UNIVERSITY OF LIVERPOOL

Analysis on the Oxidative Thermal Remodelling of Styrene-Butadiene Rubber (SBR)

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Abstract

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By Jericho de Guzman Timbol

Styrene butadiene rubber (SBR) is a synthetic rubber formed by random copolymerization of 1-3 butadiene with styrene. It is one of the earliest industrial synthetic rubbers and has established itself as one of the most widely used synthetic polymers. Heating SBR changes its physical properties as the bonds undergo a series of chemical reactions that result in crosslinking and formation of functional groups such as hydroxyls, carbonyls and hydroperoxides. Thermal oxidative degradation of SBR at 60 °C and 80 °C has been investigated by gel permeation chromatography, FTIR spectroscopy and chemical analysis of hydroperoxides, carbonyls and hydroxyls. The results showed that the degradation at this temperature range will show an induction period of 7 hours for 80 °C and 24 hours for 60 °C. The rates of degradation of SBR on oven ageing showed an increasing hydroperoxide content with increasing time of exposure. The rate of crosslinking is faster at 80 °C than at 60 °C which also has a similar pattern with the formation of hydroperoxides. FTIR results show that the oxidation is due to the aliphatic part of the rubber with a predominant growth of carbonyl and hydroxyl groups as the time of exposure increases. The reaction of 2, 4-dinitrophenylhydrazine (DNPH) with the thermally oxidized rubber at 60 °C to 80 °C confirms the presence of carbonyl groups with an increasing amount of chromophore per chain as the time of exposure increases. Attachment of anthracene on oxidized SBR via Steglich esterification shows that the presence of hydroxyl and carboxylic groups. A vast amount of work done on the mechanism and kinetics of low temperature degradation of rubbers but despite that there is still no general consensus on the mechanistic scheme of the reaction. The development of efficient synthetic protocols to attach signaling molecules to these long polymer chains is an effective method to detect the changes that has occurred as the ageing processes develop.

Acknowledgement

First of all, I would like to give my utmost gratitude to my adviser, Professor Roman Boulatov for being patient with me as I finish my PhD. This entire thing is not possible if he did not encourage me to be better and gave me freedom to explore and correct my mistakes. His suggestions, criticisms, analyses, observations, and inputs have helped me to write this piece. I learned a lot of scientific attitudes and techniques that I can use in the future as a scientist. A gratitude goes out to the Department of Chemistry of University of Liverpool for providing the funding for my work.

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This is a journey I will never forget. The hurdles I faced in working 72 hours straight while heating samples to waiting months to finally test them only for the lab to close due to Covid-19 lockdown, the amount of time I have dealt in this project is worthwhile and fruitful. Months of regret and mental breakdowns I have endured to make this possible.

Special gratitude to my family and friends who keep me sane as I work 10,728 kilometres away from you. I hope to be with you soonest.

Mabuhay ang Pilipinas!

Contents

CHAPTER I

Introduction: Thermochemical Modification of Polymers

1. Unsaturated rubbers: properties, syntheses and uses.

The prevalent property of elastomers is the ability to recover following deformation from compression or tension. The essential requirement for a substance to possess a rubbery characteristic is that it consists of long flexible chainlike molecules predominantly made from crosslinked chains of monomers [1]. The degree of deformation depends on the chemical structure and molecular weight of rubber undergoing stress and on external conditions directly affecting the rubber [1,2]. In addition, when processed for industrial purposes, synthetic rubbers are characterized by great toughness under different kinds of stresses, by having a high abrasion resistance, by its high chemical inertness and high impermeability to air and water [3].

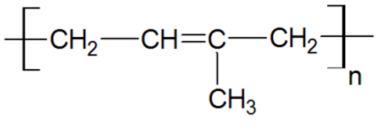
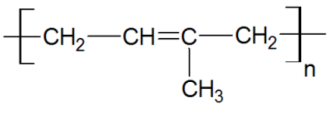
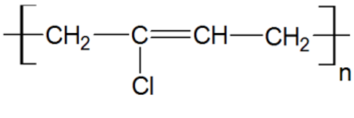
Table 1.1 Summary of properties of common synthetically manufactured unsaturated rubbers [1,4,5,6].

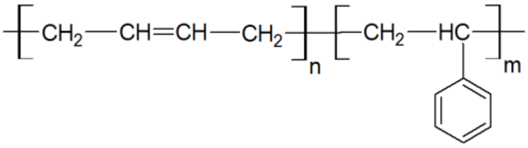
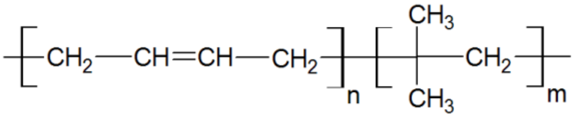
Unsaturated rubber	Chemical composition	Notable Industrial Properties	Examples of manufactured products
Polybutadiene rubber (PBR)	Polymerisation of 1,3 butadiene monomers	excellent elastic properties and low hysteresis loss, resistance to low temperatures	Tyres; plastics; additives for impact resistance of other elastomers; golf balls;
Ethylene propylene diene monomer rubber (EPDM)	copolymer of ethylene, propylene, and a small amount of conjugated diene monomers	High resistance to UV, ozone oxidation and weathering.	Roofing; tubing, pond liners, washers, belts, electrical insulation, solar panel heat collectors
Neoprene	polymerization of chloroprene	Heat resistant; High flame resistant; excellent sealant	Used as sealant; electrical insulators; shock absorbent materials or clothing;
Synthetic polyisoprene	Polymerisation of 2-methyl-1,3-butadiene	excellent mechanical properties with a high resistance to tearing and abrasion; high resilience at ~200 °C; low heat build-up	Tyres; latex products, footwear, belts and hoses and condoms
Nitrile butadiene rubber	Acrylonitrile combined with	Excellent abrasion resistance. Good	Oil seals; automotive transmission belts;

	various butadiene monomers	rebound. Good tear resistance. Cheaper than fluoroelastomers	hoses; synthetic leather; disposable non-latex gloves; printer’s form rollers and cable jacketing.
Styrene butadiene rubber (SBR)	Copolymers of styrene and butadiene	has better processability compared to natural rubber, heat aging and abrasion resistance but is inferior in terms of elongation, hot tear strength, hysteresis, resilience, and tensile strength	Rubber tyres; shoe heels; bubble gum; belts, hoses; adhesives

Generally, elastomers are classified into two types: unsaturated and saturated elastomers [2]. The unsaturated elastomers have available double bonds that can be further reacted to form products. Examples of unsaturated rubbers are the natural and synthetic polyisoprene, polybutadiene, chloroprene rubbers, nitrile rubbers, and styrene butadiene among others [1,2]. A list of structures of commonly known unsaturated rubbers are shown in table 1.2. Saturated rubbers are also called non-diene rubbers as they have no available double bonds after polymerisation process. Saturated elastomers have a very high resistance against ozone, heat, oxygen and radiation. Examples of saturated rubbers are polyacrylic rubber, silicone rubber, polyether block amides, ethylene-vinyl acetate and more [5].

Table 1.2. Type of unsaturated rubbers.

Rubber	Chemical Structure
Natural Rubber	 $-\!\left[CH_2-CH=\underset{\underset{\displaystyle CH_3}{|}}{C}-CH_2\right]_n\!-$
Polyisoprene	 $-\!\left[CH_2-CH=\underset{\underset{\displaystyle CH_3}{|}}{C}-CH_2\right]_n\!-$
Polychloroprene	 $-\!\left[CH_2-\underset{\underset{\displaystyle Cl}{|}}{C}=CH-CH_2\right]_n\!-$

Polybutadiene	$\left[-CH_2-CH=CH-CH_2-\right]_n$
Styrene butadiene	
Isobutylene isoprene	 $\left[-CH_2-CH=CH-CH_2-\right]_n\left[-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\right]_m$

Synthetic rubbers are often vulcanised to give a more rigid form suitable for industrial uses. Vulcanisation is the range of processes in hardening rubbers by chemical modification of unsaturated elastomers [4,6]. Vulcanisation of rubbers generally increases the strength of materials, lowers the water absorption, increases the resistance to oxidation, organic solvents, and abrasions [7]. Unsaturated rubbers are easily vulcanised because of the availability of double bonds that can be used to react with an agent such as sulphur [6]. Saturated rubbers are not reactive to sulphur vulcanisation thus other methods are employed such as the use of metal oxides [6].

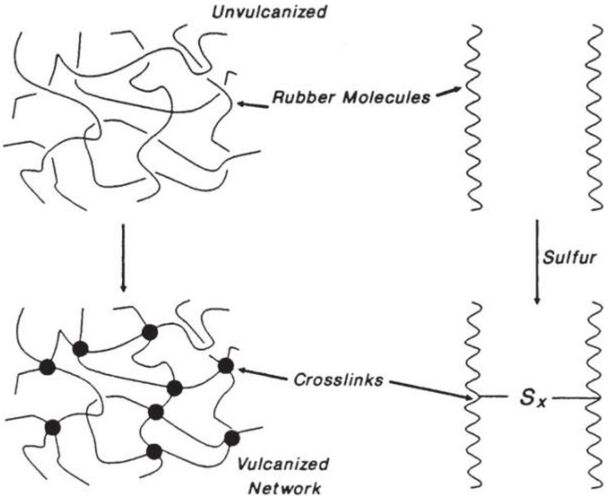


Figure 1.1 Network formation of sulphur vulcanisation of rubber composites [6].

Raw material elastomers need to be modified into different products to meet the necessary demands for consumption [6,7]. Synthetic rubbers like polybutadienes and polyisoprene are soft when warm but turn brittle when cold. By vulcanising these rubbers, these disadvantages are proportionally studied, and the rubbers are subjected to varying chemical modifications to meet the desired properties. Elastomers can be made available in different molecular weights, saturation, purity, or collectively called in industrial terms as grades or quality. Primary uses for elastomers include sealants, adhesives, polymer additives, thermal and electrical insulation, and mechanical support [9]. Table 1.2. summarizes the most common synthetically manufactured elastomers with their notable physical properties and uses.

Rubbers are ubiquitous and one of the most extensively manufactured materials on earth. However, many synthetic polymers are produced from limited resources derived from petrochemicals [1,2]. The viable recycling of waste tyres is a major challenge that industries are facing given the fact that most rubbers are extremely durable and tedious to be degraded into smaller components [1-8]. Therefore, recycling of rubber waste is a very important problem as such waste is not biodegradable and can pose negative impacts on our ecosystem. Worldwide tyre production is increasing by 3.8% annually, thus making the landfilling of waste tyres unsustainable due to resource wastage, their lack of biodegradability and the potential environmental risks involved [10]. Several attempts have been made to alleviate tyre wastage worldwide by recycling and increasing the shelf life of the rubbers [1,2,10].

Rubbers have high bulk modulus which allows their physical structure to retain their volume when deformed. Similar to incompressible liquids, they have low Poisson's ratio of around 0.5 [1-3] which is very useful for industrial applications [11]. Rubbers in their raw form often have very limited applications due to their amorphic characteristics. To become more useful, chains of these polymeric materials are processed, organised, and mixed shown in the schematic diagram below [12].

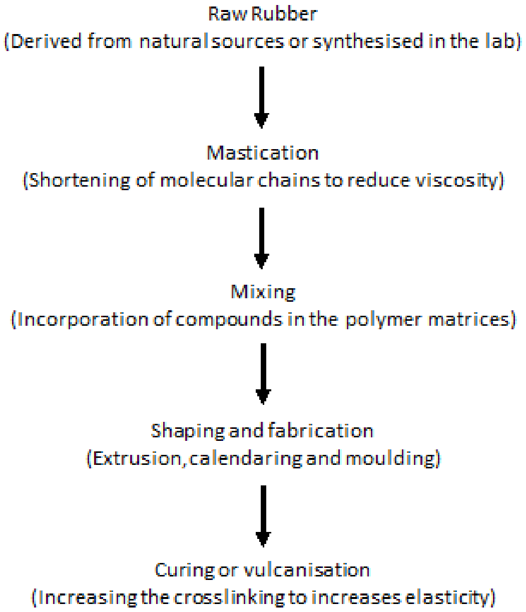


Figure 1.2. Schematic flowchart of rubber processing. The steps are not specific to all kinds of rubbers. Retrieved from [12].

2. Styrene Butadiene

1. Chemistry of SBR

Styrene butadiene rubber (SBR) is a synthetic rubber formed by polymerisation of 1,3-butadiene with styrene. It is one of the earliest industrial synthetic rubbers and has established itself as one of the most widely used synthetic polymers [1,3,13]. SBR being a cheap (around $2-3 per kg) synthetic general-purpose elastomer, it is sometimes used as a substitute for natural rubber (NR). Styrene–butadiene rubber (SBR) has the largest consumption among various general-purpose synthetic rubbers due to its notable properties such as abrasive resistance, heat resistance, and ageing resistance. These properties are superior to those of natural rubber alternatives, resulting in SBR replacing NR practically in many industries [14]. The annual world consumption of synthetic rubbers is estimated to exceed 5 million tonnes with a total value of over $30.64 billion in 2021 and is expected to reach $ 38.5 billion by 2027 [15]. In the context of rubber production, SBR holds 55% market share as of 2021 and has been seen to grow steadily in the foreseeable future [16].

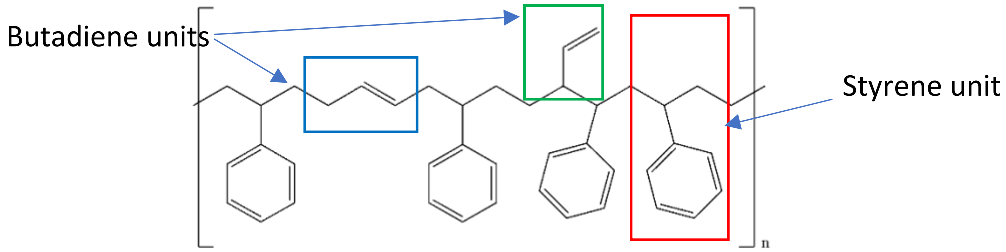


Figure 1.3 The chemical structure of styrene butadiene random copolymer that forms the basic molecular component of SBR. Repeat units derived from styrene and butadiene which can be attached via 1,4-addition (blue box) and 1,2-addition (green box) during polymerisation [14].

SBR is produced by copolymerisation of 1,3-butadiene with styrene in the approximate proportion of 3:1 by weight [3,8]. The attachments of the butadiene can go in two ways either by 1,4-addition or 1,2-addition. Figure 1.3 shows the product of two butadiene monomers added differently. Currently there are two predominant methods in SBR production: Emulsion SBR (e-SBR) and solution SBR (s-SBR). In the emulsion process, the polymerisation is initiated by free radicals where the feedstocks are suspended in a large proportion of water in the presence of an initiator or a catalyst and a stabiliser. The initiators can be potassium persulfate or hydroperoxides in Iron II salts. The emulsion process can be done in hot (~60 ^{o}C) or cold (~5 ^{o}C) media [18]. During polymerization, parameters such as temperature, flow rate and stirring are monitored and controlled to obtain optimum product conversion [18,19,20].

For the solution SBR production, the copolymerisation proceeds in a hydrocarbon solution in the presence of an organometallic complex or anionic initiator. This can be either a continuous or batch process. In solution polymerization, the monomer, initiator, and the resulting polymer are all soluble in the solvent or solvent blend. In the case of free radical polymerization, the rate of the reaction is directly proportional to the monomer concentration [18,20]. Emulsion SBR still accounted for the majority of global SBR production as of 2015 but more and more SBR is produced by solution polymerization which is better suited for high-performance tyres [14].

The styrene pendants of SBR absorb from 240-290 nm with λ_{max} at 254 nm which can be used to calculate the amount of styrene groups in the rubber [21,22,23]. The variation of the absorbances can be a method in determining the % styrene contents in the manufactured rubbers [21, 23]. Like natural rubber, SBR is swollen and weakened by hydrocarbon oils and is degraded over time by atmospheric oxygen and ozone. In SBR, however, the main effect of oxidation is increased interlinking of the polymer chains, so, unlike natural rubber, it tends to harden with age instead of softening. The most important limitations of SBR are poor strength without reinforcement by fillers such as carbon black (although with carbon black it is quite strong and abrasion-resistant), low resilience, low tear strength (particularly at high temperatures), and poor tack or sticky to the touch. These characteristics determine the use of the rubber in tyre treads; essentially, its proportions decrease as the need for heat resistance increases until 100 percent natural rubber is reached in the heaviest and most severe uses, such as tyres for buses and aircraft [18]. SBR has taken the place of natural rubber in terms of its benefits and ease of production. Its advantages include excellent abrasion resistance, crack resistance, and generally better aging characteristics [15,16].

2. Industrial Demand for SBR

Styrene-butadiene rubber has the highest volume of general-purpose synthetic rubber production today [15]. The majority of the SBR production is used in manufacturing tyres and tyre products which accounts for 70% of the global SBR production. Other uses include footwear, belts, flooring materials, surgical tools like tubes, hoses and gloves, and as additives to improve toughness, impact resistance and quality of other elastomers [15,16].

The global demand for industrial rubber is projected to increase by about 5% from 2017 to 2022. In the last several decades, SBR has overtaken Natural Rubber in terms of global production because of its overall advantage [9,15,18]. These rubbers have well-established fatigue-crack growth (FCG) characteristics in field performance of tyre treads, with NR exhibiting the higher FCG resistance at high region of tearing energies, whereas the advantage of SBR over NR can be realized in terms of the higher fatigue threshold for SBR occurring in the low range of tearing energies [18,24].

Figure 1.4 Different products derived from the manufacturing of SBR.

3. Remodelling of Polymers

The value of polymeric materials is attributed to their mechanical properties and in particular their ability to withstand any applied stress. Industries are developing ways to remodel polymers to enhance these properties for the benefit of the end products distributed worldwide. Degradation of polymers is characterized by changes in the polymer structure caused by physical, mechanical or biological factors which can lead to chain scission and/or the formation of new functional groups [25,26]. These changes can affect the service life and properties of the rubbers and can only be retarded or prevented by the addition of UV stabilizers and antioxidants or storage in an inert environment at low temperatures [27].

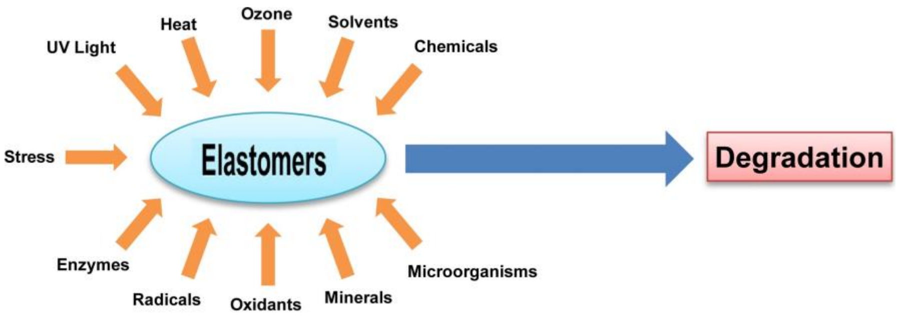


Figure 1.5. General description of elastomer degradation aided by different factors that lead to degradation of polymer chains into different products.

Synthetic rubbers such as SBR, polybutadiene and polyisoprene are susceptible to degradation. This is ascribed to the presence of reactive double bonds, and the low glass-rubber transition temperature (T_g) [1, 14, 28]. The glass transition temperature demarks the transition from a brittle glassy state to its rubbery form and is an important property that determines the usability of polymers [30]. The concentration of crystalline regions in amorphous polymers affects the rigidity of the polymer. If a polymer is degraded, its molecular structure will alter and its mechanical properties will also be affected, thus limiting useableness [31]. The T_g of a given elastomer depends on the chemical structure of the elastomer. The presence of an electron donor, bulky side groups, prevalence of crosslinks and longer chains significantly reduces its mobility thus increasing the overall T_g of the material. A 2002 paper showed the changes in the relaxation times of SBR containing varying percent composition of styrene which was done through the analyses of their glass transition. The glass-transition temperature affects a number of important technological properties such as strength, damping, low temperature flexibility, rolling resistance and wet grip [31]. The T_g of polymers allows industries to measure the limits of their products, crucial for the development of rubber-based products [32].

4. Chemically-Assisted Degradation of Elastomers

Degradation of rubbers under specific conditions such as increasing in temperature, oxidation, exposure to UV light and shearing has been extensively studied for many years. There are different methods in degrading rubbers in subtle conditions such as room temperature reactions, neutral pH environment and catalyst-assisted reaction, to gradually observe the changes in the molecular level [33-39]. The resistance to degradation depends on many factors, such as polymer chemical composition, length of the polymer chains (MW) and crosslink density. Some elastomers have double bonds that are sources of relatively reactive pi-electrons, which make them vulnerable to degradation, consequently having poor heat, ozone and UV resistance [33].

Oxidative and thermal aging of a rubber is greatly accelerated by stress and exposure to reactive gases such as ozone (O_3). Polymers with high unsaturation will suffer from oxidation degradation because the double bonds in unsaturated polymers readily react with oxygen [37-39]. The reaction of ozone with double bonds causes chain scission as shown in figure 1.6 below. Physical deformities such as embrittlement, softening, cracking and changes in color are observed [33,34].

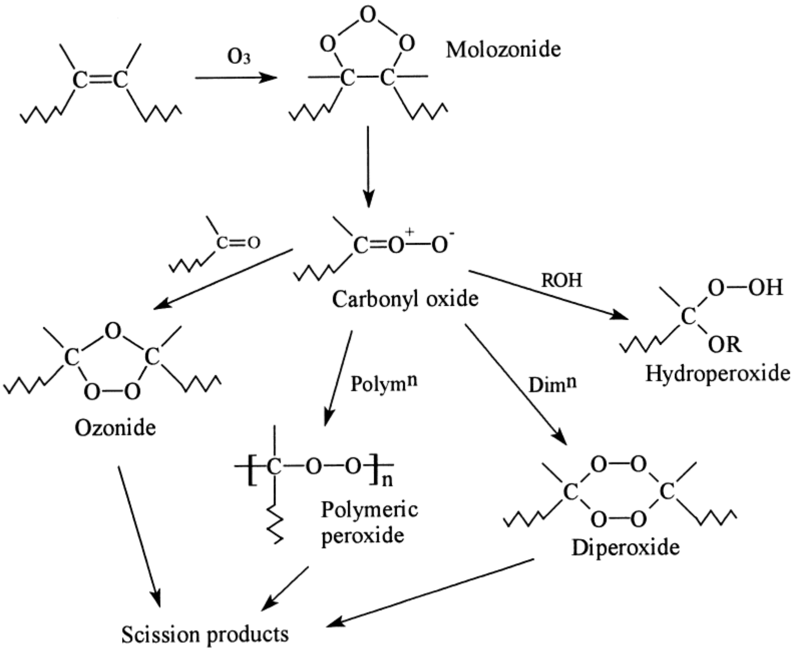


Figure 1.6. Ozonolysis of olefins. Cleaving the C-C double bonds to form carbonyl compounds are observed when elastomers are reacted to ozone. Image retrieved form [34].

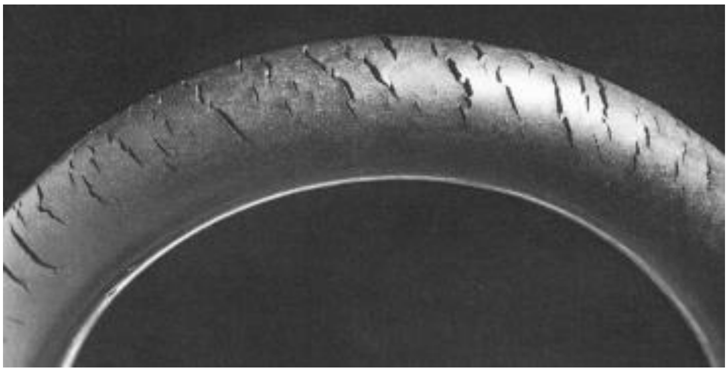


Figure 1.7. Ozone cracking in rubber tubing. Retrieved from [32].

As a typical carbon-backboned polymer, SBR and other elastomers are observed to follow the basic auto-oxidation scheme which generally involves initiation, propagation, and termination [33,37-40]. As shown in figure 1.8, addition of O_2 in the system of polymers undergoing rearrangement (scheme 1-2) can lead to the production of reactive species POO• (scheme 3). Autocatalysis can be seen as the hydrogen is abstracted from the next substrate by the peroxy radical, POO• (Figure 1.8) [37].

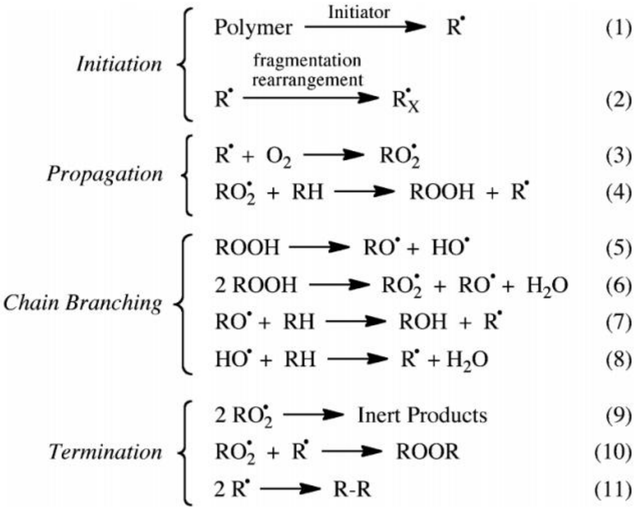


Figure 1.8. Basic Autooxidation Scheme of Polymers. Retrieved from [33].

M. Coquillat et al. [37-39] proposed a detailed mechanistic and kinetic scheme for thermal oxidation of polybutadiene which apparently suggests that the radical O_2• addition to double bond is faster than hydrogen abstraction, which suggested forming POOP• is the key feature of polybutadiene oxidation (Figure 1.9). In the propagation stage, a polymer radical (P•) reacts with an oxygen molecule to form a peroxy radical (POO•), the peroxy radical will abstract a hydrogen from another polymer chain to form polymer hydroperoxide (POOH). The POOH will split into two new free radicals (PO•) + (•OH), which abstract hydrogens from another polymer chain. Lastly, termination will be achieved by pairing two radicals. Recombination of two chain radicals will result in an increase of molecular weight and crosslinking density. Many competing reactions exist in these steps that give way to the formation of different functional groups such as alcohols, anhydrides, carbonyls, aldehydes, peracids, lactones and carboxylic acids. However, there is still a lot to understand about the specificity of these reactions and researchers are working to discriminate chemical equations that form functional groups with each other [39].

