microns and as all results for Occlusin were less than 35 microns there was scope for error. Overall Figures 5-4 and 5-7 indicate a similar pattern of diffusion between the two experiments. These results will be discussed in greater detail together with the sorption results in Chapter 6.

THE CAUSE OF THE STAINED LAYER

Although silver nitrate has been used as a histological stain throughout this century and is often quoted as causing a brown counterstain (Humanson 1979, Smith & Bruton 1977), an extensive search of the histology literature cast no light on the reason for this colour. Unpolished silver particles are usually black as seen in black and white photographic films and radiographic plates. An alternative explanation could have been a nitrate stain in the composite. However, as the stain was not present on removal from the silver nitrate, but developed after exposure to daylight, it seemed more likely that the cause was silver as this element is known to be photosensitive. To confirm this, a sample of Profile was removed from the silver nitrate after 72 days, dried, and ground to create a cross section with the stained layer around the periphery. The specimen was carbon coated and examined by scanning electron microscopy (Jeol 100 CX (Jeol UK Cambridge.). Energy dispersive analysis by X-ray (EDX) was used to analyse 50 $(\mu m)^2$ areas of the stained layer and the material deep to it. The result is shown in Fig. 5-8. There is a definite L alpha peak for silver in the stained zone confirming the presence of this element.

An extensive search of the literature on silver finally found an article indicating the various colours of colloidal silver (McWilliam 1967). There was a reference to Mie Theory which was postulated by G.Mie in 1908 to explain the complex colours caused by the scattering of light by colloidal metal particles. As the brown and yellow layers were viewed by scattered light, the hypothesis was advanced that the colour resulted from the scattering of light by colloidal silver particles which had precipitated in the composite.

MIE THEORY

Optical scattering was discovered by John Tyndall (1820 - 1893) who noted its effect with particles up to one tenth the wavelength of light (Brill 1980). The result of "Tyndall scattering" is generally a blue colour such as the appearance of an extremely dilute solution of milk. The mathematics concerning the scattering of light by larger particles was calculated by Mie (1908). These calculations are extremely complicated (Born & Wolf 1975) and only the essence of the theory can be explained here.

At any surface the percentage reflectivity is given by

$$R = 100\frac{(n-1)^2}{(n+1)^2} \qquad (1)$$

where n = refractive index of the surface.

Metals strongly absorb light and therefore the extinction coefficient (K), which is the ratio of absorption to transmission, is high. As a result of absorption the electromagnetic radiation (light) induces alternating currents on the metal surface which immediately reemits the light out of the metal thus providing strong reflection (Nassau 1983). To allow for this "paradoxical reflection", as a result of absorption, the previous equation has the refractive index n replaced by the complex refractive index (N)

$$N = n + iK \qquad (2)$$

where i = imaginary square root of -1.
K = extinction coefficient.

Therefore in Equation 1

$$R = 100\frac{(n-1)^2+K^2}{(n+1)^2+K^2} \qquad (3)$$

When metal is present as a colloidal distribution in a transparent or translucent medium (eg. glass or a dental composite), the particles are small and there is a limitation on the size of alternating currents developed. Therefore, K (the extinction coefficient) is much lower and depends upon the particle diameter. Mie formulated the mathematical solution for this situation by calculating the relationship between K and the particle size and density. A highly simplified form of this solution is given by Schulman & Compton (1962).

$$K = \frac{6\pi NV}{\lambda'} \; \mathrm{Im}\left[u \frac{\left(\frac{\mu}{\mu_0}\right)^2 - v}{\left(\frac{\mu}{\mu_0}\right)^2 + 2w} \right]$$

Where N is the number of colloid particles per unit volume.
V is volume of a colloid particle
λ' is the wavelength of light in the suspension medium.
μ is the complex refractive index of the colloidal metal.
μ_0 is the complex refractive index of the suspension medium.
u,v,w are coefficients which depend on the particle size of the colloids. They differ from unity by quantities of the order α where α is a parameter to λ' and to the particle diameter $2p$, such that $\alpha = 2\pi p/\lambda'$.

From a practical point of view the above equation predicts firstly that K depends on the wavelength of the light and secondly on the size of particles. Doremus (1964, 1965) demonstrated these effects for gold and silver particles (Fig. 5-9). The various wavelengths of visible light were absorbed to differing extents resulting in an absorption spectrum. The shape of the spectrum varied with the size of the particles. With gold, larger particles caused a more peaked distribution (Fig 5-9 A) whereas with silver there was a net shift of the spectrum to the right (Fig 5-9 B). This latter shift was also observed by Morris and Collins (1964) and Skillman and Berry (1968). Another factor that can influence the colour of materials is the scattering angle; although with depolarized light in amorphous polymers scattering is independent of this angle (Wendorf 1982).

The practical result of differential absorption is that when white light is scattered by a colloidal dispersion of metal in a sheet of glass it "loses" the maximally absorbed wavelengths. The resultant colour is the addition of the remaining wavelengths. A beautiful example of this is seen in Plate 63 which shows the effect of scattering by colloidal silver and gold. I am indebted to J. Wiley & Sons for their kind permission to reproduce this Plate from their publication "The Physics & Chemistry of Colour - The Fifteen causes of Colour - Nassau K". The yellow colour of silver is virtually the same as that seen in the microfilled composites (Plate 64) which is strong evidence for my hypothesis.

SILVER DISTRIBUTION IN THE STAINED LAYER

It is necessary to understand the process whereby the silver particles form in the composite. After removal from the silver nitrate solution the silver is in the form of molecules Ag^+. On exposure to daylight some of these are reduced to metallic silver Ag. This corresponds to the formation of the latent image in black and white photography. As further silver molecules are reduced they aggregate around the initial grains. In photography developer is used to cause the latter reduction. Black aggregates of silver particles form very readily if molecules are available. The fact that only smaller brown particles formed in the composites layer was because their growth was limited by the space available in the composite. A second limiting factor was the diffusion of the silver ions which is determined by the segmental mobility of the polymer (see Chapter 2). The site of the silver particles has not been directly determined. Plates 61 and 62 indicate an accumulation of particles in the filler resin interface; but the particles may also be in the free volume of the polymer. This is discussed more fully in Chapter 8 which deals with electronmicroscopy. These studies indicated that the size of the brown silver particles was 20-30 nm diameter.

The colour of the stain

In the microfilled materials the colour was yellow whereas in the other materials it was initially brown with the exception of Occlusin which was black. As it has not been possible to directly observe the particles in dental composites the following explanation is theoretical. The yellow colour results from the particle scattering effect of colloidal silver similar to that seen in the vase (Plate 63). The brown colour results from the combined effects of the absorption spectra from a wider range of particles. The black colour results from both the absorption effects of a larger range and a high density of particles. These situations are illustrated in Fig 5-10.

Previous use of silver nitrate staining

To the best of my knowledge this is the first direct use of silver nitrate to directly stain the structure of polymers and composites. Silver nitrate was used in a two stage procedure to stain the structure of wool, regenerated cellulose, poly(vinyl alcohol), polyesters and acrylics (Sotton 1970, Hagege et al 1979). In the latter technique the specimens were subjected to 30 Kg/cm pressure of H_2S gas, sectioned and immersed in silver nitrate to precipitate silver sulphide. At present the main reagent for staining the structure of polymers is Osmium tetroxide which enhances contrast in electronmicroscopy by scattering of the electron beam (Sawyer and Grubb 1987b).

Pilot experiments have indicated that silver nitrate can be used to directly stain the epoxy-resin Araldite MY 753 (Ciba-Geigy, Cambs UK,) and the BIS-GMA resins used as bonding agents for dental composites. The acrylic resin filling material Sevriton (De Trey UK) stains; but with bulk cured PMMA (Perspex), the staining with aqueous silver nitrate is extremely limited. However with an alcoholic solution there is a stained layer in all types of PMMA. Whilst it was not the original intention of this thesis to develop staining techniques for polymers it is thought that the present finding may be useful in this area.

Experiments are presently in hand to study the staining of acrylic bone cements.

CHAPTER 6

SORPTION IN DENTAL COMPOSITES

INTRODUCTION

The results from the previous chapter indicated that silver nitrate diffused into composites resulting in a stained layer. The depth of stain increased with time and the colour of the layer was uniform although in some materials there was evidence of a lighter stained area at the advancing front (Plates 58, 59). From a practical point of view it was necessary to determine the relationship between the stained layer and sorption. As discussed in Chapter 2 sorption is the overall penetration of a fluid into a material and has contributions from both diffusion and accumulation of the penetrant in structural flaws within the material. The experiments in this chapter were instigated as a preliminary step to establishing the relationship between stain depth and water sorption. It was hoped that the results would help to determine if the stained layer represented the limit of fluid penetration into the material. This was considered to be of importance because previous studies on dental composites have assumed a "Fickian" distribution of the penetrant (Braden and Clarke 1984, Braden 1984, Braden et al 1976, Peterson et al 1966). The accumulation of penetrants in surface layers is indicative of Case II sorption and may favour surface degradation. In the experiments on Case II sorption, iodine was used as a "passive marker" to identify the sorption of alcohol into PMMA, marking the extent of alcohol penetration without influencing the pattern of sorption (Thomas & Windle 1978, 1980, 1981). It was thought that silver nitrate may have acted in a similar manner and marked the depth of water sorption. It is important to restate that silver diffused into the material as the ion Ag^+ and not as colloidal particles. These were formed after the material had been removed from the silver nitrate and exposed to daylight.

As the silver staining had indicated a significant difference between the resin rich and ground layers, separate sorption experiments were conducted using testpieces with and without this layer. Therefore a total of four sorption experiments were instigated measuring water or silver nitrate sorption from resin rich or ground surfaces.

The uniform stained layer (Plates 55, 56, 57, 60, 61) appeared to indicate a well defined diffusion layer. This is one of the characteristics of Case II sorption. One theory for this type of sorption is that it results from stress swelling at the diffusion boundary (Thomas & Windle 1981), with a resulting increase in thickness of the testpiece (Thomas & Windle 1980). To help determine this behaviour in dental composites, dimensional changes resulting from sorption were measured.

A pilot experiment using discs 5mm diameter x 2.5mm had to be abandoned because the weight gain at each interval was too small for accurate measurement. The testpiece size was changed to conform to ADA Spec 27 (1977). Later there was some concern that the geometry of these specimens may influence the sorption curves. Thomas & Windle (1978) had recognised the importance of the edge/planar surface ratio on sorption curves. To determine whether this was significant with the ADA specimens, a number of large slabs (40 x 20 x 1.0 mm) were fabricated and the sorption curves compared with those of the disc testpieces.

A final experiment reported in this chapter determined the depth of silver staining with various concentrations of silver nitrate. This was one of a number of experiments, instigated soon after the discovery of the silver sorption layer, to determine factors which influence staining. It is included in this chapter because the results are relevant to the discussion.

METHODS

Sorption Experiments

Discs of each of the seven materials were prepared using a PTFE mould (20mm diam x 1.5mm). The discs for the ground surface testpieces were moulded to 2.5 mm thickness and then 0.5 mm was removed from each face using 120 grain silicon carbide slurry on a cast iron lapping wheel. Finally the discs were wet ground down to 1200 grit. This latter procedure was adopted because other procedures, such as machining or paper grinding, caused considerable frictional heat, potentially damaging to the surface. Five discs of each material were prepared for the four test conditions. Because of a shortage of material, testpieces for the ground surface silver nitrate sorption were limited to three materials. To ensure that the faces remained separated during sorption the discs were placed in plastic holders which "held" the discs upright, separated by small friction grip separators. Prior to immersion all discs were stored for 14 days at 37°C in the presence of calcium sulphate to remove any moisture incorporated during fabrication. The thickness of the discs was measured with a micrometer and they were weighed to 4 places of gram decimals. At 1, 5, 11, 35, 60, 110 and 180 days the discs were removed, surface dried with filter paper and weighed.

The effect of silver nitrate concentration

The method was as described in Chapter 5 using concentrations of 0.5, 1, 2, 3 & 5 Mole/litre $AgNO_3$. Samples were processed after 10, 26 and 90 days.

RESULTS

A number of comparisons were possible and these are presented and discussed individually prior to a general discussion of the results. Sorption curves are illustrated by plotting the mean weight gains at each time interval.

The standard deviations were small and are not shown on the figures, but all of the individual points were considered in the statistical analysis (Multiple Linear Regression). This test is extremely powerful because it uses all the data points to compare slopes and is therefore a time dependent comparison rather than a snap-shot analysis at individual times (See Appendix 2). Although strictly speaking the model for regression was not fulfilled because the same testpieces were measured at each time interval; it was felt that there was sufficient "a priori" evidence to justify regression as a valid analysis of sorption behaviour.

Comparison of testpieces Discs vs. Slabs.

The means of the sorption values for each material up to 110 days are shown in Fig. 6.1. The individual values were entered into the multiple linear regression analysis giving dummy scores 0 and 1 for the condition of discs and slabs respectively in equation 1.

$$\text{Wt gain} = B_{it}(\text{time})^{0.5} + B_{ic}(\text{condition}) + B_{ii}(\text{interaction}) + B_o.$$

where

B_o=origin [1]

The results of this analysis are shown in Table 6-1 and indicate that there was no significant difference between the slopes, although the value for the interaction of Clearfil is almost significant. As discussed in Chapter 5

MULTIPLE REGRESSION ANALYSIS
DISCS V SLABS

MATERIAL	INTERACTION (SLOPE)		CONDITION (ORIGIN)	
	T	P_T	T	P_T
CLEARFIL	1.972	0.06	0.762	0.52
OCCLUSIN	0.25	0.91	0.314	0.88
P-30	0.39	0.75	0.624	0.59

Table 6-1

these minor discrepancies probably result from variations in the depth of the resin rich layer caused during fabrication. It was felt that the results of this experiment justified the assumption that the edge effect of the disc testpieces was negligible and that further results could be analysed by comparison with the "Fickian" model.

Comparison of water and silver nitrate sorption.

The slopes of the sorption curves of weight gain vs. $\text{time}^{0.5}$ are given in Table 6-2 together with the results of a multiple linear regression using the condition scores 0 and 1 to represent water and silver nitrate respectively in equation 1. In the table the T values for the interaction indicate differences between the slopes for water and silver nitrate. From the associated P values it can be seen that for the resin rich surface the materials divide in three categories. With Occlusin, P-30 and Silux there was no significant difference between the slopes (Fig. 6-2A). For Concise and Heliomolar the differences were greater (Fig. 6-2B) and for Profile and Clearfil there was a highly significant difference (Fig. 6-3A). For the ground surface only three materials could be compared and the slopes were similar (Fig. 6-3B). It is interesting to note that whereas the resin rich surface of Clearfil showed a highly significant difference, the ground surface sorption was very similar ($P_{Ti} = .742$). This is further evidence that the "erratic" results for the resin rich surface of

SLOPES OF WEIGHT GAIN (Mg Cm^2) v $TIME^{(0.5)}$
DIFFERENCE IN SLOPES BY MULTIPLE REGRESSION

RESIN RICH LAYER

MATERIAL	SLOPE WATER	SLOPE SILVER	T (INTERACT)	P_T
CLEARFIL	.078	.060	3.42	.000
CONCISE	.077	.066	2.03	.045
HELIOMOLAR	.103	.083	2.28	.025
OCCLUSIN	.072	.070	-0.16	.987
P-30	.087	.088	1.243	.217
PROFILE TLC	.071	.139	-6.86	.000
SILUX	.210	.188	1.48	.144

GROUND LAYER

CLEARFIL	.072	.074	0.29	.742
OCCLUSIN	.068	.061	0.12	.964
P-30	.072	.068	1.94	.041

Table 6-2

Clearfil result from the thickness of this layer.

With the exception of Profile, water sorption was slightly higher than silver nitrate sorption. Overall the results indicate a similar pattern of sorption with silver nitrate and water. The highly significant difference for Profile suggests a specific reaction between the silver nitrate and Profile causing breakdown of the filler-matrix bonds and allowing clustering at this interface. In the staining experiment reported in Chapter 5 Profile had the highest depth of stain and this concurs with the present finding. Profile has strontium glass fillers and the reaction may have been between the glass and the silver nitrate.

Comparison of Sorption at Resin Rich and Ground Surfaces

This was compared by multiple regression of the two conditions: resin rich and ground surfaces. The results shown in Table 6-3 and Fig. 6-4 (A & B) indicate that with the exception of Profile there was no significant difference between sorption at the two surfaces. The result for Profile is interesting (Fig. 6-4 B) because the difference occurred as a result of a rapid rise in the sorption at the ground surface between 60 and 110 days. A possible explanation is swelling stress cracking within the advancing diffusion zone. If cracks form they quickly fill up with penetrant causing slope increases on the sorption curves. In the silver sorption experiments cracking has

SLOPES OF WEIGHT GAIN (Mg Cm^2)vs TIME$^{0\cdot5}$

DIFFERENCE IN SLOPES BY MULTIPLE REGRESSION.

WATER SORPTION

MATERIAL	Slope RR	Slope GR	T Interact	P_T
Clearfil	.078	.072	0.26	.841
Concise	.077	.080	-0.19	.923
Heliomolar	.103	.099	0.29	.816
Occlusin	.072	.068	0.24	.834
P-30	.087	.072	0.74	.446
Profile TLC	.071	.097	3.37	.001
Silux	.210	-.204	-0.33	.746

SILVER NITRATE SORPTION

	RR	GR	T	P
Clearfil	.60	.74	1.26	.104
Occlusin	.70	.61	.74	.446
P30	.88	.68	.76	.439

RR - Resin Rich Surface GR - Ground Surface

Table 6-3

been seen in some specimens of this material. Plate 65 illustrates such a case where a crack was present after 135 days in $AgNO_3$. The swelling stresses that occurs in polymers are highly influenced by the geometry of the testpiece (Thomas & Windle 1980) and the large discs used in the sorption experiment may have been more susceptible to this effect than the small testpieces used for silver staining.

Comparison of Depth of silver stain with Water Sorption

This comparison is extremely important because it helps to determine whether the depth of silver stain in Chapter 5 represents the limit of water penetration with the ions acting as passive marker. Water sorption at 10, 42, 90 and 180 days was assessed from the sorption curves Fig. (6-2/6-3) and plotted against the depth of stain which occurred at these times (Chapter 5). The relationship was analysed using Pearsons Correlation Coefficient (r). A scatterplot of the points is shown in Fig 6-5 and the slope + r^2 for individual materials given in Table 6-4. The r^2 value are extremely high and indicate that there was a very high correlation between the depth of stain and water sorption. Considering the overall relationship, with the exception of Profile, there was a good correlation between stain depth and water sorption (Fig. 6-5). The reason for the aberrant results for Profile has already been discussed. Regression of all the points except those for

PEARSON CORRELATION DEPTH OF STAIN V SORPTION

RESIN RICH SURFACE

	SLOPE*	R^2
CLEARFIL	.015	.93
CONCISE	.009	.89
HELIOMOLAR	.017	.95
OCCLUSIN	.013	.91
P-30	.013	.93
PROFILE	.004	.86
SILUX	.038	.92

GROUND SURFACE

CLEARFIL	.014	.95
CONCISE	.013	.95
HELIOMOLAR	.013	.92
OCCLUSIN	.013	.91
P-30	.015	.95
PROFILE	.009	.82
SILUX	.049	.88

*Depth of Stain(X) Sorption (Y) axis

Table 6-4

Profile gave a high correlation $r^2 = 0.87$ (resin rich) $r^2 = 0.89$ (ground surface). Although this "indirect" result cannot definitely confirm that the stain depth marks the limit of water sorption it is strong evidence for the hypothesis.

Dimensional Changes during Sorption

Table 6-5 shows the dimensional change at 360 days. These results were taken from the original small diameter discs. The differences were extremely small. Significance was tested using a T test to test the null hypothesis that the difference between dependant samples was <= 0. In no case could this hypothesis be rejected.

The effect of Silver Nitrate Concentration on Depth of Stain

The results are given in Table 6-6/6-7 and shown as histograms in Figs 6-6/6-7. The depth of stain at 90 days was analysed by ANOVA with the Scheffe Multiple Comparison Test (0.5 Level) used to determine homogeneous subsets. The result of this analysis is given in Table 6-8 and indicates that with the exception of P-30 (resin rich) the three concentrations above 1 mole/litre were homogeneous. This is important because it indicates that above a threshold the "diffusion coefficient", determining depth of stain was independent of concentration. Qualitatively the stain with the two lower concentrations was feinter than the other groups. There was no obvious reason for the low

THICKNESS OF DISCS BEFORE AND AFTER 360 DAYS SORPTION (N=10)

WATER SORPTION

	BEFORE	AFTER	DIFF um	T	P
CLEARFIL	3631	3635	4	0.35	NS
CONCISE	3352	3361	9	0.31	NS
HELIOMOLAR	3605	3609	4	0.24	NS
OCCLUSIN	3531	3525	6	0.17	NS
P-30	3439	3441	2	0.53	NS
PROFILE TLC	3317	3324	7	0.31	NS
SILUX	3358	3357	1	0.41	NS

SILVER SORPTION

CLEARFIL	3660	3665	5	0.27	NS
CONCISE	3440	3448	8	0.62	NS
HELIOMOLAR	3641	3650	9	0.41	NS
OCCLUSIN	3459	3470	11	0.38	NS
P-30	3345	3551	6	0.57	NS
PROFILE TLC	3378	3396	18	0.33	NS
SILUX	3446	3465	19	1.00	NS

NS - Not significant

Table 6-5

RESIN RICH SURFACE

MATERIAL	DAYS	Concentration $AgNO_3$ (Mols/Litre)				
		.5	1	2	3	5
OCCLUSIN	10	10.0	9.9	9.9	9.7	11.5
	26	16.9	16.8	17.8	17.4	16.2
	90	18.7	22.6	20.0	23.4	23.7
P-30	10	23.4	19.4	19.6	22.3	19.4
	26	18.4	20.0	26.3	27.4	26.2
	90	48.2	48.6	54.3	57.6	42.7
PROFILE TLC	10	48.3	52.1	76.4	78.4	74.2
	26	60	96.2	106.2	109.6	111.6
	90	120.1	150	179.2	175.3	176.4
SILUX	10	28.6	38.2	42.3	38.6	38.8
	26	44.2	40	52.6	50.0	49.8
	90	58.9	71.6	70.0	72.6	70.0

Depth of silver sorption layer (um) at 10, 26, 90 days for various concentrations of silver nitrate.

Table 6-6

GROUND SURFACE

MATERIAL	DAYS	Concentration A_gNO_3 (Mols/Litre)				
		.5	1	2	3	5
OCCLUSIN	10	0	0	3.6	5.0	2.4
	26	6.1	5.0	5.0	7.4	9.0
	90	11.2	12.1	11.2	10.0	13.1
P-30	10	0	0	0	8.4	7.6
	26	0	0	13.1	12.2	10.0
	90	18.6	18.6	18.9	18.1	18.4
PROFILE TLC	10	32.3	28.6	38.4	49.3	32.4
	26	30	62.4	68.4	71.4	70.0
	90	94.2	101.6	141.3	136.3	150
SILUX	10	19.4	23.7	26.3	26.8	24.2
	26	17.3	28.6	23.2	29.7	27.4
	90	39.3	48.7	56.7	56.2	53.7

Depth of silver sorption layer (um) at 10, 26, 90 days for various concentrations of silver nitrate.

Table 6-7

ANOVA & SCHEFFE MULTIPLE COMPARISON TESTS (0.5 LEVEL)

RESIN RICH SURFACE

MATERIAL	F	P_F	SS	CONCENTRATION GROUPS				
OCCLUSIN	2.641	.047	NS					
P-30	14.061	.000	1	.05	1.0			5.0
			2			2.0	3.0	
PROFILE	11.041	.000	1	.05				
			2		1.0			
			3			2.0	3.0	5.0
SILUX	3.456	.016	1	.05				
			2		1.0	2.0	3.0	5.0

GROUND SURFACE

OCCLUSIN	2.637	.047	NS					
P-30	1.368	.262	NS					
PROFILE	12.06	.000	1	0.5	1.0			
			2			2.0	3.0	5.0
SILUX	6.124	.000	1	.05				
			2		1.0			5.0
			3			2.0	3.0	5.0

F = F Ratio P_F = Associated Probability

SS = Subset No. NS = No significantly different groups

Table 6-8

result for P-30 with 5 mole/litre at 90 days. The reason for the low depths with 0.5 & 1 mole/litre may have been because the number of silver ions deep to the stained front was too small to aggregate to a "scattering" size. An alternative explanation is that for the silver ions to diffuse into the bulk polymer, an adequate concentration must develop in the immediate subsurface of the composite. This development of a subsurface boundary layer, in equilibrium with the surrounding fluid, was noted in 1955 (Baglee and Long). More recently this two-stage sorption was found in the higher epoxy resin TGMDA [Tetra-glycidyl-methylene- dianilide] (Illinger & Schneider 1980). Higher concentrations would have favoured the formation of such a layer and the threshold would depend on the structure of the material.

<u>DISCUSSION</u> - Sorption in Dental Composites.

Taken together the results indicate that there was a correlation between water sorption and the depth of silver stain, although at present it is not possible to state definitely whether the depth of silver stain indicates the limit of water penetration. Despite the correlations noted in this chapter there are a number of reasons why this may not be the case and these will now be discussed. For five materials there was a similarity between silver nitrate and water sorption. The densities of the two solutions are 1.66 and 1 respectively, therefore if both diffused as simple solutions, for equal masses the volume of sorped water would have been 1.66 times that of silver nitrate (Kulkarni & Mashelkar, 1981). As it is volume rather than mass that determines stain depth this would predict that for the same mass water would pentrate deeper into the material. However if the composite acted as a semi-permeable membrane then the number of silver ions diffusing would have been greatly reduced and the density much closer to that of water. In this case the volumes of diffusant would have been closer and the stain depth more closely related to the penetration depth of water. Epoxy resins have been shown to act as semi-permeable membranes (Fedors 1980a) and the concentration results are direct evidence for this because above a threshold of 1 mole/litre the depth of silver stain was independent of the concentration of silver nitrate.

There is a possibility that the depth of silver stain does not represent the limit of silver ion penetration; but that the concentration of ions deep to the stain was too low to aggregate into large enough particles to cause light scattering. To produce the L alpha peak for silver in the EDX analysis it was necessary to count for 100 seconds over a comparatively large area (50 μm^2). This indicates that the amount of silver present in the stained layer was small and there may have been some undetectable silver ions deep to the stain.

Another explanation for the distribution of staining is that it occured as a result of swelling and accumulation of silver in the solid swollen layer (Fig 2-3). However the increases in thickness after 360 days were extremely small (Table 6-5), and did not correspond with the stain depths. Moores et al (1983) and Hansen & Asmussen (1989) also found that dimensional changes during sorption were extremely small. Therefore it seems unlikely that this could have been responsible for the result.

Water sorption from both the resin rich and ground surfaces was similar (Fig 6-4), whereas the depth of silver stain was greater on the resin rich surface (Fig 5-4). The reason for this is that the penetrant accumulated in filler-resin interfaces. As the resin rich layer has a lower effective area of these interfaces, a fixed volume of silver nitrate could diffuse further in this layer. When the solution had diffused through the resin rich layer into the bulk of the material the two rates approximated and this is seen in Fig. 5-5 A & B where after a slow start the diffusion rates in the ground surface catch up. This finding endorses the view that the resin is the rate controlling factor in diffusion (Maron 1985).

SORPTION KINETICS IN DENTAL COMPOSITES.

When the silver stained layer was first observed its appearance resembled the iodine stain in Case II sorption experiments. Wu and McKinney (1982) stated that pilot experiments had demonstrated "unambiguously that the diffusion of chemicals within dental composites was an extreme case of so-called class-II diffusion".

Although the exact mechanism of Case II sorption is not fully understood, a number of theories have been advanced (Windle 1985). An important factor is the rate of polymer relaxation and segmental motion at the diffusion front. If this is relatively fast compared to the flux of the penetrant then the diffusion front can advance freely, but is limited by the rate of diffusion behind the front. The net result is a concentration gradient of diffusant behind the front and weight gain that is proportional to time$^{0.5}$. In Case II sorption the reverse is true: the relaxation rate is relatively slow and hence the polymer behind the front "fills up" before the front has advanced. There is uniform concentration of penetrant behind the front and weight gain is proportional to time. The two systems are illustrated in Fig 6-8. The importance of relaxation and segmental mobility was demonstrated by Thomas and Windle (1978) when they demonstrated Case II sorption of methanol in PMMA at 24^{o}C but "Fickian" sorption for the same system at 62^{o}C. This was attributed to greater relaxation and mobility at the front as a result of the increased thermal energy of the system (Windle 1984). Before considering the present results it is necessary to summarise the behaviour normally associated with Case II sorption.

These are

1(The mass of absorbed penetrant increases linearly with time.

2(A sharp boundary separates the inner glassy core of unpenetrated polymer from the outer swollen shell and that there is a uniform concentration of penetrant across the swollen layer

3(The boundary advances at a constant velocity.

(Thomas and Windle 1980)

To determine the relation of weight gain with time the following equation was evaluated by plotting Log(Weight gain) against Log(Time). The slope of the regression equals the exponent n.

$$M_t=Kt^n$$

Where

K=constant.
M_t= Sorption at time t

The results are given in Table 6-9

Similarly to determine the velocity of the advancing stain layer the equation

$$D_t=Kt^n$$

was evaluated

Where D_t= Depth of Silver stain at time t

The results are given in Table 6-10

To fulfil the first and last criteria for Case II sorption n should be closer to 1 than 0.5 (Windle 1985). Clearly this was not the case and the values were much closer to 0.5 which corresponds to classical "Fickian"

EVALUATION OF n in $M_t = Kt^n$

By Log (weight) v Log (Time)

RESIN RICH SURFACE

MATERIAL	R^2	Slope$^{(n)}$
CLEARFIL	.93	.49
CONCISE	.22	.22
HELIOMOLAR	.77	.37
OCCLUSIN	.71	.53
PROFILE	.89	.39
P-30	.88	.48
SILUX	.96	.40

GROUND SURFACE

CLEARFIL	.86	.57
CONCISE	.41	.34
HELIOMOLAR	.71	.32
OCCLUSIN	.64	.69
PROFILE	.91	.58
P-30	.83	.61
SILUX	.88	.47

Table 6-9

EVALUATION OF n in $D_t = K_t^n$

BY LOG (DEPTH) v LOG (TIME)

RESIN RICH SURFACE

	R^2	Slope (n)
CLEARFIL	.88	.73
CONCISE	.88	.71
HELIOMOLAR	.94	.73
OCCLUSIN	.96	.54
PROFILE	.88	.73
P-30	.87	.89
SILUX	.97	.83

GROUND SURFACE

CLEARFIL	.65	.72
CONCISE	.73	.64
HELIOMOLAR	.86	.66
OCCLUSIN	.60	.62
PROFILE	.98	.68
P-30	.80	.91
SILUX	.97	.80

Table 6-10

sorption. This corresponds with the findings of previous work on dental composites (Braden and Clarke 1984, Braden 1984, Soderholm 1984, Braden et al 1976, Peterson et al 1966). In a review of water permeability in composites Marom (1985) states that sorption in composites is usually Fickian even when it is anomolous in the pure resin. With these points in mind it is difficult to understand McKinney & Wu's certainty about Case II (1982). However they did not state the penetrant in their pilot studies: as their publication concerned the effect of alcohol on hardness, this may have been the penetrant. As will be discussed in Chapter 7, silver nitrate is soluble in alcohol and with this solution, sorption rates increase. When considering all these results it is important to realise that Case II sorption is a relatively recent concept and far from fully understood. Most of the results are derived from studying the sorption of organic solvents in polymers, which are unlikely to be directly comparable with the sorption of water. In time it may become clear that the important aspect of Case II sorption is that diffusion is constrained by segmental motion at, rather than behind, the diffusion front leading to the step concentration profile seen in Fig 6-8. The importance of segmental motion was found by Migliaresi et al (1984) who studied water sorption in copolymers of MMA and HEMA. They found that increasing the HEMA fraction increased the rate of sorption and most importantly noted a sharp boundary between the swollen and unswollen regions. However the rate of weight gain was proportional to Time$^{0.5}$ and they also concluded that the advancement of the boundary was more important than swelling.

An attempt was made to measure the concentration profile of the silver sorption zone using microradiography and microdensitometry. However, the radiopaque fillers of the composites absorb far more X-Rays than the silver particles and it was impossible to determine the silver concentration by this method. Another attempt was tried using backscattered electrons (in the electron microscope) to produce a map of the silver concentration. This was also unsuccessful because of the small amount of silver present in the samples. Therefore, as yet the concentration profile remains undetermined.

When the position of a penetrant can be visualized in a system it is often located far closer to the surface than might be expected from weight gain experiments (Marshall 1982). Obviously this is an exciting field of research and much more information needs to be aquired as to the exact location of water and other penetrants in dental composites. If, as the silver sorption layer suggests, water does not permeate throughout the composite but localizes close to the surface then this may help to understand the relationship between permeability and wear. It is hoped to continue this work using tritiated water (^3H_2O) and thin film autoradiography.

SUMMARY

The experiments in this chapter indicated that the silver sorption layer may represent the limit of fluid penetration into the material; but this has not been confirmed. The results did not fulfill the three criteria for Case II sorption.

CHAPTER 7

FACTORS EFFECTING PERMEABILITY AND DEGRADATION

INTRODUCTION

Exposure to moisture and heat may result in deterioration of the mechanical properties and integrity of the filling. This "hygrothermal aging" has contributions from both physical and chemical reactions (Marom 1985). Many in-vitro investigations of wear have used recently prepared samples, or ones that had been stored in a static environment. The experiments reported in this chapter used silver nitrate staining to investigate the effects of thermal or mechanical cycling on the surface of composites. In addition, the action of solvents (Food Simulating Liquids) was investigated.

1 THE EFFECT OF THERMAL CYCLING AND TEMPERATURE

Marcos-Montes (1986) found that thermal cycling caused an increase in the solubility and abrasion rate of dental composites. In epoxy resins the combined effect of heat and water caused a network of microcracks throughout the matrix of industrial composites (Kaelble & Dynes 1977) and it was anticipated that these cracks would be susceptible to staining. The effect of thermal cycling rather than constant temperatures was studied because it was more comparable to the clinical situation. A problem with thermal cycling is that it is not possible to distinguish between the effects of cycling from those attributable to the individual temperatures. Therefore a second experiment investigated the effect of temperatures alone. Two additional experiments were performed to enable clinical interpretation of the results. The temperature changes at the surface of a restoration in-vivo were determined and compared with temperature profile in the thermal cycler.

METHODS

Thermal Cycling

Silver nitrate is extremely caustic and it was considered too dangerous to use an open beaker of hot silver nitrate in the thermal cycler. Therefore, the samples were placed with silver nitrate (3 mole/litre) in an opaque plastic bottle. It was anticipated that the rate of temperature change in the bottle would be more gradual than in the open beaker situation. To compare the two situations, a second set of samples was directly cycled in water, after which the testpieces were dried and immersed in $AgNO_3$ for 42 days. The control group was stored uncycled in $AgNO_3$ at room temperature. The thermal cycle was 2.25 min at 60^oC (±1) and 2.25 min at 6^oC (±3) with two changeover times of .75 min. Samples were removed after 4.2, 21, 42 and 210 days corresponding to 1000, 5000, 10,000 and 50,000 cycles. At each time interval nine samples were processed as previously described (Fig 5-2).

Individual Temperatures

Only four materials were used in this experiment (P30, Occlusin, Silux, Profile). Samples were prepared and divided into groups of twelve. One group was placed in a water tight opaque bottle containing silver nitrate and this was placed in a 60°C water bath. Group 2 was placed in a similar container at 6°C. The third group was stored in silver nitrate at room temperature. A fourth group was thermal cycled in silver nitrate for comparison. Samples from each group were removed and processed after 14, 21, 42 and 90 days (Fourteen days is equivalent to the time in the 60°C water bath during 42 days thermal cycling).

Details of these experiments are summarised in Table 7-1

Measurement of Temperature changes in-vivo

A thermocouple probe (KM1202 Kane-May Ltd. Welwyn Garden City. Herts. U.K.) was placed on the surface of a composite restoration inserted into the occlusal surface of a temporary premolar post crown. The volunteer patient was asked to drink some hot soup and then to eat a hot toasted cheese sandwich followed by some ice cream. Finally he was asked to eat part of another hot sandwich. This particular snack was chosen because hot cheese maintains its temperature. The volunteer was asked to eat the food when it was as hot as reasonably possible and to ensure that he bit into both foods with the temporary crown. A second

SUMMARY OF EXPERIMENTAL CONDITIONS

	GROUP NO	**THERMAL CYCLING**				
EXPT 1	1	Stored Uncycled in $AgNO_3$ at Room Temperature				
	2	Thermal cycled in $AgNO_3$ $(60^{\circ}C \leftrightarrow 6^{\circ}C)$				
	3	Thermal cycled in H_2O followed by 42 days in $AgNO_3$				
Samples removed at		4.2	21	42	210	DAYS
Corresponding to		1000	5000	10000	50000	Thermal cycles
		INDIVIDUAL TEMPERATURES				
	GROUP NO					
EXPT 2	1	Stored in $AgNO_3$ at $60^{\circ}C$				
	2	Stored in $AgNO_3$ at $6^{\circ}C$				
	3	Stored in $AgNO_3$ at room temperature				
	4	Thermal cycled in $AgNO_3$				
Samples removed at		14	21	42	90	DAYS
Corresponding to (Group 4 only)		3333	5000	10000	50000	Thermal cycles

Table 7-1

probe of the thermocouple was used to monitor the temperature of the food on the plate.

Characterisation of The Thermal Cycle.

One probe of the multichannel thermocouple was placed on the surface of a specimen in the plastic bottle containing the sample cycling in silver nitrate. A second was placed on the surface of a specimen openly cycling in water and a third was buried in the middle of this specimen. The recording apparatus was set to simultaneously record the three temperatures every 10 sec during immersion and every 2 seconds during changeover.

RESULTS

Thermal cycling and prolonged storage at elevated temperatures produced both quantitative and qualitative effects. The former resulted in increased depth of diffusion whereas the latter caused the formation of different coloured layers in the surface of the materials. The colours observed included various shades of silver, black, yellow, green, orange and brown. The most pronounced example of layering occurred with samples of Profile and Occlusin stored in silver nitrate for 90 days at 60°C. (Plates 66/67, 68/69). In both these materials silver coloured silver appeared in the surface. In two samples of Occlusin the surface layer had "bubbled away" from the underlying material (Plates 68,69). With bright field incident light (Plates 67,69) the silver can be seen reflecting like a mirror.

The results of the experiments are presented separately and followed by an overall discussion. In all experiments standard deviations were within 12% of mean values and are not represented on diagrams.

The Effect of Thermal Cycling

A Thermal Cycling in Silver Nitrate (In the bottle)

The most significant effect of thermal cycling was to increase the depth of penetration of the silver nitrate. The mean depth of the stained zone for the cycled and uncycled samples are given in Table 7-2 (Resin Rich) and Table 7-3 (Ground) The mean depth at 210 days is shown in Fig. 7-1. The depth of stain for the individual materials varied, but in general, the ranking order between materials was maintained, with Occlusin having the lowest and Profile the highest. The depth of stain in the ground surface was less than in the resin rich surface, but (the with exception of Clearfil) thermal cycling decreased the difference and the depth of stain for both surfaces after thermal cycling was similar.

The progression of stain was analysed by linear regression of the depth of stain v $(\text{time})^{0.5}$. The slopes of the regression + R^2 are given in Table 7-4.

The differences in the diffusion rate between cycled and

RESIN RICH SURFACE (UPPER TABLE) DEPTH OF STAINED ZONE (MICRONS) AFTER (N) THERMAL CYCLES IN $AgNO_3$

No. Cycles	1,000	5,000	10,000	50,000
No. Days	42	21	42	210
CLEARFIL	43 (7)	77 (7)	60 (0)	71 (3)
CONCISE	58 (7)	108 (3)	127 (8)	123 (5)
HELIOMOLAR	92 (4)	109 (3)	120 (5)	118 (7)
OCCLUSIN	18 (4)	25 (2)	41 (2)	60 (0)
P-30	20 (2)	53 (7)	79 (6)	137 (10)
PROFILE TLC	42 (6)	231 (3)	248 (3)	399 (3)
SILUX	78 (4)	141 (3)	188 (24)	233 (9)

(LOWER TABLE) DEPTH OF STAIN WHEN STORED UNCYCLED IN $AgNO_3$ AT ROOM TEMPERATURE

CLEARFIL	0 (0)	25 (4)	26 (9)	60 (5)
CONCISE	7 (5)	21 (6)	28 (7)	48 (4)
HELIOMOLAR	3 (3)	10 (0)	20 (6)	36 (7)
OCCLUSIN	0 (0)	12 (6)	15 (2)	20 (0)
P-30	7 (4)	15 (2)	20 (0)	19 (2)
PROFILE TLC	60 (0)	72 (7)	94 (5)	189 (3)
SILUX	30 (2)	38 (4)	49 (7)	90 (5)

Figure - mean value
Figures in parenthesis (standard deviation)
N = 9 for all cells

Table 7-2

GROUND SURFACE (UPPER TABLE) DEPTH OF STAINED ZONE (MICRONS) AFTER (N) THERMAL CYCLES IN $AgNO_3$

No. Cycles	1,000	5,000	10,000	50,000
No. Days	42	21	42	210
CLEARFIL	58 (7)	102 (4)	114 (12)	128 (13)
CONCISE	86 (7)	121 (8)	137 (13)	142 (11)
HELIOMOLAR	133 (10)	122 (7)	131 (8)	122 (8)
OCCLUSIN	24 (2)	31 (2)	41 (2)	74 (5)
P-30	32 (4)	70 (5)	97 (7)	149 (14)
PROFILE TLC	49 (2)	229 (9)	270 (0)	394 (9)
SILUX	170 (0)	197 (21)	198 (14)	241 (3)

(LOWER TABLE) DEPTH OF STAIN WHEN STORED UNCYCLED IN $AgNO_3$ AT ROOM TEMPERATURE

CLEARFILL	33 (10)	74 (9)	76 (5)	12 (7)
CONCISE	22 (4)	46 (11)	45 (6)	64 (6)
HELIOMOLAR	19 (2)	41 (7)	46 (4)	80 (5)
OCCLUSIN	15 (0)	22 (4)	23 (5)	30 (0)
P-30	18 (3)	28 (6)	43 (4)	78 (3)
PROFILE TLC	70 (0)	96 (7)	112 (7)	205 (11)
SILUX	37 (3)	59 (4)	80 (0)	132 (8)

Figure - Mean Value (microns)
Figures in parenthesis (standard devidations)
N = 9 for all cells

Table 7-3

RESIN RICH SURFACE

MATERIAL	SLOPE* ROOM TEMP	SLOPE* T/CYCLED	T CON	T INTER
CLEARFIL	5.2 (81)	4.6 (60)	4.9 [.00]	-1.177 [.24]
CONCISE	2.8 (69)	3.7 (53)	12.35 [.00]	1.25 [.21]
HELIOMOLAR	4.6 (92)	.66 (11)	35.5 [.00]	-13.31 [.00]
OCCLUSIN	1.07 (66)	4.1 (97)	-1.10 [.27]	17.80 [.00]
P-30	4.86 (96)	8.9 (91)	4.16 [.00]	8.327 [.00]
PROFILE TLC	10.9 (97)	24 (83)	1.426 [.15]	7.20 [.00]
SILUX	7.56 (97)	5.3 (79)	32.47 [.00]	-4.23 [.00]

GROUND SURFACE

CLEARFIL	4.4 (89)	1.45 (24)	13.1 [.00]	-5.88 [.00]
CONCISE	3.1 (83)	4.06 (43)	10.4 [.00]	1.16 [.25]
HELIOMOLAR	2.5 (84)	1.65 (42)	30.94 [.00]	-2.43 [.02]
OCCLUSIN	1.3 (61)	3.3 (92)	5.10 [.00]	8.28 [.00]
P-30	.81 (42)	9.0 (95)	0.13 [.89]	21.26 [.00]
PROFILE TLC	10.8 (97)	25 (85)	1.77 [.08]	7.89 [.00]
SILUX	4.9 (95)	11.3 (84)	3.17 [.00]	6.68 [.00]

*Slope of Depth of Stain vs. (Time)$^{0.5}$

Figures in Parenthesis = For Slopes (R^2)
For T Values [P_T]

Table 7-4

uncycled samples was analysed by multiple linear regression entering $(\text{Time})^{0.5}$, condition (cycled or not) and the interaction between the latter two into the regression equation.

$$\text{Depth} = B_{it}(\text{Time})^{0.5} + B_{ic}\text{Condition} + B_{ii}\text{Interaction} + B_{o}$$

where B_i 's = regression coefficients
B_o is the constant.

For all of the uncycled samples the regression line passed close to the origin; whilst the regression line of the cycled samples indicated two patterns of diffusion. In some materials (Occlusin, P-30, Profile and the ground surface of Silux) the diverging regression lines indicated a steady increase in the rate of diffusion with time. The difference in slopes of these regression lines, tested using the T value of the B_{ii} regression coefficient, was highly significant (P=0.000) (Table 7-4). For other materials thermal cycling caused a rapid initial increase in diffusion which then slowed down. The regression line of this pattern showed a high intercept with the slope either parallel to, or less than the corresponding slope of the uncycled samples. The significance of this difference, tested using the T value of the B_{ic} coefficient, was high (P=0.000). These two patterns are illustrated in Fig 7-2.

Qualitatively, thermal cycling in silver nitrate appeared to cause a concentration gradient in the diffusion layer.

Plate 70 shows the stained layer in Silux after 50,000 cycles. Layering was not prominent except in Clearfil which developed a dark surface layer over a golden brown layer after 50,000 cycles (Plate 71).

B Thermal cycling in water +42 days in Silver Nitrate.

With the exception of Heliomolar, the depth of silver stain after thermal cycling was greater than in the unconditioned samples. The stain depths are shown in Fig 7-3. Qualitatively, this treatment resulted in much greater layering than cycling in silver nitrate. (Only in Concise and Heliomolar was no layer present). Plate 72, 73 show Profile and Occlusin respectively both after 50,000 cycles. The development of the surface layer in Silux is seen in Plates 74 & 75, where fronds of green/yellow stain are seen at 10,000 cycles and the whole layer is stained at 50,000 cycles. The colour layers and depths after 10,000 and 50,000 cycles are shown in Table 7-5 (Any discrepancy between the reported colour and that shown in the Plates arises because of the photographic processing).

The Effect of Constant Temperatures

For all materials both heat and thermal cycling increased the depth of the stained layer, whilst a decrease occured at 6^{o}C. The depth of stain after 90 days is shown in Fig 7-4. Layering was most pronounced for those samples stored in silver nitrate for 90 days at 60^{o}C (Plates 66 & 68).

COLOUR LAYERS AND DEPTH OF STAIN (μ m) AFTER (n) THERMAL CYCLES FOLLOWED BY 42 DAYS IN AgNO3

RESIN RICH SURFACE				
CYCLE NO (n)	10,000 cycles		50,000 cycles	
CLEARFIL	DARK BR BROWN	20 70	GREEN/BR BROWN	50 60
CONCISE	BROWN	80	BROWN	90
HELIO	BROWN	40	BROWN	40
OCCLUSIN	YELLOW BROWN	10 30	YELLOW/WH DARK BR LIGHT BR	50 10 10
P-30	BLACK BROWN FAINT	20 30 20	ORANGE/YEL BR/BL FAINT	15 15 15
PROFILE TLC	YELLOW BROWN BR/BL	20 100 40	BRIGHT YEL DARK BR	70 90
SILUX	GREEN/YEL BROWN	25 90	GREEN/YEL BROWN	60 70

GROUND SURFACE				
CYCLE NO (n)	10,000 cycles		50,000 cycles	
CLEARFIL	BROWN	50	BLACK/BR DARK BR	30 50
CONCISE	BROWN	80	BROWN	90
HELIO	BROWN	30	BROWN	35
OCCLUSIN	YELLOW BROWN	10 20	YELLOW/WH DARK BR	40 25
P-30	BLACK BROWN FAINT	15 10 40	GREEN/BR DARK BR	20 5
PROFILE TLC	YELLOW BROWN DARK BR	20 90 40	BRIGHT YEL BROWN	40 120
SILUX	GREEN/YEL BROWN	5 90	GREEN/YEL BROWN	40 90

/ INDICATES A COMBINATION OF COLOURS WITH THE FIRST NAMED COLOUR PREDOMINANT

BR=BROWN BL=BLACK YEL=YELLOW WH=WHITE
FAINT = FAINT TRACES OF LAST NAMED COLOUR

Table 7-5

Thermal Cycler Temperature Changes

The temperature profile of the thermal cycles is shown in Fig. 7-5 and demonstrates that the total mass of the samples cycled in water attained virtually the same temperature extremes although the rate of change was slower deep in the sample. The material used in this experiment was Occlusin, the rate of temperature change in the quartz filled materials may have been faster as a result of their higher thermal diffusivities (Watts et al 1987). For those samples cycled in silver nitrate both the temperature extremes and rates of change were diminished.

Temperature Changes in the Mouth

The results of this investigation are shown in Fig.7-6 and demonstrate that although the temperature of the snack was 90 °C, the surface of the composite did not exceed 55°C, however when in contact with ice cream the surface temperature dropped to 4°C. Drinking hot soup had little effect on the surface temperature. Generally, the rates of temperature change were comparatively low although at the cold/hot transition a rapid change of 30°C occured (arrowed).

DISCUSSION

Silver Staining

Many more colours and layers were observed in these experiments than in the unconditioned specimens (Chapter 5). This was most pronounced in the samples which were stored at 60°C and likely to have undergone surface degeneration. The result supports the hypothesis that the colour of the stained layers depends upon the size of metallic silver grains formed in the degraded surface layers. This discussion will be continued in Chapter 8 which compares the staining effects with SEM's of the same specimens. The appearance of the stained layer in Silux (Plate 70) suggests a concentration gradient in the diffusion zone. This corresponds to the finding of Thomas & Windle (1978) that increased temperatures favour "Fickian" diffusion because of increased segmental mobility at the diffusion boundary. Although "classical" Case II sorption was disproved in Chapter 6, it is still contended that penetrants have a higher concentration in the surface than predicted by the "Fickian" model. The present finding of greater apparent concentration gradients with increased temperatures supports this hypothesis.

The increased depth of stain and layering that occurred after conditioning by thermal cycling and subsequent immersion in silver nitrate indicated that surface changes occurred as a result of cycling rather than through the chemical action of silver nitrate. If the silver colour hypothesis is correct then greater degeneration occurred in the samples cycled in water. The reason is explained in the next paragraph.

There were two main differences between the treatments: firstly the temperature extremes in the silver nitrate bottle were less and the secondly the rate of temperature change was much slower (Fig 7-5). Consequently, the samples which were cycled in silver nitrate warmed up and cooled down more gently whereas the surface of the water cycled samples were subject to an immediate transition from 8°C to 60°C. This sudden transition resulted in thermal shock at the surface and rapid dimensional change of the surface over the unchanged deeper layers. These rapid dimensional changes may have caused microcracking and degeneration of the surface layer. Browning (1978) found that microcracks formed in epoxy resins as a result of repetitive 60°C temperature "spikes"; however in the latter investigation the temperature extremes were much higher (71°C- 148°C). In the present study there was no direct relationship between degradation and the coefficient of thermal expansion [CTE] of the composites: both Heliomolar and Concise (with no layering) have comparatively high CTE's (58 & 37 ppm/°C respectively) compared with Occlusin and Profile (24 & 30 ppm/°C) which showed the most degeneration. Hashinger & Fairhurst (1984) found that the CTE's of dental composites increased in the temperature range 25-60°C; but the rate of increase was proportional to the average CTE across the range. Therefore, it seems unlikely the differential increase in

CTE between materials could account for the changes. Whereas the CTE determines the dimensional change of the material, the progress of heat into the material is determined by the thermal diffusivity. There was no relation between this factor and degradation because Concise has a very high diffusivity compared with Occlusin (Watts et al 1983, 1987), but showed less evidence of surface change.

The results indicated that the effect of thermal cycling was not to sum the effects caused at 60°C and 6°C alone. The cold phase of the cycle "neutralised" the destructive effect of prolonged storage at high temperature. The main effect of cycling was to increase the depth of diffusion and this would have resulted from the well established dependance of the diffusion coefficient on temperature (Windle 1985). This result is extremely important in the interpretation of in-vitro experiments. Occasionally materials are stored at high temperatures to accelerate aging. This has always been open to criticism on the grounds that it is clinically unrealistic. The present finding entirely endorses this criticism.

It is necessary to determine which of the laboratory findings may have clinical significance, increased diffusion depth or microcracking as a result of rapid dimensional change. The graph of the restoration surface temperature (Fig 7-6) more closely resembles the graph of the temperature in the silver nitrate bottle (Fig 7-5).

However, as indicated by the arrows rapid surface temperature change is possible; although this change was produced by the rather false circumstance of the subject biting into hot food immediately after cold. This situation would be infrequent in normal eating. Therefore, it seems that the main effect of temperature change in the mouth would be to increase the depth of penetration of fluids rather than cause degradation through microcracking. It is important to recognise that thermal cycling has been studied in isolation. Clinically, microcracking may be induced by other mechanisms (eg masticatory stress) and subsequently potentiated by temperature changes.

The results of the short clinical experiment are interesting. It was anticipated that the temperature changes would have been much greater. The thermocouple was right at the surface and to check this the crown was removed and placed in a beaker of water at $90^{o}C$. The probe immediately reached this temperature. The reason for the clinical result was given by Jacobs et al (1973). They realised that the temperature rise at the surface depends not only on the flow of the food and thermal diffusivity of the restoration; but also on heat transfer coefficient. This coefficient determines the rate at which heat transfers from one material to another. It was higher for ice cream than for a hot roll with respect to the enamel. The coefficient for gravy was very high but in the present study hot soup had very little effect on the surface temperature, probably because the flow of hot liquid was directed away from the teeth by the soft tissues.

2. THE EFFECT OF MECHANICAL CYCLING.

Locations on the surface of a restoration are subjected to cyclic mechanical stress during mastication or empty movements. Lutz et al (1984) has indicated that the loss of surface in these areas of attrition may be 2.5 x greater than the general loss through abrasion. The experiments in this section investigated subsurface degradation and permeability caused by cyclic mechanical stress.

Pilot Studies

The initial concept was to subject the surface of composites to cyclic compression in a tensile tester and to stain the damaged subsurface with silver nitrate. Initially it was necessary to determine the load, cycle number, cross head speed, shape of the indenter and staining procedures.

Many factors influence the stress vectors at any tooth surface, the most important being the physiological masticatory load and the total area of tooth/restoration surface. Profit et al (1983) found that normal masticatory load on an adult molar during chewing at 2.5mm opening was 130 N ± 104 N. Maximum biting effort caused loads of 300 N ± 200 N. It was decided to use a load of 120 N. Three shapes of indentors were tried as illustrate in Fig. 7-7. The most pronounced stain occurred with the chisel indentor but the shape was not comparable to occlusal anatomy. The indentation made be the U indentor was difficult to identify during sectioning of the testpiece. Therefore the V indentor was selected. Two alternative methods of staining were tried. Firstly staining during cycling (the specimen was immersed in a small stainless steel bath containing silver nitrate during cycling), and secondly after cycling. A much larger area was stained by the latter method and subsequent experiments indicated the maximum staining was completed in 24 hours (this is discussed later). Originally it was proposed to measure the stained area after 500, 1000, and 2000 mechanical cycles; but there was difficulty identifying the stained area in some materials when only 1000 cycles had been completed. Therefore, the cycle number was set to 2000 with a cross head speed of 1 mm/sec.

METHOD

Five disc testpieces (3mm diam x 2.5 mm) of the seven materials were placed in a jig clamped on the compression plate of a tensile tester (JJ Lloyd, Southampton UK). The indentor was slowly lowered onto the surface. The tensile tester was programmed to give 2000 compression cycles between 0 and 120 N with a cross head speed of 1 mm/sec. After cycling all the testpieces were collected and stained in 3 mole/ litre silver nitrate for 24 hours.

The testpieces were sectioned through the indentation scar, embedded and polished as described previously. The stained areas were photographed (in black and white). Negatives were placed in an enlarger and projected onto graph paper. A photomicrograph of the calibrating slide was used for scaling and the cross sectional stained area "calculated" manually.

RESULTS

Plates 76, 77 & 78 show the stained areas for Clearfil, P-30 and Heliomolar respectively. Fig. 7-8 shows the mean and standard deviation of cross sectional damage. (The values for Heliomolar and Silux were 2163 ± 587 and 1064 ± 818 sq μm respectively). Results were analysed by ANOVA using the Scheffe Multiple Range Test. In view of the unequal variances Log values were used in the analysis. The homogeneous subsets are shown Table 7-6.

DISCUSSION

An interesting result from the pilot experiment was that the area of stain caused by cycling in silver nitrate was less than when the specimens were stained after completing the cycle. It appeared that the silver nitrate was absorbed into the layer at a slower rate than the damage was occurring. This indicates that the stress did not cause an advancing network of connected microcracks (Fig. 7-9 A). In the latter case the cracks would have filled up

Cross Sectional Area of Stain After Mechanical Cycling

ANOVA (Log Transform) F=12.86 P=.0000

Sub. Set							
1	Silux (1064)	Helio (2163)					
2			Occlusin (18942)				
3				P-30 (54987)			
4					Profile (194612)	Concise (219486)	Clearfil (225917)

Analysis of Variance and Homogenous Sub-sets determined by Scheffe M.C.T.

Figures in parenthesis = Area of stain [μm^2]

Table 7-6

during each cycle. It appeared that the cycling caused a stress field below the surface which became more permeable with successive cycles (Fig 7-9 B). As staining took 24 hours to complete some of the degradation may have been crazing. This supports the concept of Suh (1977) & Jahnimar & Suh (1977) that fatigue cracks develop in the subsurface rather than at the surface and propagate laterally. Further evidence for this was that, in the pilot experiments, it was often difficult to identify the stained zone after 1000 cycles whereas after 2000 a definite area was present. The MCT indicated four statistically different subsets; but from Fig 7-8 it seems reasonable to combine Occlusin & P30. The materials in the three resulting subsets (1,2,4) have similarities.

Silux and Heliomolar were similar showing very little subsurface stain or evidence of plastic deformation of the surface. It appears that in these microfilled materials compression caused elastic rather than plastic deformation. Oysaed and Ruyter (1986a) found that Heliomolar had a very definite yield point and considered that the material was tough as opposed to the conventional composites which should be regarded as brittle. However, under continuous load the microfilled materials exhibit higher creep than the conventional materials (Cock & Watts.1985); but this was not studied in the present investigation. The materials in Subset 2 (Occlusin, P-30) have similar filler loadings and both use glass fillers as opposed to the quartz fillers of Concise & Clearfil; Profile also has glass fillers and this was in Subset 4. The glass in these materials is different which may explain the result. The average particle size of all the fillers in all the materials in Subset 4 are all larger than those of Subset 2. However, the particles in P-30 are smaller than those of Occlusin and therefore particle size alone doesn't account for the ranking order. Besides the size and type of fillers, the components of the resin are important in the distribution of stress. Occlusin has a modified urethane dimethacrylate which may account for its slightly better performance than P-30. At this stage it is necessary to note the result of the clinical trial (Chapter 9) which found that although Occlusin had superior attrition resistance to P-30; Clearfil was superior to both the latter materials. This illustrates that the experiment reported in this Chapter does not rank the materials according to their clinical performance. The finding that Silux was superior to all the other materials appears to conflict with clinical experience and also with the work of Roulet (1987c) who found large indentations in the experimental microfilled materials which had been subjected to stress cycling. In the experiment of Roulet the attrition scars appeared to indicate that the indentor (Cu-Ni-Zn) had a rough surface compared with with the smooth stainless steel finish in the present study. Also the cycling was performed under water which may have allowed plastic deformation in the microfilled materials.

3. THE COMBINED EFFECT OF THERMAL & MECHANICAL CYCLING.

METHOD

Discs of composite were thermal cycled in water for 210 days (50,000 cycles), then mechanically cycled and stained as described in the previous section.

RESULTS

Plates 79, 80, 81 show Profile, Occlusin and Silux after this treatment. The staining resulting from mechanical cycling appeared to be superimposed on the effect of thermal cycling but there did not appear to have been any interaction. Table 7-7 gives mean values and the results of a Behrens-Fisher T test for equality of means. The result indicates there was no difference for any materials.

DISCUSSION

This result suggests that the degradation caused by thermal cycling is confined to the surface layer and that degradation is not potentiated by compression. The results from the first section of this chapter indicated that the thermal cycle used in this experiment was more severe than the clinical situation. Therefore it seems reasonable to conclude that temperature changes in the mouth do not potentiate attrition.

COMPARISON OF MEAN DEPTH OF DEGRADATION [μm^2]

WITH AND WITHOUT THERMAL CYCLING

MATERIAL	Without T/Cycles	With T/Cycles	T	P_T
CLEARFILL	225917	208176	0.18	NS
CONCISE	219486	198437	0.31	NS
HELIOMOLAR	2163	3178	.91	NS
OCCLUSIN	18942	30097	1.21	NS
P-30	54987	27361	2.15	.060
PROFILE	194612	200614	0.13	NS
SILUX	1064	1041	.04	NS

T / Cycles = Thermal Cycles

T = T value from Behrens - Fisher Test

P_T = Probability of T

NS = Not Significant

Table 7-7

4 THE EFFECT OF FOOD SIMULATING LIQUIDS ON PERMEABILITY AND DEGRADATION.

Food simulating liquids (FSLs) are solvents recommended by the Bureau of Food, Food and Drug Administration USA (BFFDA 1976) as suitable to simulate various types of food. The main purpose of FSLs was to enable manufacturers of food packaging to test the reaction between their material and foodstuffs. McKinney and Wu (1985) investigated the effect of two FSLs, ethanol (which simulates food containing alcohol) and n-heptane (which simulates fatty foods) on surface hardness and wear. They found that 75% ethanol caused the greatest softening and increase in wear, whereas heptane had no effect. Pilliar et al (1987) reported that aging in ethanol increased the fracture toughness of dental composites by plasticisation at the crack front. Wu et al (1982) noted that the effect of alcohol was reversed by reimmersion in water. The experiments reported in this chapter investigated the effect of ethanol and heptane on permeability and degradation. As silver nitrate is soluble in ethanol, but not in heptane, two experiments were necessary, firstly to compare the penetration of aqueous and alcoholic solutions of silver nitrate and secondly to determine the degradation caused by conditioning in alcohol or heptane. In the latter experiment the four materials used by McKinney and Wu (1985) were investigated alongside the usual seven.

The additional materials were

Adaptic (Johnson and Johnson,Slough UK.).
Profile [Chemical Cure] (SS Whites, Philedelphia USA.).
Prisma-fil (L.D. Caulk, Milford Delaware, USA.).
Silar (3 M Company, Minnesota, USA.).

METHODS

i(The penetration of an alcoholic solution of silver nitrate.

Samples of each material (Fig. 5-3) were prepared and placed in a solution prepared by a 50% dilution of absolute ethanol with 5 mole/litre $AgNO_3$. Samples were processed, photomicrographed and measured after 10, 26, 42, 90, 180 and 360 days.

ii(Conditioning of composites in ethanol or heptane.

Samples were prepared and placed in 50% ethanol, n-heptane or water for 42 days, removed, washed and dried. Subsequently they were stained in silver nitrate (3 mole/litre) for 42 days.

RESULTS

i(Penetration depths in alcoholic vs. aqueous silver nitrate

Quantitatively stain depth with the alcoholic solutions was far greater than with the aqueous solutions. The slopes for the resin rich surfaces of Profile, Silux and P-30 are shown in Fig. 7-10 A and for the ground surface of

Heliomolar, Concise and Occlusin in Fig. 7-10 B To compare the pattern of diffusion between the two solutions the equation

$D = Kt^n$ (see chapter 6)

was evaluated.