Alkyl radicals:

Radical rearrangement: $P^{\bullet}+PH \longrightarrow PH+P^{\bullet}(-PH)$ (1)

Binding oxygen: $P^{\bullet}+O_2 \longrightarrow PO_2^{\bullet}$ (2)

Intermolecular binding double bonds:

$P^{\bullet}+F \longrightarrow P^{\bullet}(2\text{-}PH)+x,$ (3)

where F=double bond, x=crosslink.

Intramolecular binding double bonds:

$P^{\bullet} \longrightarrow P^{\bullet}(-F,-PH)$ (4)

Peroxy radicals:

Hydrogen abstraction:

$PO_2^{\bullet}+PH \longrightarrow POOH+ P^{\bullet}(-PH)$ (5)

Intermolecular binding double bonds:

$PO_2^{\bullet}+F \longrightarrow POOP+ P^{\bullet}(2\text{-}PH)+x$ (6)

Intramolecular binding double bonds:

$PO_2^{\bullet} \longrightarrow \text{cyclic } POOP +P^{\bullet}(-F,2\text{-}PH)$ (7)

Figure 1.9. Reaction schemes of thermal oxidation of Polybutadiene. Retrieved from [37]. The generally accepted reaction mechanism of elastomers follows the basic auto-oxidation scheme. Researchers are still understanding the overall behavior of polymer melts as they undergo degradation in aerobic environment.

In the thermal degradation of SBR done by Guo et, al [40], polyisoprene samples were heated at 140 °C in air and the formation of functional groups was monitored by 2D FTIR spectroscopy. With increasing heating time, the polymer samples gradually lose their elasticity and the color slightly changes. Based on the IR results, carbonyls and hydroxides are formed essentially at the same time and the carbonyl region produce different peaks as time progresses (Figure 1.10). The oxidation of the aliphatic part of SBR generated conjugated carbonyls; saturated carbonyls and carbonyls of peresters and/or anhydride. The degradation kinetics of SBR was studied by differential scanning calorimetry and the parameters were measured by the Friedman method [40,41]. Guo et al determined the activation energy (E_a) of thermal oxidation of SBR at different heating rates (5, 10, 20 and 30 °C min^{-1}). The experiments showed that the E_a is higher at low conversion of SBR to crosslinked products which suggests a complex-multistep mechanism [34,37,40]. Figure 1.10 shows the evolution of functional groups on the oxidative degradation of polyisoprene done under IR analysis coupled with a heating plate [40].

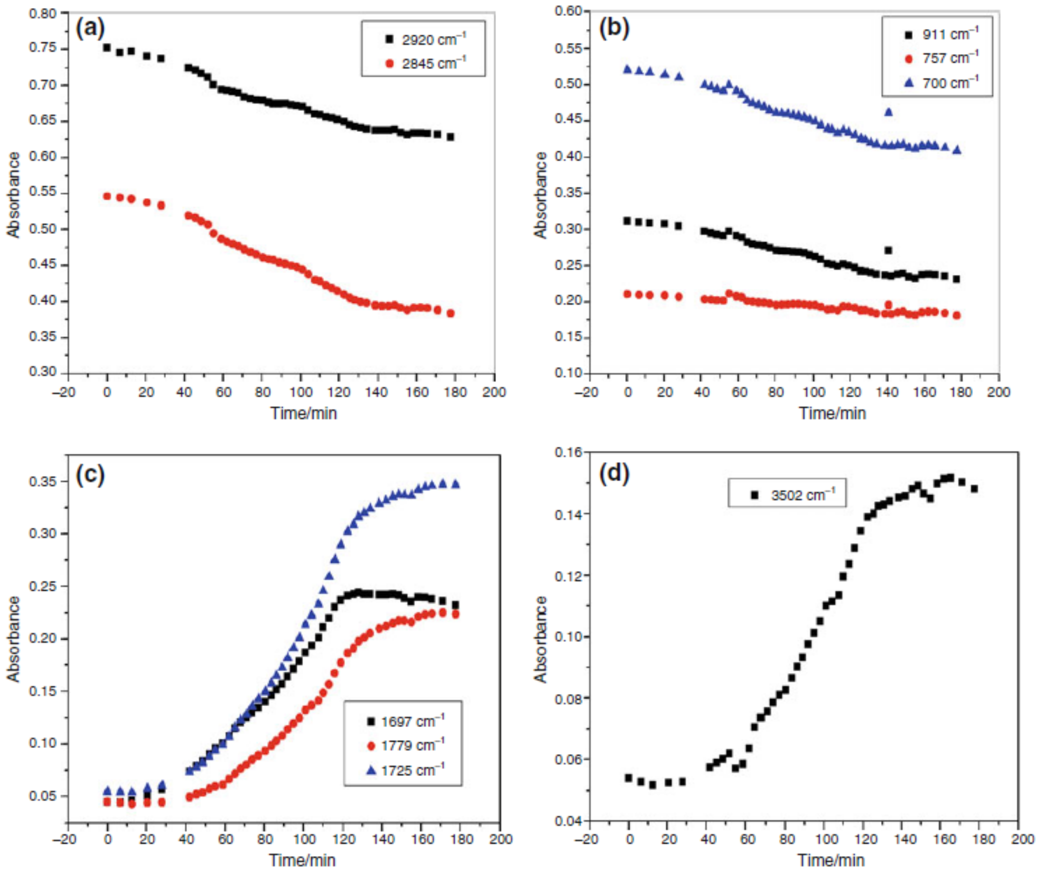
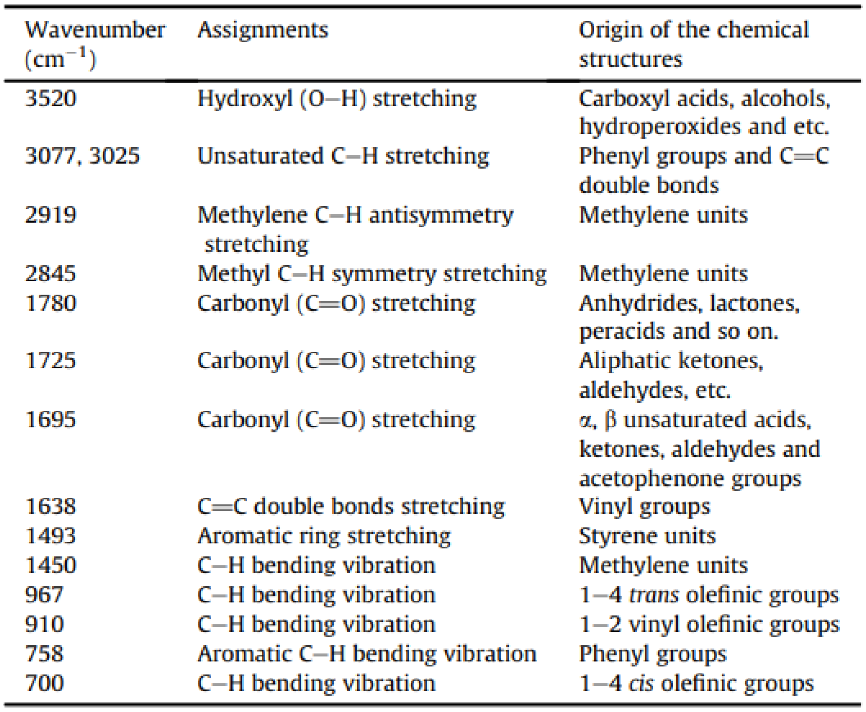


Figure 1.10. The intensity variation versus aging time from in situ FTIR (a) intensity of C–H vibration; (b) intensity of =C–H deformation vibration; (c) intensity of carbonyl vibration; (d) intensity of hydroxyl vibration. Images retrieved from [40].

The 2D infrared analyses showed the different peaks at the carbonyl region from 1660-1800 cm^{-1}. The formation of different types of carbonyls is seen to develop independently from each other. A study conducted by Guo et al [40] found that the intensities of peaks at 1697 and 1272 cm^{-1} increases simultaneously while the peak at 1777cm^{-1} only appears after 40 minutes of heating. As heating continued, the conjugated carbonyl peaks decreased, the aliphatic carbonyl peaks increased and the peaks of α, β-unsaturated carbonyls remained constant. Similar results were obtained by Xiang et al [41] who monitored composition of SBR heated in air at 130 °C by 2D IR and DSC. In addition, they found that the peaks in the aliphatic region (2845-3077 cm^{-1}) decreased during heating, which they attributed to the loss of C-H bonds and the formation of C=O bonds (Figure 1.8). Xiang also studied the relaxation behavior of thermally degraded SBR in DSC, which yielded widening of the relaxation curves or the width of the glass transition region *ΔT*, suggesting the crosslinking reaction dominated thermal degradation [41].



Wavenumber (cm^{-1})	Assignments	Origin of the chemical structures
3520	Hydroxyl (O–H) stretching	Carboxyl acids, alcohols, hydroperoxides and etc.
3077, 3025	Unsaturated C–H stretching	Phenyl groups and C═C double bonds
2919	Methylene C–H antisymmetry stretching	Methylene units
2845	Methyl C–H symmetry stretching	Methylene units
1780	Carbonyl (C═O) stretching	Anhydrides, lactones, peracids and so on.
1725	Carbonyl (C═O) stretching	Aliphatic ketones, aldehydes, etc.
1695	Carbonyl (C═O) stretching	α, β unsaturated acids, ketones, aldehydes and acetophenone groups
1638	C═C double bonds stretching	Vinyl groups
1493	Aromatic ring stretching	Styrene units
1450	C–H bending vibration	Methylene units
967	C–H bending vibration	1–4 *trans* olefinic groups
910	C–H bending vibration	1–2 vinyl olefinic groups
758	Aromatic C–H bending vibration	Phenyl groups
700	C–H bending vibration	1–4 *cis* olefinic groups

Figure 1.11 List of carbonyl groups and their FTIR absorbance observed on thermally oxidized SBR. Retrieved from [41].

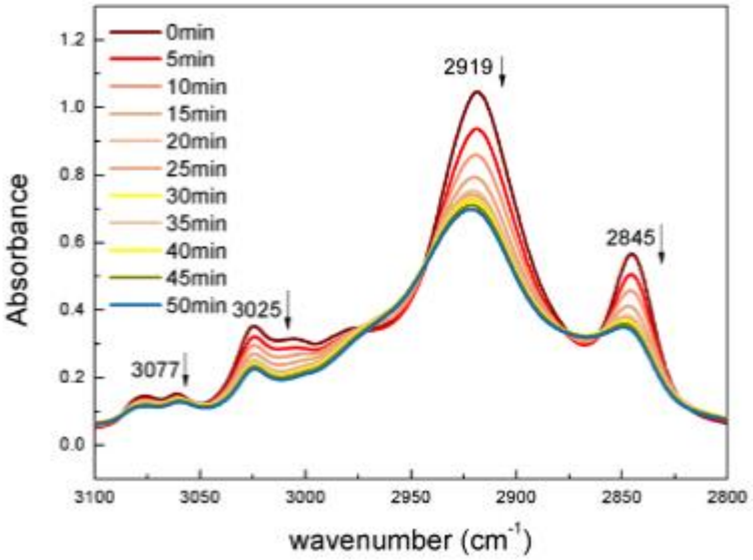


Figure 1.12. Transmission spectra in the C-H stretching of oxidized SBR at 140°C. Absorption at 3077 cm^{-1} is assigned to the phenylic C-H, 3025 cm^{-1} is to vinylic C-H while 2919 cm^{-1} and 2845 cm^{-1} are from saturated C-H stretching. Retrieved from [41].

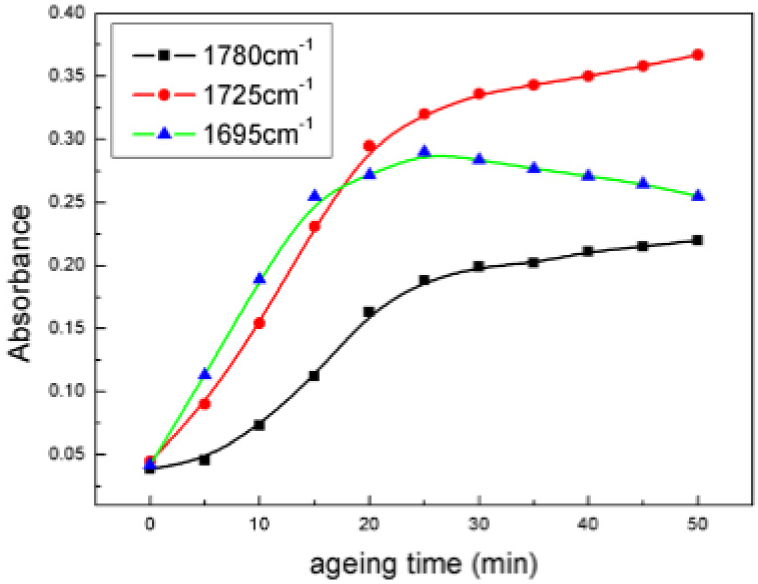


Figure 1.13. Absorbances in carbonyl regions of thermally heated SBR at 140 °C. The gradual increase of carbonyl carbons is observed vs the time of ageing. These absorbances are assigned to C-O stretching with specificity describe in Table 1.2. Retrieved from [41].

Allen et al [42] heated high styrene content SBR at 90 °C and 110 °C in air and analyzed the samples for the presence of hydroperoxide, carbonyls, the amount of crosslinked material and degree of yellowness or discoloration. The group also studied photooxidation of SBR under polychromatic light, 365 nm and 254 nm light. In the thermal experiments the carbonyl growth, hydroperoxide concentration and degree of yellowness increase with increasing temperature and an induction period is observed (Figure 1.14). The concentration hydroperoxide increased with increased exposure time. However, it is shown that the concentration of hydroperoxide gradually decreases as the crosslinking increases [42].

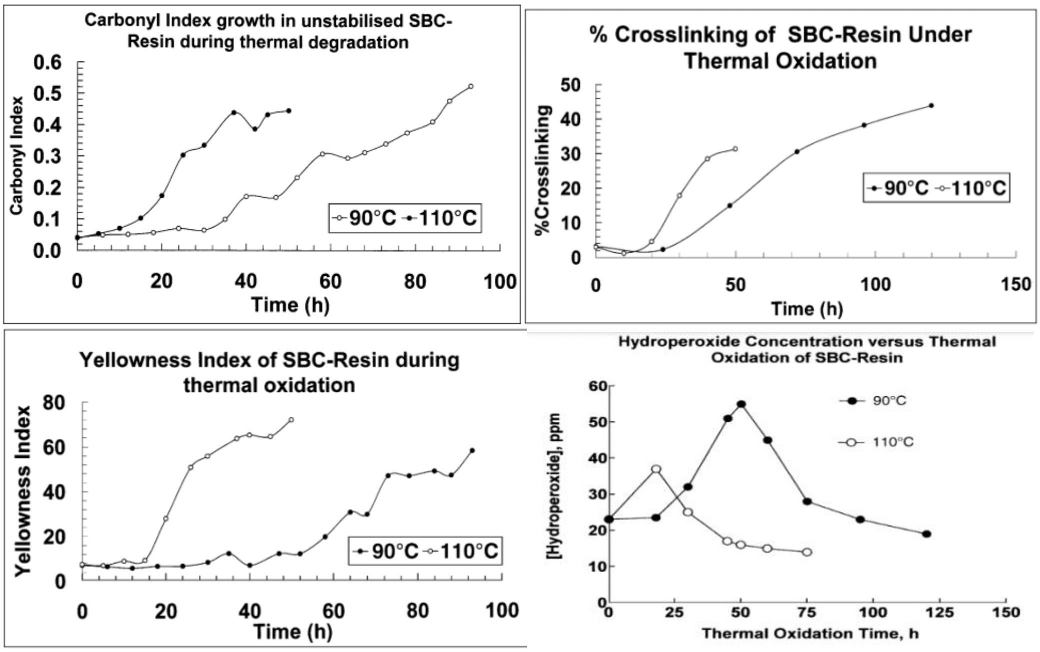


Figure 1.14. Analyses on the thermal degradation of high styrene content SBR at two specified temperatures. Retrieved from [42].

In photooxidation experiments, three light sources were used for irradiating SBR samples: Black Body Temperature 50 ^{o}C (Microsal), mercury lamp (254 nm) and fluorescent tube (365 nm). Regardless of the wavelength and length of exposure, induction periods preceded the appearance of carbonyl groups (Figure 1.14) [42,43] .

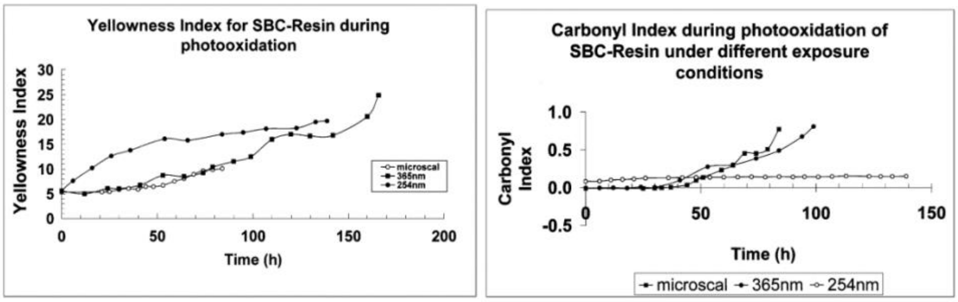


Figure 1.15. Analyses on the photooxidation degradation of high styrene content SBR at different light sources. Retrieved from [43]

Hydroperoxide concentration increased slightly initially and then achieved a steady state in all conditions. Weak crosslinking was evident only under 254 nm light while excimer aggregates were destroyed rapidly for polychromatic light and 365 nm irradiations. Irradiation at 254 nm caused more extensive discoloration than the other wavelengths [43].

For lower temperature oxidation of polymers such as polyisobutylene, the formation of oxidized species are slower and fewer and the induction periods observed are longer. R. Pazur et al [43] analyzed thermal oxidation of poly-isobutylene at 23-100 °C by Fourier Transform Infrared (FTIR) spectroscopy. The formation of carbonyl and hydroxyl groups in the rubber oxidized at temperature range from 40-60 °C is seen to have evolved from days to weeks at compared with the pristine rubber samples (Figure 1.16) [43].

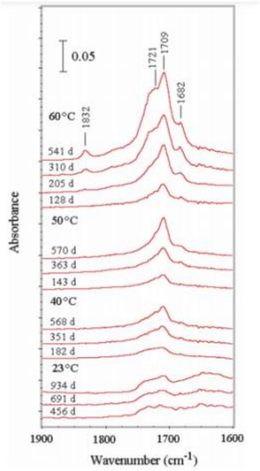


Figure 1.16. Evolution of IR active bands for carbonyl region for thermal oxidative aging from 23-60 °C of poly (isobutylene). Retrieved from [43]

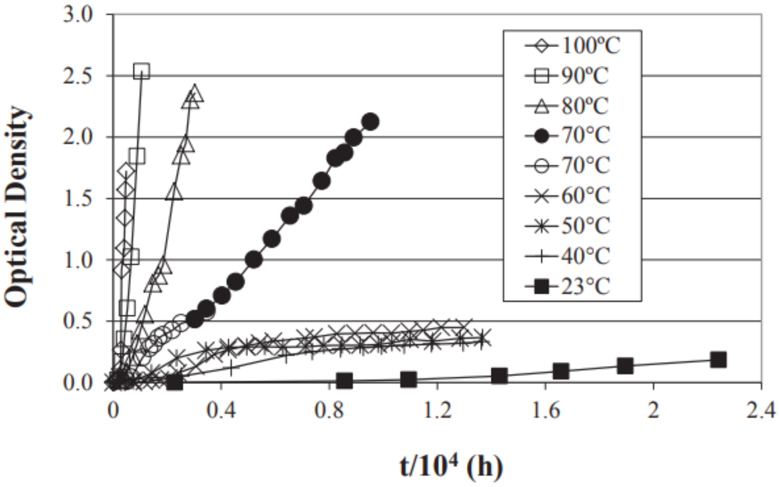


Figure 1.17. Carbonyl growth as a function of aging time from room temperature to 100 °C of polyisobutylene. Retrieved from [43].

5. Random chain scission and crosslinking on polymer oxidation

Chain scission is a term used in polymer chemistry describing the degradation of a polymer main chain into two or more smaller polymers. This process is often a consequence of reactions that are induced in the polymer such as thermal stress, radiation, oxidation, and shearing. During chain cleavage, the polymer chain is broken at a random point in the backbone to form two smaller polymer chains [1,9,17]. All unsaturated elastomers are susceptible to attack by oxygen which eventually leads to chain scission accompanied by changes in physical properties. Since almost all the elastomers being manufactured contain unsaturated bonds, many industries are focusing on the prevention of chain scission of their materials by making the elastomers resistant to heat, oxidation and other kinds of degradation by addition of anti-oxidants and vulcanisation methods [39,41,44].

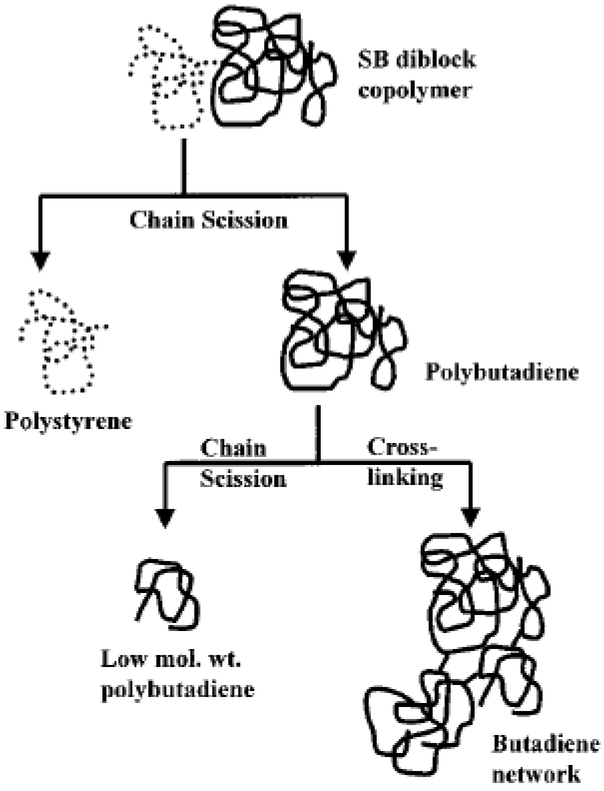


Figure 1.18. A simplified reaction scheme, showing chain scission and cross-linking reaction in a Styrene-Butadiene diblock copolymer [17].

Figure 1.18 showed a scheme of how styrene-butadiene diblock polymers are behaving in elevated temperatures while exposed in air. It is observed that the polystyrene chains are separated with the polybutadiene chain eventually creating polybutadiene networks of different masses. Reaction kinetics of thermos-oxidative degradations in Styrene-butadiene rubbers is an autocatalytic process. There are different kinds of SBR depending on how they are created industrially. Fan et al [45] studied how styrene-butadiene diblock copolymer behaves as it is oxidized with changing temperature. The gel permeation chromatography (GPC) studies revealed that the chain scission not only lowers the overall molecular weight of the copolymer but also drive macrophase separation between polystyrene-rich copolymer and polybutadiene segments. As evidenced in the gel content determination, the molecular weight increases rapidly when the cross-linking reaction becomes dominant [17].

6. Retardation of polymer degradation

Antioxidants and UV stabilizers are often added to elastomers to prevent degradation. The two main classes of antioxidants added to rubbers are free-radical scavengers and peroxide scavengers [47]. The free-radical scavengers are sometimes called primary antioxidants or radical chain terminators whereas peroxide scavengers are often called secondary antioxidants or hydroperoxide decomposers [49]. The most common rubber antioxidants are the phenylene amines or phenolic antioxidants. Amine derived antioxidants have good synergistic effects on rubbers thus increasing its shelf life.

Vulcanisation is another method of preventing the degradation of elastomers. Elastomeric raw materials are often an entanglement of varying high molecular weight polymers which are often soft and very flowy which is not a good quality for a rubber. By vulcanising it, the rubber will develop a good form that can be easily transformed into varying rubber products from tyres to hoses and pencil erasers [7]. Rubber can be cross-linked by heating with sulphur (S_8) in heated reaction system. Several methods have been done to control the rate of vulcanisation based on the desired output. This can be done by adding accelerants or retardants in the reaction mixture. In a general vulcanization scheme as in Figure 1.19, sulphur linkages form bridges between rubber chains by breaking the double bonds [50]. The chemical networks formed by the crosslinking of rubbers by sulphur vulcanisation are irreversible reactions which results in the formation of thermoset materials. These end products are not easily recyclable and often end up as rubber wastes.

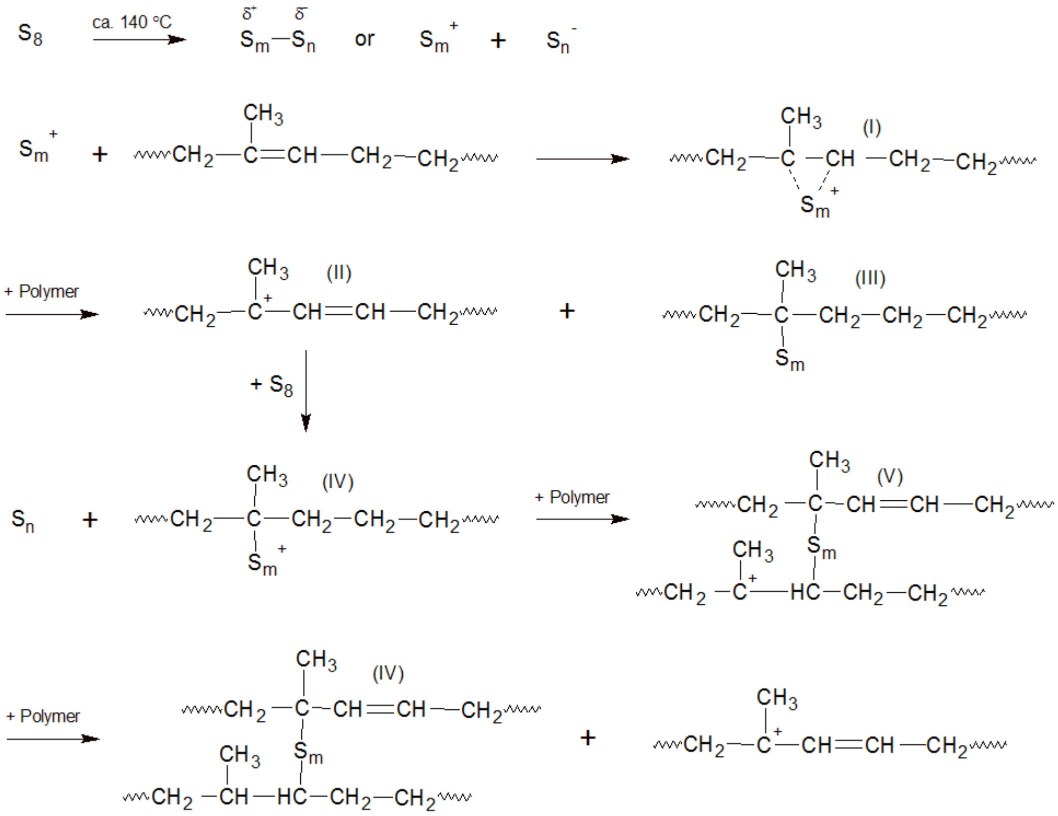


Figure 1.19. A vulcanisation scheme of elastomers with sulphur starts with the formation of monomeric sulphur ion, S_m, that then forms a cyclic bond with the allylic carbon of an elastomer unit. The polymer-sulphur ion then reacts with another polymer to attain a polymer carbocation. [50]

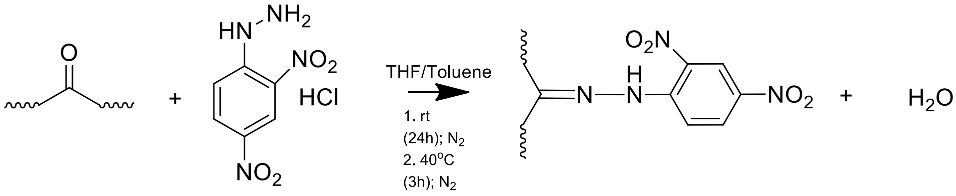
7. Methods of Detecting Functional Groups in Elastomers.