The results are given in Table 7-8 (the n values for the aqueous solution are from Table 6-10) and indicate that the progression rate of the stained boundary for alcoholic solutions was approaching unity. Qualitatively the colour of the stained layer was darker with the alcoholic solution; but layering was not a significant feature. Plates 82/83 show Heliomolar and Occlusin respectively after 360 days in alcoholic silver nitrate.

ii(Conditioning in food simulating liquids)

The results of conditioning in water, heptane or 50% ethanol are given in Table 7-9 & Fig. 7-11. Table 7-10 and Fig 7-12 show the results for the four additional materials. The standard deviations were all within 10% of means and are not shown. It is apparent that alcohol had the most effect, increasing the depth of stain by a factor of 3 (except for Heliomolar) (Plates 84/85, 86/87). The Behrens-Fisher T test was used to test significance between the groups conditioned in water and heptane. Although the differences with heptane appear small, the values were significantly different because the standard deviations

Evaluation OF $D = Kt^n$ for Aqueous and Alcoholic Solution

	AQUEOUS		ALCOHOLIC	
	Slope (n)	R^2	Slope (n)	R^2
Clearfil	.73	.88	.89	.92
Concise	.71	.88	.98	.94
Heliomolar	.73	.94	1.0	.96
Occlusin	.54	.96	.85	.86
P-30	.73	.88	.92	.90
Profile TLC	.73	.87	.98	.96
Silux	.89	.97	.96	.97

(Top) Resin Rich Surface

Clearfil	.72	.65	.84	.85
Concise	.64	.73	.96	.85
Heliomolar	.66	.86	1.05	.93
Occlusin	.62	.60	.85	.91
P-30	.68	.98	.91	.93
Profile TLC	.91	.80	.99	.59
Silux	.80	.97	.91	.98

(Lower) Ground Surface

Table 7-8

DEPTHS OF SILVER NITRATE STAIN AFTER PRECONDITIONING IN 3 SOLUTIONS (μm)

MATERIAL	42 Days in water +42 Days $AgNO_3$	42 Days in heptane +42 Days $AgNO_3$	42 Days in alcohol +42 Days $AgNO_3$	Ratio Depth Alcohol/ Depth Water
CLEARFIL	53	60	136	3.1
CONCISE	57	59	162	2.8
HELIOMOLAR	37	59	77	2.1
OCCLUSIN	20	20	76	3.8
P-30	38	50	109	2.9
PROFILE TLC	120	169	359	3.0
SILUX	50	97	172	3.44

(Top) Resin Rich Surface

CLEARFIL	26	34	71	2.7
CONCISE	37	45	133	3.5
HELIOMOLAR	21	30	71	3.3
OCCLUSIN	10	15	69	6.9
P-30	26	32	87	3.3
PROFILE TLC	108	157	357	3.3
SILUX	43	79	186	4.3

(Lower) Ground Surface

Table 7-9

DEPTH OF STAIN IN THE FOUR "ADDITIONAL" MATERIALS (μm)

MATERIAL	42 Days in water +42 Days $AgNO_3$	42 Days in heptane +42 Days $AgNO_3$	42 Days in alcohol +42 Days $AgNO_3$	Ratio Depth alcohol/ +42 Days $AgNO_3$
ADAPTIC	37	39	137	3.7
SILAR	64	61	157	2.4
PRISMA-FIL	20	25	40	2
PROFILE CHEM	69	70	176	2.5

(Top) Resin Rich Surface

ADAPTIC	34	30	134	3.9
SILAR	48	49	160	3.3
PRISMA-FIL	10	15	37	3.7
PROFILE CHEM	50	65	184	3.68

(Lower) Ground Surface

Table 7-10

were small. There was some evidence of a surface layer after conditioning in alcohol; but no definite layering. In Plate 86 there is evidence of a swelling crack (arrowed).

DISCUSSION

The results indicated that 50% ethanol diffused into composites at a greater rate than water. As the rate of the advance of the stain boundary was close to unity (Table 7-8) the diffusion of this solution fulfilled two of the requirements for Case II sorption. In many ways this experiment resembled those of Thomas and Windle (1978, 1980) except that an ethanol solution of silver nitrate was used as opposed to a methanol solution of iodine.

The conditioning experiment indicated that both alcohol and heptane caused permanent changes in the composite surface which subsequently allowed greater diffusion of silver nitrate. Although the stain depth increased, layering was not a prominent feature with this treatment. Mc Kinney & Wu (1985) ranked the hardness ratio of four materials before and after conditioning in 75% alcohol. The decreasing ranking order was Adaptic, Profile (Chem), Silar & Prisma-fil. If the same materials are ranked by the ratio of depth of stain with ethanol to depth of stain in water, the ranking is identical. This may indicate that the latter ratio is an indicator of the effect of ethanol in a material. Assmusen (1984) found that materials with low TEGDMA/BIS-GMA ratio's were more susceptible to softening by ethanol. He postulated two causes: firstly that the solubility parameter was related to the TEGDMA/BIS-GMA ratio, and secondly that softening occurred as a result of the interaction between ethanol and the unreacted double carbon bonds. A possible explanation for the increased diffusion may have been that ethanol reacted with the double bonds reducing the inter-chain Van de Waals forces and increasing segmental mobility. However, it must be remembered that with the conditioned specimens, the increase in diffusion depth occured after the alcohol had evaporated out of the testpieces. Also there was no relationship between the increases in depth of stain noted in this study and the degree of conversion of the materials given by Ruyter (1985). It therefore seems more likely that the explanation of an increased solublity parameter was the reason. McKinney (1985) also attributed matrix degeneration primarily to the solubility parameter. This also explains the darkened colour of the sorption zone because larger silver crystals could form in the enlarged microcavities caused by solution of the matrix. McKinney also noted the possible degradation of glass fillers as a result of hydrolysis of the silane bonds as described by Charles (1958). Although the effect of heptane was much less than that of ethanol it did increase the diffusion depth. The small darkened layer at the surface of these samples may indicate that heptane acted as a solvent at the surface; the increases in stain depth being accounted for by this damaged layer. Heptane was supposed to simulate the effect of fatty foods but in the very recent publication of the United States Division of Chemistry and Technology (Sept 1988) it has been replaced by corn oil. The effect of this new FSL is to be investigated.

SUMMARY

The experiments in this chapter investigated some of the physical and chemical agents that might effect a composite restoration in the mouth. Although it was possible to cause considerable degradation of the surface by extended storage at 60°C or high rates of temperature change; the clinical experiment indicated that these processes are unlikely to be effective clinically. The temperature fluctuations in the mouth may increase the depth of penetration of oral fluids. Mechanical cycling caused deeper penetration in the region close to the point of application of the load. The area of penetration was highly dependant upon the individual material. Thermal cycling did not potentiate the effect of mechanical cycling. The Food Simulating Liquid ethanol increased the depth of penetration of the silver stain. Both ethanol and heptane caused chemical degradation of the surface which potentiated the subsequent penetration of fluids.

CHAPTER 8

ELECTRONMICROSCOPY

The investigations reported in this chapter are in three sections. Firstly, analysis of the element profiles of composites by energy dispersive analysis (EDX); secondly, the identification of silver particles in polymers and thirdly, the electronmicroscopic appearance of the stained layers which had been observed with light microscopy.

1. EDX ANALYSIS

It was hoped to identify the materials of the composite "biopsies" reported in Chapter 4 because this would have helped to establish whether individual materials were more prone to degradation. By light microscopy many of the composites had a similiar appearance and it was impossible to distinguish between them. The rationale behind this experiment was to establish EDX "finger prints" of commercially available composites for comparison with the "prints" of the biopsies.

Energy Dispersive Analysis by X Ray (EDX)

When the electronbeam of an electronmicroscope collides with the specimen, electrons from the specimen are removed from their orbit. Electrons from a higher energy shell "drop" to fill the gap liberating a precise amount of energy as X-rays. Each atom has a characteristic emission

(KeV) and this is used to determine the elements present in the specimen (Robinson 1982). Quanta of energy are released for each electron orbit of the atoms and these give corresponding peaks (K, L etc).

METHODS

Small discs (2.5 mm dia x 2.0 mm) of the commercial materials were prepared, carbon coated and examined with the microscope in its scanning mode (Joel 100 CX). The scanning area was set to 10 sq µm and counting continued until the relevant peaks were visible above background emission. Thin sections of the "biopsies" were analysed in a similar manner.

RESULTS

In the interpretation of these results it is important to note that the relative size of the peaks for individual elements do not indicate their density in the material. This is because the potential for electron displacement in individual elements varies as a result of their electron configurations.

Commercial Products

Peaks were identified for all the individual elements stated in the manufacturers literature together with a few "unexpected" elements. Plates 88 - 95 show the traces for Clearfil, Occlusin, P-30, Concise, Heliomolar, Profile, Prisma-fil and the glass ionomer Ketac-Fil. The major elements identified in the materials are given in Table 8-1.

Clinical Biopsies

The analysis of the biopsies was of limited value because the majority of materials were quartz filled anterior composites with similar profiles. Plate 96 shows an early result taken at the stained edge of a specimen (V40). The calcium and phosphorus peaks are characteristic of calcium phosphate and at first it was thought that "calculus" had formed in the micropores of the degenerated composite. However, as discussed in Chapter 4, the correct explanation was the presence of a thin layer of calculus on the specimen edge. The very prominent peak for silver was also indicative of surface silver compared to Plate 97 which shows the rather imprecise evidence of silver in a specimen. The specimen (V32) in Plate 97 was confirmed as a glass ionomer by the peak for calcium. The majority of the composites had the pattern shown in Plates 98 and 99 with a single peak for silicon. This peak was characteristic for the quartz fillers of the early composites: Adaptic, Concise, Exact and Smile. The material in Plate 99 was a microfilled composite. This was obvious with light microscopy; but there was no apparent difference in the EDX between this material and one with conventional fillers (Plate 98). Another microfilled material is shown in Plate (100). This has a peak corresponding to the L emission for ytterbium. Plate 101 shows the profile of a

ELEMENTS IDENTIFIED IN COMMERCIAL COMPOSITES BY EDX

MATERIAL	ELEMENTS	
Adaptic	Silicon	
Concise	Silicon	
Clearfil	Silicon	
Heliomolar	Silicon	Barium Zinc Lanthanum
Occlusin	Silicon	Barium Zinc Aluminium
Miradapt	Silicon	Aluminium Barium
P-10	Silicon	
P-30	Silicon	Aluminium Zinc
Prisma	Silicon	Aluminium Barium Zinc
Profile-Chem	Silicon	Aluminium Strontium
Profile TLC	Silicon	Aluminium Strontium
Silar	Silicon	
Silux	Silicon	

Table 8-1

composite with conventional fillers including barium.

DISCUSSION

As a means of identifying the composites in the silver staining experiment the EDX was not very helpful. The original quartz filled composites had similar EDX profiles and it was impossible to distinguish between them. Although this part of the investigation was not successful, the ability to detect characteristic elements may be of greater benefit in the retrospective analysis of the present generation composites. These have many different types of fillers which give characteristic emissions.

Whether EDX is the best method of analysis is questionable. With the technique a number of peaks are possible for each orbit of electrons. In Plates 89/90 it is impossible to determine whether the left side Zn peak was the $L\alpha$ peak for zinc or the $K\alpha$ peak for Aluminium which both occur at 1.0 KeV. The decision that it was zinc depended upon the presence of the $K\alpha$ peak for Zn at 8.6 Kev. Barium and lanthanum also have $L\alpha$ peaks which are very close. Alternative methods of analysis were reported by Lilley & Molokhia (1986), Molokhia and Lilley (1986) who used neutron activation; and Oysaed and Ruyter (1986b) using optical emission spectroscopy. Both these studies were concerned with trace elements rather than expected elements. An important factor has emerged during the present study which must be taken into consideration. The analysis of one material indicated the presence of aluminium although it was not expected from the manufacturer's literature. This was explained to the technical department of the company concerned. In confidence an employee revealed that the company share a crucible with another firm who use alumino-silicate glass. He was sure that there was sufficient "cross-contamination" to allow detection by EDX. Obviously if this practice is common then identification by trace elements would be impossible.

In the present investigation a peak for ytterbium was noted in the sample (V34)(Plate 100). There was a peak for zinc and silicon which was characteristic of Heliomolar (Plate 92). Lilley & Molokia (1986) found ytterbium in Heliomolar, but the sample V34 was an anterior restoration and too old to have been this material. It may have been an anterior composite made by the same firm (Vivadent). This investigation also noted peaks corresponding to lanthanum (Plates 92/101). The element antimony noted by Molokia and Lilley (1986) was not identified.

The fillers in the present generation composites vary macroscopically in their size and distribution. Observation of the latter detail by light microscopy appears to be the best initial approach to identification followed by some procedure for element analysis. Perhaps the most important factor is that dentists should always record the brand of material which is essential for retrospective analysis.

2. DETERMINATION OF SILVER PARTICLE SIZE AND DISTRIBUTION

Having discovered the silver sorption layer in dental composites and postulated the cause to be light scattering; it was necessary to determine the size of the silver particles. Mie theory predicts a particle size of 1-40 nm: gold particles of this size had been observed in a hydrosol by Morris & Collins (1964) using Transmission Electron Microscopy (TEM). Dental composites cannot be prepared for TEM because the filler particles are far larger than the thickness of the sections (100 nm). Consequently it was hoped to observe the diffusion layer in unfilled polymers that could be sectioned. Rectangular samples of Perspex (ICI), Araldite MY 753 (Ciba-Geigy) and Spurr's resin (Spurr 1964) were immersed in 3 mole/litre silver nitrate, removed and processed for light microscopy at monthly intervals. A dark black stain was apparent in MY-753 at 1 month; but no stain occurred in the other polymers until 1 year when a thin brown stain was present in Spurr's resin. The stained layer in the two materials is shown in Plates 102/104. Silver-gold sections of both materials were cut in an ultramicrotome (Ultracut-E, Reichert-Jung Vienna, Austria), placed on copper grids, and viewed by TEM (Jeol 100CX). The results are shown in Plates 103/105. The particles causing the brown stain were of uniform size and symmetrically distributed (Plate 105) whereas the "black particles" were of varying size and higher density (Plate

103). The size and distribution of these particles support the theoretical model proposed in Fig 5-10.

3. SCANNING ELECTRON MICROSCOPY OF DEGRADATION

Specimens were mounted on aluminium SEM stubs and splutter coated with gold (EMscope AE 1231, Kent, UK). The scanning electron microscope was a Joel JSM-35C with anode voltage 15 KV.

Electronmicroscopy of degraded surfaces

Surface preparation has a profound effect on the appearance of the section. This is illustrated in Plates 106 and 107 which show Profile prepared by wet grinding on 1200 (UK) grit and polished with 1 µm alumina respectively. It is apparent that polishing preferentially abrades the matrix and polishes the fillers. The preparation effect with degraded surfaces can be seen in Plates 108 and 109 which show Profile preconditioned by 50,000 thermal cycles in water and corresponding to the light micrograph (Plate 72). Although surface degradation is apparent in the ground section (Plate 108) the preferential abrasion of this layer shows more clearly in the polished section (Plate 109). However, polishing tends to "fill up" holes caused by particle displacement. Plate 110 shows a similar section polished on 1µ alumina for longer and then placed in an ultrasonic bath for 2 minutes. Both plates 109 and 110 indicate the surface slope that occurs because of preferential abrasion of the specimen edge.

Thermal cycling.

Plate 111 is a higher magnification of the degraded surface. As noted by Marcos-Montes & Draughn (1985), thermal cycling caused dissolution of the matrix and microcracks at the filler matrix interface. The polishing process 'plucks' out fillers from the degraded matrix (O'Brien & Yee, 1980) and the corresponding holes are clearly visible. The areas corresponding to yellow and brown silver stain by light microscopy are marked on Plate 109. It is apparent that yellow silver stain corresponds to considerable degradation whereas the brown layer has no characteristic features by SEM. Clearly, the surface damaged layer does not correspond with the level of fluid penetration caused by thermal cycling. Although Plates 109, 110, 111 indicate considerable surface degradation, the experiments reported in Chapter 7 indicated that the treatment of these specimens was far more severe than would occur clinically. The effect of cycling in silver nitrate, which is more comparable to the clinical situation, is shown for Profile in Plate 112. Although the appearance is different from the unconditioned material (Plate 107) there is no evidence of microcracking and filler displacement. Plate 113 shows Clearfil after the same treatment: with light microscopy this material had a definite black surface layer (Plate 71); but there was no obvious change on the SEM. The large "holes" may be an indication of interfacial degradation allowing displacement of the larger filler particles. However, there is no obvious difference between Plates 114 and 115 (corresponding to the black surface layer and the deep unstained material), nor any evidence of microcracking in the surface layer. The white "flecks" in Plate 114 may be deposits of silver (this is discussed later). To illustrate the severe effect of cycling directly between 6°C and 60°C Plates 116 and 117 show Silux after 10,000 and 50,000 thermal cycles respectively. The degradation after 10,000 cycles was localised and corresponded to the coloured fronds seen with light microscopy. Microcracks were evident at the prepolymerised particle interface. After 50,000 cycles there was considerable degradation. The degraded surface layer has partially polished away and microcracks are seen extending into the bulk of the material. Microcracking and displacement of fillers is typical of hygrothermal aging (Marom 1985, Kaelbe & Dynes 1977); but the experiments reported in this thesis indicate that this is unlikely to occur clinically.

Mechanical cycling.

Plate 118 is exactly the same specimen seen in Plate 76 (the left side of the indentation). Careful examination reveals tiny microcracks in the material (arrowed). These are shown by higher magnification in Plate 119. The appearance of the crack is characteristic of a craze having filaments of polymer across the gap (Kambour 1973).

However, the size of the structure is far greater than that usually associated with crazes (20-40nm). Although small cracks (as illustrated in Plates 118 & 119) were found in the materials which had the greatest volume of staining (Chapter 7, Table 7-6 Subset 4), they were not present on every specimen of these materials. No specimens indicated a radiating network of microcracks and the cracks appeared to be in the subsurface and to radiate upwards. This supports the fatigue theory of Suh (1977) and Jahminar & Suh (1977). When present, cracks tended to pass along the filler resin interface (Plate 119). This was found to be characteristic of fracture surfaces in conventionally filled composites (Pilliar et al. 1986) although Lloyd & Mitchell (1984) noted that some resin remained adherent to the particles. With P-30 and Occlusin there was little evidence of cracks. Plate 120 shows P-30. Although there was some evidence of crack formation (arrowed) in the area corresponding to the stained zone (Plate 77) it could be a polishing effect. There was no evidence of microcracking in the microfilled materials (Plate 121).

Effect of alcohol

Whereas with silver nitrate and light microscopy there was obvious evidence of penetration (Plate 83), with electronmicroscopy there was little evidence of the effect of ethanol (75%). Plate 122 and 123 show an unconditioned specimen of Occlusin and a specimen after 360 days in 75% ethanol. Although there is no macroscopic difference, the lighter contrast area (LL) may indicate a preferential polishing of this area as a result of matrix softening. Whilst not disputing the finding of Kao (1989) that ethanol caused some dissolution of the matrix at the surface, there was no evidence of degradation in the subsurface.

Evidence of Silver Particles

When the silver sorption layer was first discovered it was postulated that the silver crystals formed in microcavities within the matrix. Browning (1978) had noted micropores associated with microcracks in epoxy resins after hygrothermal aging. However in dental composites there was evidence of these pores in the unconditioned material. Plates 124 & 125 show unconditioned Silux and Profile respectively (x7200). There were obvious pores in the material and the pore sizes in Silux appeared to be uniform in size in the region of 40 nm which corresponds to brown scattering size for silver particles. An alternative explanation is that the pores represent displaced colloidal silica particles (d = 40 nm). The pores in Profile were larger and more irregular. It would be convenient to postulate that silver particles grew in these pores; but high powered magnification of the silver sorption zone indicated a range of particles which did not correspond with the porosity. Plate 126 shows the silver sorption zone in Profile. A range of particles were present together with open pores (arrowed). Plate 127 shows a similar situation in the silver sorption zone of Occlusin where the open pores are more numerous. Some of the particles may be silver; but similar particles were evident in the unstained Profile specimen (Plate 111) which had not been in silver nitrate. It is probable that some of these particles are polishing debris. The silver particles in the silver layer that formed after 90 days in silver nitrate at 60°C (Plate 66) were very obvious with the scanning electron microscope (Plates 128/129). These ranged in size from 0.02 - 1 micron. They do not appear to be in obvious flaws within the composite. In Plate 128 small 'white' particles are in the layer corresponding to the golden yellow layer (Plate 66). Although these may be silver particles which developed as a result of silver sorption an alternative explanation is that they were smeared over by the polishing procedure.

SEM of composite 'Biopsies'

Scanning electron microscopy did not reveal any definite microcracks in areas corresponding to black or brown silver stain in the subsurface. Plates 130 and 131, corresponding to light micrographs 31 and 32, show specimen V23. It is interesting to note that there was little evidence of surface protruding particles. This may be explained because this was the labial surface of a Class 111 restoration and not vulnerable to the masticatory slurry. Plates 132 and 133 show a microfilled material (the large voids indicate a two paste chemically curing material). In this specimen there was evidence of abrasion of the surface matrix but no evidence of subsurface microcracks.

Of the four biopsies which had a stain depth greater than 900 microns, two were identified as glass ionomers. Plates 134 and 135 show the SEMs of the two composites (V9 and V26) corresponding to plates 47/49 and 48/51. In both specimens there was a network of microcracks. In the conventionally filled material (Plate 134) the cracks were distributed throughout the stained zone. It is suggested that the cracks were induced by swelling stresses as the oral fluids permeated the material (Windle 1985). The presence of the cracks may have been responsible for the great depth of stain in this specimen because silver nitrate would have perfused through the cracks by capillary action. An alternative explanation was that the material was a glass ionomer; but the presence of an unstained core and no calcium peak on the EDX analysis made this unlikely. Why this material should have cracked in this way remains unknown. The cracks in the microfilled composite were more limited and certainly not responsible for the stain which occurred all round the specimen (Plate 48). The local cracks may have been in a zone of attrition but there was no evidence of a definite attrition scar.

The mechanism of silver crystal formation.

In Chapter 5 it was noted that ionic silver Ag^+ is reduced to metallic silver Ag by daylight after the testpieces have been removed from silver nitrate. Therefore, the amount of silver available for crystal growth is determined by the size of microcavities and the rate at which silver nitrate can diffuse into the cavities from the free volume of the resin. Obviously the amount of silver nitrate present in any particular pore cannot support the growth of a crystal equal to the pore size. Therefore, in the plates 114, 126, 127 the silver doesn't fill the pores. It was noted that two materials (Profile, P-30) often appeared dark on removal from silver nitrate indicating reduction of the Ag^+ ions during storage. This situation was accelerated when the silver nitrate was at 60°C enabling larger crystals of silver to form in the enlarged microcavites caused by degradation (Plates 128/129).

A comparison of light and electron microscopy

The "starting point" of all the investigations reported in this thesis was to examine the silver staining technique of Wu and Cobb (1981). Although many researchers have used scanning electron microscopy to observe composite surfaces after in-vivo wear (Abell et al 1983, Xu et al 1984, O'Brien & Yee 1980, Leidal et al 1985); there has been little investigation of the subsurface. The work reported in this chapter was intended to complement the light microscopy and not as an exclusive SEM investigation. From these initial experiments it appears that light microscopy with staining is useful for the identification of permeability layers and degradation, whereas SEM investigates the structure of the degraded material. This can be understood by comparing plates 74 & 116, 72 and 110/111, 76 and 118/119. SEM gives an indication of three dimensional effects such as cracks, but is unable to detect the ultra structural changes that allow increased diffusion. This can be seen by comparing Plates 83 which shows the increased permeability of alcohol with the corresponding SEM (Plate 123). The results of this study indicate that both techniques should be used in the study of degradation. Chapter 10 reports on the analysis of restorations which "failed" on the clinical investigation.

CHAPTER 9

THE CLINICAL INVESTIGATION

INTRODUCTION

At present the clinical performance of dental materials can only be established by a clinical trial. An extensive evaluation of three posterior composites (Clearfil, Occlusin and P-30) and two amalgams[1,2] had been commissioned by the Department of Health and this was the basis of the clinical investigation reported in this chapter. Restorations were placed by three dentists and these were designated CRA, PRA 1 and PRA 2 (Clinical Research Associate - L H Mair, Practitioners 1 & 2). Both practitioners placed the restorations at their practices in Merseyside. The CRA was responsible for the day to day management of the trial and for data processing. The remit of the investigation was to evaluate the likely performance of the materials if they were approved for use within the NHS. To this end the two practitioners were asked to use the materials as they would in a busy general practice. The CRA was told to use rubber dam and asked to work at a rate compatible with placing 150 restorations within four months. As the protocol was therefore "flexible", at the end of the placement stage the CRA designed a questionnaire

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1. New True Dentalloy, SS Whites, Harrow, UK.
2. Solilia Nova, DeTrey, Weybridge, Surrey.

to determine the clinical procedures adopted by each operator. All restorations were placed within the first five months of 1985.

Indirect Evaluation

As discussed in Chapter 2, chairside evaluation is of limited value in the assessment of wear. Models were prepared for the indirect measurement of both abrasion and attrition. In addition, as part of the contract, epoxy resin replicas were examined by scanning electron microscopy at each recall.

Impressions and Models

Epoxy resin models (MY 753 , Ciba-Geigy) were prepared for the SEM studies and stone models (Vel-mix, Kerrs, Peterborough UK.) for wear measurement. In the preparation of replica models the surface detail of the impression is of vital importance. Abell et al (1983) and Smith et al (1987) found that a preliminary impression was necessary to remove surface plaque and debris. Whilst not disputing this; it was felt that as the majority of impressions would be taken within the busy schedule of general practice, the double impression would have been too time consuming. There has been some discussion regarding the accuracy of replica models: Lilienthal (1977) quoted an accuracy of 0.1 µm and Lambrechts et al (1981) achieved 0.24 µm using copper plated impressions. Vossen et al (1985) were unable to reproduce this degree of accuracy and indicated that 0.3

µm was a more realistic figure. As abrasion is determin to an accuracy of 25 µm and attrition to 35µm (Lambrechts et al 1984), these sub-micron variations may be ignored in the measurement of wear. With any replication technique it is necessary to ensure no reaction between the impression and model material. Extensive pilot investigations indicated that the addition silicone impression material Reprosil (DeTrey, Weybridge, Surrey) and MY 753 were compatible.

Measurement of Abrasion.

As discussed in Chapter 2, the most commonly used technique for the measurement of clinical abrasion is the "Goldberg" technique (commonly called the Leinfelder technique). This involves establishing a set of standard models having 100µm increments of marginal wear. Abrasion is then measured by categorising the model under consideration to the nearest standard model, or placing it in a "between" category. As there are 10 possible intervals (0, 50, 100, 150, ... 500 µm), Leinfelder et al (1986a) considered that this could be classed as ratio rather than categorical data. In view of the large number of restorations in the present study it was hoped to establish a set of reference models early in the trial so that abrasion could be measured at each six month recall. With this in mind the margins of all the one year models were examined with a stereomicroscope. Abrasion was not uniform around the margin: in some cases the buccal margin had abraded more than the lingual, or vice-versa and sometimes abrasion was localised to one specific area (Plate 136). This irregularity of the margin was noted by Mc Comb (1985) at the International Conference on posterior composites (St Maarten, Netherlands) and she commented that it compromised the precision of the "Goldberg" technique. Vann et al (1988) also reported problems and found it necessary to resort to "mental averaging" of the wear at individual parts of the margin prior to categorising the model. It was felt that an alternative method of measurement was necessary.

To allow measurement of enamel exposure by each cusp a stone "step-wedge" was fabricated with 100 µm steps up to 500 µm (Plate 137). The device was first made in aluminium by precision milling steps into five separate wedges. These were cemented together and an impression taken with a hydrophilic polysulphide impression material (Permalastic, Kerrs, Peterborough UK.). The impression was cast in exactly the same die stone as the restoration models. This is of extreme importance because visual acuity is affected by the colour and texture of a surface (Brill 1980, Moffa and Lugassy 1986). After casting, the stone wedge was trimmed to 1 cm width x 0.6 cm depth. The step wedge was permanently mounted in the field of view of a stereomicroscope (x10) and the hand held model moved to focus exposed enamel alongside the wedge cusp by cusp.

Four measurements were made for each large molar restoration, one by each major cusp, while for premolars and small molar cavities only two measurements were possible. As with the "Goldberg" technique it was possible to allocate a "between" score resulting in 10 possible categories for each location. Overall abrasion per restoration was taken as the mean of the four (or two) measurements. Although this data was strictly speaking discrete with 12.5 micron intervals, it was considered justifiable to regard it as a random varible in the statistical analysis. There is considerable "a priori" justification for this as the "Goldberg" technique gives discrete 50 micron intervals and this has usually been used as ratio data (Leinfelder et al 1986a, Boksman et al 1986, Sturdevant et al 1986,1988, Robinson et al 1988, Wilson et al 1988 a&b). To assess the precision of the technique, all the models of the CRA were measured independently by the CRA and a research assistant. Agreement was assessed by the test statistic Kappa (Fleiss 1982). Table 9-1 shows the contingency table and indicates good agreement (Kappa=.802 $P_K<0.001$). The majority of differences were of one unit. When measuring the remainder of the models, if the difference was one unit the lower value was used; but for greater differences the model was reassessed by both evaluators and a consensus agreed. The majority of the cases of the CRA were analysed together with an equal number of each of the practitioners cases. A number of cases had to be discarded because the models were inadequate for measurement. The total number for each

Agreement Matrix for CRA's Values

		Clinical Research Associate							
		25	75	125	175	225	275	325	375
Research Assistant	25	81	3						
	75	1	117	12	2				
	125		5	46	7				
	175		3	6	26	5			
	225			1	3	9	1		
	275					2	2		
	325							3	1
	375								2

Border Number = Class Mid-marks 0 - 49
50 - 99
etc.

Kappa = .802 P = .0000

Table 9-1

material was Clearfil 70, Occlusin 76 and P-30 75.

Measurement of attrition.- Laser interfereometry

As discussed in Chapter 3, attrition has frequently been overlooked in the evaluation of wear because it is difficult to measure. In this evaluation it was measured by laser interfereometry. The measurements were made by the scientific research associate (Mr R Vowles) who played a major role in the development of Laser Contouring and developed the softwear to compute the maximum depth of wear.

Laser Interfereometry

If a beam of light is split and then recombined after the two beams have travelled different distances, then in areas where the wave amplitudes summate there is brightness, whereas in areas of cancellation dark bands occur. From a practical point of view, if a flat screen is placed in the recombined beam a pattern of black (cancellation) and white (summation) lines form on the screen. If however the flat screen is replaced by a cone then the pattern is of regular curves. This differentiates diffraction from a projected pattern of black and white lines which would still appear as lines on the cone.

The separation of the lines Δh is given by

$$\Delta h = \frac{\lambda Z}{a}$$

where λ = wavelength of light (laser)
z = distance from illuminating source to object
a = separation of two beams.

In the assessment of attrition the "screen" was formed by the replica model of the tooth. Provided the successive models of each case were replaced in exactly the same position with reference to the beam, then successive interference fringes were identical provided no wear had occured. Deviation indicated that the surface had changed and the lost volume could be computed from the displacement of the fringes. However, as pointed out by Roulet (1985), the measurement of volume loss can be misleading because it doesn't indicate the area over which loss has occurred and therefore the computer was programmed to calculate maximum depth of wear. Early in the development of the technique, the diffraction pattern was formed by beam splitting and the interference fringes were photographed and mapped (Atkinson et al 1982, Williams et al 1983). More recently the diffraction fringes have been produced by a diffraction grating and the successive patterns analysed directly by computer. This latter modification was achieved using a "diode array" camera. The output from the camera array is input into the frame store of a computer via a flash A to D converter. From this data the computer calculates the maximum depth of wear. In the original investigation epoxy models were used; but recent work (unpublished) has indicated that stone models are superior as sharper interference lines are possible. In view of the time taken for this procedure only a representative sample were analysed, the numbers being: Clearfil 42, Occlusin 45, P-30 43.

CLINICAL PROCEDURES

At the initial visit the teeth in need of restoration were identified and the filling material for each restoration allocated from a random numbers chart. Prior to restoration the condition of the tooth, previous restorations and the periodontium were scored and photographed. The clinical procedures adopted by each operator are summarised in Table 9-2 (the CRA placed the rubber dam either before or after cavity preparation). The baseline assessment was made within two weeks of placement but not on the same day. At each recall visit assessment clinical parameters were scored and photographs taken together with the impression. The clinical parameter most relevant to wear was the presence of negative ledges at the margins and this was determined with a sharp probe. All data, photographs (slides) and impressions were collated at the Dental School where models were made by a research technician. Data was stored and processed by Dbase III and where necessary uploaded to the University main frame computer (IBM 3083) for statistical analysis using the package SPSS^{X} (Chicago USA).

CLINICAL PROCEDURES ADOPTED BY EACH OPERATOR

LOCAL ANALGESIC		
PREWEDGE	PRA 1	NEVER
	PRA 2	FREQUENTLY
	CRA	OCCASIONALLY
CAVITY (Margins finished with)	PRA 1	Slow speed diamond
	PRA 2	TC Bur with White Stone for bevel
	CRA	Tapered TC Bur
LINING	PRA 1	$Ca(OH)_2$ DYCAL (Caulk) $ZnPO_4$(De Treys)
	PRA 2	LIFE (Kerrs) PolyF (Lumicon)
	CRA	LIFE (Kerrs) $ZnPO_4$ (De Treys)
MATRIX	PRA 1	Siquveland (Ash)
	PRA 2	Siquveland (Ash)
	CRA	Siquveland (Ash) 80% Tofflemire 20%
WEDGES	PRA 1	Oral B
	PRA 2	Wizard
	CRA	Wizard
ETCH WASH DRY		According to manufactures instructions
BONDING AGENT	CLEARFIL	Bonding agent not cured separately.
	OCCLUSIN	Bonding agent cured separately.
	P-30	Bonding agent not cured separately.
PLACEMENT	CLEARFIL	Cavex Syringe
	OCCLUSIN	Amalgam Condensers
	P-30	Amalgam Condensers
PRE-CURE CONTOURING	CLEARFIL	PRA 1 / PRA 2 Wet cotton wool CRA no attempt at this
	OCCLUSIN	PRA 1 Wax Carver PRA 2 Plastic CRA Amalgam Condenser
	P-30	As for Occlusin
FINISHING	PRA 1	High Speed White Stone + Vaseline
	PRA 2	Discs and H/S White Stones
	CRA	High Speed White stone
POLISHING	PRA 1	Slow Speed White Stone + Vaseline
	PRA 2	Green silicone points
	CRA	Slow Speed White Stone

Table 9-2

RESULTS

Abrasion

Table 9-3 shows the number of negative ledges detected at each recall together with Chi^2 for trend. The mean and standard deviation for abrasion, measured with the step wedge are given Table 9-4. Figure 9-1 is a graph of the overall abrasion and Fig 9-2 shows the plot for individual operators. It is apparent that the rate of abrasion before one year was greater than the later rate; this is a recognised feature of abrasion in posterior composites (Leinfelder 1987, Jendrenson 1988). The relative rate of abrasion of the individual materials to each other was maintained over the three years. Statistical analysis indicated that individual values at each recall had a non-parametric distribution and it is apparent that the standard deviations were large. Fig 9-3 shows the frequency distribution of the values at 36 months together with the skew and kurtoise. A non-parametric analysis of variance test (Kruskal-Wallis) indicated a highly significant difference ($Chi^2 = 48.24$ $P = 0.0000$). The difference was caused by the high values for Occlusin whereas P-30 and Clearfil were not significantly different ($Z = -1.72$ $P_Z = 0.84$). Fig. 9-4 shows the median values for each practitioner and the total. Both Figs. 9-2 and 9-4 indicate that Occlusin had the highest abrasion rate for all operators; but that the value was particularly high for

Cross tabulation of number of cases with negative ledges 00 - 36 months

Months	00	06	12	24	36	CHI^2 Trend	P
Clearfil	1 (120)	0 (1110	0 (113)	3 (103)	2 (103)	2.44	0.12
Occlusin	2 (120)	2 (117)	2 (113)	10 (97)	22 (80)	27.84	<0.001
P30	2 (117)	0 (117)	0 (112)	3 (102)	10 (92)	14.14	<0.001

Cell Score

(n) - number with no negative ledges

Table 9-3

Mean Abrasion to 36 Months [µm]

Material	OP	06	12	24	36
CLEARFIL	PRA 1	15.8 (23.3)	39.2 (50.1)	53.30 (54.5)	66.3 (58.0)
	PRA 2	24.5 (26.1)	52.6 (50.1)	67.55 (58.9)	85.0 (68.2)
	CRA	23.2 (21.3)	45.0 (22.3)	72.81 (43.7)	85.7 (43.5)
	TOT	21.1 (23.4)	45.26 (41.3)	64.9 (51.9)	79.2 (56.0)
OCCLUSIN	PRA 1	57.1 (55.8)	115.9 (98.2)	183.8 (136.3)	232.7 (143.8)
	PRA 2	30.04 (29.51)	69.6 (55.5)	110.5 (92.5)	136.1 (99.6)
	CRA	54.57 (35.6)	96.1 (52.1)	127.8 (70.3)	164.8 (90.0)
	TOT	47.3 (42.4)	93.4 (71.7)	139.0 (104.4)	175.9 (117.1)
P-30	PRA 1	18.3 (22.5)	44.8 (44.0)	80.8 (55.1)	96.4 (62.0)
	PRA 2	18.8 (20.5)	38.6 (30.6)	60.5 (38.9)	77.7 (53.1)
	CRA	21.9 (22.9)	58.0 (36.0)	86.7 (50.7)	112.3 (63.2)
	TOT	19.7 (21.8)	47.6 (37.6)	76.4 (49.5)	96.1 (60.6)

Figures in parenthesis Standard Deviations
OP = Operator TOT = Total
PRA = Practitioner CRA = Clinical Research Associate

Table 9-4

PRA 1. Although the data had a non-parametric distribution, Multivariate Analysis of Variance (MANOVA) indicated that logarithmic transformation of the values resulted in a reasonably normal distribution of residuals. Consequently, MANOVA was used to assess the effect of Material, Operator, Cavity Type, Tooth Type, Quadrant and their respective interactions on the overall variance [see Appendix 2]. The result of the MANOVA is given in Table 9-5. Whereas the variable Material was highly significant (P=0.000), with one exception the interactions with Material were not significant. This indicates that the distribution of Materials by Cavity, Quadrant and Tooth Type did not account for the difference between materials. The relatively high F values for the Mat by Operator interaction results from the high abrasion rate of PRA 1 for Occlusin (Figs 9-2, 9-4). In the MANOVA, tooth type (i.e. Molar or Premolar) was highly significant (P=0.003). However a histogram of the median values for this variable indicated that the difference was mainly between the restorations of Clearfil and P-30 (Fig. 9-5). Although this analysis gave an indication of the relative effect of these variables on the overall variance (Fig. 9-1), together they explain only 40% of the total variance (r^2= 0.399).

Attrition

The values for attrition are summarised in Table 9-6. The frequency distribution is shown in Fig 9-6 and the values are graphed in Fig. 9-7 together with values from a sample

MULTIVARIATE ANALYSIS OF VARIANCE

COVARIANCE OF LOG WEAR (36 MONTHS) WITH VARIABLES AND INTERACTIONS

Source of Variation	SS	DF	MS	F	Sig of F
Within cells	11.21	140	.08		
Cav	.01	1	.01	.14	.709
Quad	.57	3	.19	2.36	.074
Type	.74	1	.74	9.23	.003
Mat	4.86	2	2.43	30.35	.000
Op	.29	2	.14	1.80	.168
Mat by Cav	.06	2	.03	.39	.678
Mat by Quad	.08	6	.01	.16	.986
Mat by Type	.02	2	.01	.11	.899
Mat by Op	.81	4	.20	2.52	.044

R-Squared = .399

Cav = Cavity Type Occlusal or proximal
Quad = Quadrant
Type = Tooth type - premolar/molar
Mat = Material
Op = Operator
X By X = Interactions

Table 9-5

SUMMARY STATISTICS FOR ATTRITION AT 36 MONTHS

	MEAN	STD	MEDIAN	SKEW	KURTOISE
CLEARFIL	153.4	25.2	152.3	-0.33	1.37
OCCLUSIN	207.8	33.4	212.0	0.39	0.29
P-30	255.54	56.10	248.9	0.62	0.06

Values in μm.
STD = Standard Deviation

Table 9-6

at 24 months. The data had a parametric distribution, but a provisional one-way ANOVA indicated inequality of the variance. This was resolved by a Logarithmic transformation resulting in Bartlett-Box F = 1.337, P_F =0.263. ANOVA of the transformed values was significant (F= 63.89 P_F = 0.000) and the Scheffe MRT (0.01 level) indicated that the materials were all significantly different from each other. Fig 9-8 shows the breakdown by tooth type. T tests indicated that the differences between molar and premolar restorations were significant for all materials (P_T<0.01). Fig 9-9 plots the values of attrition and abrasion for a sample of restorations, with the attrition values indexed in ascending order. It is apparent that there is no consistent pattern between attrition and abrasion indicating that their causes are independent. A summary of the attrition to abrasion ratio is given in Table 9-7.

Electronmicroscopy

The two processes of wear are illustrated in Plate 138 which shows an attrition scar involving enamel and the restoration surface with superimposed abrasion exposing the enamel margin. This scar had not been noted clinically. Plate 139 illustrates an obvious scar in the mesial central fossa. The distal fossa is also a site of occlusal contact but no obvious scar is present. Plate 140 A & B illustrate the relationship between the scanning electronmicroscopy

COMPARISON OF ATTRITION AND ABRASION

MATERIAL	MEAN	STD	MIN	MAX
CLEARFIL	2.66	1.46	0.60	5.64
OCCLUSIN	1.44	0.75	0.34	3.88
P-30	4.39	2.85	0.62	11.56

Value = Attrition/Abrasion

STD = Standard Deviation

Table 9-7

and the clinical findings. Three areas of attrition are present: two are very obvious, but attrition on the disto-lingual cusp was not noticed clinically. On the clinical photograph staining is present in association with the major scars.

The previous plates illustrated gross evidence of attrition. The number of obvious scars found on examination of all the x10 micrographs from the clinical trial is given in Table 9-8. For comparison the number of scars found on the amalgam restorations (Page 171) is included. The total number of scars with the two amalgam materials was compared with that for composites using Fishers exact test: there was no significant difference (p=0.296).

Two features occasionally noted in association with attrition are illustrated in Plates 141,142 and 143. These indicate loss of entire fragments from the surface: a feature known as "spalling" in fatigue wear (Pugh 1973). The surface loss in Plate 143 appears to be laminar and corresponds to the delamination concept of Jahnimar and Suh (1977). Plate 144 is from a contact free site of the same restoration: the matrix appears partly intact over the large protruding particle and there is still evidence of finishing lines. Spall marks were noted in the OCA by Roulet (1987c) and Hirt et al (1984). These gross defects were not common findings and it was often difficult to distinguish between the OCA and the CFA as illustrated in

Number of restorations with clearly identifiable wear scars on SEM at 36 months

	NTD	SN	CP	OCC	P30
Total number available for analysis	99	99	105	109	103
No. with clear wear scar at 36 months	8	2	6	10	6
First evidence at 12 months or less	8	2	4	8	6
First evidence after 12 months	0	0	2	2	0

NTD	New True Dentalloy
SN	Solila Nova
CP	Clearfil Posterior
OCC	Occlusin

Table 9-8

Plates 145/146 and 147/148. All of the features of filler particle exposure recognised by (Kusy and Leinfelder 1977, O'Brien and Yee 1980, Lambrechts & Vanherle 1982, van Dijken 1983, Abell et al 1983, Xu et al 1984, Leidal et al 1985, van Groeningen 1985, Bream et al 1986) were present on these micrographs; but matrix cracking was not a common finding. The micrographs did not indicate gross deterioration of the filler resin interface. This is supported by the finding in Chapter 7 that thermal cycling, within the limits likely to be experienced clinically, may increase permeability but does not cause gross degradation.

Examination of the tooth restoration interface indicated some evidence of the "ditching" as noted by Mc Comb (1985): this is apparent by the mesio-buccal cusp in Plate 140. Laboratory experiments, not presented in this thesis, have indicated that this occurs as a result of a "filler free" resin layer around the margin of Occlusin caused by curing the bonding resin before placement of the bulk restorative material.

DISCUSSION

These results entirely support the contention of Lutz et al (1984), Roulet (1985, 1987b&e, 1988), Lambrechts et al (1984), Bream et al (1986) and others that attrition and abrasion must be considered separately. However, it is necessary to restate from Chapter 2 that these processes are the clinical manifestation of many different wear processes, some of which are interdependent. Another misconception is that attrition manifests well defined wear facets as illustrated in Plates 138, 139, 140. Table 9-8 shows that obvious flaws were relatively uncommon and Fisher's test indicated no difference in the number between amalgams and composites. These scars were caused when a cusp tip opposed the restoration whereas often the occlusal contact was between two inclined cuspal surfaces. In the latter case attrition was less obvious and only apparent when the depth of wear was measured over successive time intervals. In this study 88% of the facets were clearly demarcated after 12 months and of these the majority were present at 6 months. This agrees with the finding of Roulet (1987b&e, 1988). The findings of this study do not support the concept of McCabe & Ogden (1987) that air-bubbles are very important in the determination of occlusal contact wear through fatigue: the two paste material Clearfil had the highest proportion of air voids but the lowest rate of attrition. This agrees with the later finding of Ogden et al (1985) that there is no relationship between porosity and abrasion. Many factors influence both attrition and abrasion and these may be divided into factors related to the masticatory apparatus and general factors. The former includes the occlusal relationship of the individual teeth which determine the food shedding pathway, the overall occlusal relationship and masticatory stress. The general factors include the abrasivity and chemical nature of the diet together with plaque metabolism which determines the local chemical environment. Many of these factors are interdependent.

By comparing the results for abrasion and attrition it is possible to gain some understanding of the contributions of these factors. Fig. 9-9 indicates that the two process are largely independent because there was high abrasion with low attrition and vice-versa. It may have been supposed that masticatory stress would be extremely important; but if so, there would have been a general tendency for both processes to increase. If chemical degradation predisposed to both abrasion and attrition then the same argument applies and a general relationship between the two processes should have been present. The frequency distributions for the two processes indicate different patterns (Figs 9-3, 9-6). For attrition there was a relatively normal distribution (Fig 9-6) whereas for abrasion the distribution was positively skewed. Comparing the materials with the highest abrasion and attrition (Occlusin & P-30 respectively); for abrasion, the high value for Occlusin was caused by many more individual restorations in the right hand tail of the distribution. For attrition the high value for P-30 was caused by an overall "shift" of the distribution to the right. The frequency distributions suggest that abrasion is influenced by factors local to the individual cases, whereas attrition is predominantly influenced by the material. Evidence for the latter was found by Aziz & Harrison (1988) who found that increasing the impact element of an in-vitro wear cycle increased the wear of all materials; but the overall ranking of the materials did not change.

One local factor that predisposed to abrasion was the presence of buccal and lingual extensions. This was also reported by Sturdevant et al (1988) and Wilson et al (1988b). The reason for this is the enhanced effect of the masticatory slurry as it is squeezed through the extension. Evidence for this was found in the laboratory study of DeGee et al (1989): the amount of wear with any individual material was found to be dependent on the thickness of the slurry layer. This may also explain the greatly reduced rate of abrasion after five years (Wilder et al 1987, 1989), because as the restoration submerges the thickness of the slurry increases and the force applied to it is decreased. The effect of the variable tooth type (ie molar or premolar) has also been noted by other workers (Brunson et al 1989, Sturdevant et al 1988, Wilson et al 1988b, Bayne et al 1987). During the course of this investigation another local factor has been noted, namely the cavo-marginal relationship of the restoration. An advantage of the step wedge evaluation is that margins are scrutinised under the stereomicroscope rather than with a magnifying glass in the "Goldberg" technique. It was noted that in many areas with high abrasion the cavo-marginal restoration was such that only a thin edge of material was present at the edge (Fig. 9-10a). These "thin edges" abrade far more rapidly than the "bulk" marginal finish (Fig. 9-10B) resulting in greater depth of marginal exposure. The relationship between cavo-marginal contour and abrasion is to be studied in detail by another associate to determine its effect on the overall variance. That thin marginal edges abrade more rapidly was noted by Davidson (1987) who questioned the reliability of the "Goldberg" technique with bevelled margins. Although the bevel reduces marginal leakage (Moore & Vann 1988); it predisposes to abrasion. The cavo-surface effect may explain the high rate of abrasion during the first year as any thin edges were worn away exposing the cavity margin. In successive years the apparent rate of abrasion decreased because larger volumes of material had to be abraded to expose the margin. The cavo-surface finish is a function of the cavo-surface angle and the final contour of the restoration. This may explain the high abrasion value for PRA 1 (Fig. 9-4). Occlusin had the highest overall abrasion and if the contour of PRA 1's restorations predisposed to abrasion it would have manifested more easily in this material.

The uneven abrasion around the margins indicates a change in the pattern of abrasion. The "Goldberg" technique was developed by measuring abrasion in composites placed before 1981 (Powers et al 1983). In these materials the overall abrasion was high and the effect of the material outweighed local factors acting at individual cusps. This resulted in the appearance of a submerging surface with equal enamel exposure around the margin (Kusy & Leinfelder 1977). The present generation of posterior composites have improved abrasion resistance and local factors exert a much greater influence. The reasons for the improved abrasion resistance were discussed in Chapter 1.

Comparing these results with those of other investigations it is apparent that the mean values for the abrasion of Occlusin are higher than those recorded by Robinson et al (1988) and Wilson et al (4 year data 1988a) (Table 9-9). The reason for this is almost certainly the measuring technique. Soderholm et al (1988) compared the results of categorisation (as used with the "Goldberg" technique) with direct measurement and found that the former resulted in statistically lower values. With the "Goldberg" technique the model must be categorised according to its general appearance; but as illustrated in Plate 136 abrasion can be much higher at various points along the margin. Many cases in this study indicated three readings of 50 or 100 µm with the remaining value being much higher. Vann et al (1988) took this into account by mental averaging, but without this the restoration may have been categorised by its lowest values. The effect of technique on the assessment of wear can be seen in Table 9-9 by comparing the results for Occlusin in this study with those of Robinson et al (1988), Wilson et al (1988a) (using the

ABRASION AND ATTRITION IN DENTAL COMPOSITES [1985 - 1989]

ABRASION

					YEARS		
INVESTIGATION		MATERIAL	1	2	3	4	5
DHSS EVALUATION	1989	CLEARFILL	45	47	49		
LUTZ et al	1985	ESTIC-MICRO	46	75			
LEINFELDER	1986	ESTILUX-POST	94	100	125		
STURDEVANT et al	88/89	ESTILUX-POST	106	127	164		169
BRAEM et al	86/87	ESTILUX-POST	23	34	45		
LEINFELDER	1986	FUL-FIL	85	85	100		
STURDEVANT et al	88/89	FUL-FIL	100	119	145		158
BOKSMAN et al	86/87	FUL-FIL			135		163
BRUNSON et al	1989	FUL-FIL	100	119	145		
HEYMAN et al	86/87	NIMITEC		199			228
HEYMAN et al	86/87	NIMITEC-DISPERS		111			150
DHSS EVALUATION	1989	OCCLUSIN	93	139	176		
LEINFELDER	1986	OCCLUSIN	57				
WILSON et al	1988	OCCLUSIN				97	154
ROBINSON et al	1988	OCCLUSIN			70		
BRAEM et al	86/87	OCCLUSIN	21	32	40		
ROOSEN et al	1988	OCCLUSIN			113		
NORMAN & WILSON	1988	OCCLUSIN			76		
LEINFELDER	1986	P-10	110	140	150		
LEIDAL et al	1985	P-10	20	40			
LUTZ et al	1985	P-10	46	70			
BRUNSON et al	1989	P-10	121	108	154		
BRAEM et al	86/87	P-10	18	29	39		
DHSS EVALUATION	1989	P-30	48	76	96		
LEINFELDER	1986	P-30	130	175			
LUTZ et al	1986	P-30	65				
LEINFELDER	1987	PROFILE-C	111	140	149		
HEYMAN et al	86/87	VISIO-DISPERS		113			126
HEYMAN et al	86/87	VISIO-FIL		198			247
HEYMAN et al	86/87	VISIO-R/OPAQUE		150			242

ATTRITION

DHSS	1989	CLEARFIL		107	153
LUTZ et al	1985	ESTIC-MICRO	60	145	
BRAEM et al	1987	ESTILUX-POST	89	175	245
DHSS	1989	OCCLUSIN		133	205
BRAEM et al	1987	OCCLUSIN	81	164	208
BRAEM et al	1987	P-10	58	107	143
DHSS	1989	P-30		156	255
LUTZ et al	1985	P-30	140		

Table 9-9

"Goldberg" technique) and Bream el al (1987) using direct z coordinate measurement as described by Lambrechts et al (1984): there is clearly a tremendous difference in the results. The latter technique appears to underestimate wear because it is constrained to assess CFA abrasion at only one site on the surface whereas wear varies at all locations on the surface (Bloem et al 1988). The accuracy of the "Goldberg" technique is questioned by the results from a multiclinic trial of Occlusin (Norman & Wilson 1988): the overall result for abrasion at three years was 76+45 but two (/11) centers scored 41±27 and 112±39.

The step-wedge was devised purely as an expedient technique to determine the relative rates of wear of the materials in this trial. As yet no claim is made to its superiority over other techniques nor has any attempt been made to compare methods as such a comparison is beyond the scope of this investigation. All investigations measuring abrasion agree that there is a high overall variance (Sturdevant et al 1987, 1988, Wilson et al 1988a&b, Robinson et al 1988, Norman & Wilson 1988, Boksman et al 1986). Sturdevant et al (1988) also noted the non-parametric distribution. It is surprising therefore that they plotted mean values and standard errors resulting in a graph that appears to indicate a clear difference between two materials. This is entirely misleading because the standard error does not indicate the variance of the population. If the values are corrected to standard deviations then the error bars would show a large degree of overlap as in Fig. 9-1. Leinfelder (1987) found that the distribution of abrasion wear for Profile (Chemical) was normally distributed and claimed that the pattern for P-10 was similar. However his frequency distribution indicated a high kurtoise with P-10 which can have an significant effect with parametric analysis. The large standard deviations and non-parametric distributions preclude the use of small sample trials in the evaluation of wear.

The preceeding discussion illustrates the importance of frequency distributions in the analysis of wear. The mean and its standard deviation or the median value, do not indicate how many individual restorations have undergone a high amount of abrasion. In deciding the overall performance of a material, the frequency distribution may be more important because it indicates the number of restorations that are tending toward unacceptable wear.

There are very few in-vitro studies using all the three materials reported in this study although the study by Fingar & Thiemann (1987), using a wear machine designed to simulate clinical three body abrasion, showed a ranking order of the three materials identical to the present clinical result. In a two body abrasion tests P-30 had the highest wear of all the composites tested; but Clearfil and Occlusin were not included in the study (Lappalainen 1989).

Lambrechts et al (1984) stated that any material with an attrition rate exceeding 60 um per year (the attrition rate of enamel) is contraindicated as a material for a posterior composite. Neither P-30 or Occlusin measure up to these criteria, however, it is the subjective opinion of all three operators involved in this trial that the materials are performing adequately. Clearfil had the highest wear resistance but none of the operators would entertain the routine use of this material because its colour match and handling were appalling. Although the argument concerning the use of chairside or indirect measurement still continues there is now a general consensus that indirect measurement is necessary (Taylor et al 1989 a). The ADA has requested that manufacturers supply measurements of mean abrasion based on indirect techniques when applying for licensing of the material by the ADA (Sturdevant et al 1988). Unfortunately the distinction between abrasion and attrition is still frequently ignored and authors give the impression that wear can be measured solely as exposure of enamel margins. This discussion is continued in the next chapter which reports on the investigation of subsurface degradation.

CHAPTER 10

SUBSURFACE DEGRADATION IN THREE POSTERIOR COMPOSITES

METHOD

The silver staining technique developed in Chapter 4 was used together with scanning electromicroscopy to study surface degradation in eleven restorations which were removed because of failure on the clinical trial. Details of the restorations are summarised in Table 10-1. The method for silver stain was as illustrated in Fig. 4-9, except that the specimen was immersed in $AgNO_3$ for 42 days. The reason for this modification was to determine whether the depth of the silver sorption layer had increased as a result of exposure to the oral environment. After sectioning the remaining stub was embedded and polished using the regime given in Fig. 5-2. These were mounted on specimen holders for scanning electronmicroscopy and splutter coated with gold as described in Chapter 8.

RESULTS

The three materials are discussed individually prior to an overall discussion. P-30 had the most apparent degradation and is discussed first.

DETAILS OF RESTORATION WITH FRAGMENTS FOR ANALYSIS

Material	OP	R/C	Cav	Pat Age Years	Sex	Reason	Res Age Months	Last Rec	Wear at LR
Clearfil	1	214/44	DO	41	F	Pulpitis	17	12	50
Clearfil	C	726/15	DO	22	M	Ortho	29	24	25
Clearfil	1	228/46	MO	31	M	Retention	36	24	50
Occlusin	1	116/15	MO	22	F	Ortho	12	12	50
Occlusin	1	164/38	MOD	43	M	Fracture	12	6	0
Occlusin	2	449/26	MOD	44	M	Pulpitis	12	12	100
Occlusin	2	435/17	MO	25	F	Abrasion	27	24	50
Occlusin	1	125/36	DO	40	M	Pulpitis	28	24	300
P-30	1	156/18	MO	48	M	Fracture	24	24	100
P-30	C	706/17	MO	21	M	P/Abscess	27	24	100
P-30	C	726/25	MO	22	M	Ortho	31	31	100

Op = Operator 1 PRA 1, 2 = PRA 2, C = CRA

CAV = Cavity Type PAT = Patient, Res = Restoration

Rec = Recall LR = Last Recall, R/C = Identification code.

Table 10-1

SC 156/18/05 In-vivo service = 24 months

Plate 149 is a low power micrograph of the embedded specimen. There is a wide permeability layer on the exposed surfaces and the gingival margin. The thickness of the layer is less occlusally than proximally. Plates 150/151 show the junction between the proximal surface and the marginal ridge. Although with scattered light (Plate 150) the permeability appears very black, by bright field illumination there is little evidence of degradation (Plate 151). This was confirmed by the SEM (Plate 152) which shows no evidence of gross degradation compared with the appearance of the material deep to the permeability layer (Plate 153). The localised porosity in the centre of the field may be the site of an interface between two successive packing increments. This would explain the resin rich delta which is arrowed. It is apparent from Plate 152 that the resin rich layer had not been removed by abrasion.

SC 706/17/05 In-vivo service = 27 months

Plate 154 shows the staining of a P-30 restoration removed after 27 months service. The appearance was similar to that seen in 24 months specimen although the width of stain of the proximal surface is thinner toward the occlusal rather than the gingival surface. The restoration had a wide proximal box and the occlusal part of the proximal surface would have been subject to abrasion from the masticatory slurry. Plate 155 shows the proximal surface viewed by incident scattered light.

SC 726/25/05 In-vivo service = 31 months.

The silver sorption layer on this restoration was so well defined that at first it was thought to be a thick layer of adsorbed silver (Plate 156). However, Plates 157 and 158 indicate the layer is definitely a permeability layer within the surface. Plates 159 and 160 show SEMs of the proximal surface. The ragged edge indicates degradation of the surface. At the very edge in Plate 159 there appears to a zone of microporosity but no evidence of microcracking. Plates 161/162 are of the occlusal surface which is, by comparison, much flatter. The white surface "layer" in Plate 162 is not an actual layer but has been caused by preferential abrasion of the surface resulting in a trough between the specimen and the embedding plastic. Surface projecting particles are present on the occlusal surface.

OCCLUSIN

SC 449/26/04 In-vivo service 12 months.

This restoration was replaced because of pulpitis and an impression was taken before removal. Plate 163 shows the surface SEM with an attrition scar on the occlusal surface. Plate 164 is a magnified view of the surface of the scar: there appears to be surface cracks. The silver stained specimen (Plate 165) appears to indicate that a "laminar plate" has been lost from the surface but there was no indication of gross subsurface degradation. The sorption layer occlusally was thinner than at the proximal margin (Plate 166). The absence of gross subsurface damage, at the occlusal surface, was confirmed by the SEMs (Plates 167/168). It was apparent that the resin rich layer had been worn away and that there were surface projecting particles. These were obvious on the surface SEM (Plate 164).

SC 116/15/04 In-vivo service = 12 months.

The comparatively thin sorption layer at all margins of the Occlusin restorations is shown in the low power micrograph of this specimen (Plate 169). The apparent depth of the brown layer occlusally resulted from a thin layer of adsorbed silver on the surface.

SC 125/36/04 In-vivo service = 28 months.

This restoration had the greatest abrasion at the time of removal (300 um); but there was no difference in appearance between this and the other Occlusin restorations. An incidental finding with this restortion was the presence of a large sub-surface void between two packing increments. (Plate 170/171). It appears that a crack may have nucleated down to the defect (arrowed). The resin rich layer was well defined and there is evidence of micropores (Plate 172).

The two remaining Occlusin restorations had a similar appearance, but no evidence of incremental interfaces.

CLEARFIL

SC 214/44/03 In-vivo service = 17 months.

Macroscopically the appearance of these restorations was similar to those of Occlusin (Plate 172). The silver staining technique indicated no gross degradation of the occlusal surface (Plate 173) and this was confirmed by SEM (Plate 174).

SC 726/15/03 In-vivo service = 29 months.

This specimen had a similar appearance. The apparent subsurface degradation staining seen in Plate 175 was caused entirely by a layer of surface adsorbed silver (Plate 176). On the SEM there was no obvious indication of subsurface degradation (Plate 177/178).

SC 228/46/03 In-vivo service = 36 months

Plates 179/180 indicate the proximal and occlusal surfaces respectively. There is evidence of a resin rich surface on the proximal surface although it is not as well defined as in the other two materials. Surface projecting particles are evident on the occlusal surface.

DISCUSSION

It is apparent that the permeability layer of P-30 was very much greater than that of the other two materials. The stained layer was deeper and the whole layer appeared black whereas in the in-vitro specimens of this material the stain was predominantly dark brown (Plate 59). The difference in the thickness of the silver sorption layer between the occlusal and proximal surface can be partly explained by the differences noted between the permeability depths for resin rich and ground surfaces (Chapter 5). The occlusal surface corresponds to a ground surface because the resin rich layer was removed firstly during finishing of the restoration and secondly by in-vivo abrasion. Normally the proximal surface requires little finishing and remains "as placed" (Patterson & McLundie 1986). The scanning electron micrographs indicated that the resin rich layer was still present proximally but had been lost occlusally. This would be predicted by the pattern of occlusal wear associated with occlusal surfaces (Kusy and Leinfelder 1977). As the proximal surface was not constantly being removed, it was subject to the development of a permeability layer with subsequent dissolution and enlargement of the microcavities. The very black stain in this material (Plate 156) can be explained by the theory of colour dependence on the size of precipitated silver grains in these cavities. The increased degradation of P-30 over the other two materials can be compared with the finding of Watts et al (1986) that the surface hardness of P-30 specimens, stored in water, decreased between one day and one month after the initial cure whereas the values for

Occlusin remained constant. This was attributed to the increased water sorption as a result of the polymeric constitution of the two materials, which agrees with the finding in Chapter 6 that the water sorption of P-30 was greater than that of Occlusin. The relationship between microhardness and water sorption had previously been recognised by Hansen (1983).