Several methods have been employed to determine the oxygen-containing compounds in oxidized rubbers by reacting them with an indicator molecule. The most popular method is to attach a molecule that can be detected spectroscopically and further quantified. These are considered non-destructive approaches as we can still obtain the rubbers without destroying them in the process. For reactions to be considered non-destructive, milder conditions are employed, limiting the temperature, and prohibiting other unwarranted chemical reactions that can lead to hydrolysis, reduction and further crosslinking and chain scission [51].

a. The DNPH analysis for carbonyl group

2, 4-dinitrophenylhydrazine (2, 4-DNPH) or commonly called as the Brady's reagent is generally used to quantify aldehydes and ketones. The solution is prepared from dissolving DNPH in ethanol and adding concentrated sulphuric acid. This method is commonly used as qualitative identifier for aldehydes and ketones for laboratory experiments and analyses. The reaction is an addition-elimination reaction through the addition of the $-NH_2$ and the elimination of water in the process [52].

The hydrazone derivatives of small molecules are often precipitated out of the solution and later quantified. For polymers such as oxidized polybutadiene, 2, 4 DNPH is used to quantify the carbonyls present in samples. A method designed by Burfield et al [53,54] shows the reaction (Figure 1.20) of oxidized polyethylene (1) with 2, 4-DNPH (2) to produce the polyethylene-hydrazone (3) product, which was analysed by UV absorption at 367 nm (Reaction 1, the experimental ε for the hydrazone derivative at λ_{max} = 367 is 22,000 $M^{-1}cm^{-1}$) [47]. Dinitrophenylhydrazine does not react with other carbonyl-containing groups such as carboxylic acids, amides, esters, anhydrides, and acyl phosphates [53,54]. One main reason is that other types of carbonyls form resonance structure thus delocalising some positive charges away from the carbonyl carbon on to the adjacent heteroatom. Carbonyl carbons of aldehydes and ketones are electrophilic enough for the nucleophilic DNPH to react [52,53,54].



2 1 3

Figure 1.20. Reaction between 2, 4 DNPH with the carbonyl groups oxidized polyethylene [52,53].

Since there are different oxygen-containing species present in the oxidized SBR, interferences should be checked and if possible, corrected. A work done by Arnold et al [54] shows that the presence of hydroperoxide in the oxidized rubber does not react with DNPH in the solution. The experiment was done by adding equimolar amounts of triphenylphosphine in the solution of oxidized rubber before performing the DNPH reactions [54]. The reactivity of polymeric carbonyl groups towards DNPH appears to be markedly affected by steric factors, determined by the polymeric microstructure so the limitation of the reaction mainly focused on the solubility of the polymers in the reaction solution and the rate of stirring as DNPH is slightly soluble in water and many organic solvents such as THF and ethanol. Reactions are often maintained at room temperature to prevent further degradation of polymers when the reaction system heats up. The efficiency of this substitution reaction to the analysis of oxidized rubbers will be discussed in this study .

Typical reactions of DNPH to detect carbonyls are done at elevated temperatures (~50 °C). However, in this project, the experiment was done at two temperatures, (40 °C and 25 °C) to prevent SBR from further degradation. Interferences are also checked to make sure that no other functional groups are reacting with DNPH. One reaction that is tested is the presence of hydroperoxides in the solution [54]. By reacting the oxidized rubber with triphenylphosphine (PPh_3), the hydroperoxide groups are decomposed to alcohols at room temperature. Oxidized SBR samples that are treated with PPh_3 did not show different results from the untreated ones [54].

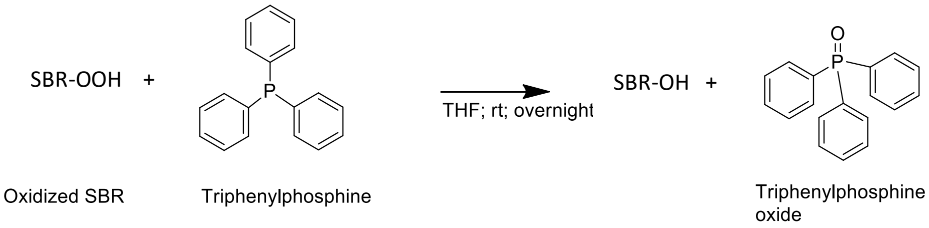
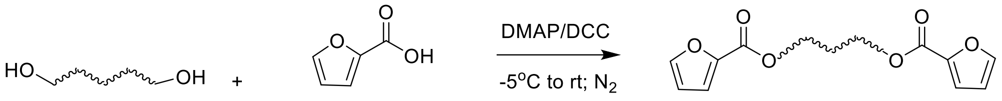


Figure 1.21. Reaction of hydroperoxides with triphenylphosphine [54].

b. Steglich esterification of alcohols and carboxylic acids

Esterification of polymers bearing either -OH or $-CO_2H$ groups is efficient using dicyclohexylcarbodiimide (DCC) or 1-N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide (EDC), which activates the carbonyl group in the acid. 4-dimethylaminopyridine (DMAP) is used as catalyst. A work done by Liang et al. shows the reaction of 2-furoic acid (2) with hydroxyl terminated polybutadiene (1) to obtain the furfuryl-terminated derivative (3).



1 2 3

Figure 1.22. An example of efficient esterification of a polymer using the DCC/DMAP protocol. hydroxyl terminated polybutadiene with 2-furoic acid [55].

For this research, 9-anthracene carboxylic acid and 9-anthracenemethanol will be used as the acid and alcohol sources respectively and the product will be run in GPC to measure the apparent amount of anthracene attached to the oxidized SBR. The experimental ε for the anthracene pendant at λ_{max} = 360 is 9,800 $M^{-1}cm^{-1}$. The main advantage of this reaction is that it can be done at 0 ^{o}C to room temperature and the rubber can be easily separated through precipitation methods [55,56,57].

c. **Iodometric Titration of Hydroperoxide in Polymers**

Hydroperoxides that are produced in the oxidation of rubbers can be measured by titration of potassium iodide (NaI) following the equation:

$$3I^{-}\ (aq) + H_2O_2\ (aq) + 2H^{+}\ (aq) \rightarrow I_3^{-}\ (aq) + 2H_2O$$ [58,59].

Figure 1.23. Iodometric reaction of hydrogen peroxide.

Recent works have shown that the weight of iodine liberated when an organic peroxide is added to an acidified solution of potassium iodide is the most effective tool in determining the amount of hydroperoxides formed in oxidised polymers [37,40,41]. This method is also used to determine the content of oxygen as peroxide in manufactured products such as fats, oils, fragrances, and food flavourings.

The concentration of the hydroperoxide can be measured from the triodide ion, I_3^{-1}, via UV-vis spectroscopy at 360 nm and an ε of 25,000 M^{-1} cm^{-1} [38,43,44]. Most substances do not interfere with this method thus making this as an effective tool in determining free organic peroxides in the solution [58,59,60].

8. Definition of the Project

The modification of SBR in different environments can be fully understood by analysing the individual chemistry of each reaction. Several studies have shown that the oxidation of SBR produced different products, but none has finalised the exact kinetics of the said processes. The main challenge for this project is to formulate a definitive mechanistic scheme whilst the reaction processes are simultaneously occurring.

The degree of deformation done on elastomers can be crucial to decide a possible application in industrial purposes. It is well-known that these behaviours depend on the presence of functional groups in the polymer chains which also affect the overall properties of the manufactured product. Understanding these deformations vis-à-vis the production of functional groups is the key to the development of stronger and longer-lasting polymeric materials in the future [61].

At the core of many applications of elastomeric materials such as SBR are their mechanical properties, specifically their capacity to endure any applied stresses. The wear and tear of rubbers lies exclusively on the bonds that they contain and how they are degraded in time. These bonds are to be studied and calculated by understanding the products of reaction after exposing pristine SBR at specified conditions.

Figure 1.24. Ageing of rubbers.

The overall goal is to analytically determine the components of the degradation of SBR in air at a specified temperature. To achieve that, the project has to devise a working experimental method in determining hydroperoxides, carbonyls, hydroxyls and carboxylic moieties in oxidised rubbers. Understanding the mechanism of this degradation can help in the determination of possible ways of slowing the process of ageing of SBR in specific conditions [10,61].

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CHAPTER II

Approach: Functional Group Modifications on Oxygen-Containing Polymers and Standardization Processes

1. Introduction

a. Oxidation of elastomers and its products

As discussed in the previous chapter, the degradation of elastomers in the presence of oxygen leads to the formation of different oxidized functional groups. These reactions are considered multi step and simultaneously occurring within the entire system [1]. The oxidation process is complex, and several factors are considered such as time of reaction, thickness of the sample, surface exposure and the pressure of reacting oxygen species [2]. The resistance to oxidative degradation depends on many factors, including chemical composition, molecular weight, crosslink density, and type of crosslinks. Diene elastomers that have electron-donating groups attached to the polymer are usually the least stable rubber. They have poor heat, ozone, and UV resistance, whereas elastomers with a low number of double bonds have good or even excellent heat resistance [1-6].

Most elastomers are oxidized at high temperatures by auto-acceleration [3]. These repeating sequences of steps involve radical initiation, propagation and termination reactions that lead to the formation of aldehydes, ketones, ethers, alcohols, acids, etc. Simultaneously, structural changes are also occurring such as chain scission, chain branching, crosslinking that collectively alter the physical properties of rubbers such as the color, increased brittleness and reduction of gloss and cracking [2].

There are many ways to prevent these from happening to pristine rubbers. One major method of the retardation of oxidation is to introduce antioxidants. These chemicals interrupt the degradation cycle by reacting with the radicals produced in the initiation reaction thus preventing the downstream reactions. Some antioxidants are hydrogen acceptors that function as a chain donor mechanism which terminates the propagation reaction thus stopping the formation of radical groups. Other antioxidants react with the hydroperoxides, decomposing them before they cut the chains [8,9].

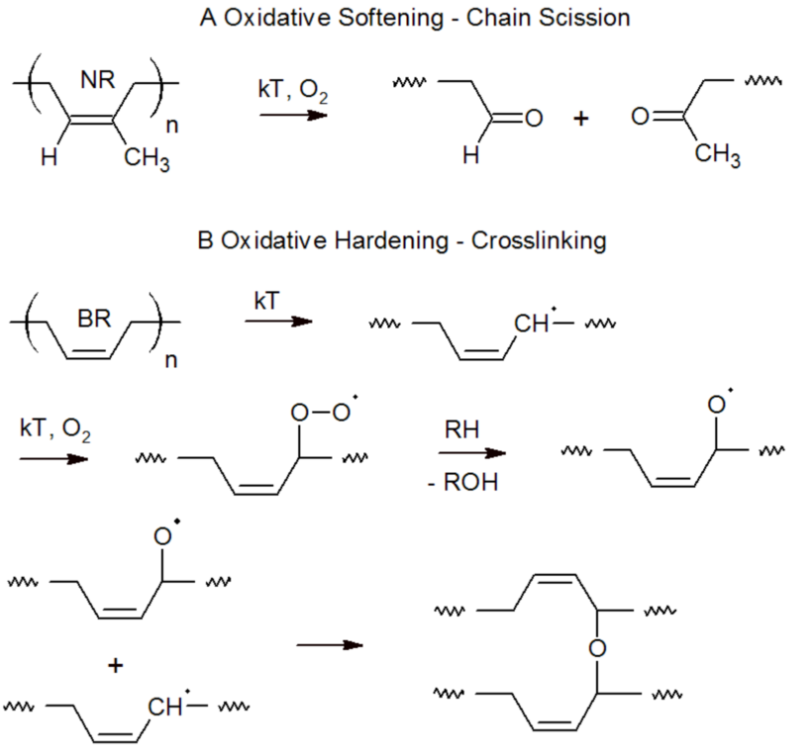


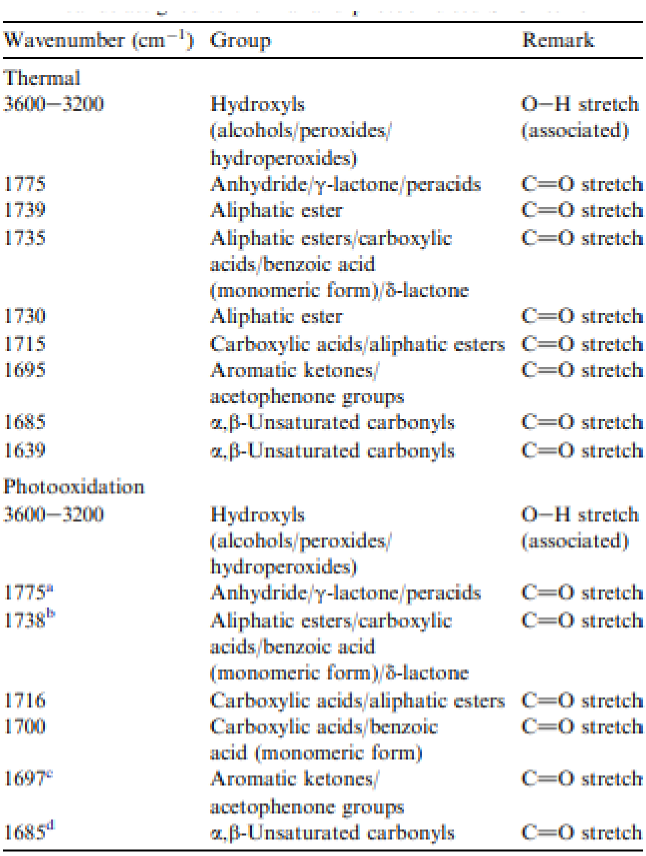
Figure 2.1. General mechanism of oxidative thermal degradation of unsaturated polymers. In general, the type of degradation depends on the composition of the polymer. Oxidative Softening happens when polymer chains are broken, and smaller molecular chains are produced. Oxidative hardening occurs when the radicals are clumped together to form branched products with larger molecular mass. Image retrieved form [2].

Polymers will change over time when exposed to pressure, radiation, and excessive heat or/in corrosive environments. These changes are the result of oxidative degradation caused by free radicals which form through hydrogen abstraction or homolytic scission of carbon-carbon bonds when polymers are exposed to heat, ozone or light. These changes can have a dramatic effect on the service life and properties of the polymer [3]. The modification on the molecular level following the ageing process exerts great influence on the mechanical properties. To correlate the molecular origin and the transition behavior, dynamic mechanical analysis has been proven to be a convincing tool in studying thermal degradation.

b. Detection and characterisation of the products of thermal ageing of unsaturated polymers

The presence of oxygen, light, heat and reactive species is known to compromise the structure of elastomers and affect its appearance, macrostructure, industrial performance and overall durability. Understanding the mechanisms involved in the degradation of SBR is crucial in improving its resistance to different factors. The elastomer degradation takes place predominantly in the aliphatic segment at the allylic position, giving rise to a maximum IR absorption at 1700-1750 cm^{-1} in the carbonyl stretching region [6,7]. Table 2.1 shows the IR spectra of thermally oxidized SBR copolymers. Extensive IR studies have been employed on oxidized elastomers. IR absorption spectroscopy has been used to measure the oxidized products and the rate of its formation during the heating process. It is visible that some regions have overlapping peaks that some IR cannot distinguish [6].

The main challenge for researchers is the individual analyses of each oxygen containing species in the mixture of end-products that sit in one container. Regardless of the complexities, there are different methods to distinguish one functional group from another. One example is the reduction of hydroperoxides with triphenylphosphine. For oxidation of elastomers such as SBR, carbonyls and hydroperoxides are produced together in one system. Hydroperoxide is a potential interference that can alter the carbonyl results. Arnold et al. developed a method to test whether hydroperoxides change the carbonyl results in oxidised rubbers. By reacting the oxidised rubber with triphenylphosphine (PPh_3), the hydroperoxide groups are decomposed to alcohols at room temperature. Oxidized SBR samples that are treated with PPh_3 did not show different results from the untreated ones [10].



Wavenumber (cm^{-1})	Group	Remark
Thermal		
3600–3200	Hydroxyls (alcohols/peroxides/ hydroperoxides)	O–H stretch (associated)
1775	Anhydride/γ-lactone/peracids	C=O stretch
1739	Aliphatic ester	C=O stretch
1735	Aliphatic esters/carboxylic acids/benzoic acid (monomeric form)/δ-lactone	C=O stretch
1730	Aliphatic ester	C=O stretch
1715	Carboxylic acids/aliphatic esters	C=O stretch
1695	Aromatic ketones/ acetophenone groups	C=O stretch
1685	α,β-Unsaturated carbonyls	C=O stretch
1639	α,β-Unsaturated carbonyls	C=O stretch
Photooxidation		
3600–3200	Hydroxyls (alcohols/peroxides/ hydroperoxides)	O–H stretch (associated)
1775[a]	Anhydride/γ-lactone/peracids	C=O stretch
1738[b]	Aliphatic esters/carboxylic acids/benzoic acid (monomeric form)/δ-lactone	C=O stretch
1716	Carboxylic acids/aliphatic esters	C=O stretch
1700	Carboxylic acids/benzoic acid (monomeric form)	C=O stretch
1697[c]	Aromatic ketones/ acetophenone groups	C=O stretch
1685[d]	α,β-Unsaturated carbonyls	C=O stretch

Table 2.1. FTIR Bands assigned to thermally and photochemically oxidized SBR [6].

c. Motivation of the study

The understanding of the behavior of elastomers in heated environment is beneficial for the preservation of the product in industrial purposes. The modification on the molecular level after thermal oxidation greatly affects the overall physical property of SBR and this is a great concern for tyre industries. Furthermore, investigating the chemical modifications on our SBR samples at 60 °C and 80 °C is a valuable area of continuing research for tyre chemistry as you can clearly see in this region the changes occurring in SBR as they begin to be oxidised. However, there is no established method in determining these functional groups insider the polymer melts. Creating a method of detection is a valuable step in understanding the complete mechanism of degradation in oxygen at elevated temperatures.

2. Experimental Objectives

As previously discussed, one method of determining the changes in the degradation of elastomers is to react a functional group that can be detectable in analytical methods available. In this project, standards are used to check the viability of the proposed method of attachments. We used three techniques to determine the chemical composition of the polymers in this project: (1) Size exclusion chromatography (SEC) with UV detector; (2) Spectrophotometric titration of hydroperoxides via UV-vis; and (3) Fourier-transform infrared spectroscopy.

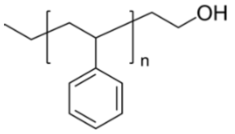
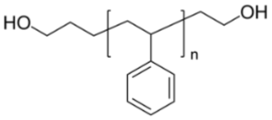
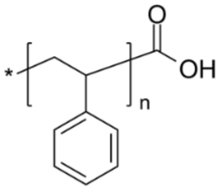
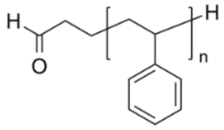
3. Experimental Approach

a. Materials

Polymer Standards:

Standard polystyrene samples of different molecular weights are acquired from Sigma Aldrich. The types of polymer standards used as listed in table 2.2.

Table 2.2. Oxygen-containing polystyrene standards.

mHTPS – monohydroxy-terminated polystyrene (25kD)	
dHTPS – dihydroxy-terminated polystyrene (50kD)	
CTPS – carboxyl terminated polystyrene (25kD)	
ATPS – aldehyde terminated polystyrene (25kD)	

Reagents:

- 2, 4 dinitrophenylhydrazine-HCl in THF
- 9-anthracene carboxylic acid in DCM
- dicyclohexylcarbodiimide (DCC) in DCM
- 9-anthracenemethanol in DCM
- 4-dimethylaminopyridine (DMAP) in DCM
- 1 M HCl (in ethanol)
- *tert*-butyl hydroperoxide
- Cumene hydroperoxide

Solvents:

- Dichloromethane (DCM)
- Ethanol
- Toluene
- Tetrahydrofuran (THF)
- Acetone
- Ethanoic acid
- Isopropanol

b. Sample Preparation

1. Polymer Standards

Polymer samples are pure and free from antioxidants and are stored in glovebox. The polymers are dissolved in THF creating a solution concentration of 50, 100 and 500 and 1000 mg per mL. The solutions are then stored in the glovebox freezer maintained at -37 ^{o}C.

2. Styrene Butadiene Samples

All SBR samples in this project used a random copolymer of styrene and butadiene of M_n = 162 ± 9 kDa, PDI = 1.07 ± 0.03 and Tg = -35 °C, synthesised by anionic polymerisation at Michelin and containing 26% by weight of styrene, 15% by weight of 1,2- butadiene with the rest being 1,4- trans butadiene. Samples are stored in freezer maintained at -37 ^{o}C.

c. Characterisation

1. Gel permeation chromatography of the polymer standards

100 µL solutions of the polymer standards are diluted to 1000 µL in THF and were shaken for several minutes and then analysed by GPC. For the styrene pendants, analyses are run at 290 nm. Analytical SEC was carried out on Waters Acquity UPLC system with an isocratic solvent manager, sample manager, column heater, photodiode array (PDA) detector and RI detector using three Waters Acquity APC columns in series (APC XT 900, 150 × 4.6 mm, APC XT 450, 150 × 4.6 mm, APC XT 200, 150 × 4.6 mm). The flow rate of THF is 0.6 mL/min. Column heater temperature is 35 ^{o}C. The PDA detector monitors absorbance of light of the wavelength from 240 to 400 nm. The temperature of the RI flow cell is 35 ^{o}C. All polymer solutions were filtered through PTFE syringe filters (pore size: 0.45 µm) prior to analysis. The SEC columns were calibrated using narrow polystyrene standards from Sigma-Aldrich and Scientific Polymers Inc.

2. DNPH Analyses

2,4-dinitrophenylhydrazine (2,4-DNPH or simply DNPH) has long been used as a reagent used to identify ketones and aldehydes. Purgotti [11,12] was the first to be credited with the initial investigation of DNPH reaction as a method to identify aldehydes and ketones. However, the reagent was made popular by Brady and Elsmie [12] when they used 2,4-DNPH to test wide samples of aldehydes and ketones, after which DNPH became known as ‘Brady’s reagent’. It has been established in journals that 2,4-DNPH does not react to other carbonyl groups mainly because the resonance structure delocalizes some of the positive charge away from the carbonyl carbon onto the adjacent hetero atom that could be a nitrogen for amides and an extra oxygen for carboxylic acids. This makes the carbonyl carbon less electrophilic in these compounds, and consequently attack by the nucleophilic 2,4-DNPH is less favoured [14,15]. This makes Brady's reagent a reliable method to distinguish ketones and aldehydes from other types of carbonyl compounds.

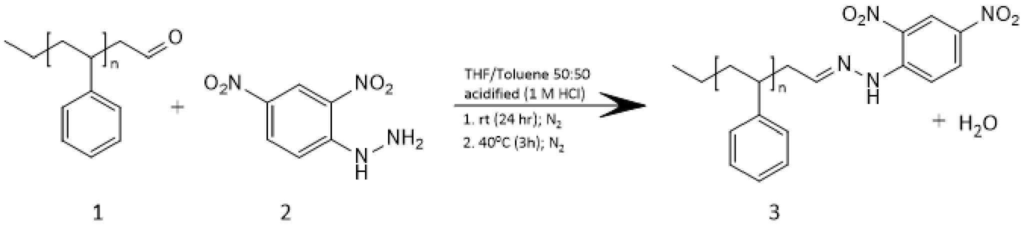


Figure 2.2 The acid-catalysed reaction of aldehyde terminated polymer (ATPS) (1) with DNPH (2) will produce the hydrazone derivative of the polymer (3).

1.0 mL solution of ATPS was pipetted in weighed vials and solution of DNPH was added. One drop of 1 M HCl was added, and the mixture was stirred at 40 °C for three hours in nitrogen atmosphere. The solvent in the resulting mixture was evaporated and unreacted 2, 4-DNPH and HCl were washed with ethanol. After drying, the final mass of the ATPS-hydrazone derivative was weighed and redissolved in THF creating a solution of 1 mg/mL. The solution containing the rubber-hydrazone was analysed in GPC and the absorbance was measured at 367 nm for the hydrazone moiety. (Figure 2.4, the experimental ε for the hydrazone derivative at λ_{max} = 367 is 22,000 $M^{-1}cm^{-1}$). Reactions done in journals are experimented in excess DNPH to make sure that all the aldehyde and ketones are fully converted to its hydrazine derivatives. For this project, the standardisation of the attachment of DNPH on aldehyde terminated polymers are done in different concentrations of DNPH: 5, 10 and 20 equivalents of DNPH. Increasing the concentration of the reacting hydrazine also increases the discoloration of the polymers but can be dealt with by repeatedly washing the polymers with ethanol [10,16,17].

The parameters considered in this project are the temperature and interferences. For the temperature, the attachment of 2,4-DNPH on carbonyl compound is enhanced in higher temperature but can work at different temperatures [11-17]. Considering the polymer melts have been converted to different products, lower temperature reactions are maintained to prevent further degradation [13]. The temperature tested in this reaction is at 0 ^oC, 20 ^oC, 40 ^oC and 60 ^oC.

3. Standardisation of Iodometric titration

Iodide titration was reported as the most accurate and general method to quantify hydroperoxides [18] which is based on the oxidation of iodide ion, I^- to triiodide ion, I_3^- by hydroperoxide in acidic solution (Figure 2.3). In a complete reaction, all P-OOH are reduced by iodide ion to produce the triiodide ion which is proportional to the change of the intensity of the absorption band at 365 nm [20,21].

$$3I^-\ (aq) + H_2O_2\ (aq) + 2H^+\ (aq) \rightarrow I_3^-\ (aq) + 2H_2O$$

Figure 2.3. Iodometric reaction of hydrogen peroxide.