Whereas the depth of stain in Clearfil and Occlusin was similar to the depth which occurred in laboratory specimens, the depth in P-30 was more than doubled. This was partly due to exposure in the mouth because the depth at the proximal surface was greater than at the gingival margin (which represents an unexposed resin rich surface)(Plates 149 and 154). As noted in Chapter 7 fluctuating temperatures increased the depth of stain; but if this was the predominant reason then the material must have been especially sensitive to this effect or it would have occurred in all three materials. The appearance of the proximal surface after 31 months service (Plate 160) appears to indicate disintegration of the proximal surface. Although this fits the model of chemical dissolution within the permeability layer (Chapter 2): there was only one specimen available of this age and the degradation may have been specific to this restoration. Roulet & Walti (1984) found chemical degradation of composite "restorations" placed in the undersurface of pontics. Although not reported in the thesis, the clinical investigation has progressed to four years and none of the dentists have reported the appearance of proximal ledges with P-30 which would occur if this surface was degrading. However, just as the "Goldberg" technique is insensitive to occlusal wear of less than 100 microns, it is unlikely that the degree of degradation noted in Plate 160 would have been apparent clinically. Nonetheless, surface roughness as a result of chemical degradation may have important long term effects on the periodontium by encouraging the accumulation of bacteria (Skjorland et al 1982). Van Groeningen (1986) also noticed surface loss and an increase in surface roughness of composites placed in the buccal flanges of full dentures which was attributed to chemical degradation. At this site the restorations would have been subject to abrasion which may have accounted for the roughness. The present result indicates that the early rate of loss noticed by van Groeningen doesn't continue because the resin rich surface was still present after three years. At present it appears that the wear rate of the proximal surface is very limited in which case a "solution layer" may develop. It is tempting to postulate that the surface microporosity seen in Plate 160 is solution cavities; but similar pores were noted in the resin rich surface of Occlusin (Plate 171) which did not appear to have degraded.

Although the silver staining and scanning electronmicroscopy of Clearfil and Occlusin indicated very little subsurface damage this does not mean that the materials are inert in the oral environment. Soderholm (1981,1983) found leaching of ions from dental composites and Marcos-Montes & Draughn (1986), Fan et al 1985, Braden and Clark (1984) demonstrated gravimetrically that the materials are subject to solution in water. This would be expected from the physical and chemical laws of solution (Brey 1978, Ueberreiter 1968). However, the present result indicates that these processes did not cause gross degradation in two materials and their effects were limited to the surface in P-30.

The results confirm the findings in Chapter 7 that hygrothermal aging in the mouth is unlikely to cause the gross degradation that can be produced by more severe conditions in the laboratory. It was noted that none of the Clearfil clinical specimens suffered the large particle displacement caused by in-vitro thermal cycling (Plate 113).

The importance of investigating the subsurface is emphasised by comparing Plate 164 to 165/167/168. The surface SEM appears to indicate that a network of cracks would be present in the subsurface although it is apparent that this was not the case. Whereas in the anterior composites a zone of subsurface stain was occasionally noted in association with attrition (Plate 45), there was little evidence of this in the posterior composites. However the appearance of Plate 165 may indicate that a surface fragment had fractured away from the stained zone. It is apparent from this small sample number that it is not possible to assess the degree of subsurface degradation from the appearance of the surface. Whilst not disputing the findings of surface cracks by Roulet (1987e), Lambrechts et al (1985) and Lutz et al (1984) it is not possible to extrapolate the extent of the damage from the surface appearance. Skeeters et al (1988) investigated the subsurface damage of Estilux-Posterior and found that stains on the surface appeared to penetrate into the subsurface; but on sectioning this was not the case. The only evidence of degradation was limited crazing within 10 µm of the surface. It was noted in Chapter 9 that facets, as described by Roulet (1987e), were not a general finding and the results in this chapter indicate that when they occur, the subsurface degradation was less than might be expected. Whilst the results for P-30 would support the theory of a degrading surface layer caused by microcracking and subsequent chemical degradation (van Groeningen et al 1985), it appears that the layer was not present in the other two materials. Brunson et al (1989), studying P-10 were suspicious of the surface layer theory on the the grounds that it did not manifest as surface textural changes and staining in their study. However, the present result for P-30 indicates that considerable ultrastructural degradation may occur without clinical evidence. Naturally this investigation will continue as more specimens become available. At present it appears that clinical abrasion and attrition are far more responsible for loss of the occlusal surface than degradation.

SUMMARY

The findings presented in this chapter indicate that in two materials there was little evidence of sub-surface degradation. Although degradation had occurred in the other material after 36 months, only one restoration was available for analysis and therefore no definite conclusions can be drawn.

Chapter 11

IN-VITRO WEAR

INTRODUCTION

As discussed in the introduction a vast number of devices have been invented to study wear in dental composites; but none have been accurately predictive of clinical performance. The objective of the experiments reported in this chapter was to assess the effect of physical and chemical conditioning on the abrasion rate of dental composites with a view to understanding the possible clinical effects of these processes. As there is much more clinical data available, it was decided to concentrate on three body abrasion, although my colleague has developed a two body device (Vowles et al 1988) so that laboratory testing of both processes can proceed side by side. As yet the latter device has been used only to determine differences between materials rather than the effect of physical and chemical agents (Vowles & Williams 1989).

Development of the Three Body Abrasion Wear Tester

In concept the device was similar to that used by Jorgensen (1982) having six samples weighted onto a revolving polishing wheel (Microcloth, Beuhler Ltd, Coventry, UK). The device is shown in Plate 181. The composite samples were fixed to the specimen holder with a cyanoacrylate adhesive (SAS 220 Dunlop, Birmingham UK).

Plate 181 shows 300 gms applied load; but during the pilot studies 150 gms was found to be adequate. The surface area of the samples was 40 mm^2 resulting in an applied force of 3.68×10^4 Nm^{-2}. Wear was determined as loss of height of the specimen measured with a comparator. Specimens were measured every minute for the first 10 minutes, then every 5 minutes up to 30 minutes and every 15 minutes up to 210 minutes. The abrasive medium was an aqueous slurry (25 gms/100 mls) of 1μm alumina which was exchanged every fifteen minutes. The speed of revolution was calibrated with an optical tachometer (Radio Spares, Corby, UK) to 180 per 1 minute.

Pilot studies were undertaken using samples of six different composites to test the precision of the device and to determine the predominant variables. The latter were found to be the speed of revolution and the age of the polishing cloth which were interrelated through the coefficient of dynamic friction between the cloth and the samples. Two test routines were tested: running six specimens of the same material together (individual test per material) or alternatively running one specimen of each material over six successive "runs" (common wear path). The result for six specimens of the same material tested together is shown in Fig 11-1 [A] whereas [B] shows the result for the alternative regime. Although the ranking order of the materials was virtually identical (Clearfil and P-30 were reversed), there was some difference in the absolute wear. Fig. 11-2 shows the individual point values for six consecutive "runs" of P-30. The differences resulted from minor variations in the speed of revolution and different change times for the polishing cloth. The resultant standard deviations for P-30, Profile and Concise are shown Fig. 11-3. From these pilot studies it was decided that the precision was sufficient to rank differences; but not to determine an absolute wear rate and that testing should always use a specimen from each condition over six consecutive "runs."

METHOD

As there were only six test stations on the machine, the effect of physical conditioning was tested separately to the effect of food simulating liquids (FSL's).

After conditioning the specimens were stored dry until testing which occurred at 210-280 days after the commencement of the experiment. The experimental conditions and codes are shown in Table 11-1. Six specimens for each group were tested.

RESULTS.

For all test conditions the materials showed a similar pattern in that any differences in abrasion were established within the first 30 minutes of testing when the surface layers were abraded. Figs 11-4 (A & B) and 11-5 (A & B) illustrate the pattern of abrasion over the full test

PHYSICAL PRE-CONDITIONS

GROUP	CONDITIONS	CODE
1*	No conditioning	Dry
2	Stored in H_2O for 42 Days	42 H20
3*	Stored in H_2O for 180 Days	180 H20
4	10^4 Thermal Cycles in H_2O^+	104 TC
5	5×10^4 Thermal Cycles in H_2O	504 TC
6	Stored at 60^oC in H_2O for 14 days	140 60oC

FOOD SIMULATING LIQUIDS

GROUP	CONDITIONS	CODE
1*	No conditioning	Dry
2*	Stored in H_2O for 180 Days	180 H20
3	Stored in 75% Ethanol for 180 Days	Alcohol
4	Stored in n-Heptane for 180 Days	Heptane

$^+$Cycled between 6^oC and 60^oC as described in Chapter 7.

*These groups were common to both experiments but separate samples were tested.

Table 11-1

period of 210 minutes. In these and the following graphs each point is the mean of the six "runs." Standard deviations were large but equal for all materials and were of the magnitude illustrated in Fig. 11- 3 . For clarity, error bars are not included on the graphs; but all data points were used in the statistical analysis.

Figures 11-6 to 11-12 show the abrasion patterns for each material over the first 30 minutes. The Y axis is scaled according to the overall wear for each material.

Statistical Analysis

The statistical comparison of multiple slopes with nominal condition values is a problem and statistics can only be used as aid to interpreting the graphs rather than as an absolute test of significance. Two statistical methods were used for this purpose. Firstly, a MANOVA of the abrasion value entering, time, condition and the interaction between these into the analysis. Secondly, a "snap-shot" analysis of the abrasion at 10 minutes using one-way AVOVA with the Scheffe Multiple Comparison Test (Appendix 2). With MANOVA two analysis' were conducted: one for early abrasion (Time <= 30 minutes) and one for late abrasion (Time > 30 minutes). As would be expected time was always highly significant and with the exception of Heliomolar and Silux both the physical and chemical conditions were a highly significant factor ($P<0.001$) on wear. However, for all materials, the interactions were not significant, indicating that the data points were insufficiently separated to determine significant differences between the individual slopes. The latter results from the high standard deviations at each time interval. The one-way analysis of variance at 10 mintues indicated that the variances were equal. However only for Clearfil, Occlusin and Profile (Physical conditions) and Concise, P-30 and Profile (FSL's) was there sufficient discrimination to determine significantly different subsets. The results of the ANOVA are given in Table 11-2.

Another way to examine the results is to examine the ranking order of the conditions over the seven materials. With physical conditioning it is apparent from the graphs that the samples conditioned by 50,000 thermal cycles ranked highest in six materials. With the FSLs the samples conditioned by alcohol ranked highest in four materials. Other than this there was no consistent pattern.

DISCUSSION.

It appears from the results that only conditioning by 50,000 thermal cycles had a consistently significant effect on the three body abrasion rate of the composites. Plates 72, 73, 75, 109, 110, 111 indicated that this regime resulted in gross surface degradation, although this treatment is far more severe than the clinical situation. If the wear machine reflects the three body wear process in the mouth; then the lack of discrimination between the

ONE-WAY ANALYSIS OF VARIANCE
THREE BODY WEAR AT 10 MINUTES

		504 TC	104 TC	108 H_2O	42 H_2O	1460oC	Dry
Clearfil F=5.83 P=0.000	1		*	*	*	*	*
	2	*	*	*		*	
Concise	F = 0.64	P = 0.67		No Significant Difference			
Helio	F = .023	P = 1.00		No Significant Difference			
Occlusin F=2.94 P=0.03	1		*	*	*	*	*
	2	*					*
P-30	F = 2.14	P = 0.09		No Significant Difference			
Profile F=7.67 P=0.00	1		*	*	*	*	*
	2	*	*		*		
Silux	F = 1.25	P = 0.31		No Significant Difference			

		Alcohol	Heptane	180 H20	Dry
Clearfil	F = 1.69	0.20		No Significant Difference	
Concise F=8.64 P=0.000	1		*	*	*
	2	*			
Heliomolar	F = .017	P = 0.97		No Significant Difference	
Occlusin	F = 1.84	P = 0.17		No Significant Difference	
P30 F=3.14 P=0.05	1		*	*	
	2	*			*
Profile F=3.78 P=0.03	1		*	*	
	2	*			*
Silux	F = 0.25	P = 0.86		No Significant Difference	

* Groups in homogeneous subsets.

Table 11-2

other groups indicates that the conditions are not a major variable influencing clinical abrasion. This statement is open to criticism: only one particle size was used in the slurry whereas De Gee et al (1986), Pilliar et al (1984) and Jorgensen (1982) noted the effect of interaction between particle size and materials on the three body abrasion. There was an extremely high abrasion rate for Heliomolar (Fig. 11-1A, Fig. 11-8), but data on file in this establishment indicates that this does not represent the clinical situation. The extremely high abrasion rate of microfilled materials has been found by other workers using three body abrasion devices (De Gee et al 1985, Aker 1982, Heath & Wilson 1976).

Of the Food Simulating Liquids: alcohol caused higher wear rates in Concise and P-30 (over the first 40 µm). As both materials use the same resin (Ruyter, 1985) this may indicate a specific effect with this formulation. The finding that Concise had a lower abrasion than all the other materials appears to be at variance with clinical experience. An important finding in this respect was made by McCabe (1985) who found a significant difference in abrasion rates between samples of this material marketed in 1978 and 1984 respectively. As ethical committees have not allowed the use of Concise as a posterior restorative material since 1985 there is no evidence as to how the present material would perform.

Taken together, the results in this chapter correspond with the findings in other chapters. The silver staining and scanning electron microscopy indicated that 50,000 thermal cycles causes much greater degeneration than any of the other conditions and this was the only treatment that consistently increased abrasion. The depth at which the initial high rate of abrasion of Clearfil, Occlusin, Profile and P-30 began to decrease corresponded to the depth of the outer coloured layer noted with this treatment (Chapter 7). This indicates that the high initial rate was a function of the degraded surface. These results agree with the findings of Pilliar et al (1984) and Heath & Wilson (1977) that in conventionally filled materials aging in water does not affect three body abrasion. This is at variance with the finding of Marcos-Montes et al (1986) that long term exposure to water increased the three body abrasion rate. The results do not contradict the work of Mc Kinney & Wu (1985) who found that 75% ethanol had a highly significant effect on the pin on disc wear of composites; but the difference in these results confirms the need to consider abrasion and attrition separately. Chadwick et al (1989) found that storage in different buffers had a significant effect on hardness but not on abrasion. They concluded the the buffers acted only at the very surface. Experiments in this laboratory are presently underway to determine the effect of repeated exposure/abrasion cycles; but so far there are no conclusive results.

CHAPTER 12

GENERAL DISCUSSION

The experiments reported in this thesis were initiated to study the permeability and degradation of dental composites within the context of understanding their effect on wear. The most important finding was that whilst composites may be degraded by physical and chemical treatments in the laboratory, clinically these processes are unlikely to be a major influence on wear in the present generation composites. The discussion in this chapter contrasts the laboratory and clinical findings and then considers the process of clinical wear in the light of this and contemporary studies. Since 1984 it has become increasingly apparent that abrasion and attrition must be considered separately (Lutz et al 1984, Lambrechts et al 1984, Roulet 1987b, Roulet 1988, Bloem et al 1988). However, some publications even in 1989 have disregarded this distinction.

A factor that has been implicated in the discrepancy between clinical and laboratory studies is water sorption (Lloyd 1982, Pilliar et al 1986, Oysaed & Ruyter 1986b). The presence of water may cause hydrolysis of the filler matrix bond thereby increasing the ease with which fillers are displaced in both abrasion and attrition (Oysaed & Ruyter 1986B, Braden and Clarke 1984, McKinney 1985). The experiments reported in Chapters 5 and 6 indicated that water sorption in dental composites may deviate from the classical "Fickian" model which has generally been accepted. Penetrants may localise relatively close to the surface by a process associated with the phenomenon of Case II sorption. Although the results did not fit the mathematical model for Case II sorption there was definite evidence of a diffusion layer. This pattern of diffusion would potentiate any effect of water sorption on wear; but in the in vitro experiment (Chapter 11), prolonged water sorption did not have a significant effect on abrasion. The latter result was also found by De Gee et al (1985), Pilliar et al (1984), Wilson et al (1981), Heath and Wilson (1977). Considering water sorption in the three materials used for the clinical trial, the ranking order (increasing) was Occlusin, Clearfil, P-30. The ranking order for the depth of silver stain was Occlusin, P-30, Clearfil. Neither of these orders corresponds to the clinical result for either abrasion or attrition in which Clearfil was superior to the other materials. In the laboratory experiments the silver stain in Clearfil was lighter than in the other materials. The hypothesis for the colour of the silver predicts that the size of microcavites in this material were smaller. As microcavites are potential sites for subsurface dissolution (Marom 1985) or cracking as a result of osmotic forces (Fedors 1980a&b), this may indicate that Clearfil was less susceptible to these processes. In the examination of restorations removed for replacement, only P-30 showed signs of increased permeability after degradation in the mouth. The silver sorption layer was deeper and blacker especially at the resin rich proximal surface. However, scanning electron microscopy indicated that only in a 3 year old specimen was there gross evidence of degradation. Oysaed & Ruyter (1986b) found that this material had the greatest ionic leaching from the filler component, the major element being boron. Although this may indicate dissolution of the glass as a result of water sorption (Soderholm 1981, 1983), the same study found considerable ion leaching from Occlusin which showed virtually no degradation in the present study. This indicates that, at present, there is no definite relationship between degradation at an ionic level and structural changes seen by microscopy.

Associated with penetration is the potential for chemical dissolution. McKinney & Wu (1985) found that 75% ethanol decreased the hardness of composites and increased the rate of attrition over the first 150 microns of wear. The former finding has recently been substantiated by Kao (1989). The experiments in Chapter 7 indicated that the penetration depth of an alcoholic solution of silver nitrate was about 3x greater than an aqueous solution. Clearly alcohol can penetrate deeper into the material, but the electronmicroscopy studies did not find evidence of gross degradation as a result of prolonged immersion in ethanol. In the in vitro abrasion test (Chapter 11), conditioning in 75% ethanol caused an increased wear rate only in three materials. Therefore, although 75% ethanol may decrease the hardness of materials, it does not necessarily increase the wear rate. The lack of association between hardness and wear was reported by Harrison & Draughn (1976) and Chadwick et al (1989) showed that although buffer solutions reduced the hardness of composites; there was no significant effect on wear. Ethanol is quoted as a simulating fluid for alcohol and alcohol containing foods BFFDA (1976, 1988). McKinney and Wu (1985) noted that the softening effect of 25% alcohol was far lower than 75% alcohol. Only the strongest of alcoholic drinks approach even the former concentration and it can safely be assumed that the exposure time of a restoration to this environment is negligible in the vast majority of the population. Furthermore, as the softening effect of alcohol is reversible (Wu et al 1982), it seems reasonable to conclude from all these results that alcohol has a limited effect on clinical abrasion.

The experiments reported in Chapter 7 indicated that in the laboratory thermal cycling and prolonged storage at 60^{o}C caused considerable degradation in the composite surface as a result of thermal cracking. However, investigation of temperature changes at a restoration surface indicated that these processes were unlikely to be effective in the clinical situation. This was again borne out by the subsurface analysis (Chapter 10) which showed no sign of "layering", an effect seen after laboratory conditioning (Chapter 7). The important factor determining surface temperature changes appears to be to the heat transfer coefficient (Jacobs 1973) and also the control of the food pathway by the soft tissues.

In the experiment reported in Chapter 5, it was found that a number of anterior restorations had a localised stained zone in association with areas of attrition. However, in Chapter 10 there was no evidence of subsurface staining in two posterior composites, even in association with a clearly defined attrition scar (Plate 163). The experiments on mechanical cycling (Chapter 7) indicated that local areas of fatigue damage could be caused by repetative compression cycles. The damaged area stained with $AgNO_3$; but was not evident with scanning electronmicroscopy indicating that the network of microcracks was extremely fine and probably more akin to crazes. Roulet (1987c) reported good correlation between laboratory attrition caused by a fatigue wear tester and clinical attrition. Whilst not disputing this finding, there was no evidence in the clinical specimens of the three posterior composites to suggest that subsurface damage was a major feature of clinical attrition. Two body abrasion and adhesive wear are probably of far more importance, although the presence of saliva as a lubricant should minimise these effects (Bloem et al 1988).

It is apparent that many factors affect abrasion and attrition. The clinical trial demonstrated that the causal factors may be independent although some will obviously be interrelated. For example, a high attrition rate allows the two occlusal surfaces to approximate thus increasing the force on the masticatory slurry. De Gee et al (1989) demonstrated a significant relationship between abrasion and the force between the two mating surfaces.

The major factors affecting wear are listed in Table 12-1. Included in the table are my opinion of the significance of each of the factors on the two processes and these are discussed below.

Materials: The material itself is still a major variable in the determination of wear. It was clear from the clinical study that Clearfil had the greatest resistance to both abrasion and attrition. In some ways this was surprising because the material has many of the features of the early composites, being a chemically cured two paste system with large quartz filler particles. The major difference from the early composites was its high filler loading: (84% by weight; 68% by volume (Appendix 1) and the incorporation of 35% TEGDMA as a diluent monomer (Tani 1985, Pilliar et al 1987). As discussed in the introduction, the flexible molecule of TEGDMA increases the degree of conversion of the material. However the filler loading alone cannot be reponsible for the performance because both Occlusin and P-30 have similar values, 85.6% & 83.9% repectively (Ruyter & Oysaed 1987), but behaved differently clinically. An explanation for this difference

Relative Importance of Variables on Wear

		ABRASION	ATTRITION
Material	Resin	3	3
	Fillers	3	3
	Coating	3	3
	Solubility Parameters	2	2
Surfaces	Contour of Centric Stops	1	3
	Marginal Contour	3	1
	Opposing Cusp Morphology	1	3
	Food Shedding Pathway	3	1
General Oral Factors	Occlusal Force	1	2
	Masticatory Movements	1	3
	Saliva/Plaque pH	1	1
General Patient Factors	Abrasivity of Diet	3	1
	Chemical Nature of Diet	1	1
	Thermal Nature of Diet	1	1
	Toothbrushing	1	0
	Oral Hygiene	1	1

3 Highly Important
2 Important
1 Limited Importance

Table 12-1

may have been the difference in hardness of the filler glasses (the Vickers hardness of the three materials are: Clearfil 130, Occlusin 122, P-30 180[1]). At present the relative importance of the various components of the materials is far from understood; but overall they contribute a highly significant variable in the process of wear. Another material factor to be considered is the depth of cure in the deeper layers of the materials. It has been shown that hardness decreases with depth (Prevost et al 1985, Watts et al 1984, Eliades et al 1987, Rueggenberg & Craig 1989). The latter study also indicated that resin leaching increased with depth. Although these two factors might be expected to increase the rate of wear at greater depths, clinical evidence shows that the converse is true (Leinfelder 1987, Jendrenson 1988). This behaviour can attributed to two mechanisms: firstly, the increased abrasion rate of the resin rich surface; and secondly, the apparent increase as thin edges of composite at the margins are worn away.

<u>Surface</u> <u>Factors:</u> As discussed in Chapter 9, the occlusal relationship between a restoration and its opposing surface is an important variable on both processes. Undercontouring of centric stops causes early attrition scars, "high spots"; this being a fault of the operator rather than the material. The latter statement is

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[1] Data on file for the DoH

collaborated by the lack of significant difference between the number of scars with amalgams or composites. The publications of Lutz et al (1984) and Roulet (1987b&e, 1988) can give the impression that attrition is synonymous with wear scars. Clearly this was not the case as there was often considerable attrition in the absence of such scars. In the laboratory contact stress has been shown to be a significant variable on wear (Baily & Rice 1981, Harrison & Moores 1985). This is determined by the contact area between the two surfaces and the occlusal load; the former being influenced by the contour of both surfaces. Of course, it is a fundamental principle of wear that no surfaces are completely flat and the roughness of the restoration will influence wear. The latter is a function of not only the material; but also its effect on the opposing surface. It has been shown that there is a significant interaction when different restorative materials opppose each other (Embong et al 1987).

Two local factors were found to have a highly significant effect on abrasion: firstly, the food shedding pathway and secondly, the marginal contour of the restoration. Another site can be where the masticatory slurry is forced out into the embrassure. The importance of marginal contour does not appear to have been previously recognised although Davidson (1987) noted the high rate of abrasion with bevelled margins. The frequency distributions for abrasion indicate that individual restorations are subject to high abrasion rates and the local contour will be a major variable in these cases. Another factor which has been associated with wear is the finish of the restoration which has been the subject of recent research (Northeast & Van Nort 1988, Tjan & Chan 1989). However it appears that, provided the restoration is finished taking precautions to minimise overheating, then the final polish will have little effect on wear because the surface layer is abraded away within one year (Leidal et al 1985, Xu et al 1984, Abell et al 1983, O'Brien & Yee 1980). Nonetheless the surface finish may be of importance in determining staining and degradation of the proximal surface. In this study the resin rich layer was intact in all materials at three years, although one specimen of P-30 was showing evidence of degradation (Plates 159/160).

General Oral Factors: The contact stress resulting from the occlusal morpholgy of the individual restoration and its opposing tooth appears to be more significant than the overall occlusal force. Although Asmussen (1984) found that the hardness of restoration surfaces was decreased by "plaque simulating" acids, Chadwick et al (1989) indicated that this does not necessarily increase the wear rate. As the analysis of the Clearfil and Occlusin "biopsies" indicated no evidence of degradation, it seems reasonable to conclude that oral pH was not a major effect on these materials. However, the increased permeability of P-30 may have had a contribution from this process.

General Patient Factors: The abrasivity of the diet, interacting with the food shedding pathway, is probably the most significant variable affecting abrasion. De Gee et al (1986) found that the abrasion rate varied with different consignments of the millet seed that he used as an abrasive medium; presumably because they varied in abrasivity. As to the chemical nature of the diet, the results discussed in this thesis suggest that the physical factors discussed above, are more significant than chemical degradation. This conflicts with the concept of Leidal et al (1985) that loss of material may be primarily a chemical process predisposing to mechanical wear.

A current trend in the study of wear is to generate general mathematical expressions for wear as functions of its causal factors (Taylor et al 1989b, Sarrett & Soderholm 1989). In my opinion this is not a valid exercise because, as demonstrated by the permeability effect with P-30 (Chapter 10), each factor may have specific interactions with individual materials or each other. To compensate for this in a general formula every factor would have to have a function for its interactions. Therefore a simple formula would be

$$\text{Wear} = F_m + F_l + F_{ilm} + F_a + F_{ial} + F_t$$

where
F_m = Function of material
F_l = Function of load.
F_{ilm} = Function of the interaction between load and material.

F_a = Function of abrasivity of the diet.
F_{ial} = Function of the interaction between abrasivity and load
F_t = Function of time

This formula does not take into account second degree interactions which may also be important. Although modern statistical computer packages are capable are solving this equation the function values [F] would almost definitely change as each new set of data was entered. Therefore besides being extremely complicated the equation has no value. The only appropriate use of the mathematical approach may be to determine dominant effects with each material and to make people aware of the complexity of the situation.

SUMMARY AND CONCLUSIONS

This work was undertaken to determine the relationship between permeability, degradation and wear. It was found that the subsurface porosity previously reported was mainly caused by artefacts. By changing the optical pathway it was possible to observe a zone of subsurface stain in twenty out of thirty four specimens. In the majority of cases the staining was limited to localised areas on the exposed surface of the restoration, sometimes in association with an attrition facet. EDX analysis was unable to determine which materials were subject to degradation. It is concluded that subsurface degradation had occurred in some of the composite biopsies; but that its occurence was not as universal as previously described.

During the development of the silver staining technique an entirely new phenomena of a " Silver Sorption Layer" was discovered. Investigation of this layer suggested that the silver ions may be acting as marker ions indicating the extent of fluid penetration into the material. It is suggested that this may indicate that sorption in dental composites doesn't follow the classical "Fickian" model; but tends to accumulate in uniform concentration layers at the surface. However the results did not fulfil the three criteria for Case II sorption.

The colour of the "Silver Sorption Layer" was predominantly brown compared to the usual black precipitates of metallic silver. Transmission electronmicroscopy of two unfilled polymers demonstrated that the silver particles giving rise to the brown colour in composites were smaller than those causing the black colour. It is concluded that the colour of the silver zone depends upon the size and distribution of silver particles in the layer. Furthermore, it is suggested that the colour is caused by the diffraction of light by small particles as predicted by Mie Theory.

In the laboratory both physical and chemical treatments caused considerable degradation of the surface, as determined by silver staining and scanning electronmicroscopy; but the composite restorations recovered from the clinical trial showed no similar features. It is concluded that whilst composites can be degraded in vitro, clinically the effect is very limited and unlikely to be a predominant variable affecting wear. However, there was a very definite difference in the in-vivo permeability and degradation of one material (P-30) and it is concluded that degradation is highly material dependent.

In line with contemporary thought, the clinical study indicated that abrasion and attrition occurred at varying rates in different materials. No definite cause for the behaviour was apparent, but it is now obvious that both processes must be considered individually. It is concluded that local occlusal factors and the abrasivity of the diet are more significant variables determining wear than physical or chemical degradation.

This study has concentrated specifically on wear which is only one aspect of clinical performance. All three operators involved with the clinical study subjectively feel that the three materials are performing adequately at the four year stage. Objective analysis of the data indicates high variances for all the parameters under investigation. This suggests that differences in the clinical performance of materials can only be determined by large scale clinical trials. There is general agreement that the number of factors interacting to determine clinical wear are too numerous to be effectively included in an in vitro wear test. Nonetheless laboratory studies have an important role towards understanding the effect of the individual factors which affect wear. It is hoped that some of the findings reported in this thesis will be the foundation for further study.

APPENDIX 1

MATERIALS USED IN THE LABORATORY STUDY

The three posterior composites Clearfil, Occlusin and P-30 had been selected for clinical evaluation by the Department of Health. The remaining four materials were chosen to represent comparative aspects of composite technology. Thus, Heliomolar utilises microfilled technology in a material designed for posterior restorations, whereas Silux is an anterior material of this type. Silux was choosen as opposed to the anterior material manufactured by Vivadent because it was decided to use three materials by the same manufacturer. Therefore, P-30, Silux and Concise are all made by the 3-M Company (Table A1) and have similar polymers (Ruyter 1985). Concise was selected partly for the latter reason and also to compare a chemically curing anterior composite with the posterior material Clearfil-Posterior. Profile-TLC was chosen as a material which represented the development stage of posterior composites. The light cured form was selected because in 1985 it was apparent that light curing was gaining wide acceptance by the dental profession.

IN THIS THESIS PROFILE REFERS TO PROFILE - TLC (LIGHT CURED) UNLESS OTHERWISE STATED. CLEARFIL ALWAYS REFERS TO CLEARFIL POSTERIOR.

Table A1 gives details of the manufacturers and summarizes the general properties and use of the materials. Table A2 shows the constituents of the materials. The references for the polymer contributions are given. Filler loadings were determined gravimetrically as part of the experiments for this thesis. Weight percentage was determined as weight before and after ashing at 600°C. Volume percentage was determined with 10 ml density bottles. The ashed composites were left in the bottles for one week to ensure complete saturation before final weighing. Weighings were to four places of gram decimals. Three separate analysis' were performed for each material and the standard deviations are included in the table. The pre-polymerised particle size of the microfilled materials were assessed by photographing polished (1μm Alumina) specimens with a Normaski microscope. The slides were magnified (x 10) in an enlarger and the filler outlines traced onto graph paper together with an image of the standard scale.

MATERIALS INVESTIGATED

MATERIAL	MANUFACTURER	TYPE	CURING	POSTERIOR USE
CONCISE	3.M. Company Minnesota, USA	CON.	CHEM	NO
CLEARFIL (Posterior)	CAVEX Haarlem, Holland	CON	CHEM	YES
HELIOMOLAR (Universal)*	VIVADENT Schaan Liechtenstein	MICRO	LIGHT	YES
OCCLUSIN (Standard)*	I.C.I. Macclesfield, U.K.	HYBRID	LIGHT	YES
P - 30 (Universal)*	3.M. Company	CON	LIGHT	YES
PROFILE TLC (Shade SS)*	S.S. WHITES Philadelphia, U.S.A.	CON	LIGHT	LIMITED
SILUX (Universal)*	3.M. Company	MICRO	LIGHT	NO

CON = CONVENTIONAL FILLERS. MICRO = MICROFILLERS.

CHEM = CHEMICAL CURE.

*SHADE

Table A1

CONSTITUENTS

MAT.	POLYMERS AND PERCENTAGES		REF	FILLERS MEAN SIZE (μm)	% FILLER BY WEIGHT	% FILLER BY VOLUME	BATCH NO.
CON	Bis-GMA TEGDMA	73 24	1	QUARTZ 50	79.65 (0.47)	61.08 (1.27)	P861112
CLE	Bis-GMA TEGDMA	65 35	2	QUARTZ 80^{+}20	84.02 (0.24)	68.15 (2.37)	43116
HELIO	Bis-GMA EGDMA	69 22	1	COLLOIDAL SILICA 10*	60.87 (1.48)	39.45 (2.61)	372201
OCC	TUDMA TEGDMA	56 54	1	BARIUM GLASS 10	85.71 (0.36)	75.53 (1.88)	PA61B
P30	Bis-GMA TEGDMA	54 46	1	ZINC GLASS 3	84.74 (0.48)	70.23 (2.39)	P8701102
PRO	Bis-GMA EGDMA	64 34	1	STRONTIUM GLASS 3.5	81.79 (1.10)	71.94 (2.37)	358702
SIL	Bis-GMA TEGDMA	40 60	3	COLLOIDAL SILICA 40*	54.55 (2.12)	39.65 (3.87)	6W1R

Figures in Parethesis = Standard Deviations

Bis-GMA	Bisphenol A Glycidyl Methacrylate
EGDMA	Ethyleneglycol Dimethacrylate
TEGDMA	Triethyleneglycol Dimethacrylate
UDMA	Urethane Dimethacrylate
TUDMA	Modified Urethane Dimethacrylate

1 (Ruyter 1985)
2 (Tani 1985, Pilliar et al., 1987)
3 (Eliades et al, 1987)
\+ This material has a biomodal distribution
* Size of prepolymerised particles

Table A2

APPENDIX 2

STATISTICAL METHODS

The routine statistical techniques used in this thesis are described in standard textbooks notably the excellent work by Chase & Bown (1986). This Appendix elaborates on the more advanced techniques.

ANOVA & MULTIPLE COMPARISON TESTS (Homogeneous Subsets.)

Analysis of Variance is a routine statistical procedure used to negate the null hypothesis that experimental groups could have been selected by chance from a single parent population. Having negated this in favour of the alternative hypothesis, that there was a significant difference between means, then Multiple Comparison Tests were used to determine which groups were significantly different. The use of the tests available was discussed by Kirk (1982) and the test used in this thesis was the Scheffe Test. This is a conservative test and was chosen to discriminate between means from groups with small sample numbers. Rather than present the results as significantly different groups, they have been presented as homogeneous subsets. These are groups, which considered together, could have arisen from a single parent population. Table A3 shows five means with their standard deviations. The means are obviously different and fall into 5 separate subsets. In B the differences are less and the means 13, 15 and 19 could have arisen by chance from a single

SUBSET NO.	GROUP MEANS (STDs)				
1	10 ±2				
2		33 ±4			
3			55 ±6		
4				76 ±3	
5					98 ±7

A

1	13 ±8	15 ±7	19 ±8		
2			19 ±8	23 ±9	27 ±8

B

Table A3

population as could the means 19, 23 & 27. It is noted that 19 is common to both subsets being the highest value in Subset 1 and the lowest in Subset 2. Means that appear in only one subset are significantly different from means that appear in the other, thus 13 & 15 are significantly different from 23 & 27. The advantage of homogeneous subsets is that they help to visualize materials that are similar and which may have common properties. Thus in Chapter 7, under Mechanical Cycling (Table 7-6), the microfills were in Subset 1 and the large filler materials in Subset 4.

MULTIVARIATE ANALYSIS OF VARIANCE (MANOVA)

This is an advanced Analysis of Variance used to determine the effect of the independent variables on the overall variance of the dependent variable. Thus in Chapter 9, the test was used to assess the effect of the independent variables, Cavity Type, Tooth Type, Quadrant, Material and Operator on the dependent variable abrasion. MANOVA indicates the significance of the variance (of the dependent variable) accounted for by each of the independent variables, when the effect of the others are taken into account. Therefore, Tooth Type and Material had significant effects on the variance of Abrasion. Each factor may interact with others. For instance, Material had a significant interaction with Operator. This means that one or more materials were specifically affected by one of more operator. The MANOVA does not indicate which

Material or Operator were involved. *However, Fig. 9-4* indicates that the interaction was between Occlusin & PRA 1. Therefore, MANOVA helps to indicate which variables may be significant or interacting rather than being an absolute test of significance.

MULTIPLE LINEAR REGRESSION

A regression equation can be built for a dependent variable as functions of the independent variables. Therefore, it is possible be to build a formula for children's height as

$$\text{Height} = B_i a\ (\text{Age}) + B_i s\ (\text{Sex}) + Bo$$

where the B_is are the slope values for Age and Sex. and B_o is the origin or constant.

In the above example Age is a ratio value (between 0 and ∞) whereas Sex cannot be given a true numerical score. However, it is possible to ascribe two "dummy" values for Sex namely 0 & 1 (It doesn't matter which way round).

If the B_is arbitarily placed at 0.25 & 0.1 respectively and the B_o at 0 then if Male = 1 and Female = 0

$$\text{Height} = 0.25\ (\text{Age}) + 0.1\ (\text{Sex})$$

From this equation the height of males and females from age 5-10 =

Age	Female	Male
5	1.25	1.25 + 0.1
6	1.50	1.50 + 0.1
7	1.75	1.75 + 0.1
8	2.00	2.00 + 0.1
9	2.25	2.25 + 0.1
0	2.5	2.50 + 0.1

If these values are plotted (Fig. A2A) then the variable sex always causes the same difference at any age. The two resulting regression lines are parallel with a difference of (0.1).

Now if the interaction between Age & Sex is introduced (Interaction = Age x Sex) the equation becomes

Height = B_ia(Age) + B_is(Sex) + B_ii(Interaction).

If B_ii is placed arbitarily 0.2, then the height for a girl aged 5 =

Height = (0.25 x 5) + (0.1 x 0) + (0.2 x 5 x 0) = 1.25

and the height for a boy aged 5 =

Height = (0.25 x 5) + (0.1 x 1) x (0.2 x 5 x 1) = 2.35

Similarly the height for boys and girls aged 5 - 10

Age	Female	Male
5	1.25	1.25 + 0.1 + 0.2 x 5
6	1.50	1.50 + 0.1 + 0.2 x 6
7	1.75	1.75 + 0.1 + 0.2 x 7
8	2.00	2.00 + 0.1 + 0.2 x 8
9	2.25	2.25 + 0.1 + 0.2 x 9
10	2.50	2.50 + 0.1 + 0.2 x 10

If these lines are plotted (Fig. A2B) the result is two diverging regression lines indicating that for each age there is a proportional increase in height. From the diagram it is seen that the two lines would be separated at the origin by 0.1 (the B_i of the condition [SEX]) and the slopes then increase by the B_i of the interaction. In the above example the B_i values were placed arbitarily, however Multiple Linear Regression calculates their true values from the data. The B_i values cannot be used to the assess significance of each independent variable because they

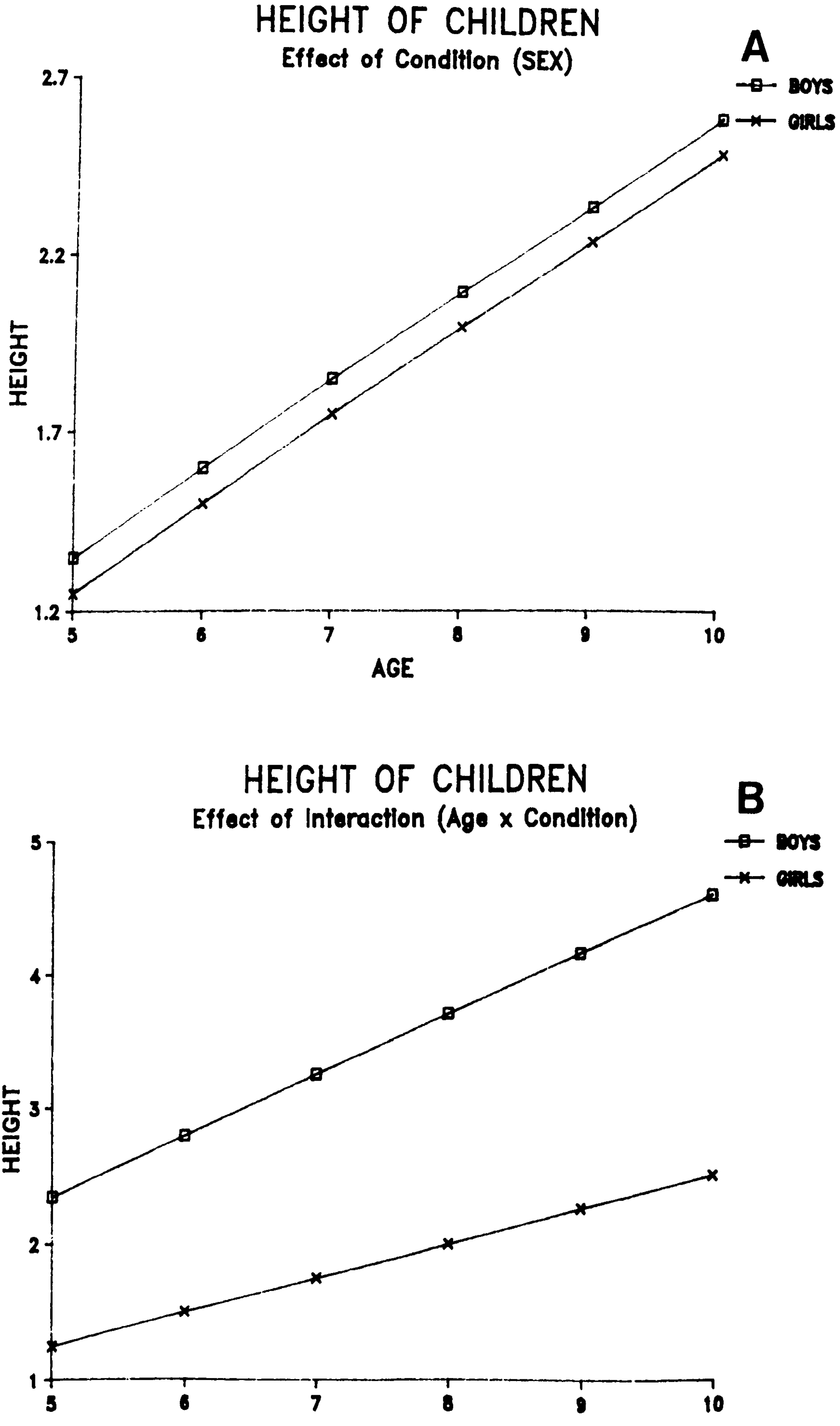
HEIGHT OF CHILDREN
Effect of Condition (SEX)
A
BOYS
GIRLS
HEIGHT
2.7
2.2
1.7
1.2
5
6
7
8
9
10
AGE
HEIGHT OF CHILDREN
Effect of Interaction (Age x Condition)
B
BOYS
GIRLS
HEIGHT
5
4
3
2
1
5
6
7
8
9
10
AGE

Figure A2

depend upon the units in which the variables were measured. However, it is possible to calculate BETA coefficients from the B_is and the ratio between the standard deviation of the independent variable to that of the dependent variable. For each BETA coefficient there is an associated T value from which the significance of each independent variable is assessed.

From Fig. A2 it can be seen that if the B_i condition [Sex] is significant then there is a difference in the two regression lines at the origin. If the B_i of the interaction is significant then the slopes are significantly different. Naturally both the B_i's can be significantly different. This test was used to test the differences of slopes in the sorption experiments (Chapter 6) and the conditioning experiments (Chapter 7). In both case only two conditions were tested and these were ascribed the dummy values 0 & 1 as in the case of Sex in the example. Significant B_i(interaction) indicated differences in slopes. The significance of B_i (condition) is discussed in the text and Figs. 5-6 & 7-2.

NON-PARAMETRIC DATA AND TRANSFORMATIONS.

ANOVA, MANOVA and Multiple Regression require that the data has a normal (parametric) distribution. If the data is not normally distributed then it should be tested by non-parametric tests. In this thesis the Kruskal-Wallis was used for the Analysis of Variance of non parametric data and the Mann Whitney U test for testing two groups. However, it is often useful to be able to use a parametric test such as MANOVA to give an insight into the significance of the independent variables. To this end it is sometimes possible to transform the data so that it has a reasonably parametric distribution. The most common transformations involve taking Logarithms or Square Root values. Any transformed data must be tested to see if fulfills the requirements for the parametric tests. For the ANOVA analysis transformed data was tested with the Bartlett-Box test and for MANOVA by examination of the detrended plot of residuals. These are explained in the Advanced Statistics Guide (Norusis 1983).

I am grateful to the three statistitians who helped me understand and apply these techniques. Of special importance was the advice that statistics should be used to prove the significance of a relationship which is apparent on a visual representation of the data, rather than to find spurious relationships in vast amounts of data.

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An investigation into the permeability of composite materials using silver nitrate

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Abstract – A new effect of silver-nitrate staining on dental composites and unfilled polymers has been observed which may be useful in the study of polymer permeability. After extended storage in silver nitrate, the materials developed a layer of brown stain in the subsurface. The color was thought to be caused by the presence of finely divided silver precipitated in microcavities within the composite. Energy Dispersive Analysis by x-ray confirmed the presence of silver in the stained zone. The width and shade of staining varied in different materials. After 90 days, layers of different shades could be seen within the stained zone. The exact shade of the stain is thought to depend upon the size of the precipitated silver particles, which is directly related to the sizes of the microcavities.

Silver nitrate has been used to stain the subsurfaces of composite fillings that had been removed for replacement (Wu and Cobb, 1981; Wu *et al.*, 1984) and to study marginal leakage (Wu *et al.*, 1983; Hammesfahr *et al.*, 1987). In these investigations, black metallic silver was grown in subsurface porosities or interfacial defects. The present investigation concerns a previously unrecognized effect of silver-nitrate staining. After extended storage in silver nitrate and subsequent exposure to daylight, samples of composite developed a zone of brown stain in the subsurface of the material. The exact shade of brown varied in different materials, and in some materials layers of various shades occurred after prolonged storage.

Most polymers absorb water from their environment (Barrie, 1968). This may result in swelling of the polymer, seen especially as a result of water bridges forming between the hydroxyl groups on the polymer chains (Spencer and Honeycutt, 1973). In some dental applications, this hygroscopic expansion is considered a useful compensation for polymerization shrinkage. In other situations, the presence of water may accelerate the diffusion of oxygen and other gases into the polymer, allow for permeation of ions, facilitate hydrolytic degeneration, and encourage the growth of molds, algae, and fungi (Perera and Selier, 1973). Methods commonly used to measure permeability are based on the weight of diffusant gained by a material and give no indication as to the location of the diffusant in the material (Crank, 1968). Although the penetration of silver nitrate cannot be directly compared with the penetration of water or ions, it may allow for an assessment of changes in the organic matrix caused by an inorganic diffusant. Silver nitrate, of course, is not an organic solvent, and in solution its ions are univalent and should be able to diffuse more rapidly than higher valency ions (Meares, 1968).

This investigation concerns seven dental filling materials in which the effect was first recognized and studied. The aim of the present investigation was therefore to confirm the presence of the brown zone, to observe its progression with time, and to identify silver within the zone.

MATERIALS

Seven dental composites were selected to include conventional, microfilled, and hybrid materials, some of which are recommended for posterior restorations (Table 1). Composites develop a resin-rich surface when they are packed in moulds or cavities resulting from the preferential flow of the resin phase over the particle phase. Both resin-rich surfaces and surfaces from which the layer had been removed were investigated. An unfilled BIS-GMA resin (Enamel Bond, 3M Company) was included for observation of the staining developed in this material.

METHODS

Rectangular bars (Fig. 1) of each material were prepared by the packing of the composite into split stainless steel moulds. The open surface of each mould was covered with a glass slide which closed the open surface of the mould and allowed a window for light-curing. Where appropriate, the composites were light-cured in sections along the bar. After removal from the mould, the bars were cured again on all surfaces to ensure complete setting. An identification groove was cut along the surface which was at right angles to the surface under the glass slide. This latter surface was designated the "resin-rich" surface. The opposite

TABLE 1

Material	Manufacturer	Type	Curing	Posterior Use
CONCISE	3M Company, Minneapolis, Minnesota, USA	Con.	Chem	No
CLEARFIL (Posterior)	CAVEX Haarlem, Holland	Con	Chem	Yes
HELIOMOLAR	VIVADENT Schaan, Liechtenstein	Micro	Light	Yes
OCCLUSIN	I.C.I Macclesfield, U.K.	Hybrid	Light	Yes
P - 30	3M Company	Con	Light	Yes
PROFILE TLC	S.S. WHITE Philadelphia, U.S.A.	Con	Light	Limited
SILUX	3M Company	Micro	Light	No

Con = Conventional fillers; Micro = Microfillers; Chem = Chemical cure.

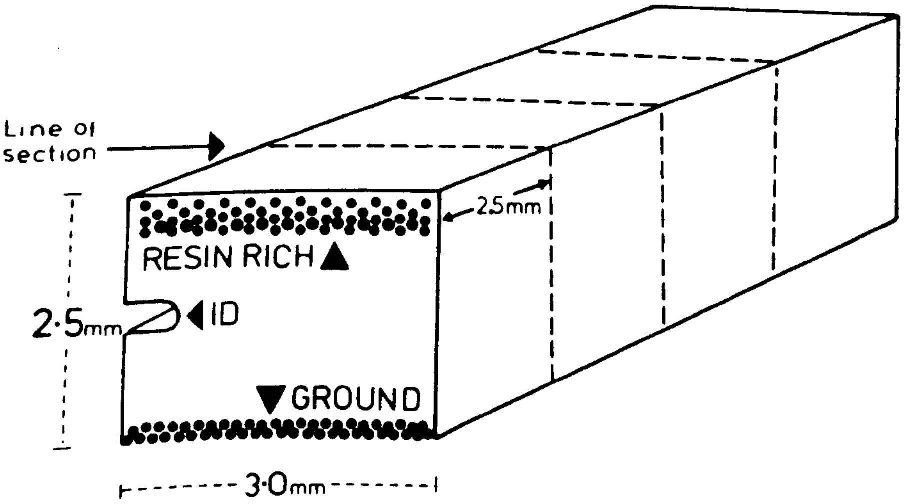

Fig. 1. A sample bar before being sectioned into four individual samples.

surface was ground on wet silicon carbide paper (240 grit) for removal of the resin-rich layer. This surface was designated "ground". Finally, the prepared bar was cut into 2.5-mm sections by means of a carborundum saw. The final size of each sample was, therefore, 3.0 mm × 2.5 mm × 2.5 mm (Fig. 1).

Twenty-five samples of each material were prepared and immersed in silver-nitrate solution (3 mol/L). The specimen bottles were filled to ensure a large volume of silver nitrate relative to the volume of the samples. The bottles were stored in complete darkness. Three samples of each material were removed after one, six, 10, 26, 42, and 90 days, respectively. They were washed in two beakers of water for removal of excess silver nitrate. In pilot experiments, the samples were then irradiated with ultraviolet light and placed in developer for 10 hours. However, this did not affect the eventual color, and it is now considered that these stages are unnecessary.

The samples were then placed in cylindrical moulds and embedded in PMMA resin. They were then ground on wet silicon carbide grits of successive fineness (240, 400, 600, 1200 UK Grit) and then polished with 1-micron aluminum oxide on microcloth by means of an ultrasonic polisher (Vibromet, Buehler UK Ltd, Coventry, England).

Microscopy and Measurement

The brown zone was observed with reflected scattered light, which shows the color rather than the reflectivity of a surface. Scattered light microscopy is usually achieved by use of the oblique illumination of dark-field techniques. The brown zone is clearly visible with dark-field illumination, but in this study a more convenient approach was devised which used a reflected light microscope with polarizing filters (Photomicroscope, Zeiss, Inc., Oberkochen, West Germany). The incident beam was polarized, and then, in the reflected beam, the second polarizer (analyzer) was set to polarize out all directly (specularly) reflected light. The scattered light passed through the analyzer and was focused to image the specimen. The advantage of this system is that scattered light microscopy (showing color) could be alternated with bright field microscopy (showing structure) simply by rotating or withdrawing the analyzer. Therefore, the brown zone could be compared with the filler distribution of the composite. Measurements were made with an eyepiece graticule that was calibrated against a standard grating. Three measurements were made at successive intervals along each surface to an accuracy of 5 microns. Color photomicrographs were taken of each material at each interval to facilitate qualitative assessment of color changes.

Energy Dispersive Analysis by x-ray (EDX)

A sample of one of the materials (Profile) was removed from the silver nitrate after 72 days and thoroughly washed. It was ground to produce a cross-section that could not have been contaminated by surface adsorption, mounted on a specimen-holder, and carbon-coated. The surface was viewed with the electron microscope (JEOL 100 CX, JEOL U.K., London, England) in its scanning mode. The electron beam scanned a 50-μm^2 area of the sample corresponding to the stained area. X-rays emitted as a result of the interaction between the sample and the electron beam were analyzed to produce a trace showing the number of x-ray pulses for each specific energy level (KeV). The trace was compared with a standard chart showing the specific energy levels associated with each element. In the case of silver, the highest count is for the Lα x-ray emission.

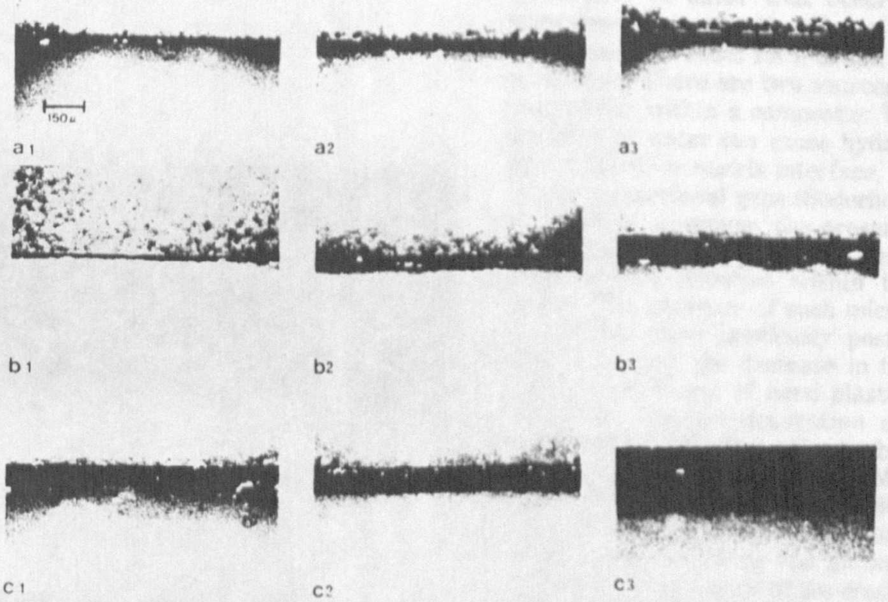

Fig. 2. **The increasing width of stain at 10 days (1), 26 days (2), and 90 days (3). Materials: (a)P – 30, (b)Silux, and (c)Profile.**

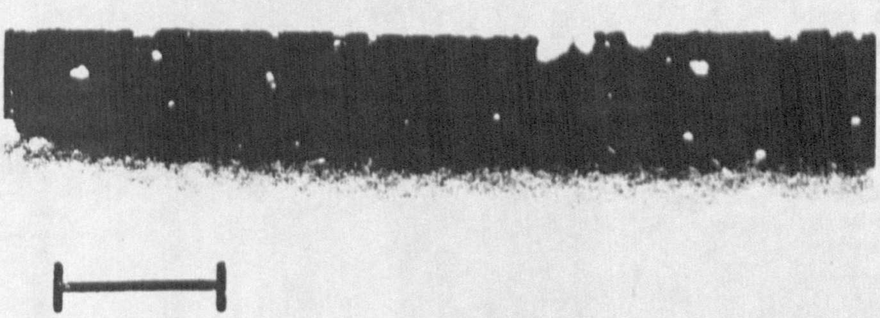

Fig. 3. **P-30 at 90 days showing layers decreasing in darkness from the surface into the depth of the material. Space bar = 60 microns.**

RESULTS

The increasing width of the brown zone and its differentiation into layers of different shades are shown for three materials in Fig. 2 (1a-3c). The differentiation into layers at 90 days was most obvious in P-30 (Fig. 3), in which the surface layer was almost black, whereas the deeper layers were much lighter shades of brown. The dark surface layer also occurred in Occlusin and Profile. With the exception of Concise, in which no layers could be discerned, the differential shade in the other materials was between lighter shades of brown. In the unfilled BIS-GMA resin at 90 days (Fig. 4), a thin surface layer stained dark brown, the much wider middle layer stained black, and the innermost layer was golden brown.

The widths (W) of the permeated zone for the resin-rich and ground surfaces are given in Tables 2 and 3, respectively. At least five of the nine measurements for the resin-rich zone were equal and the remaining four within one unit of measurement (5 μm); therefore, the figures in Table 2 are the modal values. For the ground surface, there was a greater variance, and the values in Table 3 are the means. All standard deviations were within 25% of the mean. Figs. 5 and 6 show the graph of Width *vs.* (Time)$^{0.5}$ for the resin-rich and ground surfaces, respectively.

Table 4 shows the Analysis of Variance of Width (of stain) by material at 90 days, together with homogeneous subsets as determined by Scheffé Multiple Range Comparisons (0.01 level).

EDX of the stained zone in Profile showed the Lα line for silver which was not present on analysis of material deep to the stain (Fig. 7).

DISCUSSION

Samples of composite material stored in silver nitrate for 90 days developed a brown subsurface zone. The color was thought to be caused by finely divided metallic silver deposited in the microcavities within the composite. The stain was not present when the samples were removed from the silver-nitrate solution but developed during exposure to daylight. This distinguishes the effect from one of silver colloid penetration. The mechanism for the precipitation and growth of silver particles is similar to the process used in photography (Wu and Cobb, 1981). Specialist texts on silver indicate that finely divided silver may be colored silver, black, grey, blue, yellow, or brown and that the color of a sus-

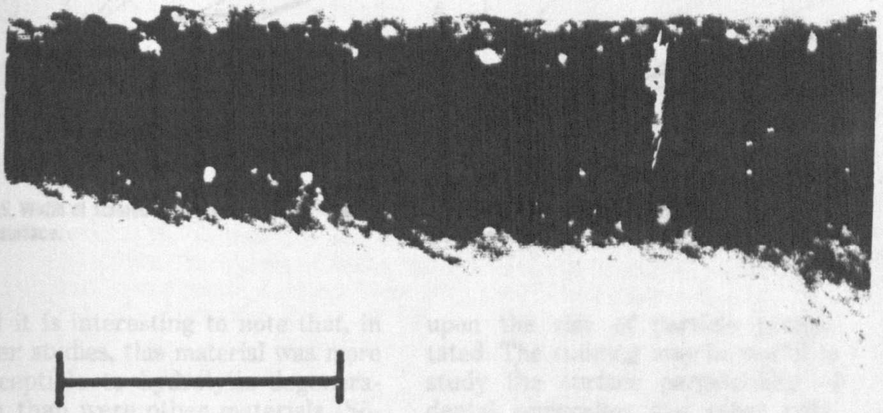

Fig. 4. **Unfilled BIS-GMA resin at 90 days showing three layers: Surface, dark brown; middle layer, black; deepest layer, golden brown. Space bar = 100 μm.**

pension of silver particles depends upon the sizes of the particles (McWilliam, 1967). The theory of color dependence on particle size was first advanced by Mie in 1908. Although not all the optical phenomena caused by metal deposits can be explained by Mie's theory, it is certain that particle size is predominantly important in color determination (Schulman and Compton, 1962). It is important to note that the color is a diffraction effect and that individual brown particles cannot be distinguished.

The sizes of the silver particles precipitated are determined by the space available for crystal growth. In order for the EDX peak for silver to be produced, it was necessary to count for a relatively large area (50 μm²) of the stained zone. This is indicative of a relatively small amount of silver. It is thought that the various colors of silver that occurred were dependent upon the sizes of silver grains that could form in the microcavities. There are two sources of microcavity within a composite: The presence of water can cause hydrolysis of the filler matrix interface, resulting in interfacial gaps (Söderholm *et al.*, 1984). However, the presence of the brown zone in unfilled resin suggests microcavities within the matrix. The presence of such microcavities has been previously postulated to explain the decrease in the diffusion coefficient of hard plastics caused by sorption-desorption cycling (Barrie, 1968). This behavior has been demonstrated in BIS-GMA epoxy resin (Brewis *et al.*, 1980). Electron microscopy of resins treated to cause microcracking has showed microvoids in the region of the cracks (Browning, 1978). Dental composites treated with organic solvents that would lead to microcavity enlargement and surface swelling developed black silver deposits in the enlarged cavities (Wu *et al.*, 1984).

The graphs of W *vs.* $t^{0.5}$ (Figs. 8 and 9) indicate that the basic mechanism governing the permeation of silver nitrate is diffusion. The initial curves and inflections of the graphs indicate a deviation from simple ("Fickian") diffusion, in which the rate of diffusion is constant. The reasons for "non-Fickian" diffusions in polymers and composites are discussed in appropriate texts (Crank, 1968; Barrie, 1968).

The findings of this investigation may be helpful in understanding the process of clinical wear. Clinically, dental composites wear by vertical loss across the whole surface (Abell *et al.*, 1983). This is determined by many interrelated factors. Abrasion of the matrix permits displacement of the fillers, which is facilitated by mechanical and chemical processes which weaken the matrix (Lutz *et al.*, 1979). *In vitro*, the organic acids of plaque (Asmussen, 1984) and food-simulating liquids (McKinney and Wu, 1985) have been shown to soften the matrix. The effects of these processes will be influenced by the depth to which the chemicals can penetrate.

The results indicate that the depth of penetration varies between materials. Profile has the greatest depth,

TABLE 2

MODAL WIDTH OF STAINED ZONE (μm) RESIN-RICH SURFACE

No. of Days	1	6	10	26	42	90
CONCISE	5	20	35	40	40	70
CLEARFIL	10	40	60	70	80	90
HELIOMOLAR	10	20	30	40	50	70
OCCLUSIN	10	15	15	20	20	30
P-30	10	20	30	30	40	60
PROFILE TLC	40	70	70	100	110	150
SILUX	20	35	50	60	80	100

TABLE 3

MEAN WIDTH OF STAINED ZONE (μm) GROUND SURFACE

No. of Days	1	6	10	26	42	90
CONCISE	5	6	9	21	28	32
CLEARFIL	0	0	14	21	26	50
HELIOMOLAR	0	5	10	10	20	24
OCCLUSIN	0	0	0	14	15	20
P-30	0	0	5	15	20	22
PROFILE TLC	30	60	40	72	94	124
SILUX	15	35	32	38	50	65

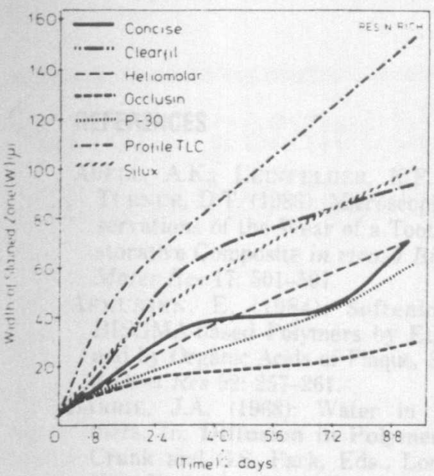

Fig. 5. **Width of stained zone (W) *vs.* (time)$^{0.5}$, resin-rich surface.**

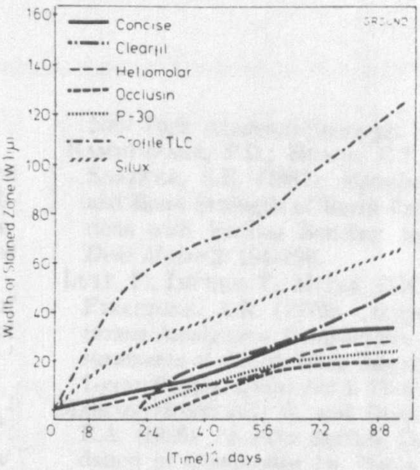

Fig. 6. **Width of stained zone (W) *vs.* (time)$^{0.5}$, ground surface.**

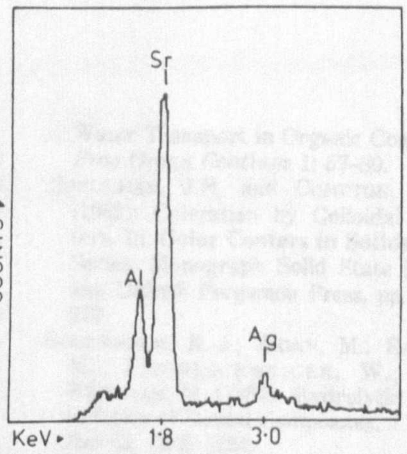

Fig. 7. **EDX trace from stained zone showing Lα peak for silver.**

and it is interesting to note that, in other studies, this material was more susceptible to hydrolytic degeneration than were other materials (Söderholm *et al.*, 1984; Marcos Montes-G. and Draughn, 1986). There was considerably less depth of penetration in the ground surfaces, and the homogeneous subset analysis showed less difference between the materials for this surface. Clinically, this surface is more likely to be removed during the occlusal adjustment of a posterior restoration than in the finishing of anteriors. The two microfilled composites stained a similar shade, which was distinguishable from the other materials. The depth of stain for the posterior microfilled (Heliomolar) was similar to that of two posterior composites with closely-packed conventional particles.