Solutions of organic hydroperoxide samples were diluted to concentrations with THF, isopropyl alcohol and acetic acid and placed in a sealed cuvette. For every 100 µL of the organic hydroperoxide solution, 900 µL of THF was used to dilute it and 300 µL isopropanol and 100 µL acetic acid were added in anaerobic condition. The absorbance of the sample in a sealed cuvette was measured at 300 – 600 nm. After collecting the first spectrum, 100 uL 150mg/ml NaI-i-PrOH solution was injected into the mixture through 100 uL glass syringe and then spectra were keeping collecting with 0.6min intervals until 30 min. The concentration of hydroperoxide per unit mass of the organic hydroperoxide (OH), was calculated by equation 2.1.

$$c_{OOH} = \frac{(\Delta\Delta A_s - \Delta\Delta A_b)V}{\varepsilon \times l \times m_{OH}}\ mol \cdot g^{-1} \qquad (2.1)$$

where ε = 25000 M^{-1} cm^{-1} is extinction coefficient of I_3^- in isopropanol at 365 nm, l = 1 cm is the length of the optical path, m_{OH} is the amount of the organic hydroperoxide in the sample, V = 1.5 mL is the volume of the sample and ΔΔA is given by equation. 2.2, where 365 nm and 600 nm are wavelengths at which the absorbance is measured, and t_{final} and $t_{initial}$ are the times since addition of NaI when it is measured; subscripts s and b refer to the sample solution and blank. For the baseline correction, the absorbance read at 600 nm is subtracted from the absorbance at 365 nm.

$$\Delta\Delta A = A(365\,nm, tfinal) - A(365\,nm, t\ initial) - \left(A(600\,nm, t\ final) - A(600\,nm, t\ initial)\right) \quad (2.2)$$

Since the reaction mixture is not stirred or disturbed, the readings are done at different time from the initial injection ($t_{initial}$). Readings are then compared and the concentration of I_3^- is calculated.

To measure the potential interferences, polymer samples are added in the solution of known organic hydroperoxides and then titrated by iodine in the same manner as above. 1 mg of sample of polystyrene or SBR are added of hydroperoxides to create a solution of 1 mg per mL polymer solution.

4. Esterification Reactions

The esterification using the amide coupling agent N,N'-dicyclohexylcarbodiimide (DCC) and organocatalyst 4-dimethylaminopyridine (DMAP) was first reported by Wolfgang Steglich and Bernhard Neises in 1978 [21]. The reaction proceeds under mild conditions usually at room temperatures and neutral pH and can afford a wide range of esters containing sterically hindered substrates [22].

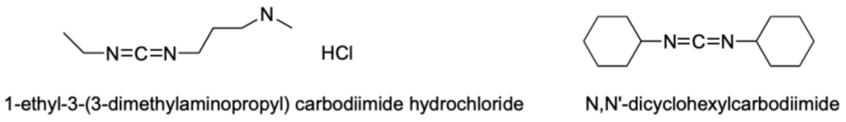


Figure 2.3 Coupling agents used in the Steglich esterification.

The reaction begins with the coupling reaction between the hydroxyl groups of the polystyrene and the carboxylic group of 9-anthracene carboxylic acid using N,N'-dicyclohexylcarbodiimide (DCC) and N,N'-(dimethylamino)pyridine (DMAP) as the coupling agents. The byproduct formed using this coupling agent, 1-ethyl-

3-(3-dimethylaminopropyl) urea, is removed more easily by extraction with dilute acid.

a. Attachment on the Hydroxyl End

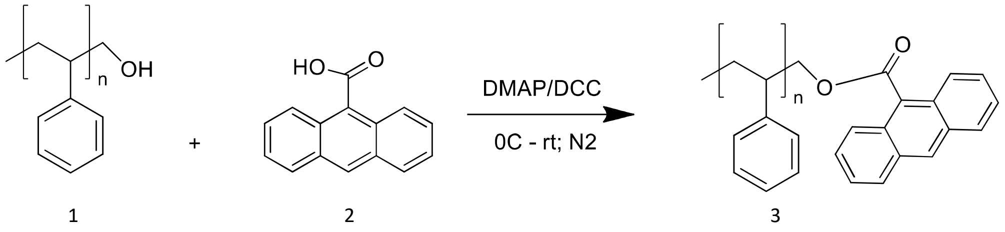


Figure 2.5. An example of efficient esterification of a polymer using the DCC/DMAP protocol. Hydroxyl terminated polystyrene (HTPS) (1) reacting with 9-anthracenecarboxylic acid (2) to produce the anthracene-derived polymer (3). The number of anthracene pendants depends on the amount of hydroxyl groups in the samples [23].

1.0 mL solution of HTPS was mixed with DCC, DMAP and 9-anthracenecarboxylic acid, was stirred at 0 ^{o}C for 5 hours and allowed to stay for 24 hours at room temperature. The reaction mixture was dried, and excess reactants were washed by acetone. After drying the acetone, the final mass of the anthracene derived HTPS was weighed and dissolved in THF creating a solution of 1 mg/mL. Finally, the solution is analysed in GPC and the anthracene absorbance is measured at 360 nm [23-24]. Experimentally, the concentrations of the reacting anthracene are 5,10 and 20 equivalent solutions.

b. Attachment on the Carboxylic End

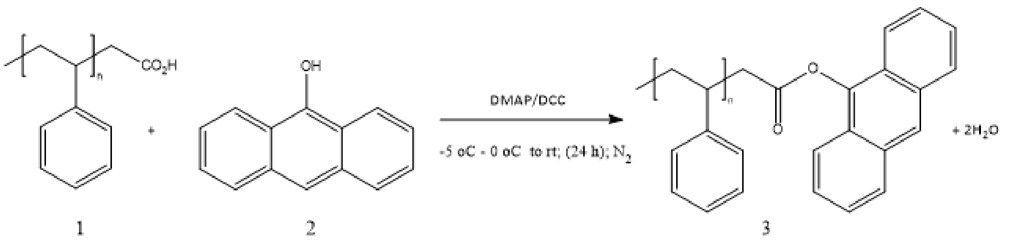


Figure 2.6. An example of efficient esterification of a polymer using the DCC/DMAP protocol. Carboxyl terminated polystyrene (CTPS) (1) reacting with 9-anthracenemethanol (2) to produce the anthracene-derived polymer (3). The number of anthracene pendants depends on the amount of hydroxyl groups in the samples [23].

1.0 mL solution of carboxyl-terminated polystyrene (CTPS) was mixed with DCC, DMAP and 9-anthracenemethanol, was stirred at 0 °C for 5 hours and allowed to stand for 24 hours at room temperature. The reaction mixture was dried, and excess reactants were washed by acetone. After drying the acetone, the final mass of the anthracene derived CTPS was weighed and dissolved in THF creating a solution of 1 mg/mL. Finally, the solution is analysed in GPC and the anthracene absorbance is measured at 360 nm.

Carbonyl, hydroxyl and carboxylic contents may be expressed as moles per mole of the polymer. The peak area of the styrene and the chromophore can be integrated in the chromatograms [24,25,26]. Using the apparent extinction coefficients of the polystyrene and the chromophore, we can calculate the amount of carbonyl or hydroxyl present in the rubber [23-27]. Experimentally, the concentrations of the reacting anthracene are 5, 10 and 20 equimolar solutions (equation 2.3 and 2.4).

$$mol = \frac{A*F}{\varepsilon*b} \qquad (2.3)$$

Where:

A = Area (mAU * min)	F = Flow rate (mL/min)
ε = extinction coefficient ($cm^{-1}*M^{-1}$)	b = path length (cm)

chromophore	λ	ε (cm^{-1}, M^{-1}) in THF
styrene	254	9800
anthracene	360	8000
diphenylhydrazone	360	25000

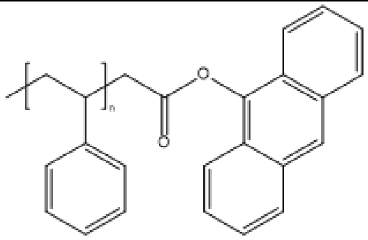
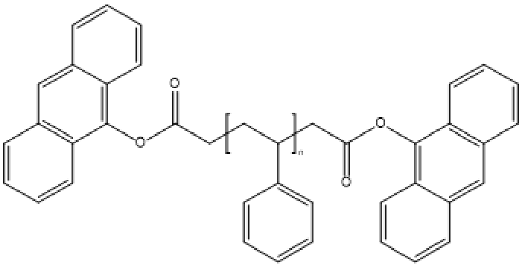
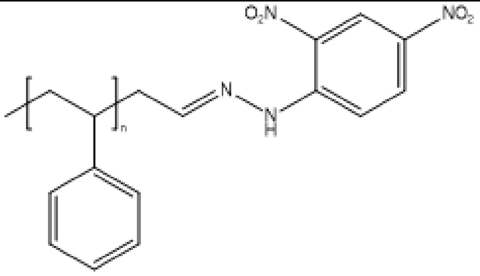
Table 2.3. List of extinction coefficients at specific wavelengths [12,13].

To calculate the amount of moles of chromophore per mole of polymer standard, the following equation is used:

$$\frac{mole\ chromophore}{mole\ polymer} = \frac{\varepsilon_{polymer}*A_{367}}{\varepsilon_{chromophore}*A_{254}} \qquad (2.4)$$

4. Results and Discussion

Table 2. 4. List of molecules formed from the reaction in section 3.

Structure	Notes
 Ant-PS	Anthracene terminated Polystyrene derived from the Steglich esterification of polystyrene with anthracene. (see section 3.c.3)
 diAnt-PS	Dianthracene terminated Polystyrene derived from the Steglich esterification of dihydroxy terminated polystyrene with anthracene. (see section 3.c.3)
 Hyd-PS	Hydrazone terminated polystyrene derived from the reaction of aldehyde terminated polystyrene with DNPH (see section 3.c.2)

a. Formation of Anthracene-Terminated Polystyrenes

1. Analysis of the Anthracene Attachments

Based on the Steglich esterification, the attachments of anthracene molecules were synthesised. The structures were characterised by SEC showing the peaks of anthracene groups at 340-380 nm range (figure 2.7). The calculation for the amount of anthracene attached is describe in section 3.c.4.

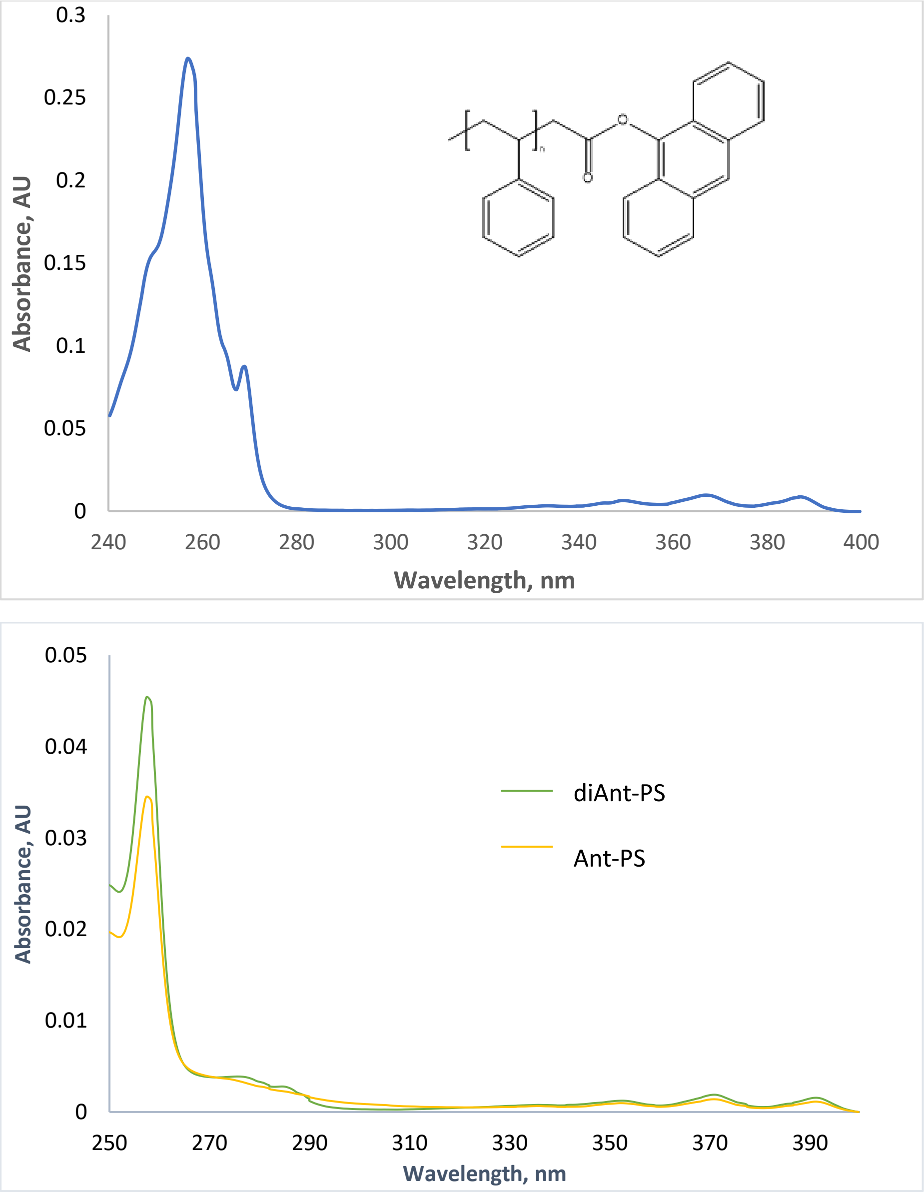


Figure 2.7. Reaction between monohydroxyterminated and dihydroxyterminated polystyrenes with anthracene to produce the anthracene-terminated polystyrene (Ant-PS and diAnt-PS).

2. Optimisation and Stoichiometry

The esterification catalysed by DMAP and DCC is a one-step reaction and produces high yields [23]. However, the reaction system in this project is relatively challenging as there are few reactive species present in long chain polymers. Several works done on polymers have been successful and were able to detect the chromophores and quantify their concentrations. To test the reaction mechanism, we have reacted the polymers with increasing equivalents of reactants. Assuming if the polymer m-HTPS contains one mole of hydroxyl per polymer chain, the percent yield for the attachment of anthracene on polystyrene is about 70 % for all tree experiments (table 2.4). The calculations are derived from the peak areas of the styrene and anthracene absorbance in the UV spectra. Similar phenomena were observed from other oxygen-containing polymers as summarized in tables 2.5 and 2.6. Increasing the concentration of the reacting anthracene and workup temperature did not affect the total yields of the products.

Sample	Prepared Concentration, mg/mL	Concentration of anthracene used, equivalents	Measured Concentration of anthracene, mole Ant per mole polymer
m-HTPS	1.0	5.00	0.700
m-HTPS	1.0	10.0	0.701
m-HTPS	1.0	20.0	0.695

Table 2.4. The amount of anthracene on the m-HTPS as analysed by SEC in varying equivalents of reacting 9-anthracene carboxylic acid. The measured amount of anthracene is derived from the peak areas of anthracene and polystyrene. m-HTPS = monohydroxy terminated polystyrene.

Sample	Prepared Concentration, mg/mL	Concentration of anthracene used, equivalents	Measured Concentration of anthracene, mole diAnt per mole polymer
d-HTPS	1.0	5.00	1.44
d-HTPS	1.0	10.0	1.45
d-HTPS	1.0	20.0	1.42

Table 2.5. The amount of anthracene on the d-HTPS as analysed by SEC in varying equivalents of reacting 9-anthracene carboxylic acid. The measured amount of anthracene is derived from the peak areas of anthracene and polystyrene. D-HTPS = dihydroxy terminated polystyrene.

Sample	Prepared Concentration, mg/mL	Concentration of anthracene used, equivalents	Measured Concentration of anthracene, mole Ant per mole polymer
CTPS	1.0	5.00	0.721
CTPS	1.0	10.0	0.730
CTPS	1.0	20.0	0.731

Table 2.6. The amount of anthracene on the CTPS as analysed by SEC in varying equivalents of reacting 9-anthracene carboxylic acid. The measured amount of anthracene is derived from the peak areas of anthracene and polystyrene. CTPS = monocarboxy terminated polystyrene.

Sample	Prepared Concentration, mg/mL	Concentration of anthracene used, equivalents	Temperature of the reaction system, °C	Measured Concentration of anthracene, mole diAnt per mole polymer
d-HTPS	1.0	10.0	0	1.40
d-HTPS	1.0	10.0	25	1.40
d-HTPS	1.0	10.0	40	1.37

Table 2.8. The amount of anthracene on the polymer as analysed by SEC in varying reaction temperatures. The measured amount of anthracene is derived from the peak areas of anthracene and polystyrene. D-HTPS = dihydroxy terminated polystyrene.

b. Formation of Hydrazone Derivative Polystyrene

1. Stability of the Hydrazone Derivatives

It has been reported that the hydrazone product is not stable at varying pH [15]. Hydrazones are seen to show stability at 7.4-9.0 pH while they are prone to hydrolysis when exposed to acidic conditions [16]. To determine the stability of hydrazones attached to the polymer, samples were analysed in SEC every 3 hours and the peak area is measured. Figure 2.8 shows the changes in the peak area of Hyd-PS in 36 hours of storage. It clearly shows that the hydrazone product is stable at neutral pH after the DNPH reaction.

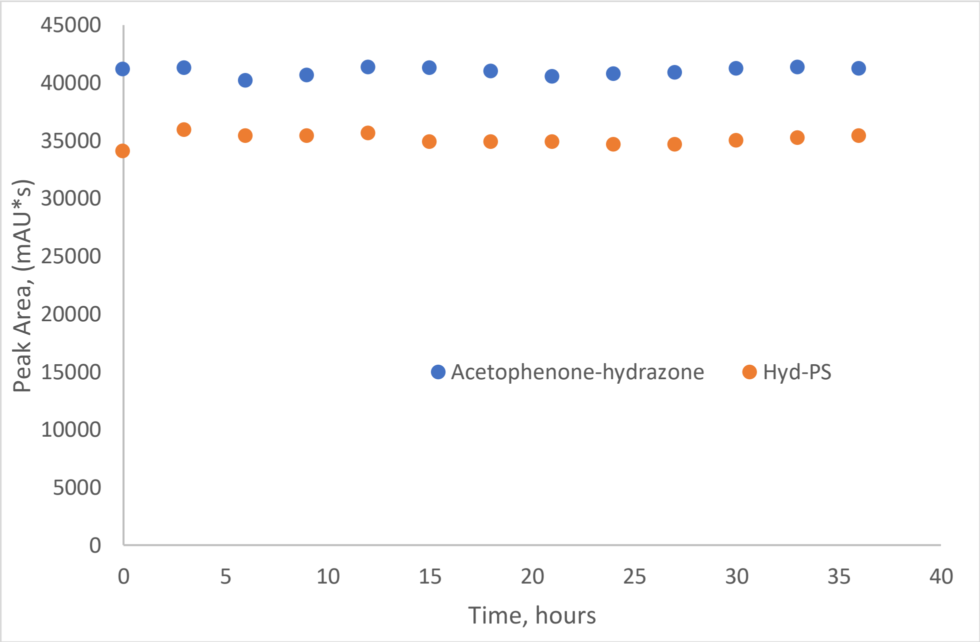


Figure 2.8. Stability of the hydrazone derivatives after the DNPH reaction.

2. Optimisation of the Reaction System and Stoichiometry

Several reported studies using the 2,4-DNPH reaction have noted that large excesses of 2,4-DNPH for reaction to go to completion [16,17]. In this project, we have established the fact that the amount of carbonyls are small, it is important to evaluate the stoichiometric requirements of the reactions to ensure that the carbonyls are fully reacted. The carbonyls are reacted in 5, 10 and 20 equivalents of DNPH and the reaction proceeded for 3 hours. Figure 2.9 shows the spectra of Hyd-PS showing the hydrazone peaks at 360 nm and the polystyrene pendants at 260 nm. Table 2.7 summarises the measured amounts of hydrazone attached to the polymer at different concentration of reacting 2,4-DNPH. It showed that there are no significant changes in the measured hydrazone in polymers.

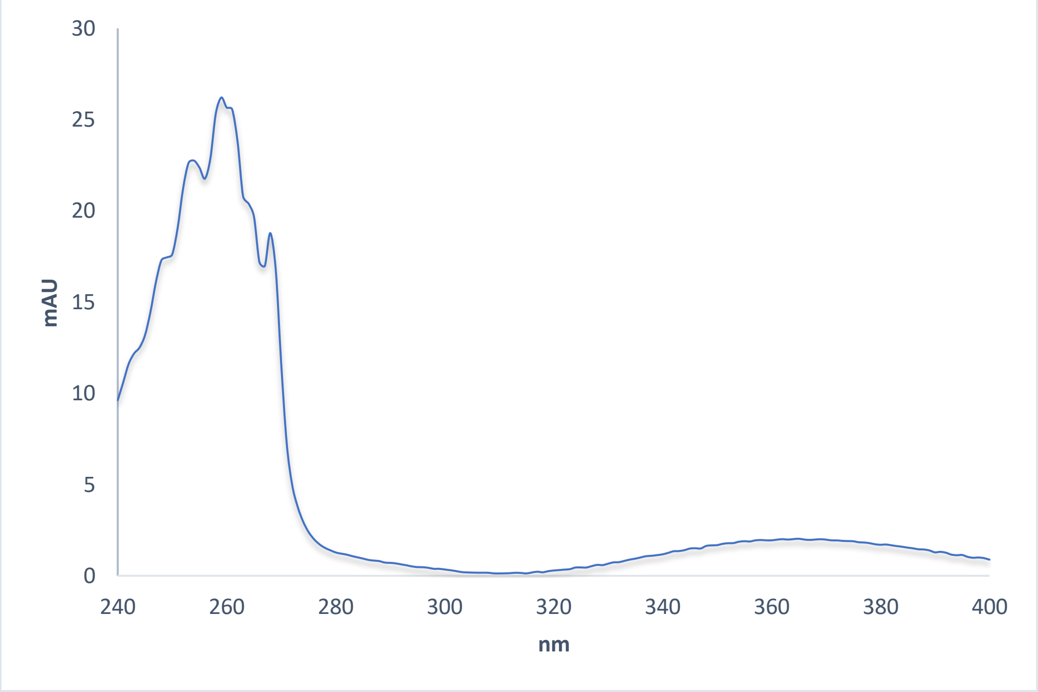


Figure 2.9. UV analysis of aldehyde terminated polystyrene reacted with DNPH in acidic media. The absorbance of the styrene pendants is measured at 240 nm and the hydrazone derivatives at 360 nm. In this experiment, the absorbance of the Hyd-PS is measured as it increases in time as C=O bonds are reacted to DNPH.

Sample	Prepared Concentration, mg/mL	Concentration of DNPH used, equivalents	Measured Concentration of hydrazone, mole Hyd per mole Polymer
ATPS	1.0	5.00	1.18

ATPS	1.0	10.0	1.19
ATPS	1.0	20.0	1.17

Table 2.7. The amount of hydrazone on the polymer as analysed by SEC in varying equivalents of reacting DNPH. The measured amount of hydrazone is derived from the peak areas of hydrazone and polystyrene. ATPS: Aldehyde terminated polystyrene

Sample	Prepared Concentration, mg/mL	Concentration of DNPH used, equivalents	Temperature of the reaction system, °C	Measured Concentration of hydrazone after 1 hour, mole Hyd per mole Polymer	Measured Concentration of hydrazone after 3 hours, mole Hyd per mole Polymer
ATPS	1.0	10.0	0	0	0
ATPS	1.0	10.0	20	0.80	1.10
ATPS	1.0	10.0	40	1.12	1.12
ATPS	1.0	10.0	50	1.12	1.11

Table 2.9. The amount of hydrazone on the polymer as analysed by SEC in varying reaction temperature. The measured amount of Hyd is derived from the peak areas of hydrazone and polystyrene. ATPS: Aldehyde terminated polystyrene.

The 2,4-DNPH reaction has always been reported as a 1:1 reaction with carbonyls and results of the current studies generally supports this [16-20]. An excess of DNPH in acidic media is needed to allow for some potential loss from protonation. Because the reaction is not stirred, excess amounts of DNPH is required to ensure efficient contact with carbonyls at the low carbonyl concentrations being analysed. The use of THF as a solvent increases the solubility of 2,4-DNPH which benefits the reaction system. With THF as a solvent and reaction pH around 2.5, a reaction stoichiometry of 5:1 (DNPH : carbonyl) is adequate for full reaction. This stoichiometry can be used as a guide when estimating concentrations of DNPH needed for quantification of carbonyls in unknown samples of polymers.

Table 2.9. shows the effects of heating the reaction solution of DNPH with aldehydes and ketones [16]. Experiments showed that heating the solution increases the conversion of aldehydes to its hydrazone derivatives. It is documented that the reaction of 2,4-DNPH is enhanced in increasing temperature. However, in this project, we have tried to maintain the reaction as

close to room temperature to prevent further degradation of the polymer melts. Experiments showed that increasing the time of reaction will lead to efficient conversion of aldehydes and ketones to its hydrazone derivatives.

c. Hydroperoxide Moieties

We quantified the concentration of hydroperoxide moieties in organic hydroperoxides by iodometric titration, which is based on oxidation of iodide to I_3^- by hydroperoxide in acidic media (see section 3.c.4) [2,18]. We assumed that all peroxy moieties are reducible by I^-, so that the concentration the hydroperoxide equals that of I_3^-, which is proportional to the change of intensity of the absorption band at 365 nm according to the Beer-Lambert law.

The systematic error on the concentration of hydroperoxide measured by iodometric titration was estimated by titrating a solution of known concertation of *tert*-butyl hydroperoxide and cumene hydroperoxide in H_2O-isopropanol solution. In other set up, samples of oxidised polymers (5 mg of each polymer in table 2.2) are added to the known concentrations of *tert*-butyl hydroperoxide to check if there will be interferences.

The results in table 2.10 show the relative systematic error of less than 1% regardless of the presence of polymers. This suggests that the iodine titration proceeded to convert hydroperoxides without being interfered by other functional groups.

Sample	Prepared concentration of hydroperoxide, μM	Measured concentration, μM	Systematic error
tert-butyl hydroperoxide	16.2	16.1	0.061
Cumene hydroperoxide	16.0	16.0	0
tert-butyl hydroperoxide	16.2	16.2	0

+ SBR rubber stock solution			
tert-butyl hydroperoxide + ATPS	16.2	16.2	0
tert-butyl hydroperoxide + HTPS	16.2	16.0	0.012
tert-butyl hydroperoxide + CTPS	16.2	16.0	0.012
Cumene hydroperoxide + SBR rubber stock solution	16.0	15.9	0.063
Cumene hydroperoxide + HTPS	16.0	16.0	0

Table 2.10. The concentrations of organic hydroperoxides determined by UV-vis through iodometric titration. The addition of oxygen-containing polymers (HTPS, ATPS, and CTPS) do not interfere with the reaction.