It is hoped that the effects seen in this investigation will be useful in the study of permeability changes in the surfaces of dental composites and other polymer systems. Investigations presently in progress have demonstrated that the layer forms in some unfilled BIS-GMA epoxy resins and PMMA.

CONCLUSION

Samples of composite and other polymers stored in silver nitrate developed a brown stain in the subsurface after exposure to daylight. The color is thought to arise from the precipitation of brown metallic silver in the composite and its shade to depend upon the size of particle precipitated. The staining may be useful to study the surface permeability of dental composites and other polymer systems.

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This research was carried out within the framework of an extensive evaluation of dental materials commissioned and funded by the Department of Health and Social Security.

TABLE 4
ANOVA VALUES* AND HOMOGENEOUS SUBSETS** AT 90 DAYS

Resin-rich Surface
ANOVA F = 216.16, P = 0.0000

Subset.							
1	OCCLUSIN (26.7)***						
2		P - 30 (56.7)	HELIO (70.0)				
3			HELIO (70.0)	CONCISE (73.3)			
4					CLEARFIL (90.0)	SILUX (100.5)	
5							PROFILE (148.8)

Ground Surface
ANOVA F = 234.02, P = 0.000

Subset.							
1	OCCLUSIN (20.0)	P - 30 (22.2)	HELIO (24.4)	CONCISE (32.2)			
2					CLEARFIL (48.9)		
3						SILUX (65.5)	
4							PROFILE (124.4)

* Width by material.
** Scheffé Multiple Range Comparison (0.01 Level)
*** Mean values.

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Surface permeability and degradation of dental composites resulting from oral temperature changes

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Abstract – The surface changes in dental composites caused by thermal cycling and different temperatures were evaluated by use of silver nitrate to stain the surface layers. Rapid temperature change resulted in the formation of layers within the surface which may have resulted from microcracking. Slow rates of change increased the depth and rate of diffusion of silver nitrate. Determination of the temperature changes at the surface of a restoration in the mouth indicated that *in vivo* temperature change is more likely to increase the depth of diffusion of oral fluids than to cause microcracking of the surface.

Composite materials, aged in solution at various temperatures, are subject to degradation as a result of chemical and physical reactions in the surface (Marom, 1985). This hygrothermal aging makes the surface more susceptible to wear and further degeneration. The depth to which these reactions proceed will depend upon the depth of penetration of fluids. This is determined by the diffusion coefficient, which has been found to be temperature-sensitive (Windle, 1985). Thermal cycling was found by Marcos Montes-G. and Draughn (1986) to cause surface degradation of dental composites. The aim of the present study was to stain the aged surface layer with silver nitrate in order to assess the extent of the degeneration.

In a recent study, it was found that silver nitrate penetrated and stained the surfaces of dental composites *in vitro* (Mair, 1989). Initially, the stain was brown, but after extended storage the surface layers stained darker and appeared black in some materials. The color was thought to result from the precipitation of metallic silver within microcavities in the composite. Based on the Mie theory for color dependence upon the size of diffracting particles, an hypothesis was advanced to explain the color of the stain in terms of the size of the precipitated particles which could form in the surface. Since hygrothermal aging was found by Kaeble and Dynes (1977) to cause a network of microdefects in the surface, it was anticipated that these would be susceptible to staining.

Three experiments were conducted, first to investigate the effect of thermal cycling, second to determine the effects of the high and low temperatures individually, and third to determine the temperature changes at the surface of a composite restoration in the mouth, so that the results of the experiments could be related to the clinical situation.

MATERIALS AND METHODS

Samples of seven dental composites (Table 1) were prepared as previously described (Mair, 1989). The concentration of the silver nitrate in all the experiments was 50% (by weight).

In the first experiment, to determine the effects of thermal cycling, 36 samples of each material were prepared. Twelve were cycled in silver nitrate, 12 in water, and 12 were stored uncycled in silver nitrate. Samples of the first group were sealed in a small opaque plastic bottle containing silver nitrate and placed in the thermal cycler, while the samples to be cycled in water were placed directly into the thermal cycler. The third group was stored at room temperature. The thermal cycle was 2.25 min at 60°C (±1) and 2.25 min at 6°C (±3), with two changeover times of 0.75 min. Samples were removed after 4.2, 21, 42, and 210 days, corresponding to 1000, 5000, 10,000, and 50,000 cycles. The water-cycled samples were subsequently dried and then immersed in silver nitrate at room temperature for 42 days. After removal from the silver nitrate, the samples were washed, embedded, and polished as described previously.

In the second experiment, to determine the effects of the individual temperatures, 48 samples of four materials (P30, Occlusin, Silux, Profile-TLC) were prepared and divided into groups of 12. One group was placed in a water-tight opaque bottle containing silver nitrate, and this was placed in the 60°C water bath of the thermal cycler. Group 2 was placed in a similar container at 6°C. The third group was stored in silver nitrate at room temperature, and the fourth group was thermal-cycled as described in experiment 1. For each material, three samples from each group were removed and processed after 14, 21, 42, and 90 days (14 days = approx. time in the 60°C water bath during 42 days of thermal cycling). The details of experimental conditions are summarized in Table 2.

All of the samples were examined by use of a reflecting light microscope with the optical system previously described by Mair (1989). The total width of the stained layer was measured by use of an eyepiece graticule. Although color photomicrographs were taken, the colors reported were assessed by direct observation, since there is always a degree of color aberration induced during the processing of films. For comparative purposes, a scanning electron micrograph of one surface was prepared.

Surface temperature changes and temperature gradients across the sample used in the investigations were determined by use of a multiprobe thermocouple (KM1202, Kane-May Ltd., Welwyn Garden City, Herts, U.K.). One probe was placed on the surface of a sample in the plastic bottle containing samples cycling in silver nitrate. A second was placed on the surface of a sample in the thermal cycling basket, and a third was buried in the middle of this sample. The recording apparatus was set to record the three temperatures simultaneously every 10 sec during immersion and every two sec during changeover.

A thermocouple probe was placed on the surface of a composite restoration which had been inserted into the occlusal surface of a temporary premolar post crown. The volunteer patient was asked to drink some hot soup and then to eat a hot toasted-cheese sandwich, followed by some ice cream and finally part of another hot sandwich. This particular snack was chosen because hot cheese maintains its temperature. The volunteer was asked to eat the food when it was as hot as reasonably possible and to ensure that he bit into both foods with the temporary crown. A second probe of the thermocouple was used to monitor the temperature of the food on the plate.

TABLE 1
MATERIALS INVESTIGATED

Material	Manufacturer	Type	Curing	Posterior Use
CONCISE	3M Company, Minnesota, USA	Con	Chem	No
CLEARFIL (Posterior)	CAVEX, Haarlem, The Netherlands	Con	Chem	Yes
HELIOMOLAR	VIVADENT, Schaan, Liechtenstein	Micro	Light	Yes
OCCLUSIN	I.C.I., Macclesfield, U.K.	Hybrid	Light	Yes
P-30	3M Company	Con	Light	Yes
PROFILE TLC	S.S. White, Philadelphia, PA, U.S.A.	Con	Light	Limited
SILUX	3M Company	Micro	Light	No

Con = Conventional fillers. Micro = Microfillers. Chem = Chemical cure.

TABLE 2
SUMMARY OF EXPERIMENTAL CONDITIONS

	Group No.				
EXPT 1	1	Stored unclcyed in $AgNO_3$ at room temperature			
	2	Thermal-cycled in $AgNO_3$ (60°C <-> 6°C)			
	3	Thermal-cycled in H_2O followed by 42 days in $AgNO_3$			
Samples removed at (days)		4.2	21	42	210
Corresponding to (thermal cycles)		1000	5000	10,000	50,000
	Group No.				
EXPT 2	1	Stored in $AgNO_3$ at 60°C			
	2	Stored in $AgNO_3$ at 6°C			
	3	Stored in $AgNO_3$ at room temperature			
	4	Thermal-cycled in $AgNO_3$			
Samples removed at (days)		14	21	42	90
Corresponding to (thermal cycles) (Group 4 only)		3333	5000	10,000	50,000

RESULTS

The different aging temperatures and thermal cycling produced both quantitative and qualitative effects. The former resulted in increased depth of diffusion, whereas the latter caused the formation of different-colored layers in the surfaces of the materials. The colors observed included various shades of silver, black, yellow, green, orange, and brown. The most pronounced example of layering occurred with samples of Profile and Occlusin stored in silver nitrate for 90 days at 60°C (Fig. 1, A1, A2, B1, B2). In both these materials, silver-colored silver (like the silver of a silver coin) appeared in the surface, and in two samples of Occlusin this layer had "bubbled away" from the underlying material (B1, B2). In Fig. 1, the three samples (ABC) are shown viewed by scattered light (left photomicrograph) and by directly reflected light (right). In reflected light, the silver in Profile (A2) and Occlusin (B2) can be seen reflecting like a mirror.

In all experiments, standard deviations were within 12% of mean values and are not represented on diagrams.

The Effect of Thermal Cycling (Experiment 1)

For specimens subjected to thermal cycling in silver nitrate, the most significant effect was an increase in the depth of penetration of the silver nitrate. The mean depth of the stained zone at 210 days is shown in Table 3 and Fig. 2. The depth of stain for the individual materials varied, but in general the ranking order be-

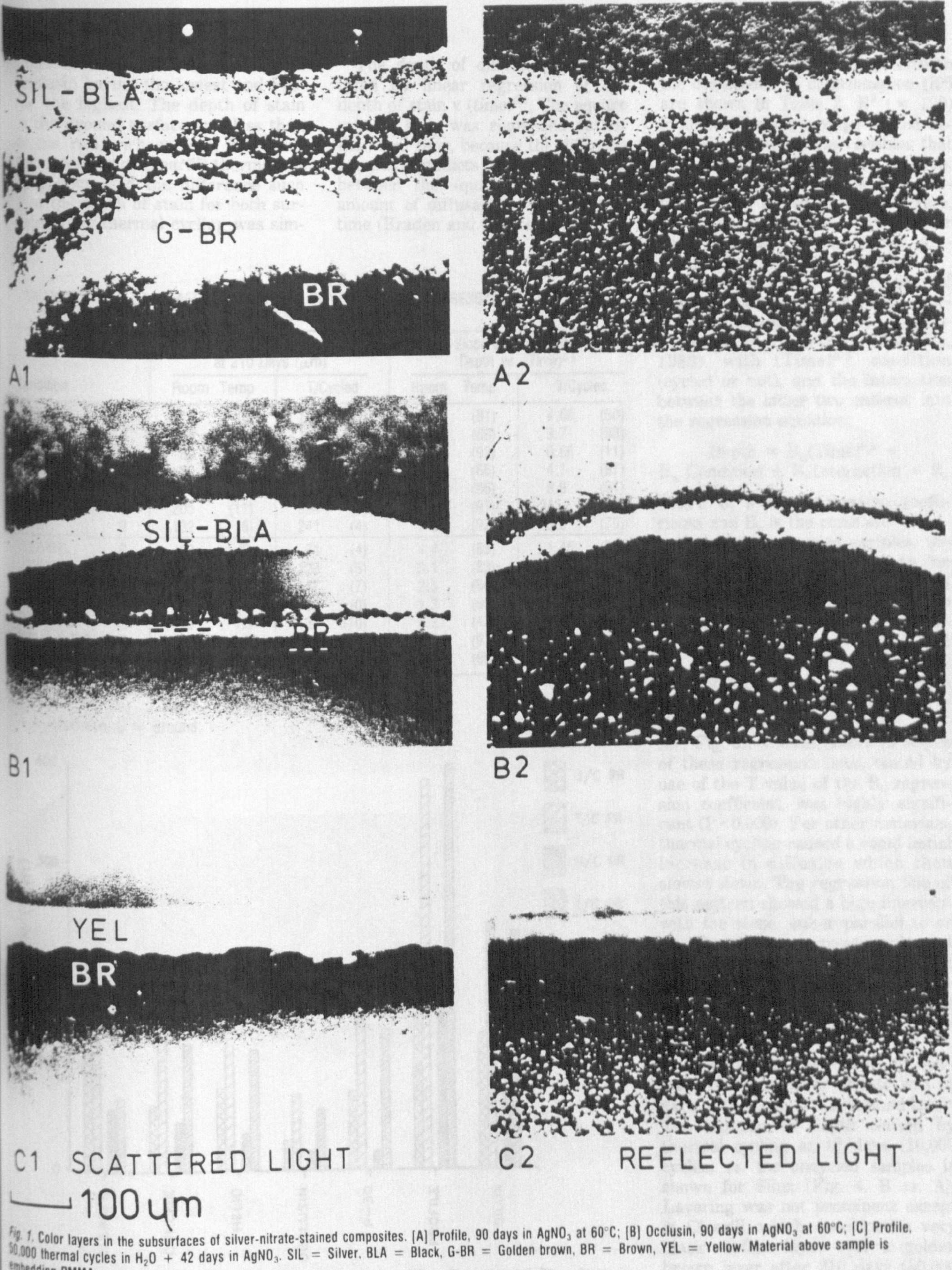

Fig. 1. Color layers in the subsurfaces of silver-nitrate-stained composites. [A] Profile, 90 days in $AgNO_3$ at 60°C; [B] Occlusin, 90 days in $AgNO_3$ at 60°C; [C] Profile, 50,000 thermal cycles in H_2O + 42 days in $AgNO_3$. SIL = Silver. BLA = Black, G-BR = Golden brown, BR = Brown, YEL = Yellow. Material above sample is embedding PMMA.

tween materials was maintained, with Occlusin having the lowest and Profile the highest. The depth of stain in the ground surface was less than in the resin-rich surface, but (with the exception of Clearfil) thermal cycling decreased the difference such that the depth of stain for both surfaces after thermal cycling was similar.

The depth of diffusion was analyzed by linear regression of the depth of stain v $(\text{time})^{0.5}$. The square root of time was regressed rather than real time, because the diffusion equation predicts a linear relation between the square root and the amount of diffusant present at this time (Braden and Clarke, 1984). The slopes of the regression together with the coefficients of determination (R^2) are shown in Table 3. R^2 ($\times$ 100) indicates the percentage of the relationship between the variables that is accounted for by a linear relation. With the exception of the Heliomolar samples cycled in silver nitrate, the R^2 values are higher and concur with a linear relationship as predicted by the diffusion equation.

TABLE 3

MEAN DEPTH OF STAIN AFTER 210 DAYS IN SILVER NITRATE; REGRESSION STATISTICS FOR DEPTH OF STAIN WITH $(\text{TIME})^{0.5}$

		Mean Depth of Stain at 210 Days (μm)				Slope of Regression, Depth *vs.* $(\text{Time})^{0.5}$			
Condition		Room Temp		T/Cycled		Room Temp		T/Cycled	
CLEARFIL	R	112	(6)	127	(13)	5.2	(81)	4.66	(60)
CONCISE	R	64	(6)	142	(10)	2.8	(69)	3.7	(53)
HELIOMOLAR	R	80	(5)	122	(8)	4.6	(92)	0.66	(11)
OCCLUSIN	R	30	(0)	74	(5)	1.07	(66)	4.1	(97)
P-30	R	78	(3)	148	(14)	4.86	(96)	8.9	(91)
PROFILE TLC	R	205	(11)	394	(9)	10.96	(97)	24	(83)
SILUX	R	132	(8)	241	(4)	7.56	(97)	5.3	(79)
CLEARFIL	G	60	(5)	71	(4)	4.4	(89)	1.45	(24)
CONCISE	G	48	(5)	123	(5)	3.1	(83)	4.06	(43)
HELIOMOLAR	G	35	(7)	117	(7)	2.5	(84)	1.65	(42)
OCCLUSIN	G	20	(0)	60	(0)	1.3	(61)	3.3	(92)
P-30	G	19	(2)	137	(10)	0.81	(42)	9.0	(95)
PROFILE TLC	G	118	(4)	398	(4)	10.78	(97)	25	(85)
SILUX	G	90	(5)	233	(9)	4.9	(95)	11.3	(80)

Figures in parentheses = Standard deviation for means.
= $R^2 \times 100$ for slopes.
R = Resin-rich; G = Ground.

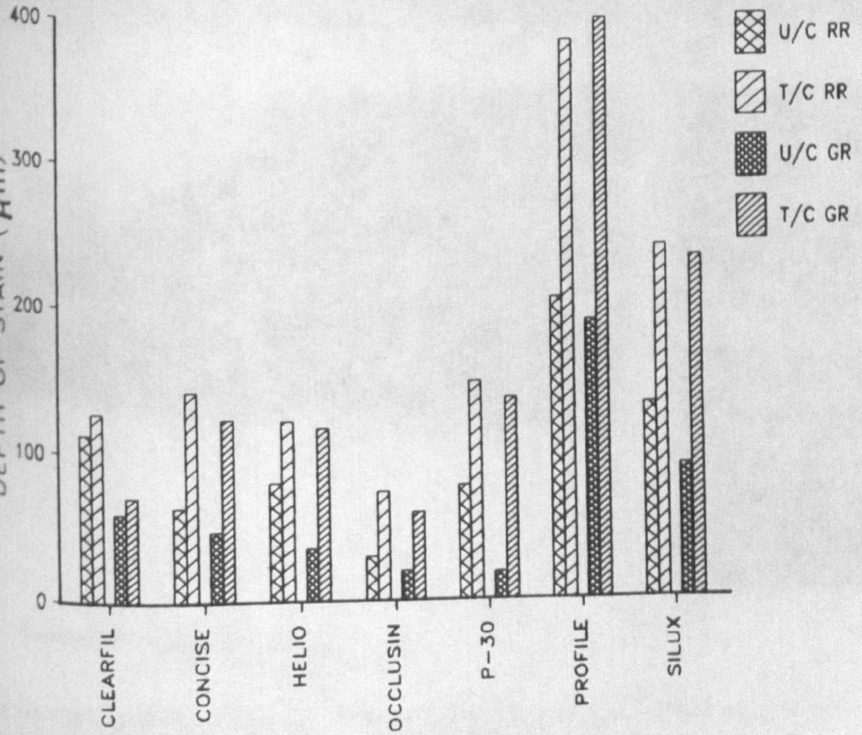

Fig. 2. **Mean depth of stain after 210 days in $AgNO_3$. U/C = Uncycled, T/C = Thermal-cycled, RR = Resin-rich Surface, GR = Ground Surface.**

The differences in the pattern of diffusion between cycled and uncycled samples were analyzed by multiple linear regression (Norusis, 1983), with $(\text{Time})^{0.5}$, condition (cycled or not), and the interaction between the latter two entered into the regression equation:

$$\text{Depth} = B_{it}(\text{Time})^{0.5} + B_{ic}\,\text{Condition} + B_{ii}\text{Interaction} + B_o$$

where B_i s are regression coefficients and B_o is the constant.

For all the uncycled samples, the regression line passed close to the origin, while the regression line of the cycled samples indicated two patterns of diffusion. In some materials (Occlusin, P-30, Profile, and the ground surface of Silux), the diverging regression lines indicated a steady increase in the rate of diffusion with time (*e.g.*, Occlusin, Profile, Fig. 3). The difference in slopes of these regression lines, tested by use of the T value of the B_{ii} regression coefficient, was highly significant ($P<0.000$). For other materials, thermal cycling caused a rapid initial increase in diffusion which then slowed down. The regression line of this pattern showed a high intercept with the slope, either parallel to or less than the corresponding slope of the uncycled samples (*e.g.*, Silux, Fig. 3). The significance of this difference, tested by use of the T value of the B_{ic} coefficient, was high ($P<0.000$).

Qualitatively, the effect of thermal cycling in silver nitrate was to darken the color of the stained layer. The increase in depth caused by thermal cycling at 42 days (10,000 cycles) *vs.* the uncycled samples is shown for Silux (Fig. 4, B *vs.* A). Layering was not prominent except in Clearfil, which developed a very black surface layer over a golden brown layer after 210 days (50,000 cycles), as opposed to uniform stain

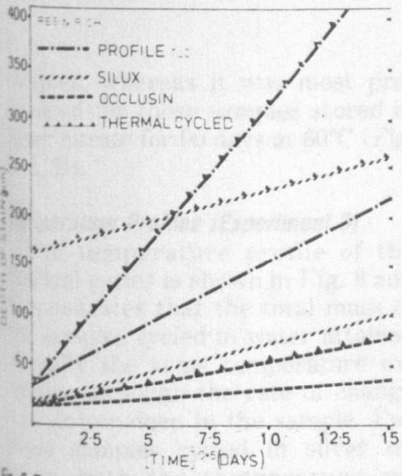

Fig. 3. Regression lines of depth of stain *vs.* (Time)$^{0.5}$.

at room temperature (Fig. 5, B *vs.* D).

For specimens subjected to thermal cycling in water plus 42 days in silver nitrate, with the exception of Heliomolar, the depth of diffusion of silver nitrate after 42 days was greater for those samples that had been preconditioned by thermal cycling (Fig. 6). Qualitatively, this treatment resulted in the greatest evidence of layering, and only in Concise and Heliomolar was this not evident. The color layers and depths after 10,000 and 50,000 cycles are shown in Table 4 (Resin-rich Surface) and Table 5 (Ground Surface). Fig. 1 (C1, C2) shows Profile after 50,000 preconditioning cycles. The development of the surface layer in Silux is seen clearly in Fig. 4 (C, D), where fronds of yellow stain are seen at 10,000 cycles, and the whole layer is stained at 50,000 cycles. The layers for the resin-rich surface of Clearfil are shown in Fig. 5C.

The Effects of Different Temperatures (Experiment 2)

For all materials, both heat and thermal cycling increased the depth of the stained layer, while a decrease occurred at 6°C. The depth of stain after 90 days is shown in Fig. 7. As in Experiment 1, no layering occurred for the thermal-cycled

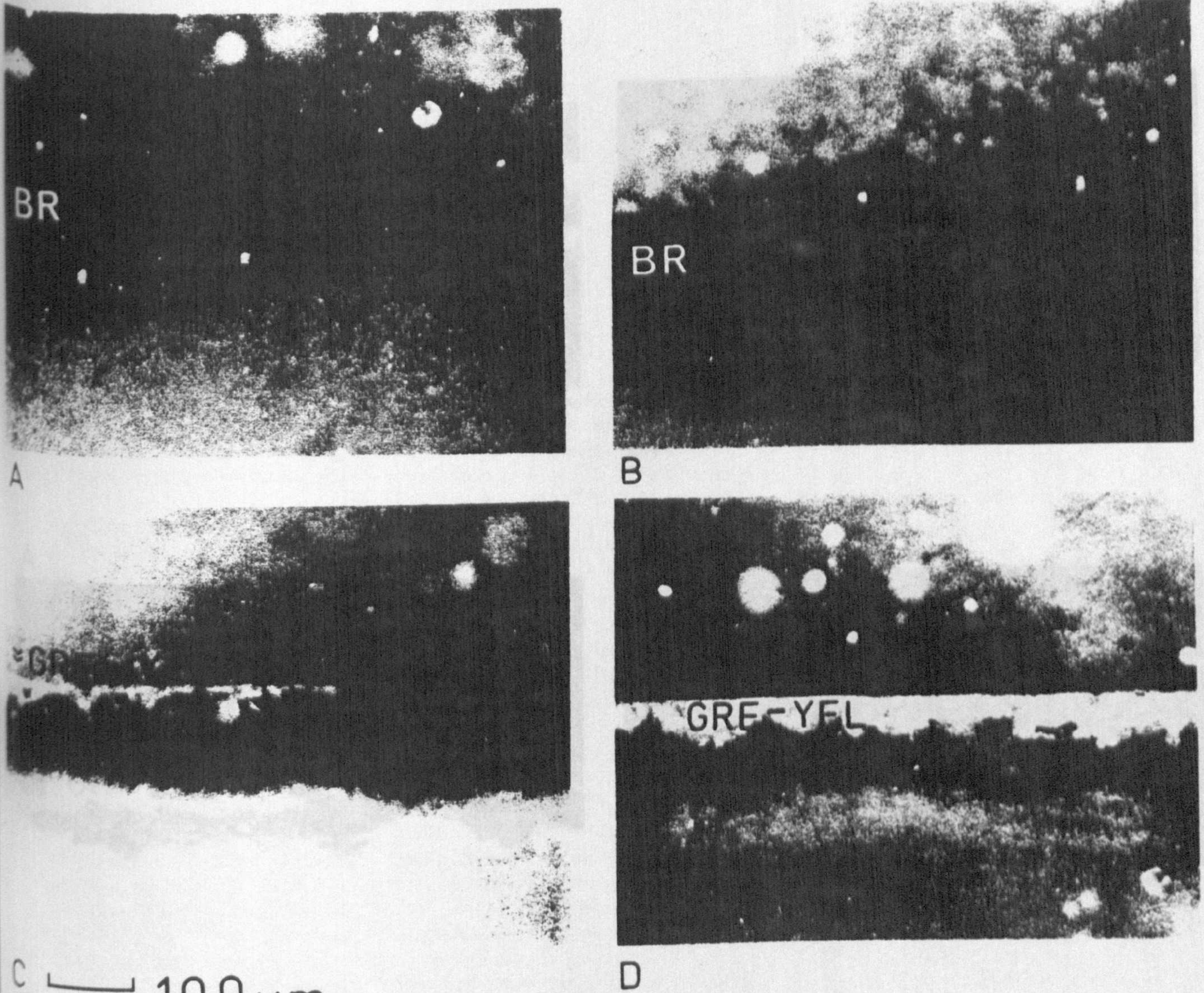

Fig. 4. The stained sub-surface of Silux. [A] 42 days in AgNO$_3$ at room temperature; [B] 10,000 cycles in AgNO$_3$; [C] 10,000 cycles in H$_2$O + 42 days in AgNO$_3$; [D] 50,000 cycles in H$_2$O + 42 days in AgNO$_3$. GRE-YEL = Green Yellow; BR = Brown.

samples, whereas it was most pronounced for those samples stored in silver nitrate for 90 days at 60°C (Fig. 1, A, B).

Temperature Profiles (Experiment 3)

The temperature profile of the thermal cycles is shown in Fig. 8 and demonstrates that the total mass of the samples cycled in water attained virtually the same temperature extremes, although the rate of change was slower deep in the sample. For those samples cycled in silver nitrate, both the temperature extremes and rates of change were diminished.

The results of this investigation of temperature changes in the mouth are shown in Fig. 9 and demonstrate that although the temperature of the snack was 90°C, the surface temperature of the composite did not exceed 55°C; however, when in contact with ice cream, the surface temperature dropped to 4°C. Drinking hot soup had little effect on the surface temperature. Generally, the rates of temperature change were comparatively low, although at the cold/hot transition a rapid change of 30°C occurred (arrowed).

Fig. 10 shows a scanning electron micrograph corresponding to the light micrograph in Fig. 1 (C1) and indicates the zones corresponding to the color layers.

DISCUSSION

Compared with results seen in the original *in vitro* investigation into silver nitrate penetration, many more colors and layers were observed. This effect was most pronounced in the samples which were stored at 60°C and therefore most likely to have undergone surface degeneration. The result supports the hypothesis that the color of the stained layers depends upon the sizes of the metallic silver grains that formed in the de-

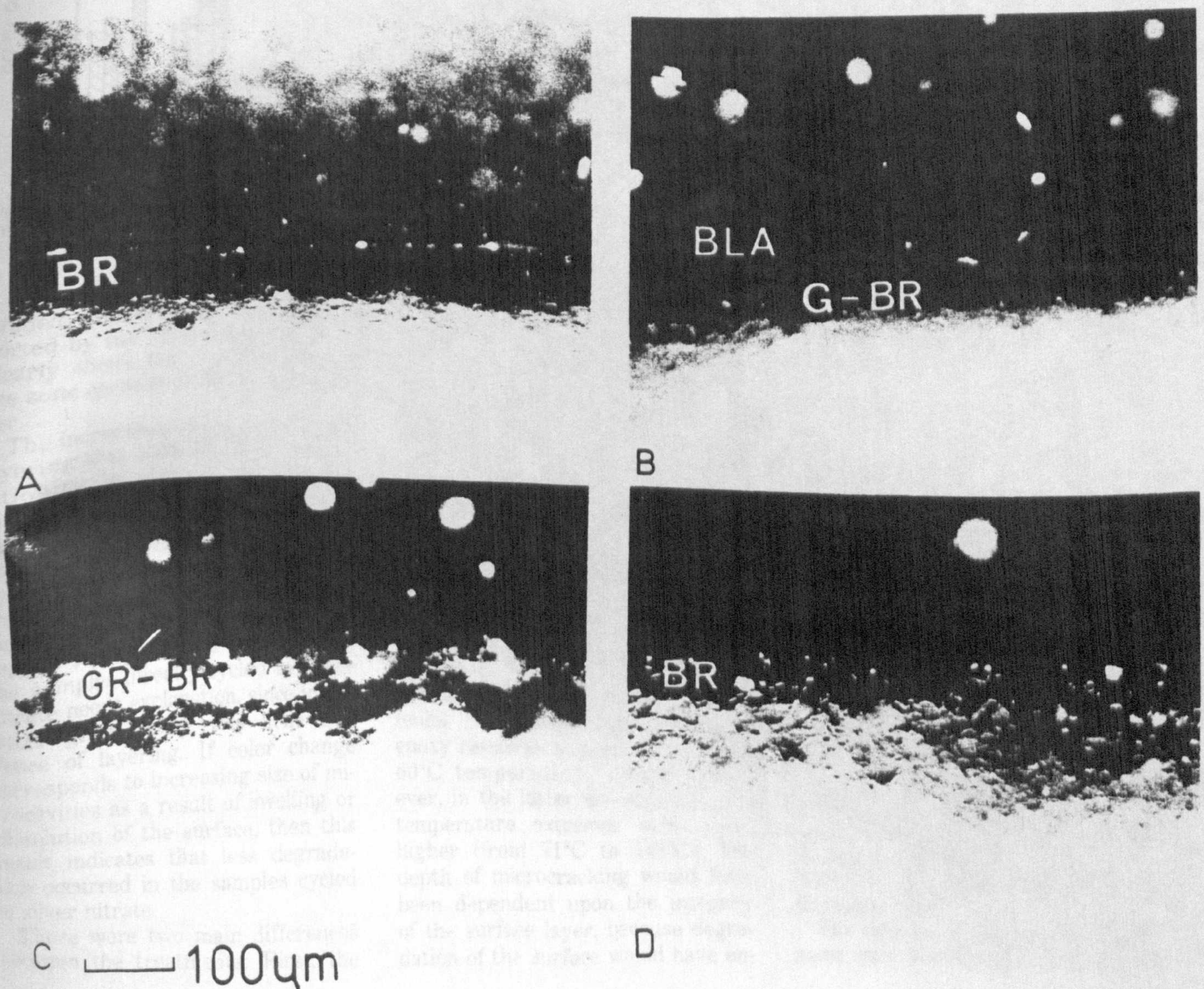

Fig. 5. The stained subsurface of Clearfil. [A] 1000 cycles in $AgNO_3$; [B] 50,000 cycles in $AgNO_3$; [C] 50,00 cycles in H_2O + 42 days in $AgNO_3$; [D] 210 days at room temperature in $AgNo_3$. BR = Brown; G-BR = Golden Brown; GR-BR = Green-Brown; BLA = Black.