5. Summary and Conclusions

Polymers can undergo chemical modification and the detection in these changes is challenging due to several factors such as the molecular mass of the polymer, potential interferences, and crosslinking tendencies. SBR and other elastomers can produce oxygen-containing species as they are exposed to heat, radiation, or pressure in the presence of air. Consequently, the production of these moieties can damage the structure of these polymeric materials. This project aims to selectively identify these functional groups through chemical analyses that could potentially be helpful in solving in understanding the mechanism of the auto-oxidation processes of elastomers. The functional groups observed are aldehydes, ketones, hydroxyls, hydroperoxides and carboxylic acids.

Concerning Aldehydes and Ketones: The detection of aldehyde and ketones on long chain polymers can be done using Brady's reagent in acidic media. As done by other research, the formation of the hydrazone derivative can be accomplished by reacting the carbonyl group with excess 2,4-DNPH. Heating the solution is favourable but not recommended for polymers with relatively reactive pi electrons. Overall, the attachment of the hydrazone moiety on polystyrene samples are effective and can be detected by chromatography.

Concerning the Steglich Esterification: The method of attaching chromophores in polymers can be achieved by Steglich esterification which is by far the most effective way to detect alcohols and carboxylic acids in polymers due to its simplicity and specificity. The attachment was made under mildly acidic conditions ran at toom temperature with yields that can be quantified.

Concerning the Iodometric Titration of Hydroperoxides: Hydroperoxides play an important role in polymer oxidative degradation and detecting them with certain accuracy is what we are trying to achieve. By carefully isolating the hydroperoxide and reacting them via iodometric titration, we can quantify the concentration of hydroperoxides in the solution. It is also determined that other functional groups such as hydroxyl, carbonyls and carboxylic acids do not interfere with the titration processes which can be beneficial in detecting the hydroperoxyl moieties in degraded elastomers with several kinds of oxygen-containing species.

6. References

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Chapter III

Analysis on the Thermochemical Degradation of SBR

1. Oxidation of Styrene Butadiene

Styrene butadiene rubber (SBR) has been extensively studied as it is one of the most important materials in our current industrialized society [1]. By manipulating the conditions such as temperature and chemical environment, SBR undergoes different transitions that lead to chemical modifications. As we discussed briefly in previous chapters, the two main forms of rubber degradation are: hardening (or embrittlement) and softening [2,3]. From a molecular perspective, these chemical processes are known as chain hardening and chain scission respectively. The chemical makeup of the polymer will determine which type of deterioration will ultimately occur (Figure 3.1) [2,3].

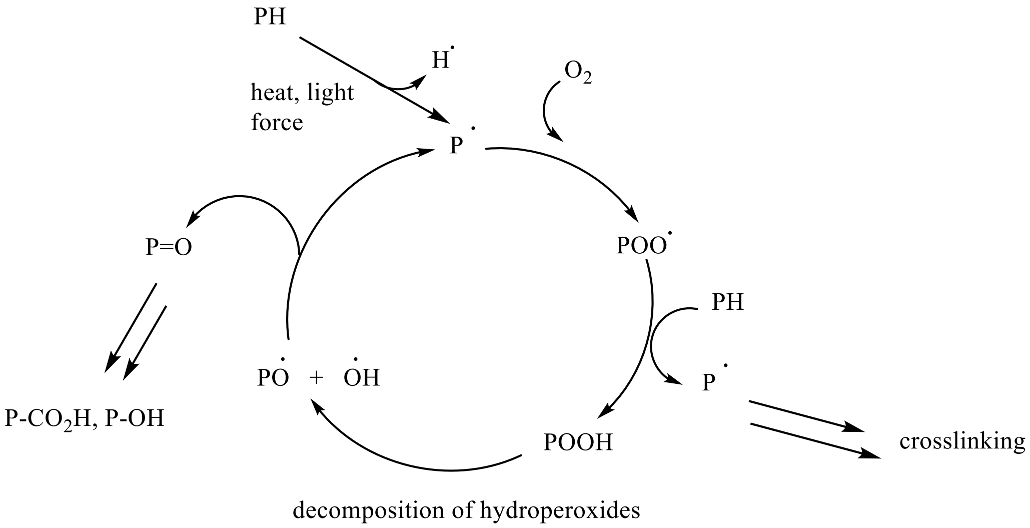


Figure 3.1. Schematic diagram for the autoxidation of unsaturated rubbers. It has been extensively studied that SBR follows the BAS (basic autoxidation scheme) but there are no defined sets of reactions on how the actual mechanistic schemes are happening as the polymer melt degrade in the presence of oxygen at elevated temperatures [4].

In many applications, elastomers such as SBR are subjected to mechanical load sufficiently large enough to induce mechanochemical reactions that gradually change the molecular structure, chemical composition, and bulk properties of the material [5]. Whilst the mechanochemistry of saturated rubbers and glassy polymers such as polystyrene or polyisoprene have been studied extensively, little is known about the mechanochemical response of unsaturated polymers. Although several studies have suggested particular mechanistic schemes, any proposal for a new one must be confirmed experimentally. To validate the mechanism, it is empirical to show that the qualitative observation is backed up with data from the experiments. As a typical carbon chain polymer, oxidation of SBR is seen to follow the basic autoxidation scheme that involves initiation, propagation, and termination. Several studies have shown that oxidation of SBR produced chemical species such as carbonyls, hydroxyls, hydroperoxides, and epoxides that are simultaneously produced. The formation of chemical pathways is studied and analyzed and monitored in the following sequences: (1) Induction Period (2) Rapid oxidation period, (2) slow oxidation and (4) diffusion forbidden period [3-10]. A common approach in understanding the mechanochemical transformations of elastomers is to determine the growth and formation of functional groups that can be tested by laboratory analyses.

2. Mechanistic Schemes on the Oxidation of SBR

Oxidative remodeling of SBR happens through competing reactions that involve abstraction of H, formation of radicals, reaction with available gases such as O_2, O_3, NO_x and SO_x or any other reactive species. Several works have suggested that the formation of macroradicals is the main driving factor that allow the reaction to happen [7]. Radical reaction mechanisms of SBR typically follows the chemical pathways in three steps: initiation, during which radicals are generated, propagation, during which radicals react with closed-shell molecules, and termination corresponding to recombination of radicals [5,6]. Following the experiment done in the last chapter, we were able to observe the evolution of functional groups that is corroborated by several research works in the past. Figure 3.2 summarizes the autoxidation processes of SBR under thermal remodeling.

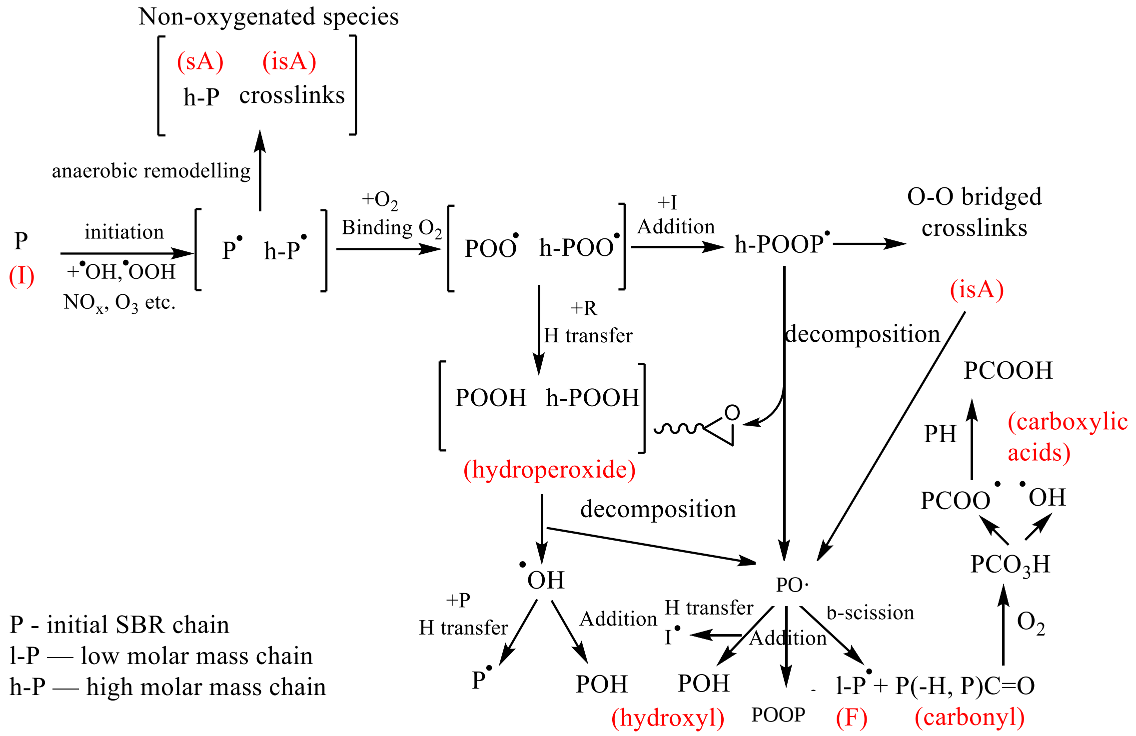


Figure 3.2. Summary of the oxidative thermal remodelling of SBR. End products marked in red are observed in this project.

a. Autoxidation

Auto accelerated oxidation in polymers has been found to proceed by a chain mechanism reaction; that is, a reaction consisting of a series of successive steps occurring in repetitive cycles, in each of which intermediate products called chain carriers are regenerated [7]. Many of the classical concepts of polymer oxidation were conveyed based on the kinetic parameters of autocatalytic reactions (Figure 3.2) [8-10]. In this project, reactions are focused on the formation of free radical after the samples are either heated or sheared in the presence of oxygen. It is a challenge to study the integral hydroperoxide forming reactions as the peroxide decomposition quickly overwhelm other reactions [11].

b. Initiation

At the start of the thermal oxidation, it inclines to generate allylic macroradicals because of the reactivity of α-hydrogen (Figure 3.3). Macroradicals are most likely generated either by H abstraction by adventitious impurities or by homolysis of much weaker bonds such as the O-O bonds in hydroperoxides in a polymer backbone introduced during polymerisation or in storage [5]. Production of macroradicals happens throughout the entire oxidation process and it is seen through several researches that the presence of hydroperoxide is the most prevalent species (r3-r5). The key species for the propagation stage is the homolytic cleavage of POOH to form PO· and ·OH that will eventually lead to the production of different functional groups. Reaction 4 was validated and the production of hydroperoxides are measured at different temperatures. In the initiation stage, the existence of POOH is the only verifiable scheme based on experimentation [3,4]. However, the plausible pathways that could lead to the propagation of species would be the homolytic cleavage of POOH (r3) [2,11,12].

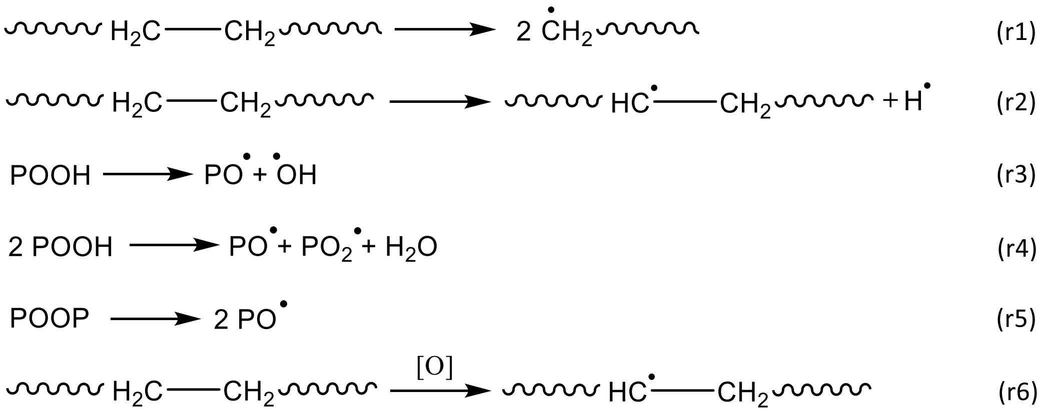


Figure 3.3. Reactions responsible for the initiation, where P is a small group or a polymer chain.

c. Propagation

Several kinds of alkyl free radicals may form in the entire process, but the allylic radicals dominate [4]. The rapid oxidation period happens on the surface as O_2 is present in the system. In an aerobic set up (figure 3.4), O_2 is reacted with the polymer macroradical at a diffusion limited rate to form the superoxyradicals POO· (r11) that can react to abstract H from a nearby polymer. The detection of functional groups done in this project is verified by the presence of alcohols, carbonyl, and carboxylic acids (r18-r20) which corroborated the existing theories about the mechanistic schemes of SBR degradation in air [5].

d. Termination

It has been established that the end point of elastomer degradation reaction would be the formation of high molar mass where all radical species are quenched to form variations of end products (Figure 3.4). As the oxidation reaction continues, the crosslinking creates polymer matrices which in turn obstruct free O_2 molecules from penetrating inside the polymer melt [3,4]. Researchers suggest that the inside of the polymer mass has a limited supply of free oxygen thus the termination happens from r11, r12 and r14 forming epoxides, esters, anhydrides and carboxylic acids. This consequently follows our observation with the production of carboxylic acids and hydroxyls [4-6].

$$P^{\bullet} + R\,[\text{-C=C-}] \longrightarrow P^{\bullet}(\text{-PH}) \tag{r7}$$

$$P^{\bullet} + R\,[\text{-H}] \longrightarrow P + R^{\bullet} \tag{r8}$$

$$P^{\bullet}\,[\text{-C=C-}] \longrightarrow \text{cyclic } P^{\bullet}(\text{-PH}) \tag{r9}$$

$$P^{\bullet} \longrightarrow P^{\bullet}(\text{-PH}) \tag{r10}$$

$$P^{\bullet} + O_2 \longrightarrow POO^{\bullet} \tag{r11}$$

$$POO^{\bullet} + R\,[\text{-H}] \longrightarrow POOH + R^{\bullet} \tag{r12}$$

$$POO^{\bullet} + R\,[\text{-C=C-}] \longrightarrow POOP^{\bullet}(\text{-PH}) \tag{r13}$$

$$POO^{\bullet}\,[\text{-H}] \longrightarrow HOOP^{\bullet}(\text{-PH}) \tag{r14}$$

$$POO^{\bullet}\,[\text{-C=C-}] \longrightarrow \text{cyclic } P^{\bullet}(\text{-PH}) \tag{r15}$$

$$POOP^{\bullet}(\text{-PH}) \longrightarrow POP\ (\text{epoxide}) + PO^{\bullet} \tag{r16}$$

$$PO^{\bullet} + R\,[\text{-C=C-}] \longrightarrow POP^{\bullet}(\text{-PH})\ (\text{ether}) \tag{r17}$$

$$PO^{\bullet} + R\,[\text{-H}] \longrightarrow POH + R^{\bullet} \tag{r18}$$

$$PO^{\bullet}(\text{-PH}) \longrightarrow PH{=}O + P^{\bullet} \tag{r19}$$

$$PO^{\bullet}(\text{-2PH}) \longrightarrow PP{=}O + P^{\bullet} \tag{r20}$$

$$HO^{\bullet} + R\,[\text{-H}] \longrightarrow H_2O + R^{\bullet} \tag{r21}$$

$$HO^{\bullet} + R\,[\text{-C=C-}] \longrightarrow HOP^{\bullet}(\text{-PH}) \tag{r22}$$

Figure 3.4. Summary of the mechanistic schemes for SBR where R represents the initial rubber and P is the rubber chains that is different from the initial rubber, R. P can be a product of different reactions along the autoxidation processes. $P^{\bullet}$ represents the radical formed of P or the macroradicals produced from the initial chain R. Groups inside the brackets represent the active site for the reaction and groups inside the parentheses represent the functional group on the terminal carbon.

Carboxylic acids showed longer induction period which suggests late formation in the thermal reaction. Our research methods are limited to the determination of molecular species in the soluble part of the rubber, so we have no measurement of the chemical pathways of the oxygen containing species in the insoluble part of the rubber [6].

e. Carbonyl Path

Several researchers have extensively studied the carbonyl growth in oxidised rubbers and have hypothesized that the growth of C=O in elastomers comes from the alkoxy radical, PO· that eventually rearranges into an aldehyde (figure 3.5 r1 and r3) [2,3]. Since allylic hydrogens are the most susceptible from being abstracted, the hydroperoxides that are formed is an α,β-unsaturated hydroperoxides which then leads to formation of α,β-unsaturated aldehydes. The main consequence of aldehyde formation is chain scission and formation of macroradical P·.

$$\mathrm{POOH} \longrightarrow \mathrm{P\dot{O}} + \mathrm{\dot{O}H} \quad \text{(r1)}$$

$$\mathrm{PO^{\bullet}} + \mathrm{R\,[\text{-}H]} \longrightarrow \mathrm{POH} + \mathrm{R^{\bullet}} \quad \text{(r2)}$$

$$\mathrm{PO^{\bullet}(\text{-}PH2)} \longrightarrow \mathrm{PH{=}O} + \mathrm{P^{\bullet}} \quad \text{(r3)}$$

$$\mathrm{PO^{\bullet}(\text{-}2PH)} \longrightarrow \mathrm{PP{=}O} + \mathrm{P^{\bullet}} \quad \text{(r4)}$$

Figure 3.5. Chemical pathways for the formation of ketones, aldehydes, and alcohols from the homolysis of hydroperoxide POOH.

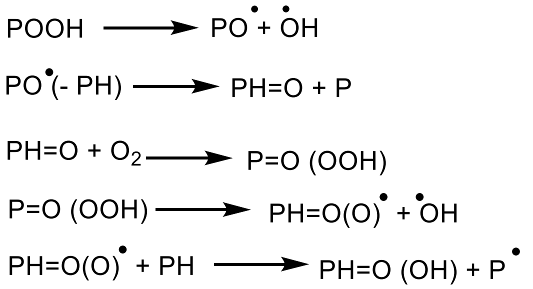
In the presence of additional reactants in the degrading polymer melt, aldehydic carbons can continue to react by letting its proton be abstracted to form the carbonyl radical PC=O· or an additional O_2 from the atmosphere can form a peracid, PCOOOH (figure 3.5). The peracid degradation can lead to a lot more kinds of carbonyl compounds like lactones, esters, and carboxylic acids [4,13].

f. Hydroxyl Path

Hydroxyl groups can be formed from the alkoxy radical coming from the hydroperoxides [7,14]. But instead of rearranging itself to form the aldehyde and chain scission, PO· can then abstract a nearby H to produce an alcohol, POH (figure 3.5 r1 and r2).

g. Carboxylic Path

As mentioned in the termination stage, the struggle to form the carboxylic moieties is due to the specificity of the reaction. Similarly, the starting point for carboxylic path is the homolytic cleavage of the hydroperoxides [2,15]. In Figure 3.6, the production of peracids leads to the carboxyl radical and the abstraction from a nearby H can produce the carboxylic acid. The diffusion forbidden method by the end stage of the oxidative degradation of SBR can explain the production of carboxylic moieties. As macroradicals are continuously being produced, the upper layer tends to be crosslinked first than the inner layers creating a barrier for O_2 to diffuse as the heating continues [13,14,15]. Consequently, the inner part of the polymer melts which are comprised of peracids are producing radicals without the presence of oxygen (Figure 3.9 r4). The RCOO radical can abstract H from nearby H to form the carboxylic acid RCOOH (Figure 3.6 r5).



$$\mathrm{POOH} \longrightarrow \mathrm{PO}^{\bullet} + {}^{\bullet}\mathrm{OH} \tag{r1}$$

$$\mathrm{PO}^{\bullet}(\text{- PH}) \longrightarrow \mathrm{PH{=}O} + \mathrm{P} \tag{r2}$$

$$\mathrm{PH{=}O} + \mathrm{O_2} \longrightarrow \mathrm{P{=}O\ (OOH)} \tag{r3}$$

$$\mathrm{P{=}O\ (OOH)} \longrightarrow \mathrm{PH{=}O(O)}^{\bullet} + {}^{\bullet}\mathrm{OH} \tag{r4}$$

$$\mathrm{PH{=}O(O)}^{\bullet} + \mathrm{PH} \longrightarrow \mathrm{PH{=}O\ (OH)} + \mathrm{P}^{\bullet} \tag{r5}$$

Figure 3.6. The formation of carboxylic acid from the homolysis of hydroperoxide POOH.

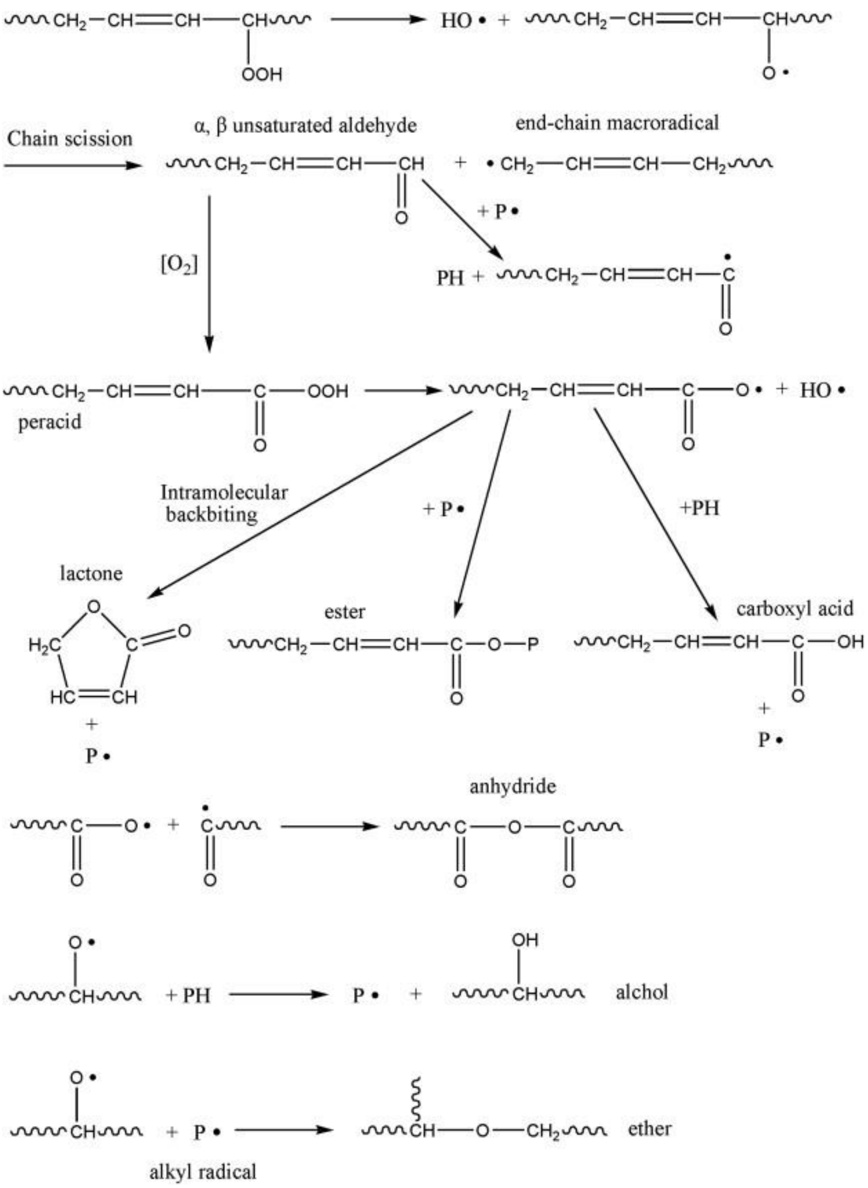


Figure 3.7. Proposed mechanistic formation of oxygen containing functional groups on SBR. Image retrieved. Image retrieved from [2].

3. Mechanochemical degradation of SBR in air

When tyre materials are exposed in mechanical loading, forces act on the polymeric material that will induce degradation [15]. Macromolecules are stretched when mechanical loads are applied on the material by extrusion, compression, elongation and sonication (Figure 3.8). Stretching, shearing, twisting and other alterations on the macroscopic shape of a polymer can initiate degradation. With the presence of O_2 in air, exposed polymeric elastomers will proceed to the formation of macroradical that will lead to autoxidation [16]. Sheared samples of SBR have been extensively studied and the mechanistic behavior is also being evaluated. With the available experimental methods mentioned in the last chapters, the functional groups produced from the shearing of SBR in air are evaluated [17,18,19].

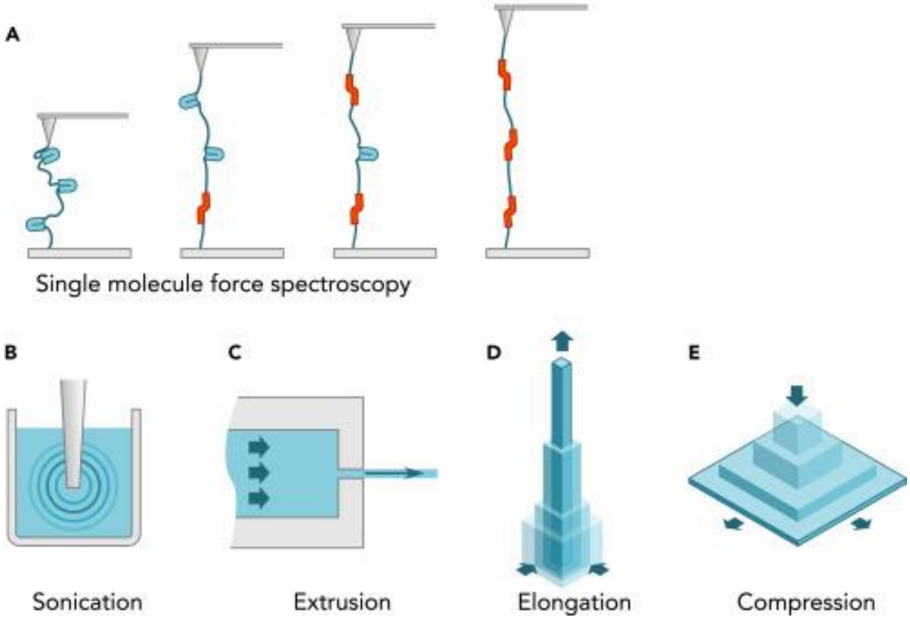


Figure 3.8. General illustration of mechanochemical degradation of polymers. Retrieved from [15].