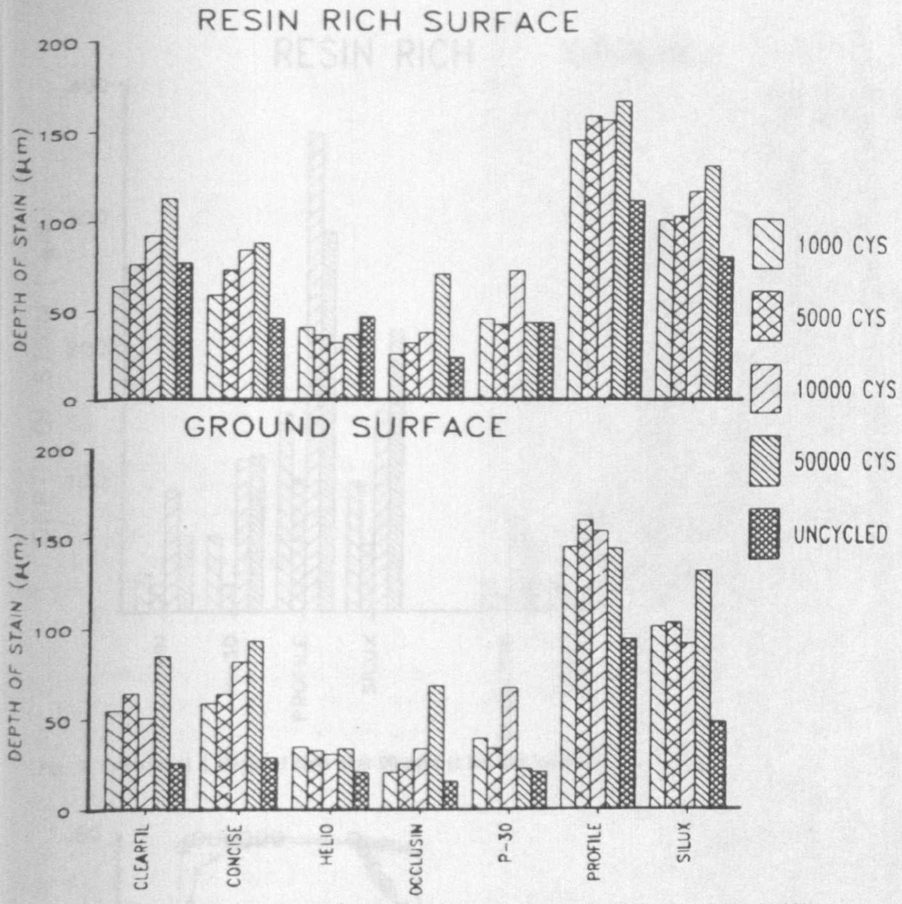

Fig. 6. **Depth of stain after n thermal cycles in water followed by 42 days in AgNO$_3$ (n = 1000-50,000). CYS = cycles.**

TABLE 4
COLOR LAYERS AND DEPTH OF STAIN (μm) AFTER (n) THERMAL CYCLES FOLLOWED BY 42 DAYS IN AgNO$_3$

	Resin-rich Surface			
Cycle No. (n)	10,000 cycles		50,000 cycles	
CLEARFIL	Dark Br	20	Green/Br	50
	Brown	70	Brown	60
CONCISE	Brown	80	Brown	90
HELIO	Brown	40	Brown	40
OCCLUSIN	Yellow	10	Yellow/Wh	50
	Brown	30	Dark Br	10
			Light Br	10
P-30	Black	20	Orange/Yel	15
	Brown	30	Br/Bl	15
	Faint	20	Faint	15
PROFILE TLC	Yellow	20	Bright Yel	70
	Brown	100	Dark Br	90
	Br/Bl	40		
SILUX	Green/Yel	25	Green/Yel	60
	Brown	90	Brown	70

"/" Indicates a combination of colors, with the first-named color predominant.

Br = Brown; Bl = Black, Yel = Yellow; Wh = White; Faint = Faint traces of last-named color.

TABLE 5
COLOR LAYERS AND DEPTH OF STAIN (μm) AFTER (n) THERMAL CYCLES FOLLOWED BY 42 DAYS IN AgNO$_3$

	Ground Surface			
Cycle No. (n)	10,000 cycles		50,000 cycles	
CLEARFIL	Brown	50	Black/Br	30
			Dark Br	50
CONCISE	Brown	80	Brown	90
HELIO	Brown	30	Brown	35
OCCLUSIN	Yellow	10	Yellow/Wh	40
	Brown	20	Dark Br	25
P-30	Black	15	Green/Br	20
	Brown	10	Dark Br	5
	Faint	40		
PROFILE TLC	Yellow	20	Bright Yel	40
	Brown	90	Brown	120
	Dark Br	40		
SILUX	Green/Yel	5	Green/Yel	40
	Brown	90	Brown	90

Legend as for Table 4.

graded surface layers. This is supported by the SEM (Fig. 10), which clearly shows the larger cavities in the zone corresponding to yellow silver.

The increases in depth of stain and layering that occurred after preconditioning by thermal cycling and subsequent immersion in silver nitrate indicate that surface changes occurred as a result of the thermal cycling rather than through the chemical action of silver nitrate. However, the difference between the results for this group and those of the samples directly cycled in silver nitrate needs explanation, since in the latter group there was little evidence of layering. If color change corresponds to increasing size of microcavities as a result of swelling or dissolution of the surface, then this result indicates that less degradation occurred in the samples cycled in silver nitrate.

There were two main differences between the treatments: First, the temperature extremes in the silver nitrate bottle were less, and second, the rate of temperature change was much slower (Fig. 8). Consequently, the samples which cycled in silver nitrate warmed up and cooled down more gently, whereas the surfaces of the water-cycled samples were subject to an immediate transition from 8°C to 60°C. This sudden transition resulted in thermal shock at the surface and rapid dimensional change of the surface over the unchanged deeper layers. These rapid dimensional changes may have caused microcracking and degeneration of the surface layer. Browning (1978) found that microcracks formed in epoxy resins as a result of repetitive 60°C temperature "spikes"; however, in the latter investigation, the temperature extremes were much higher (from 71°C to 148°C). The depth of microcracking would have been dependent upon the integrity of the surface layer, because degradation of the surface would have enabled rapid temperature change to reach deeper into the material. With successive cycles, this process resulted in increasing thickness of the damaged layer.

The results of the second experiment show that the effect of thermal

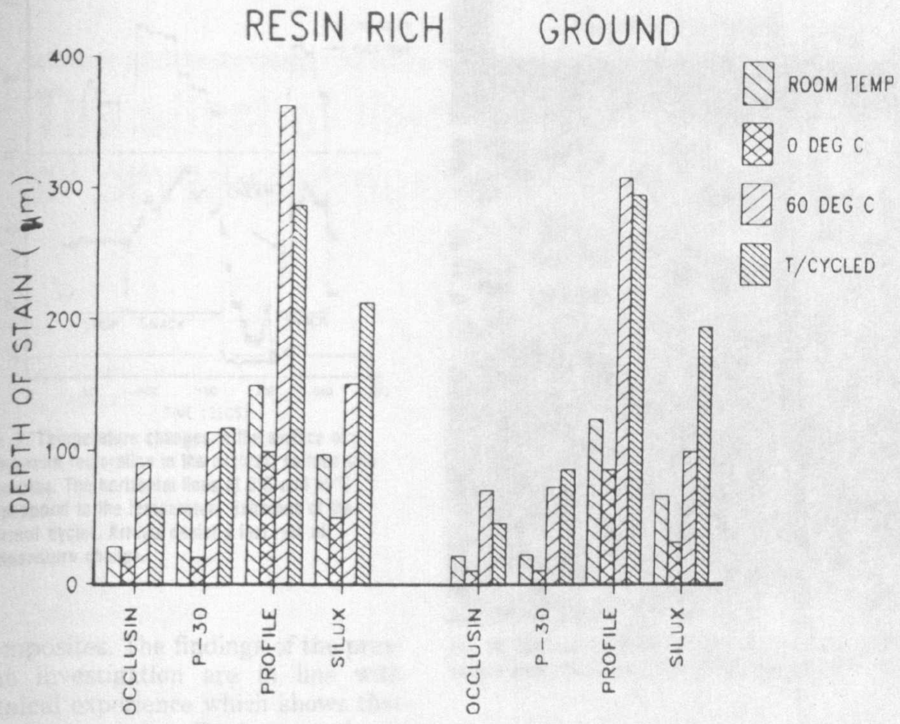

Fig. 7. **Experiment 2. Depth of stain after 90 days at the four temperature conditions.**

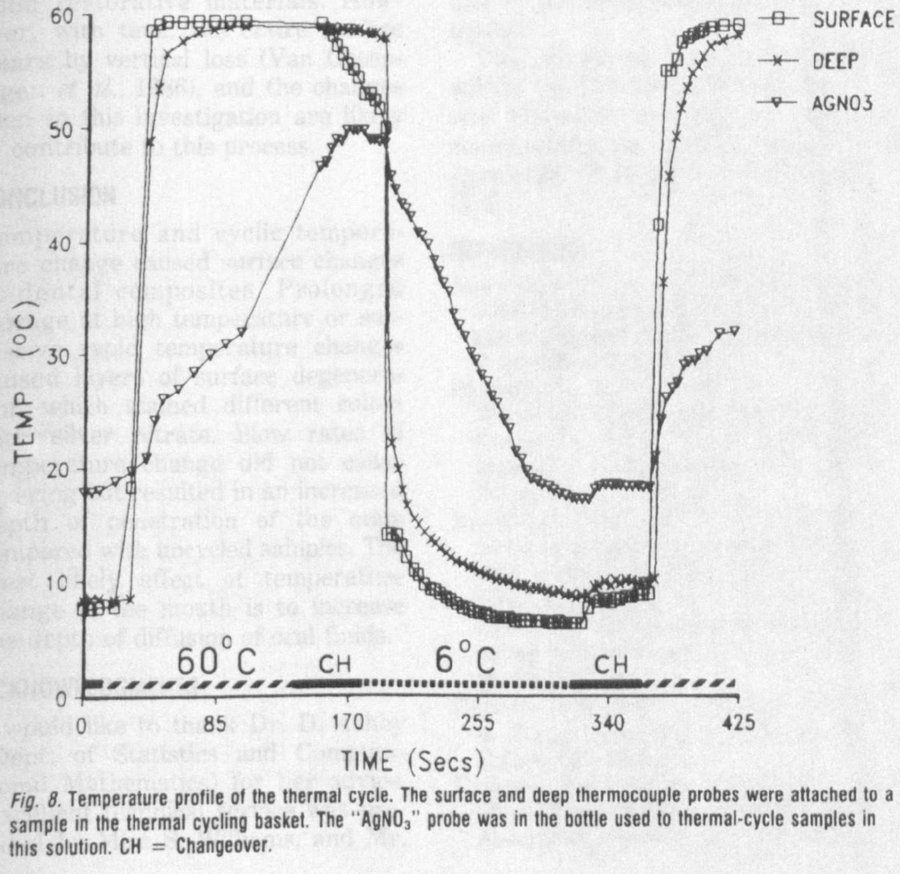

Fig. 8. **Temperature profile of the thermal cycle. The surface and deep thermocouple probes were attached to a sample in the thermal cycling basket. The "AgNO$_3$" probe was in the bottle used to thermal-cycle samples in this solution. CH = Changeover.**

cycling was not to sum the effects caused at 60°C and 6°C. The cold phase of the cycle "neutralized" the destructive effect of prolonged storage at high temperature. The main effect of cycling was to increase the depth of diffusion, and this would have resulted from the well-established dependence of the diffusion coefficient on temperature.

As yet, it is not possible to rank the colors in relation to the amount of surface deterioration that they indicate, although the SEM (Fig. 10) clearly shows that the yellow silver in Profile TLC is indicative of degeneration. It seems likely that the "silver" in the samples of Profile and Occlusin stored in silver nitrate for 90 days at 60°C also indicates considerable surface degradation.

Which of these effects is likely to predominate in the mouth–increased depth of diffusion of oral fluids or surface microcracking as a result of rapid dimensional change? The graph of the restoration surface temperature (Fig. 9) more closely resembles the graph of the temperature in the silver nitrate bottle (Fig. 8). However, as indicated by the arrows, rapid surface change is possible, although this change was produced by the rather false circumstance of the subject biting into hot food immediately after cold. This situation would be infrequent in normal eating. It is interesting to note that hot soup had very little effect on the surface temperature, presumably because the flow of hot liquid is directed away from the teeth by the soft tissues. Therefore, it would seem that the main effect of temperature change in the mouth would be to increase the depth of penetration of fluids.

The depth of penetration of fluids into the surfaces of composites is of clinical importance. Both water and plaque acids were found to cause chemical degeneration of dental composites (Söderholm *et al.*, 1984; Asmussen, 1984). Apart from thermal dimensional change, the presence of water in an epoxy resin was found by Kaeble and Dynes (1977) to cause internal stresses leading to microcracking. Fedors (1980a) found that this process was facilitated by the presence of penetrant molecules giving rise to local stresses as a result of osmotic forces. Sucrose molecules, which are common in the mouth, were found to cause discoid cracks to form in epoxy resins (Fedors, 1980b). These factors acting together are likely to cause some degree of surface degradation in dental

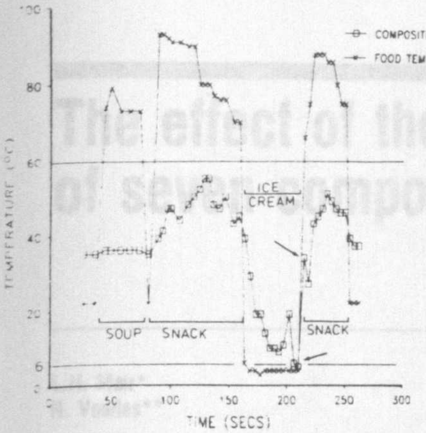

Fig. 9. **Temperature changes in the surface of a composite restoration in the occlusal surface of a premolar. The horizontal lines at 6°C and 60°C correspond to the temperature extremes of the thermal cycler. Arrows depict a fast rate of temperature change.**

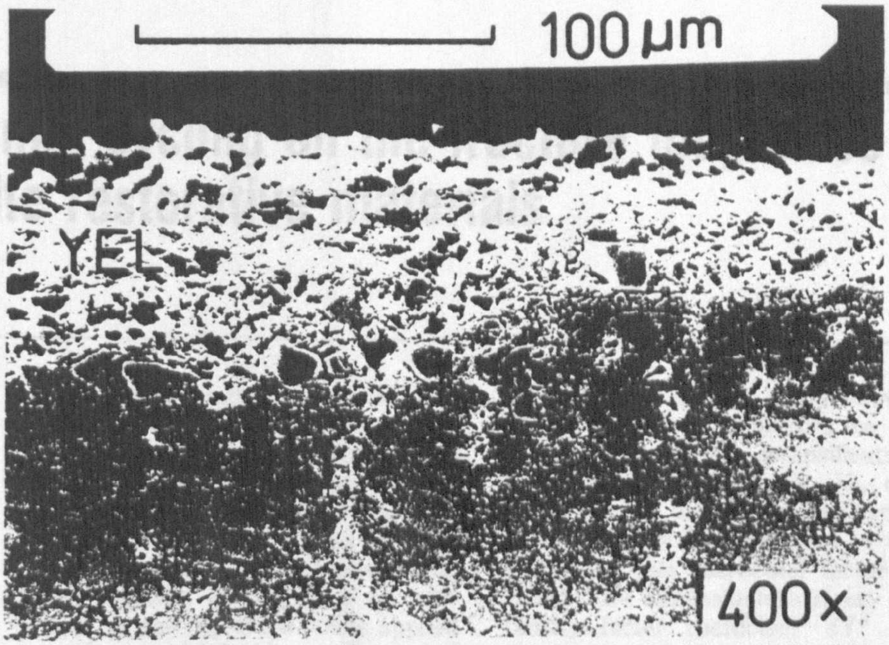

Fig. 10. **SEM corresponding to Fig. 1 (C1) showing subsurface degradation corresponding to the yellow silver-stained zone (YEL), with small loci of degeneration in the brown zone (BR).**

composites. The findings of the present investigation are in line with clinical experience which shows that composites generally do not undergo rapid surface degeneration and are good restorative materials. However, with time, the entire surface wears by vertical loss (Van Groeningen *et al.*, 1986), and the changes seen in this investigation are likely to contribute to this process.

CONCLUSION

Temperature and cyclic temperature change caused surface changes in dental composites. Prolonged storage at high temperature or successive rapid temperature changes caused layers of surface degeneration which stained different colors with silver nitrate. Slow rates of temperature change did not cause layering but resulted in an increased depth of penetration of the stain compared with uncycled samples. The most likely effect of temperature change in the mouth is to increase the depth of diffusion of oral fluids.

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The effect of thermal cycling on the fracture toughness of seven composite restorative materials

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Abstract – Short-red chevron-notch samples of seven composite materials were thermal-cycled between 0°C and 60°C. The stress intensification factor, K_{IC}, was found for four sample groups subjected to $10^1 - 10^4$ cycles, respectively. One group of uncycled samples was tested at the commencement of the investigation and another group after exposure to water for the equivalent time taken by 10^4 cycles (42 days). The K_{IC} decreased for all materials, but the decrease after 10^4 cycles was not significantly different from that after storage in water for an equivalent period of time. These results indicate that, in the determination of K_{IC}, the filler/matrix bond is of secondary importance to the presence of fillers. The effects of cyclic temperature changes likely to be encountered in the mouth are not a significant factor in reduction of the fracture strength of composite filling materials.

Fracture toughness may be characterized by the stress intensification factor (K_{IC}), which gives an indication of the resistance to fracture caused by the propagation of cracks or flaws. Cracks or flaws may be formed in materials during manufacture, or they may be initiated by the repetitive forces applied to the material during use (Crane and Charles, 1984). A crack may take some time to initiate, but, once formed, its presence may seriously decrease the strength of the material. Microcracking is important in the wear of dental composites (Abell *et al.*, 1983), and K_{IC} has been considered as a parameter which may be associated with wear resistance (Pilliar *et al.*, 1986, 1987; Ferracane *et al.*, 1987). Previous investigations have measured K_{IC} for various dental composites and determined the effects of various static environments on the value (Pilliar *et al.*, 1986, 1987; Ferracane *et al.*, 1987; Lloyd, 1982, 1983, 1984; Lloyd and Iannetta, 1982; Lloyd and Mitchell, 1984). In the oral environment, restorative materials are subjected to a wide variety of temperatures. The internal stresses developed as a consequence of the temperature changes may have a detrimental effect upon the toughness of these materials. The aim of the present study was to investigate the effects of thermal cycling on the K_{IC} of seven commercially available dental composites, by use of the short-rod chevron-notch test-piece with dimensions applicable to biomedical materials (Pilliar *et al.*, 1987).

Critical Stress Intensification Factor (K_{IC}) – Stress intensification (K) relates the tensile stress which is applied along a test-piece to the resultant stress which acts at the crack tip to open up the crack. The stress at the crack tip depends upon two factors: first, the structure of the material and, second, the geometry of the test-piece. Therefore, to determine the stress intensification, which is material-specific (K), one must correct for the intensification resulting from the geometry of the specimen. The correction factor is called "the dimensionless stress intensity factor coefficient" (Y^* for chevron-notch test-pieces, Y for straight-through cracks). Under conditions of plane strain, it is dependent on the ratio of the crack length (a) to the test-piece length (W). The relationship between Y^* and the a/W ratio for a short-rod chevron-notch test-piece and a straight-through crack test-piece (single-edge notch [SEN] or double torsion [DT]) is shown in Fig. 1. The unique "U"-shaped curve as a result of the chevron notch enables K_{IC} to be determined without the necessity for a starter crack (Newman, 1984).

The test-piece has an initial theoretical crack length (ao), being the length from the line of load application to the tip of the chevron (Fig. 1). At the commencement of load application, the geometric intensification is high (Y^*_0) and remains at this level until the intensification of load P_0 causes crack propagation to Δa_1. Now the test-piece geometry has changed: Y^*_0 is decreased to Y^*_1, the load is "detensified", and crack propagation stops until the load is increased to ΔP_1 to enable propagation to Δa_2. Again, Y^* decreases, and there must be a further increase in load to cause propagation to Δa_3. Crack propagation is sustained by this process to crack length Δa_n at $Y^* = Y^*_n$. This phase of crack propagation is called "stable" and continues until the crack length reaches *a*, which corresponds to the minimum point of the curve. The load at this point is the maximum load attainable, because any further load is again intensified and results in unstable

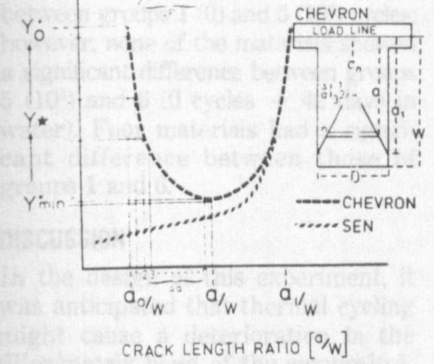

Fig. 1. **Stress intensity coefficient curves (Y^* *vs.* a/W) for the chevron-notch test-piece and the SEN test-piece.**

(catastrophic) fracture. Hence, at the point of fracture, the load is P_{max}, and the Stress Intensification Coefficient is Y^*_{min}.

K_{IC} is calculated from the formula:

$$K_{IC} = \frac{P_{max}}{D\sqrt{W}} \cdot Y^*_{min}$$

where

P_{max} = peak load at fracture,

D = diameter of the specimen (Fig. 1),

W = length of specimen from line of load application to base,

a_o = the length from the line of load application to the tip of the chevron, and

a_i = the length from the line of load application to the base of the chevron.

Y^*_{min} is determined from calibration curves of Y^*_{min} *vs.* a_o, as described by Pilliar *et al.* (1987). It is extremely important to understand that the terms "stable" and "unstable" fracture, with reference to the chevron-notch test-piece, have a meaning different from that of the same terms applied to SEN or DT samples, where they imply continuous or slip-stick fracture, respectively. This latter type of fracture occurs as a result of blunting of the crack tip (see "Discussion"), whereas the "incremental" fracture of the chevron-notch specimen is a function of its geometry. In practical terms, the increments Δa_1 to Δa_n are too small to show as steps on the stress-strain curve, and this phase of stable fracture is regarded as continuous.

MATERIALS AND METHODS

Seven materials were used in the study. These included materials for restorations in anterior teeth and five composites advocated as posterior composites (Table 1). A microfilled material was included for both categories (Silux and Heliomolar, respectively). Thirty-six samples of each material were prepared and divided into six groups of six each. All samples were stored for 14 days before the start of the investigation. The samples of group 1 were fractured at the commencement of the experiment. Groups 2–5 were subjected to 10^1, 10^2, 10^3, and 10^4 thermal cycles, respectively, between 3°C (+2) and 60°C (+1). The immersion time in each bath was 2.25 minutes *per* cycle, and the change-over was 0.75 min *per* change. Hence, the total cycle time was six minutes, consisting of two immersion phases and two changes, respectively. Group 6 was not cycled but was stored in water for the equivalent time taken by group 5 to complete 10^4 cycles (42 days).

The specimen was held in the tensile testing machine *via* wire loops threaded through the holes in the specimen rim. The sample was then loaded at a cross-head speed of 0.5 mm min^{-1} and the peak load at fracture recorded. The values needed to determine Y*m (a_o, a_1, and W) were obtained by means of a three-dimensional coordinate measuring device (S.I.P., 414M, Société Genevocia) and recorded directly on a microcomputer (BBC Acorn Computers Ltd.). Both halves of each fractured specimen were measured, and the mean was used in the determination of Y*m by computer interpolation of the polynomial compliance curves (Pilliar *et al.*, 1987). The final part of the computer program calculated K_{IC} from the equation.

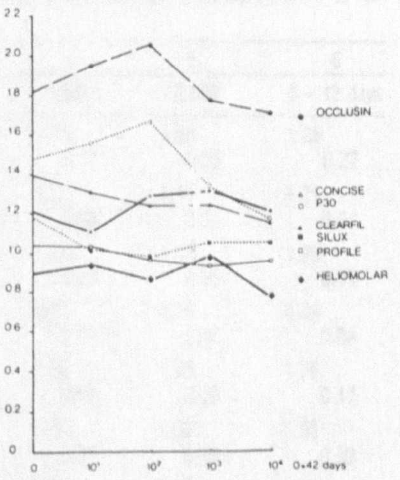

Fig. 2. **Critical stress intensity factor (K_{IC}) *vs.* number of thermal cycles for seven dental composites. The material symbols mark the K_{IC} values of the uncycled sample stored in water for 42 days.**

RESULTS

The mean and standard deviations of K_{IC} of the materials tested are given in Table 2 and shown graphically in

TABLE 1
MATERIALS

Material	Manufacturer	Average Filler Diameter (μm)	Cure	Posterior Use
Concise	3M Company Minneapolis, MN, USA	50	C†	No
Clearfil (Posterior)	Cavex Haarlem, The Netherlands	20	C	Yes
Heliomolar	Vivadent Schaan, Liechtenstein	10*	L	Yes
Occlusin	I.C.I. Macclesfield, U.K.	10	L	Yes
P-30	3M Company	3	L	Yes
Profile TLC	S.S. White Philadelphia, PA, USA	3.5	L	Limited
Silux	3M Company	40*	L	No

†C = Chemical; L = Light.
* = Average diameter of pre-polymerized particles.

Fig. 2. Table 3 shows significantly different groups as determined by Duncan's Multiple Comparison test. Except for the materials Occlusin and Concise, there was a significant difference between groups 1 (0) and 5 (10^4) cycles; however, none of the materials showed a significant difference between groups 5 (10^4) and 6 (0 cycles + 42 days in water). Four materials had a significant difference between those of groups 1 and 6.

TABLE 2

CRITICAL STRESS INTENSITY FACTOR (K_{IC}) GROUP MEANS AFTER THERMAL CYCLING (0 > = N = < 10^4)

Group No.	1	2	3	4	5	6
Cycle No.	0	10	100	1000	10,000	0 + 42 days
Occlusin	1.81* 0.19·	1.94 0.17	2.04 0.15	1.75 0.17	1.68 0.05	1.66 0.22
P30	1.47 0.12	1.55 0.12	1.65 0.08	1.32 0.08	1.15 0.21	1.21 0.04
Clearfil	1.39 0.08	1.30 0.08	1.23 0.06	1.23 0.26	1.13 0.05	1.10 0.10
Heliomolar	0.89 0.06	0.93 0.14	0.85 0.07	0.97 0.10	0.75 0.07	0.84 0.04
Concise	1.21 0.12	1.10 0.15	1.28 0.19	1.30 0.13	1.19 0.09	1.26 0.17
Silux	1.18 0.07	1.01 0.08	0.97 0.06	1.04 0.07	1.03 0.10	1.06 0.02
Profile TLC	1.03 0.06	1.02 0.06	0.96 0.06	0.92 0.04	0.94 0.04	0.99 0.05

*Mean K_{IC}, mN $^{3/2}$

·Standard Deviation, mN $^{3/2}$

DISCUSSION

In the design of this experiment, it was anticipated that thermal cycling might cause a deterioration in the filler/matrix bond of the composites. Although unexpected, the finding that 10^4 cycles caused only a small decrease in K_{IC} concurs with previous work on the effects of fillers and their interfaces on the fracture toughness of composite systems (Spanoudakis and Young, 1984a, b; Moloney *et al.*, 1984; Brown, 1980). Increasing the volume percentage of fillers (Vp) generally causes an increase in K_{IC} (Spanoudakis and Young, 1984a; Davis and Waters, 1987), and this has been attributed to pinning of the line energy of the crack front by the fillers (Lange, 1970). Early misgivings about this theory arose because the Fracture Surface Energy, G_{IC}, decreased with high filler volumes. This has been resolved by demonstration that the decrease in G_{IC} occurs as a result of the inverse relation between G_{IC} and the elastic modulus (E), which increases with filler loading. K_{IC} is directly related to E and therefore increases. The effect of the filler/matrix bond on crack pinning has been investigated by use of either experimental composites in which the fillers were either coated with a coupling agent (to promote adhesion) or a release agent to leave the fillers unbonded (Spanoudakis and Young, 1984b; Moloney *et al.*, 1984; Brown, 1980). For large particles (diam = 64 µm), it was found that K_{IC} increased with increasing volume of particles (Vp) regardless of the surface treatment. For small particles (diam = 4.5 µm), the K_{IC} for unbonded systems decreased with respect to bonded systems once the volume loading (Vp) exceeded 30% (Spanoudakis and Young, 1984a). However, these decreases were small and were considered to be of secondary importance to the overall effect of pinning.

All the composites in the present investigation had a filler loading exceeding 30% by volume. Excluding the microfilled composites, Concise had the highest large-particle loading (Table 1) and, as predicted by the above considerations, showed the least change in K_{IC}. P30, which is filled entirely with small-size fillers, had the greater decrease. The changes for Occlusin and Clearfil were intermediate to those of the previous two composites. Profile had the lowest K_{IC} of the conventional composites, and this may be explained by its friable filler particles (Moffa and Jenkins, 1978). If the particle size of the microfilled composite is taken as the size of the prepolymerized particles, then decreases in K_{IC} are similar to those of equivalent-sized conventional composites.

The initial increases found in the present study may have resulted from blunting of the advancing crack tip as it ran into the "resin cavities" of the debonded fillers (Moloney *et al.*, 1984). With SEN or DT test-pieces, crack-tip blunting manifests itself as slip-stick fracture (Spanoudakis and Young, 1984a; Moloney *et al.*, 1984; Davis and Waters, 1987). However, because of the unique Y^* *vs.* a/W ratio of the chevron-notch test-piece (see opening paragraphs),

TABLE 3

SIGNIFICANTLY DIFFERENCE GROUPS DETERMINED BY DUNCAN'S MULTIPLE RANGE COMPARISON

Group No.	4		1		5	6		1
No. of Cycles	1000		0		10,000	0 + 42 days		0
Occlusin	1.75		1.81		1.68	1.66		1.81
P30	1.32	*	1.47	**	1.15	1.21	**	1.47
Clearfil	1.23		1.39	**	1.13	1.10	**	1.39
Heliomolar	0.97		0.89	*	0.75	0.84	*	0.89
Concise	1.30		1.21		1.19	1.27		1.21
Silux	1.04	**	1.18	**	1.03	1.06	**	1.18
Profile	0.92	**	1.03	*	0.94	0.99		1.03

Significantly different groups are separated by *.

Numbers = Mean values for group.

**Difference significant with test at 0.01 level.

*Difference significant with test at 0.05 level.

slip-stick is masked by the rapidly changing compliance of the specimen and cannot be determined. An alternative explanation for the initial increase may have been the plasticizing effects of residual monomers (Lloyd and Iannetta, 1982).

The insignificant difference between groups 5 (10^4 cycles) and 6 (42 days in H_2O) indicates that a similar mechanism could have caused the decrease in both groups. The previous discussion indicates that a possible mechanism could be debonding of the filler-matrix interface. However, while thermal cycling may have caused a physical debonding as a result of differences between the expansion coefficients of fillers and the resin, it seems unlikely that water sorption for 42 days could have caused debonding to an equal extent, given that the diffusion coefficient for dental composites is extremely small (Braden *et al.*, 1976). These findings together may indicate that another mechanism – such as age-relaxation (increase in entropy) of the matrix – may have contributed to the decreases in K_{IC} seen in this study.

When one is considering the effects of thermal cycling on a material, it must be remembered that K_{IC} is determined by the structure of the bulk of the test-piece; its effect on the surface of the material may be far more significant but not determinable by changes in K_{IC}. Thermal cycling has been shown to increase the rate of toothbrush abrasion (Montes-G. and Draughn, 1986) and water to cause hydrolytic degeneration at the surface (Söderholm *et al.*, 1984). In engineering, fracture toughness is used to assess the resistance to fracture of stress-bearing materials, but fracture of dental composites is an infrequent clinical occurrence. The interest in K_{IC} seems to have developed for assessment of "crack behavior" because microcracking is an important part of the wear process. However, by definition, K_{IC} measures *critical* stress intensification, while microcracking in the wear process is sub-critical. The as-yet-undetermined relationship between fracture toughness and wear may be better resolved by the study of sub-critical stress intensification, with use of methods such as the "time-to-failure" model (Beaumont and Young, 1975), which are more directly related to microcracking.

CONCLUSION

The K_{IC} of dental composites was reduced after being stored in water for 42 days. Thermal cycling did not cause a significant reduction over and above that caused by storage in water. It appears that the fluctuating temperature in the oral environment is not a significant factor causing deterioration in the fracture toughness of dental composites.

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