4. Effects of antioxidants on SBR degradation

Antioxidants are used to protect polymers from decomposition by retarding the autoxidation processes by interfering with the radical propagation reaction [20]. There are different kinds of antioxidant that can be used to inhibit the oxidation reaction for SBR. Potential research have been developed to show the effectiveness of known anti-oxidants on polymeric materials such as tyre samples. The main concern for the usage of antioxidants would focus on the capacity of these materials to prevent further oxidation, effects on the physical properties of rubbers, potential environmental impact and price [21].

Table 3.1 summarizes the type of degradation exhibited on elastomers and the accelerating factors.

Type of Degradation	Initiating Factors	Degradation Causes	Type of Failure
Storage Aging	Surrounding conditions	O_2, light, heat and humidity	Loss of elasticity
Thermal Aging	Heat	Oxygen, O_2	Loss of elasticity
Light and weathering	Radiation (Light, UV light), heat, humidity	Oxygen, O_2	Loss of elasticity and formation of crazed surface
Soluble metal ion or catalysed oxidation	Cu, Mn, Fe, Co and Ni in their soluble fatty acid form	Oxygen, O_2	Loss of elasticity
Flex-fatigue cracking	Mechanical strains	Oxygen, O_2	Appearance of cracks
Ozone cracking	Strains	Ozone, O_3	Appearance of cracks

Figure 3.9 shows the chemical pathways where potential antioxidants can work to disrupt the cycle. Organic sulfides such as sulfenic acids, thio-di-propionates and dialkyldithio-carbamates are used as peroxide decomposers. They react with hydroperoxides to form intermediate sulfoxides thus reducing hydroperoxides to alcohols [21].

Most phenolic or amine-based antioxidants are good H-donors that can interfere macroradicals from reacting to other radical groups, moieties, and hydrogens in the polymer [22]. This inhibits further crosslinking that leads to formation of cracks on rubber tyres. Figure 3.11 shows the mechanism of hydrogen abstraction of H by ROO· radical. SBR samples that are used in this project are treated with pyrene-derived TEMPO (figure 3.10) as a radical scavenger [23,24].

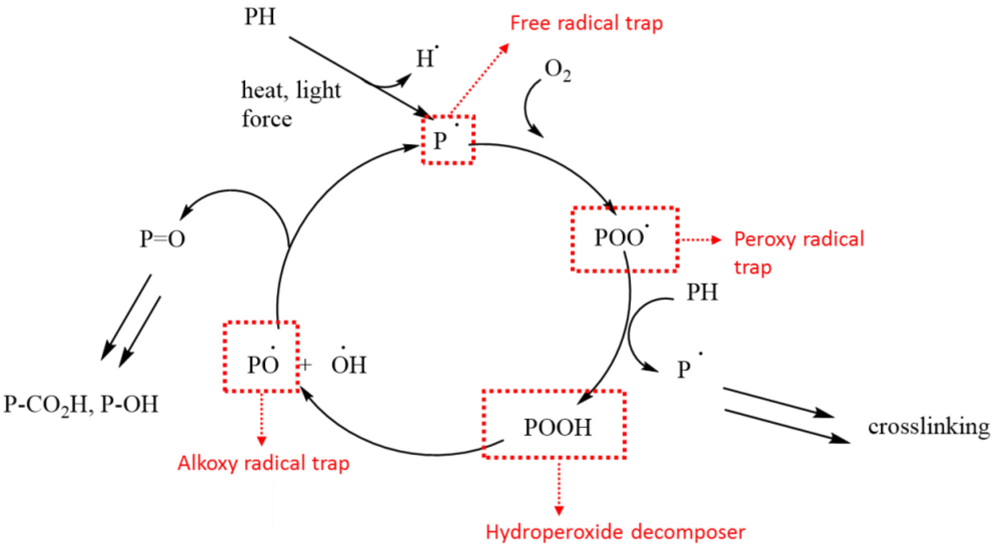


Figure 3.9. Different kinds of antioxidants based on their ability to react with the radical moieties in the polymer melt as it undergoes oxidative degradation.

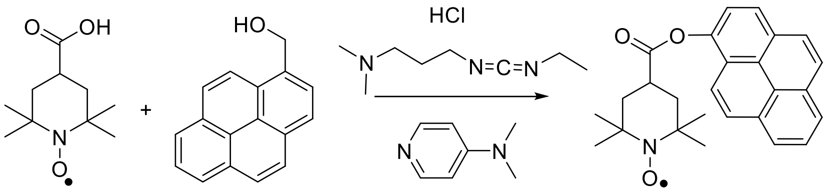


Figure 3.10. Synthesis of pyrene-derived TEMPO.

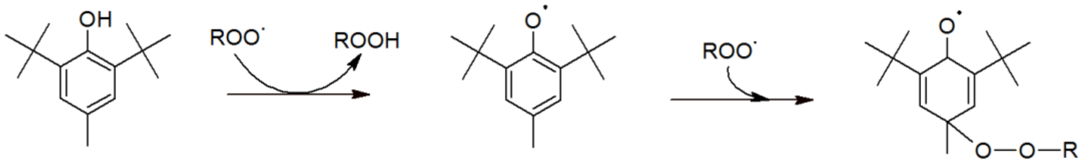


Figure 3.11. The mechanism of scavenging peroxy radicals is shown below for BHT or butylated hydroxytoluene [24].

5. Approach

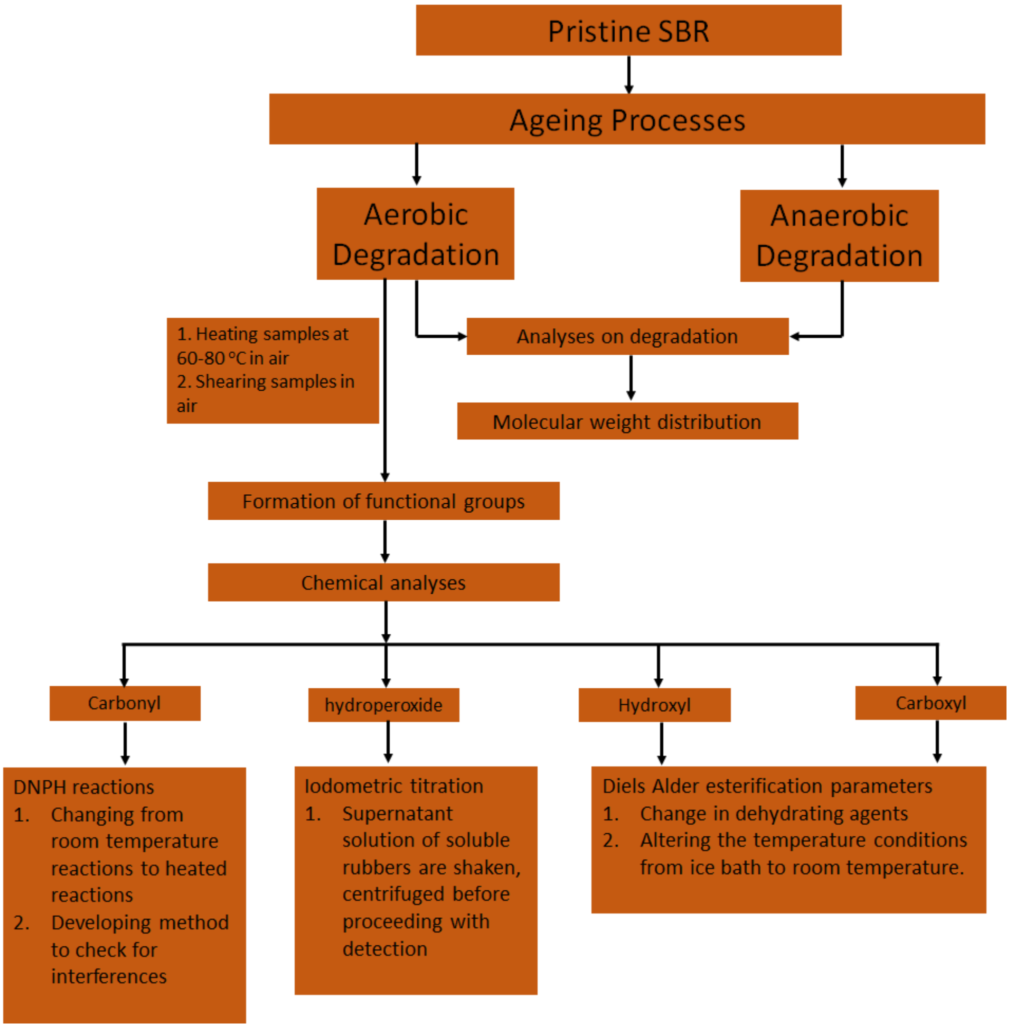


Figure 3. 12. The general experimental approach for this project. Pristine SBR samples from Michelin ® are collected and aged at specified temperature and atmospheric conditions. In this project, samples are heated in air at varying temperatures from 60 to 80 degrees Celsius both in air and N_2. Resulting rubber samples are then analysed for the changes accompanying the degradation processes.

- To determine of rate of crosslinking of SBR at 60 °C and 80 °C
- To develop a working reaction method for the detection of oxygen containing species in long polymer chains such as SBR, polybutadiene and polystyrene
- To analyse the amount of oxygen containing species (hydroperoxide, carbonyl and hydroxyl) present in thermally oxidized SBR
- To correlate the relationship of the amount of soluble material or uncrosslinked thermally SBR with the amount of oxygen containing species.
- To formulate plausible mechanistic schemes of the degradation of SBR at these conditions

6. Experimental Methods

a. Materials

Styrene Butadiene Rubber (SBR) samples were provided by Michelin containing 26% by weight of styrene, 15% by weight of 1,2-bound butadiene and 59% by weight 1,4-bound trans butadiene (M_n = 177 kDa, PDI = 1.07 and T_g = - 35°C). The SBR pristine samples were stored in airtight sealed containers and kept in freezer to prevent unaccounted degradation before the experimentation processes. These samples have M_w = 177,000 and are free of antioxidants. SBR samples were dissolved in toluene and stored as stock solutions and stored in freezer at -37°C.

Solutions:

- 5% w/v 2, 4 dinitrophenylhydrazine-HCl in THF,
- 5 mg 9-anthracene carboxylic acid in 1 mL dicyclohexylcarbodiimide (DCC)
- 5 mg 9-anthraceneethanol in 1 mL DCC
- 1.5 mg 4-dimethylaminopyridine (DMAP) in 1 mL DCC.
- 1 M HCl

Solvents:

- Analytical Grade Ethanol
- Toluene
- Tetrahydrofuran (THF)
- Acetone
- Isopropanol
- Acetic Acid

b. Sample treatment and exposure conditions

Thermal aging of SBR: Enough SBR samples were dissolved in THF to create a 50 mg/mL solution. The stock solution is stored in the fridge to prevent further degradation while the experimentation is being done. 200 µL rubber stock solution for each sample was transferred into 1.5 mL vials. The vials were placed in a sealed chamber and solvent was evaporated under high vacuum. Then all vials were transferred to a glove bag and were saturated with compressed air for 24 hours at room temperature. Samples that are to be degraded in anaerobic atmosphere are exposed in N_2 gas for 24 hours at room temperature.

c. Thermal degradation processes

Thermal degradations were done in two set ups – in aerobic and anaerobic environments. For the anaerobic set up, the vials are tightly sealed and heated under slight overpressure of N_2 gas to saturate the atmosphere. Samples for aerobic degradation are directly heated at a specified time and temperature. Individual vials were taken out periodically and kept in a refrigerator until further characterisation. The vials are protected from air as they cool back to room temperature. Degraded samples are redissolved in THF and stored in the freezer in the glovebox to prevent further degradation. The heating set-up used for the degradation of SBR is shown in figure 3.13.

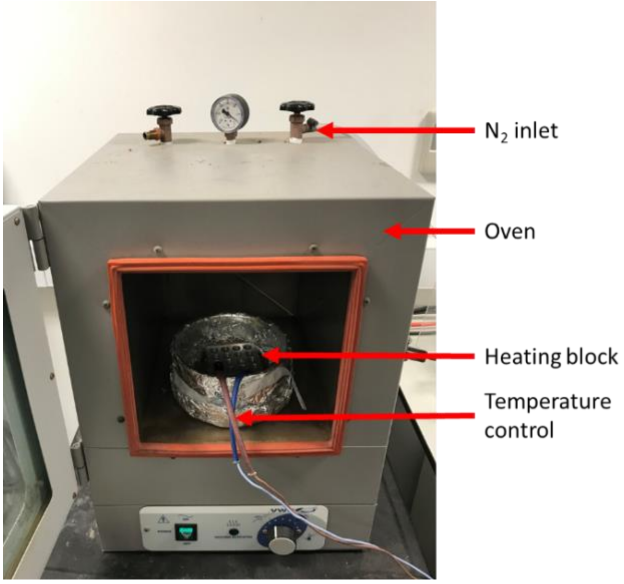


Figure 3.13. Experimental setup for the thermal degradation of SBR. The heating block is externally monitored to make sure that heating is constant, and samples are heated at identical temperature.

d. Characterisation

1. Gel permeation chromatography of SBR solution

100 µl solutions of oxidized SBR is diluted to 1000 µL and were shaken for several minutes and then analysed by GPC. For the styrene pendants, analyses are run at 290 nm. Analytical SEC was carried out on Waters Acquity UPLC system with an

isocratic solvent manager, sample manager, column heater, photodiode array detector and RI detector. The flow rate of THF is 0.6 mL/min. Column heater temperature is maintained and controlled at 35 ^{o}C. The PDA detector monitors absorbance of light of the wavelength from 240 to 400 nm. The temperature of the RI flow cell is 35 ^{o}C. All polymer solutions were filtered through PTFE syringe filters prior to analysis. The SEC columns were calibrated using narrow polystyrene standards from Sigma-Aldrich and Scientific Polymers Inc.

2. Iodometry for hydroperoxide determination

The complete methodology for this experiment is detailed in chapter 2 section 3.c.3. Solutions of oxidized SBR samples were diluted to concentrations with THF, isopropyl alcohol and acetic acid and placed in a sealed cuvette. For every 100 µL of the rubber solution, 900 µL of THF was used to dilute it and 300 µL isopropanol (Fisher, HPLC grade) and 100 µL acetic acid (Sigma-Aldrich, >99.9995% pure) were added in anaerobic condition. The absorbance of the sample in a sealed cuvette was measured at 300 nm to 600 nm. After collecting the first spectrum, 100uL 150mg/ml NaI-i-PrOH solution was injected into the mixture through 100 uL glass syringe and then spectra were keeping collecting with 0.6 min intervals until 30 min [13,14,26].

3. Mechanochemical treatment of samples

SBR samples were sheared in a capillary rheometer, comprised of a purpose-made capillary flow cell coupled to an 831 Elastomer test system EM1020 from MTS Systems Co. Ltd. The instrument is located at the Michelin global R&D headquarters in Clermont-Ferrand. This tester controls the magnitude and rate of the vertical displacement and measures the force needed to achieve them. The cylindrical flow cell consists of two reservoirs of 1 mL capacity each connected by a capillary of 1 mm diameter and 10 mm length and two pistons fitting the reservoir chambers. During the operation the two pistons were maintained at a constant vertical separation of 30 mm and the cell was moved up and down by 10 mm at a linear rate of 0.625 mm/s so a single cycle took 32 s. All mechanochemical remodelling experiments were done at the Michelin R&D headquarters in France by Dr. Sergey Akbulatov. All sample preparation and analysis were performed at Liverpool by Dr. Chenxu Wang. The chemical tests are performed here in the University of Liverpool. Sheared samples are dissolved in THF and were tested for the presence of oxygen containing-functional groups. All sheared samples were stored at -37 ^oC and saturated with N_2. Solid samples were dissolved in THF creating a 1mg/mL concentration.

4. DNPH analysis on oxidized SBR

The complete methodology for this experiment is detailed in chapter 2 section 3.c.2. 100 µL solutions of oxidized SBR is pipetted in weighed vials and solution of DNPH is added. One drop of 1 M HCl was added, and the mixture was stirred at 25 ^oC for three hours in nitrogen atmosphere. The solvent in the resulting mixture was evaporated and unreacted 2, 4-DNPH and HCl were washed with ethanol. After drying, the final mass of the rubber-hydrazone was weighed and redissolved in THF. The solution containing the rubber-hydrazone was analysed in GPC and the absorbance was measured at 367 nm for the hydrazone moiety. Typical reactions of DNPH to detect carbonyls are done in elevated temperatures (<50 ^oC). However, in this project, the experiment was done at room temperature (25 ^oC) to prevent SBR from further degradation [26-28].

To check for the interferences, 100 µL of the oxidised SBR solution was reacted with 5 equivalents of PPh_3 solution and the mixture was stirred at 0 ^oC gradually until room temperature for 24 hours. After the reaction, the rubber is precipitated with ethanol to remove the unreacted PPh_3. The recovered rubber was then redissolved in THF and DNPH reaction was done. Further processes were similar as mentioned above. For this project, the reacted oxidized SBR samples are ran in GPC and the peaks at 254 nm and 367 nm for the styrene and hydrazone group respectively will be used to calculate the number of carbonyls present in the chain [28].

5. Attachment of anthracene on oxidized SBR

a. Detection of hydroxyl groups

The complete methodology for this experiment is detailed in chapter 2 section 3.c.4.a. A 100 µL solution of oxidized SBR was mixed with DCC, DMAP and 9-anthracenecarboxylic acid, was stirred at 0 °C for 5 hours and allowed to stay for 24 hours at room temperature. The reaction mixture was dried and excess reactants were washed by acetone. After drying the acetone, the final mass of the anthracene derived SBR was weighed and dissolved in THF. Finally, the solution was analysed in GPC and the anthracene absorbance was measured at 360 nm [29]. Carboxylic and hydroxyl contents may be expressed as moles per mole of the polymer. The peak area of the styrene and the chromophore can be integrated in the chromatograms. Using the apparent extinction coefficients of SBR and the chromophore, we can calculate the amount of carbonyl or hydroxyl present in the rubber [30,31,32].

b. Detection of carboxylic groups (-COOH)

The complete methodology for this experiment is detailed in chapter 2 section 3.c.4.b. A 100 µL solution of oxidised SBR was mixed with DCC, DMAP and 9-anthracenemethanol, was stirred at 0 °C for 5 hours and allowed to stand for 24 hours at room temperature. The reaction mixture was dried and excess reactants were washed by acetone. After drying the acetone, the final mass of the anthracene derived SBR was weighed and dissolved in THF. Finally, the solution is analysed in GPC and the anthracene absorbance is measured at 360 nm [30,31,32].

6. IR Measurements

Thermally degraded SBR samples are dissolved in the toluene for 24 hours and centrifuged to make a clear supernatant solution. The clear solution is dried in a vacuum. Pieces of solid SBR samples were scratched from the vial and placed on the sample plate of PerkinElmer Spectrum 100 FT-IR Spectrometer with Universal ATR Sampling Accessory. Scanning range is from 600 cm^{-1} to 4000 cm^{-1} and scan number is set as 4.

7. Results and Discussions

a. Analysis on the thermally oxidized SBR samples

1. Calculations for the fraction of insoluble material

As the polymeric material starts to degrade, the amount of crosslinking is seen to have increased over time. This resulted in a larger molecular mass that could not be dissolved by common organic solvents such as toluene and THF. Remodeling of SBR through oxidative heating alters the chemical composition of the molecular chains and this is evident from the insoluble materials that have been crosslinked. The detection of the changes in structure is challenging as there are several functional groups that can be formed during the processes. Thermal remodeling of SBR converts significant fraction of soluble SBR into its insoluble counterpart thus deemed uncharacterisable with the methods viable to us. However, what we can monitor, and measure is the processes by which these macromolecules form from quantification of soluble fraction, molar mass distribution and the concentration of the oxidized species heated in air.

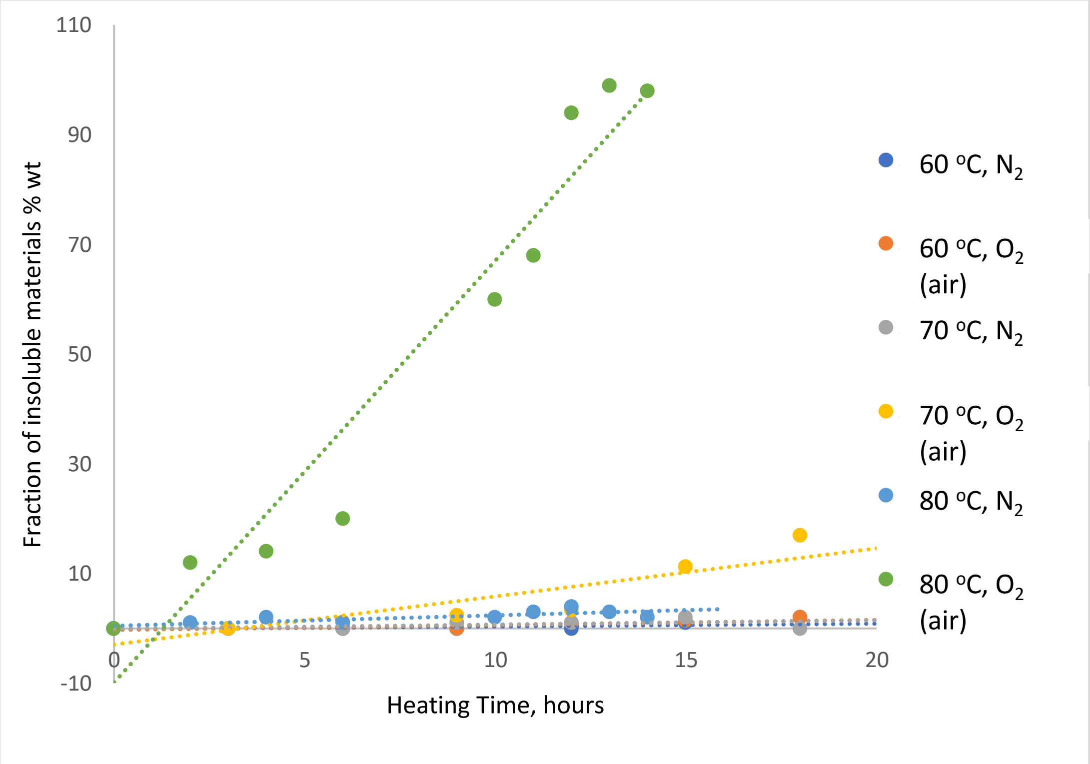


Figure 3.14. Mass fractions of the insoluble material in heated SBR as a function of the heating time. The data points are averaged from sequential weighting and SEC and the error bar are the

statistical errors. The dash lines for anaerobic heating are linear least square fit, and for aerobic remodeled sample is a simple connection of each data point. Dotted line: linear fit correlation.

The fraction of insoluble material from the degradation of SBR at 80 ^{o}C increased dramatically after 7 hours while the rest of the tested samples increased approximately linearly with the heating time (Figure 3.14). Accumulation of insoluble materials in air at 80 ^{o}C shows an induction period where there is a slow conversion at the beginning followed by a rapid increase of insoluble material. There is no significant difference for SBR samples degraded in air or N_2 at lower temperatures in the first 21 hours of the experiment.

Figure 3.15 shows the evolution of the spectra of the thermally degraded SBR at different temperatures. It shows the drastic decrease in the amount of soluble component as the temperature increased from 60 ^{o}C to 80^{o} C. To determine the degree of degradation at 60 ^{o}C, the amount of time needed is increased to 240 hours. Moving forward with the experiment, tests are focused on two temperatures, 60 ^{o}C and 80 ^{o}C heated at different times in air and N_2.

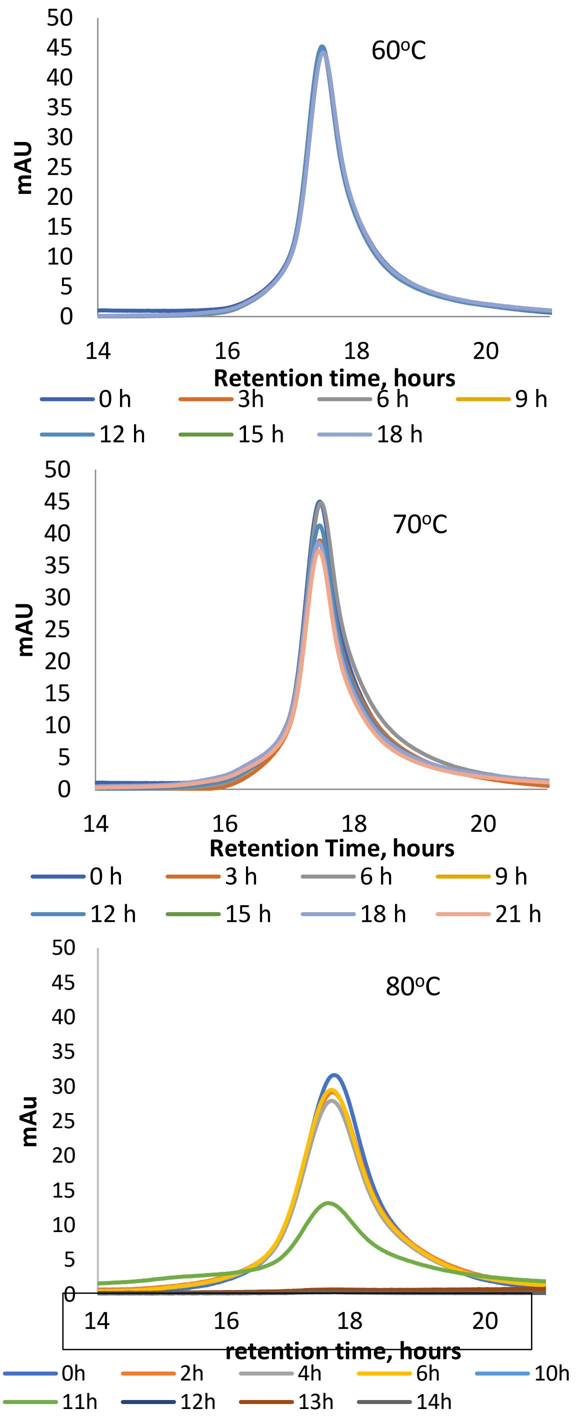


Figure. 3.15. Evolution of SEC traces of SBR samples during thermal remodelling at different conditions. RI intensity is proportional to the mass fraction of each molar mass species and longer retention time reflects smaller molar mass.

2. Molecular Mass Distribution

Following the increased time of exposure for samples heated at 60 ºC, the changes in the fraction of insoluble materials have been observed past 120 hours (see section 4.a.1). Experimental Size exclusion chromatography (SEC) traces of SBR samples collected at different time of heating at 60 ºC suggest a low conversion to crosslinked products (Figure 3.16). Experimental SEC traces of samples collected at different heating times suggested thermal oxidation at 80°C generated only higher molecular weight fractions with two well defined peaks (Figure 3.17). Note for these two analyses, 60°C samples were ran in Shimadzu SEC and 80°C in Acquity SEC.

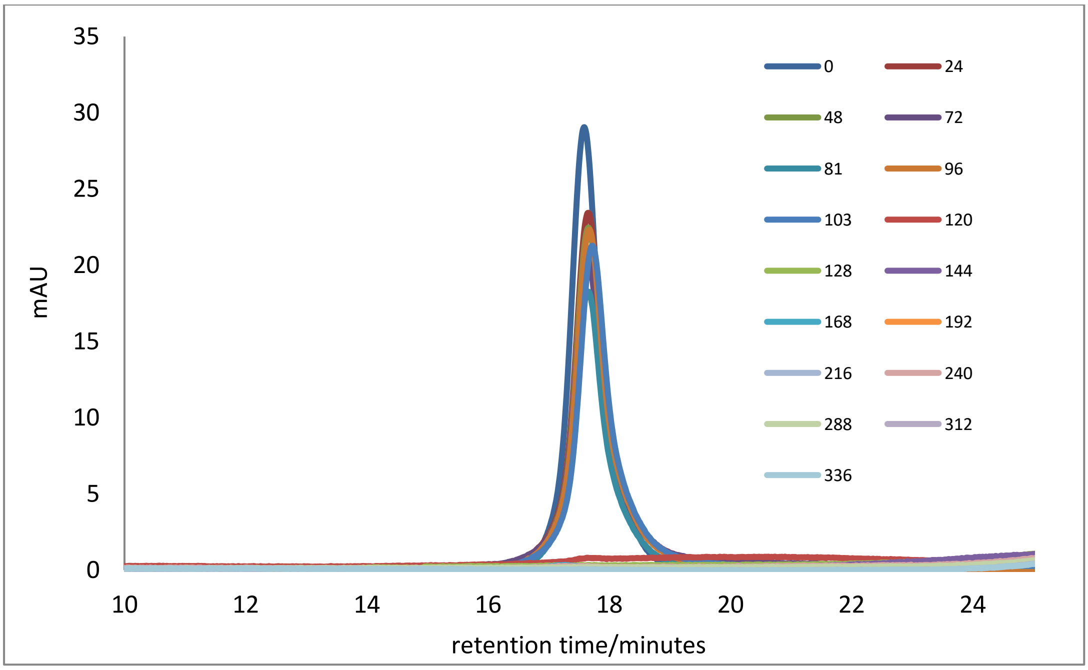


Figure 3.16. GPC results of SBR samples which were heated in O_2 under 60°C. Each SEC trace is corresponding to specific sample at specific time points.

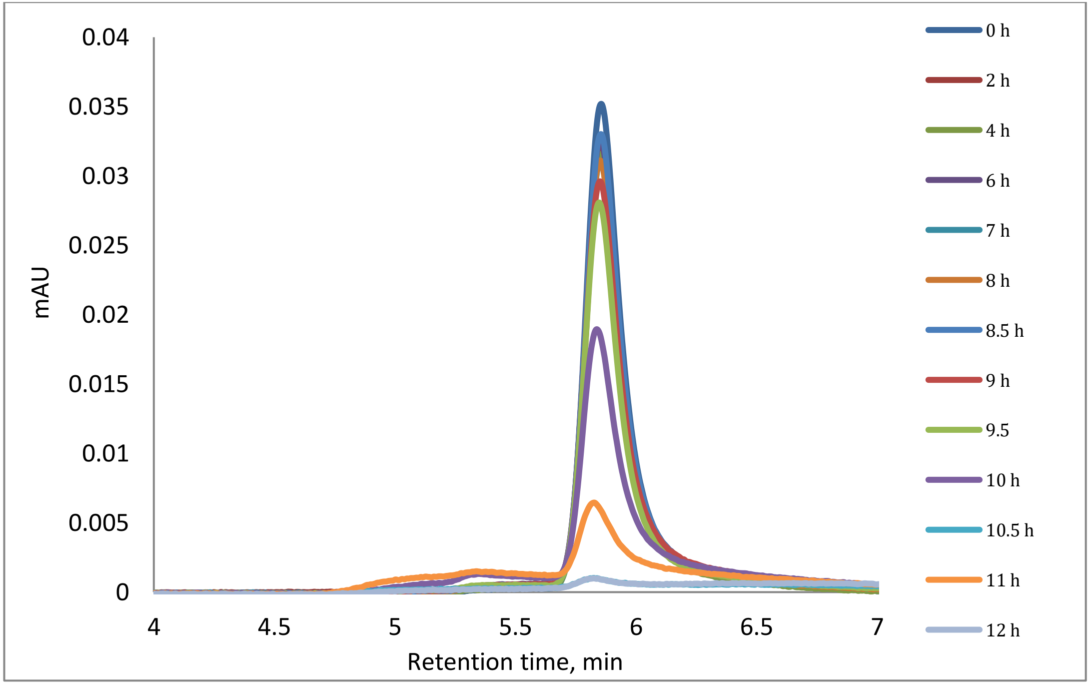


Figure 3.17. SEC traces of samples which were heated in O_2 under 80°C. Each SEC trace is corresponding to specific sample at specific time points.

3. Crosslinking

Calculating the area of the peaks at 254 nm of the samples, the fraction of crosslinked materials for 60 °C and 80 °C show a slow conversion of the products. As seen below, for three separate experiments, thermally oxidized SBR showed slow increase of insoluble material until it goes almost fully crosslinked after 120 hours. For samples oxidized at 80°C, the increase in fraction of insoluble material happened after 7 hours (Figure 3.18 and 3.19 respectively).

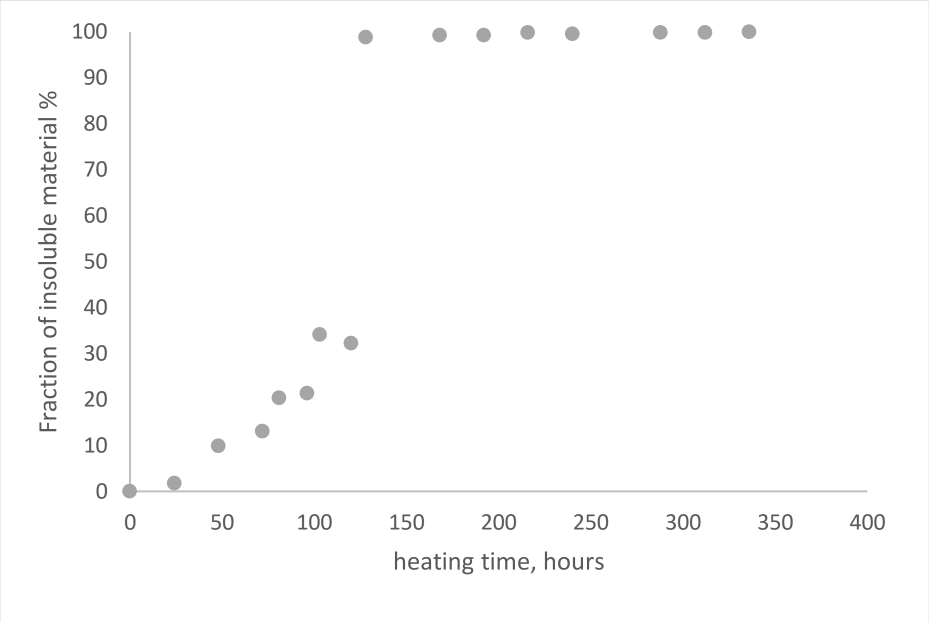


Figure 3.18. The fraction of the insoluble material as a function of the heating time at 60 °C.

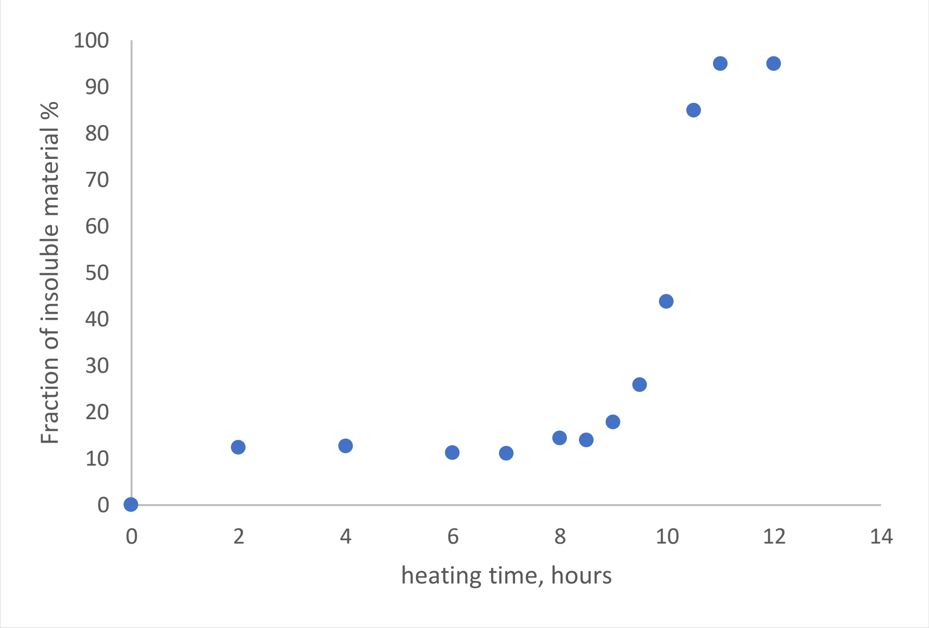


Figure 3.19. The fraction of the insoluble material as a function of the heating time at 80 °C.

b. Determination of hydroperoxides in oxidized SBR samples

The concentration of hydroperoxides was measured by iodometric titration. Peroxide content of rubbers oxidized at 60 °C and 80 °C showed an induction period of 24 and 7 hours, respectively. After the induction stage, the concentration of hydroperoxide increases together with the level of crosslinking and nearly linearly with heating time (Figure 3.20 and 3.21). The concentration of the hydroperoxy radical increases exponentially with heating time until all soluble SBR are converted to its insoluble products.

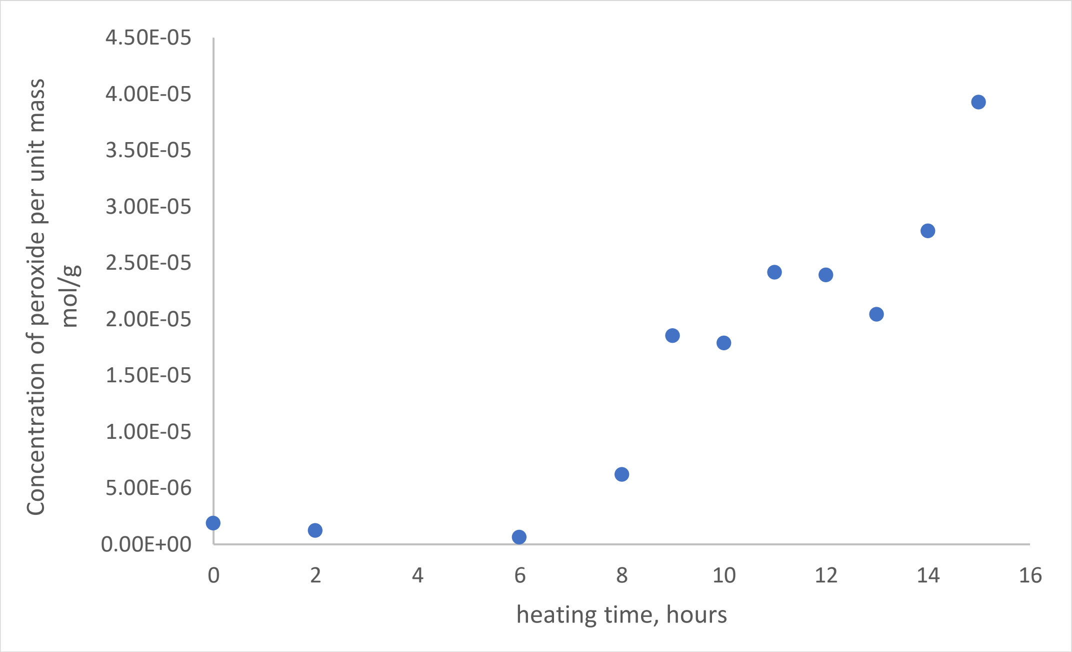


Figure 3.20. Concentration of peroxides in SBR samples during heating at 80°C in air. Dotted line: linear fit correlation.

For samples degraded at 60°C, it is necessary to increase the time of exposure as the concentration of peroxide did not change in the first 24 hours in three trials (Figure 2.14). At the 120th hour, hydroperoxide concentration is seen to start decreasing with heating time but still has a higher concentration compared to the first four days of reaction. This phenomenon is evident many researches done at similar or higher temperatures [2]. There are possible reasons for the presence of hydroperoxides in solution with almost no rubber left. Hydroperoxides might exist in the low molecular mass product after the thermal reaction [3].

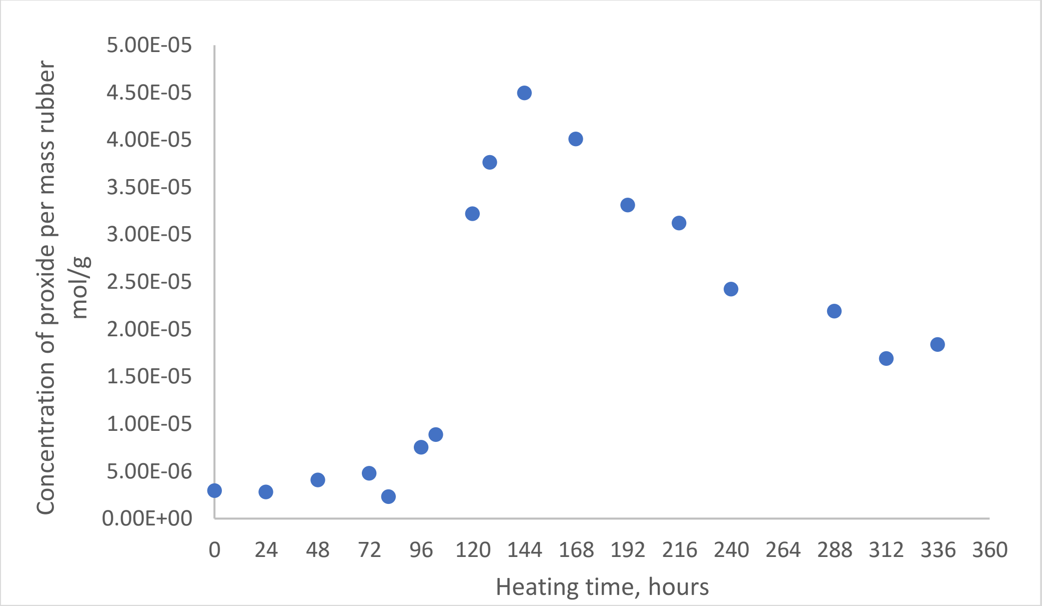


Figure 3.21. Concentration of peroxides in thermally oxidized SBR samples at 60°C versus time of heating.

c. Analysis of DNPH-derived SBR

The determination of the amount of carbonyl in oxidised SBR was measured by DNPH reaction (see section 3.d.4). GPC analysis was done to determine 2,4-DNPH on oxidized rubber. The SBR-hydrazone derivative is analysed at 367 nm with ε = 22,000. The styrene region is in the 245 nm to 270 nm and the hydrazone region is peaking at 367 nm. By calculating the peaks of the samples at 254 nm and 367nm, the amount of hydrazone that is attached in the SBR can be estimated. Carbonyl content may be expressed in moles per carbonyl per mole of rubber.

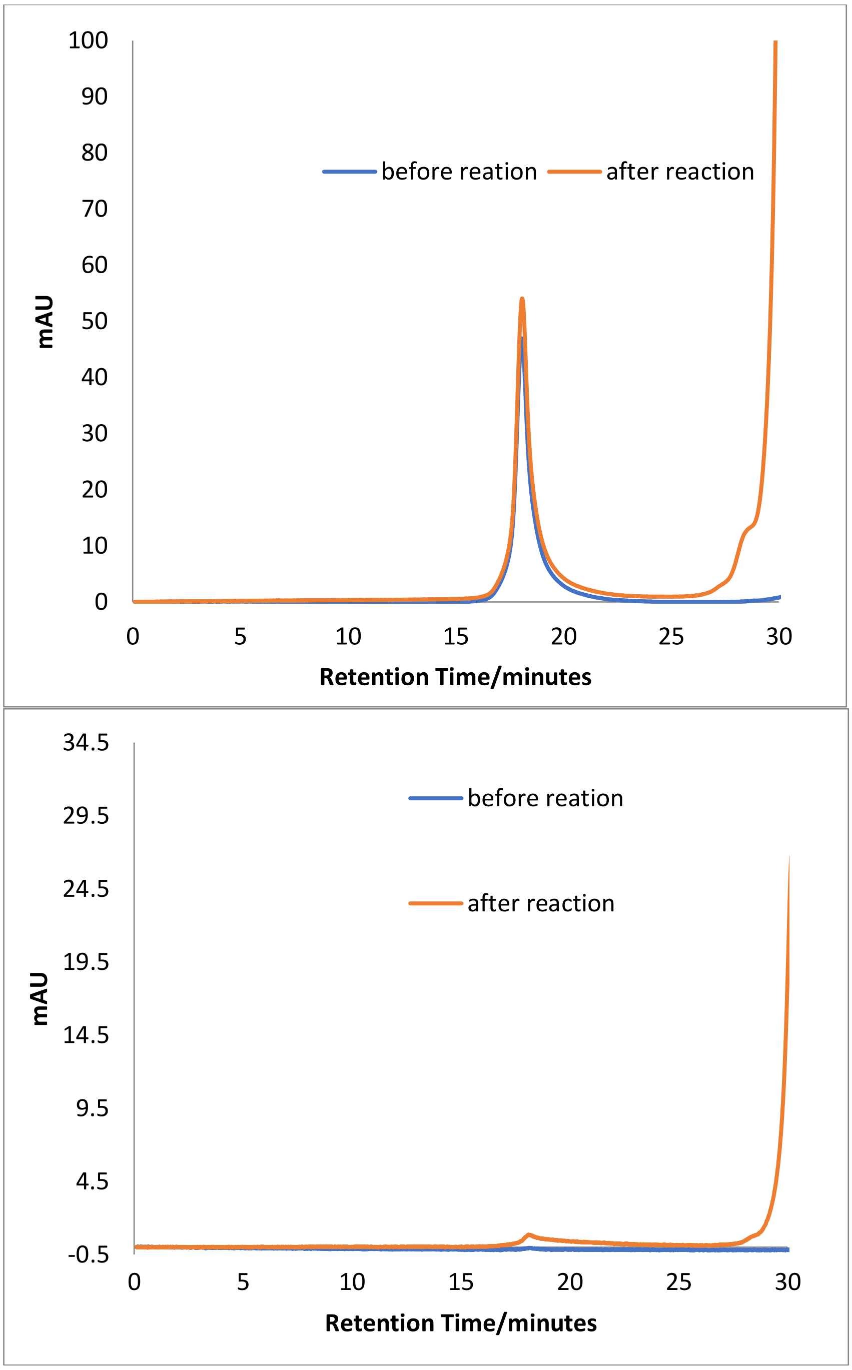


Figure 3.22. SEC traces of SBR-hydrazone and unreacted oxidised rubber seen at two wavelengths 254 nm (top) for styrene and 367 nm (bottom) for the hydrazone derivative.

The calculated amount of hydrazone corresponds to the amount of carbonyl present in the samples. To calculate the amount of carbonyls, the peak area for the oxidised rubbers is calculated and compared with that of the unreacted samples (See section 3.d.4). Figure 3.22 shows the SEC traces of SBR-hydrazone at two wavelengths, 254 nm and 367 nm. For the two separate experiments, the induction period is observed (Figure 3.18). Similar to the results in hydroperoxides, the induction period for samples degraded at 60 °C and 80 °C in air is evident in the first seven hours which apparently affects the linearity of the graph.

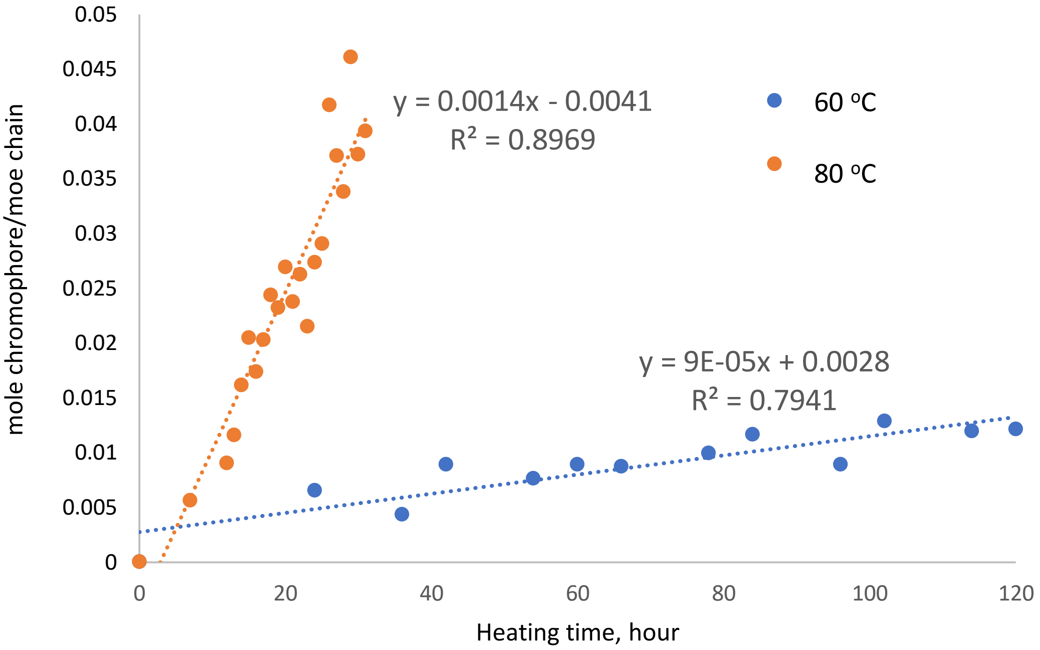


Figure 3.23. shows the difference in evolution of carbonyl groups between two temperatures. Experiments done at 80°C clearly showed an increase of carbonyls as the samples have fully crosslinked. Dotted line: linear fit correlation.

d. Analysis on the anthracene derived SBR

Following the Steglich esterification of alcohols and carboxylic acids, similar end products of anthracene derived molecules can be formed (See section 3.d.5). Figure 3.24 shows the complete spectra of anthracene derived SBR clearly showing the the styrene and anthracene peaks. The calculation for the approximate values of hydroxyl and carboxylic acid per chain is similar to that of the carbonyl and the results show that there is less hydroxyl than carbonyls in rubber analysed at 60 °C and 80 °C at varying times (Figure 3.26). Similar patterns are observed in growth of hydroxyl (R-OH) and Carboxylic (R-CO_2H) groups in the oxidised SBR samples. For experiments done at 80 °C, there is a slight increase in the accumulation of R-OH than R-CO_2H which shows that alkoxy groups have higher concentrations than the carboxylic acids (figure 3.24).

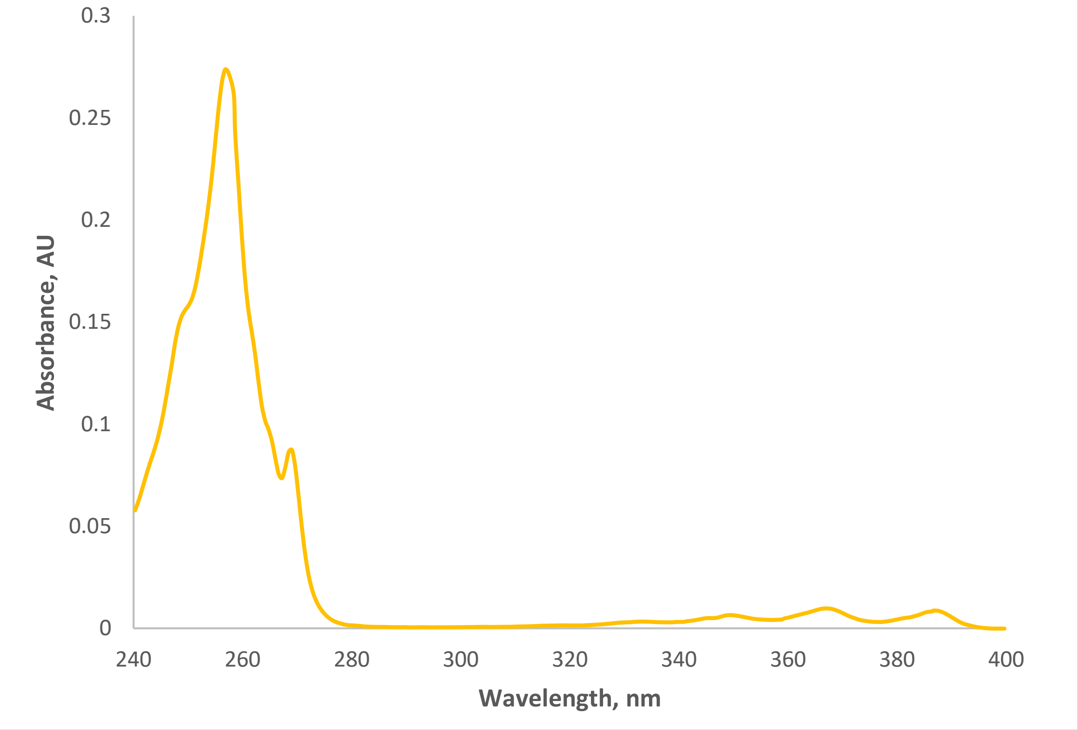


Figure 3.24. UV-vis spectra of anthracene derived SBR.

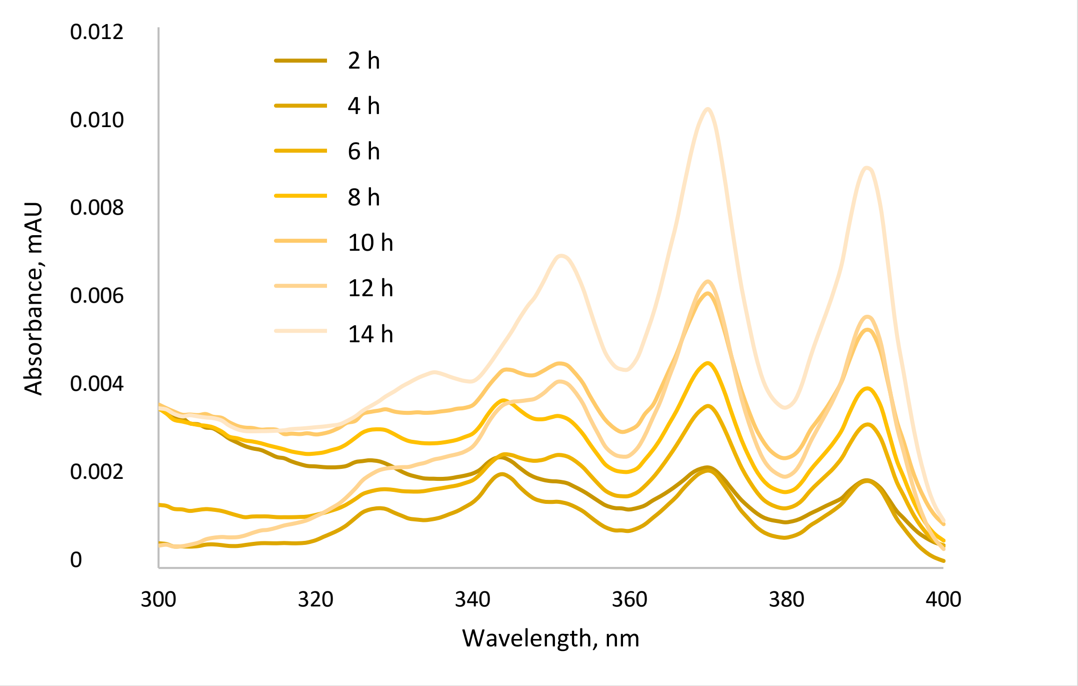


Figure 2.25. Spectra of the UV-vis of SBR-Anthracene magnified at the anthracene region. These SBR samples are heated at different times in air 80 ^{o}C.

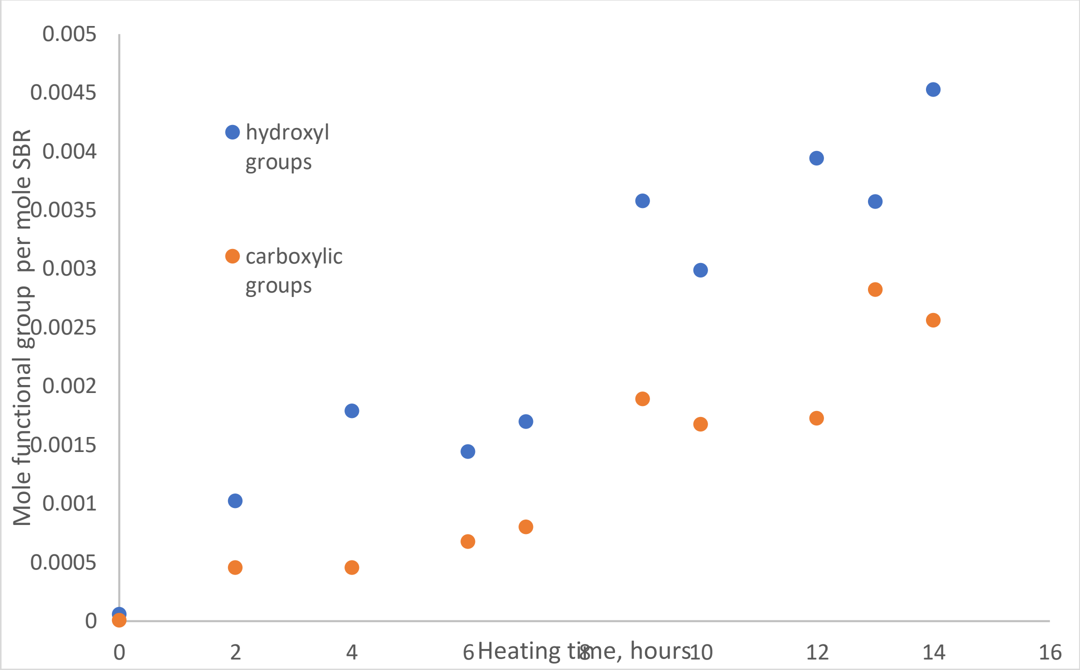


Figure 3.26. Approximation of the amount of hydroxyl (R-OH) and carboxylic (R-CO_2H) in oxidized SBR thermally oxidized at 80 °C at varying time of exposure. Dotted lines: Linear fit correlation.

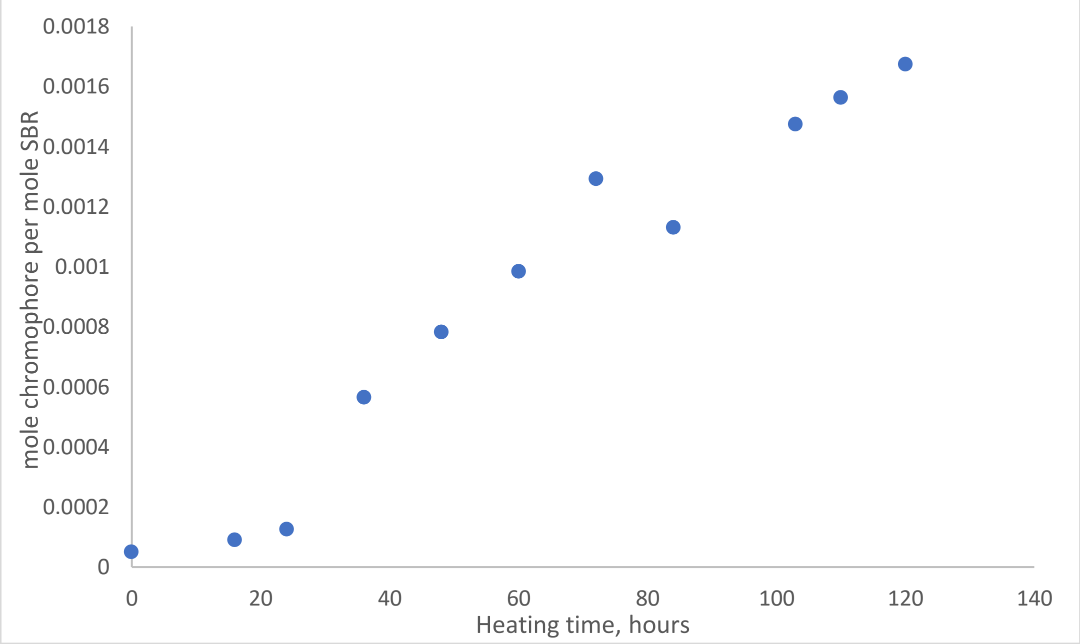


Figure 3.27. Hydroxyl growth as a function of time on oxidized SBR at 60°C. Dotted lines: Linear fit correlation.

e. Influence of Temperature and Chemical Treatment on Carbonyl Groups

Figure 3.28 shows the variation in the amount of carbonyls attached to the SBR after oxidation at 80 °C. PPh_3 as a hydroperoxide scavenger is seen to quench the –OOH in the SBR melt without affecting other functional groups particularly the carbonyls.

Treating the oxidized SBR with solution of PPh_3 solves two cases in this experiment: (1) hydroperoxides do not interfere with DNPH reaction. It does not react with DNPH nor in acidic media of the solution. The amount of carbonyls in the samples represents the aldehydic and ketonic carbons. (2) PPh_3 does not change the carbonyl component of the system.

The textbook method for the DNPH reaction with carbonyls is to heat the solution as high as 50 ^oC to allow a quick conversion of C=O to its DNPH derivative. We know from the previous section that hydroperoxides are still in its induction phase at 60 ^oC. Using this information, we can say that at 50 ^oC, we should not be expecting any dramatic changes in the carbonyl content. As seen in figure 3.25, fewer carbonyl groups are detected when the reaction is heated at 50 ^oC.

The reason for this is the formation of crosslinking when the DNPH reaction are done. Heating the reaction system allows the oxidation reaction to occur. Considering the reaction schemes in presented, the formation of carbonyls is dependent on the hydroperoxides in the lower mass radical chains meaning the faster the crosslinking, the lower the carbonyl content. The introduction of heating and stirring creates new competing reactions thus lowering the carbonyl products.

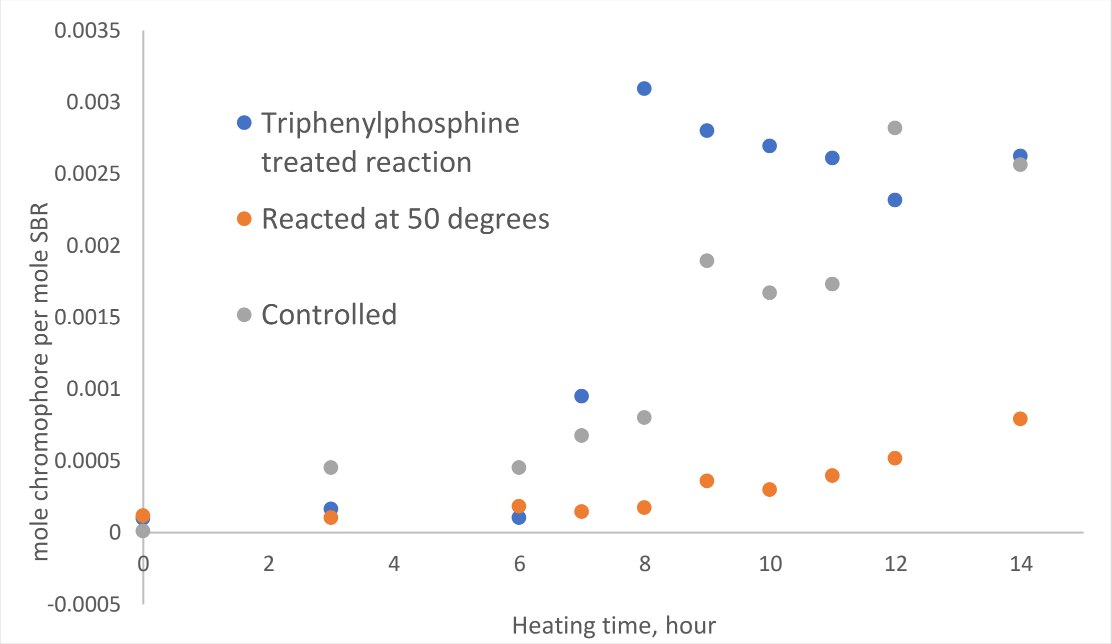


Figure 3.28. The controlled set up is done where oxidized SBR is reacted with DNPH in acidic media and stirred for 24 hours at room temperature (see section 4.d.4.). The controlled set up is altered by (1) changing the reaction temperature (orange plot) to 50 °C and (2) treating the oxidised SBR with PPh_3 before proceeding with the reaction (blue plot). Dotted lines: linear fit correlation.

f. Influence of temperature and chemical treatment on hydroxyl groups

The increase in the temperature of the reaction system on the esterification of hydroxyl groups are shown in figure 3.29. It was noted that there is no significant difference with the amount of anthracene moieties on the oxidized rubber samples. The SBR melt done in short period of time has been observed to go fully cross-linked if stirred for 24 hours. The ideal reaction for the esterification of hydroxyls and carboxylic acids would be at zero degrees to room temperature but the reaction time takes 24-48 hours.

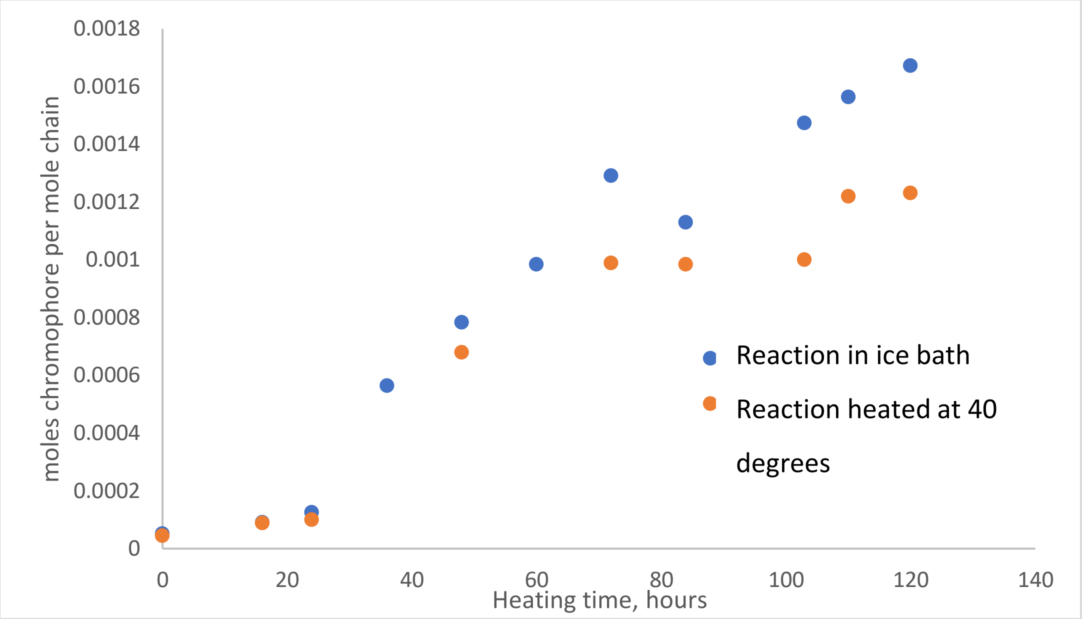


Figure 3.29. Diel-alder esterification of SBR-OH to SBR-Ant in ice bath(blue) and 40 °C (orange).

g. Influence of disturbance of the solution – stirring and centrifugation discussed

It was observed that following the dissolution of the oxidized rubbers, the rubbers tend to form suspension in the solution in THF. In reexamining the experimental procedures, solutions were then centrifuged to observe the effect of decanting the insoluble materials before proceeding with the detection processes. Figure 3.30 and 3.31 shows the effect of shaking and centrifugation in the dissolved polymer melts. When a polymer system is disturbed, the possibility of introducing new elements can alter the end product. It has been experimented that there are no significant changes in the amount of hydroperoxide in the solution of oxidized samples regardless of the stirring processes (Figure 3.31). The GPC analyses of the samples also did not show significant changes in the amount of soluble material regardless of whether the solution is centrifuged or shaken.

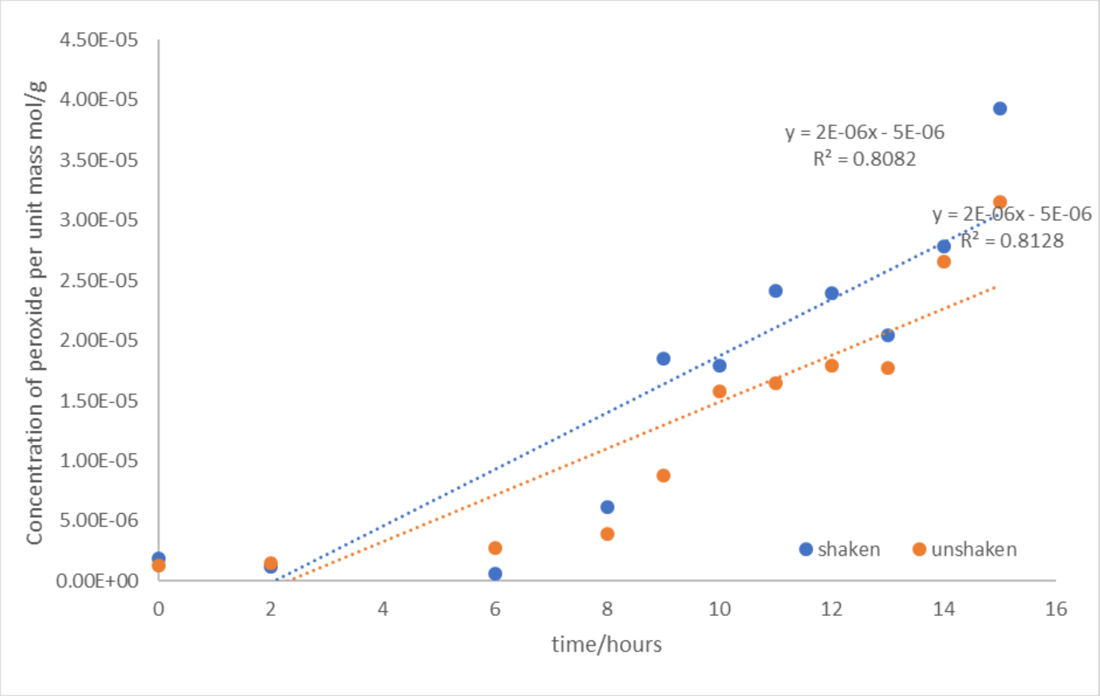


Figure 3.30. Analysis of the peroxide content on the oxidized SBR heated at 80 °C. Both set up are allowed to be dissolved in THF for 24 hours but samples in blue are shaken at 150 rpm. Dotted line: linear fit correlation.

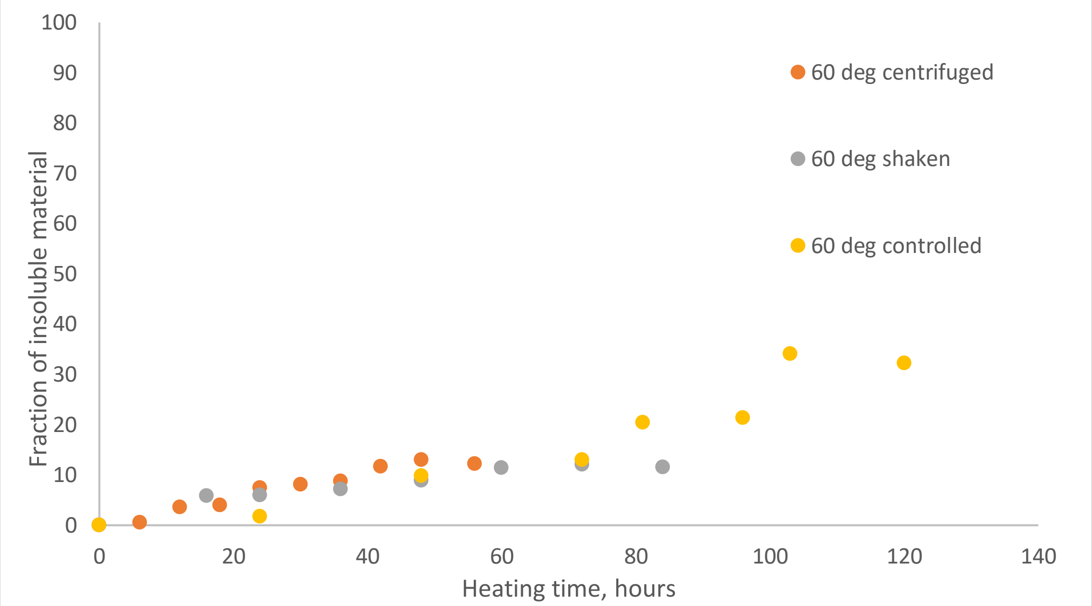


Figure 3.31. Analysis on the fraction of insoluble material of oxidized SBR at 60 °C. All of the set ups are allowed to be dissolved in THF for 24 hours. Samples in orange are centrifuged for 5 minutes. Samples in grey are shaken for 24 hours at 150 rpm then centrifuged for 5 minutes. Dotted line: Linear fit correlation

h. Influence of shearing and antioxidants.

Shearing SBR in air changes the chemical composition of the polymer chains. These changes are increasing over time and are quantifiable by different methods. We measured the amount of oxygen-containing species in the sheared samples in air and compared it with the sheared samples with added antioxidants. The summary on the analysis of sheared rubbers is detailed in Table 3.2. The method on the shearing process is explained in section 4.d.2. SBR samples used from this experiment were collected form the Michelin laboratory in France where the entire mechanochemical degradation process has taken place. The chemical analyses showed that SBR samples treated with antioxidant showed smaller amounts of carbonyl and hydroperoxides than those with no antioxidants. Shearing times in general increases the amount of oxygen containing species in the SBR samples. TEMPO effectively inhibits the production of oxygen containing functional groups by scavenging the macroradicals whilst the degradation is occurring.

The amount of oxygen containing functional groups observed are lesser than those that are thermally degraded in air. This result is substantiated because hydroperoxides are thermally decomposed at high temperature producing alkoxy and hydroxyl radicals, which can be finally converted into carbonyl groups and hydroxyl groups. However, at lower temperatures, hydroperoxyl groups are relatively stable kinetically.

Table 3.2. Table summary of the shearing analysis of SBR. Some polymer melts have no usable soluble samples to be tested. The antioxidant (AO) added is pyrene-derived TEMPO.

Sample	Shearing time/h	Antioxidant (AO)	Mole carbonyl per mole SBR	Mole peroxide per mole SBR	Mole hydroxyl per mole SBR
1	2.638	Without AO	0.002236	1.4475	0.00000892
2	2.601	Without AO	0.00198	2.025	0.00000652
3	3.11	With AO	No soluble samples	0.0347	No soluble samples
4	2.586	With AO	0.0000652	0.00961	No soluble samples
5	2.571	With AO	No soluble samples	0.00342	No soluble samples
6	1.78	With AO	0.00000832	0.00231	No available samples

7	2.221	With AO	0.00010076	0.00312	No available samples
8	2.13	Without AO	0.00315254	0.8355	0.000871
9	2.40	With AO	0.00009821	0.00032	No available samples
10	3.73	With AO	0.0001098	0.007632	0.00000532
11	3.73	With AO	0.000123	0.00632	0.00002121
12	3.73	With AO	No soluble samples	0.00234	No soluble samples

i. Evolution of IR spectra of oxidized SBR samples

Different strategies were undertaken to detect the presence of oxygen-containing species in thermally degraded SBR. The growth of the carbonyl peaks can be observed in IR which is an indication of the oxidation reaction. IR results of thermally degraded samples are compared with the pristine SBR and showed a very weak absorbance on O-H and C=O regions which suggests that the composition of carbonyls and hydroxyls groups in SBR are relatively low. There are weak peaks around 3000 cm^{-1} corresponding to an OH group and around 1750 cm^{-1} region, suggesting carbonyl groups on the oxidised SBR. Figure 3.32 shows the IR spectra of degraded SBR at 60 ^{o}C in air, and the range between 3100 to 3700 cm^{-1} and 1600-1900 cm^{-1} were zoomed in.

With crosslinking proceeding, a broad peak appeared at 3300 cm^{-1} to 3600 cm^{-1}, which was indicated as hydroxyl group. Also, a sharp peak appeared at less than 1700 cm^{-1}, which indicated an unsaturated carbonyl group like ketones, aldehyde etc. This observation is consistent with several studies on SBR and other elastomers [1,2,4].

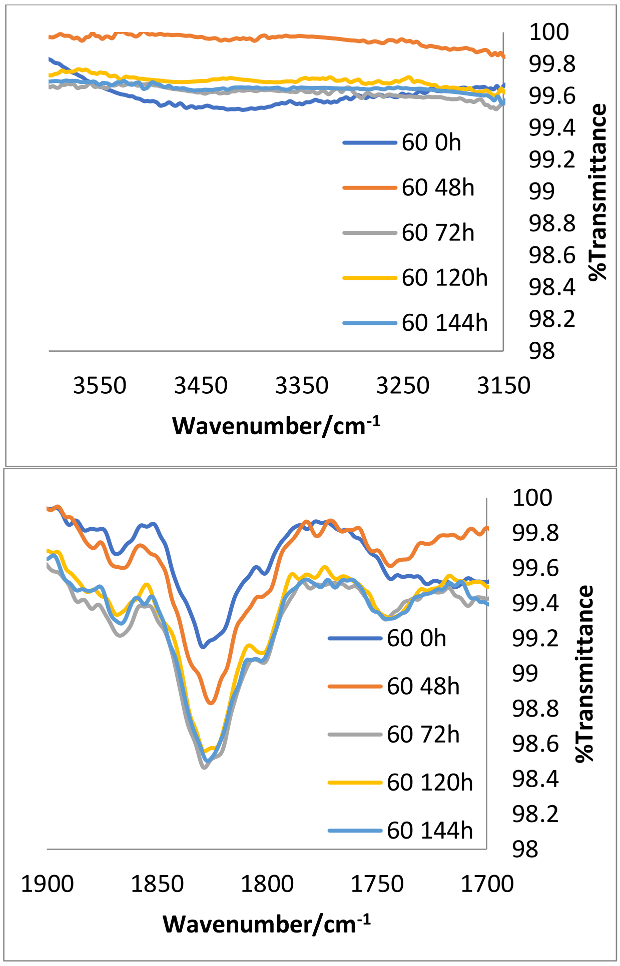


Figure 3.32. Evolution of IR spectra of pristine SBR samples during thermal remodelling 60 °C under aerobic condition.

8. Discussion

Table 3.3. Summary of the reaction of the experiment for thermally oxidized SBR at 60 °C and 80 °C.

	60 °C	80 °C
Formation of insoluble material	Induction period is observed from 0-24 hours and went fully cross linked at 120 hours.	Induction period is observed from 0-7 hours and went fully cross linked at 30 hours.
Formation of hydroperoxides	Accumulation peroxides starts on the 24th hours, gradually increasing until the 120th hour and suddenly decreasing right after.	Accumulation –OOH starts on the 7th hour until the 14th hour where there are no available insoluble materials.
Carbonyl formation	Formation of hydrazone is observed at 48th hour until it went fully cross linked after 120 hours	Formation of hydrazone is observed at 9th hour until it went fully cross linked after 31 hours
Hydroxyl formation	Induction period is observed until the 36th hour then a sudden increase in hydroxyl growth until the 120th hour.	Induction period is observed until the 8th hour and very slowly increasing until the 14h hour
Carboxylic acid formation	Not enough samples for testing the reaction.	Induction period is observed until the 7th hour and very slowly increasing until the 14h hour

The results are obtained from the analyses of SBR at two temperature (60 °C and 80 °C) in air at atmospheric pressure. These results call for the following comments:

a. Role of induction period in thermal remodeling of polymers

Rates of thermal oxidation show carbonyl, hydroxyl and hydroperoxide growth with increasing temperature and time of exposure. As the temperature is increased, the rate of crosslinking also increases and the retrieval of uncrosslinked material is difficult. At lower temperature however, reactions are much slower, and an induction period is evident. As seen in several experiments, induction period is observed at samples heated in 60 °C and much less at 80 °C. All the growth curves done in this experiment display an induction period for samples heated at 60 °C and 80 °C (See table 3.3 for reference). As expected, the production of hydroperoxides, carbonyls, hydroxyls and carboxylic acids are seen to be very slow in the first few hours then increasing abruptly past inflection point as the rubber is converted into its insoluble form.

b. Evolution of functional groups as a function of time of exposure in SBR

As observed, the formation of functional groups is significantly higher in samples heated at 80 °C than 60 °C. Table 3.4 summarizes the results of the detection method for the oxidative degradation of SBR at two specified temperatures. The data gathered in this experiment obeys the same general principle as standard schemes for autoxidation: initiation is exclusively due to the formation of the hydroperoxides decomposition. As the oxidative remodeling of SBR converts the product into high molar mass chains, the production of functional groups occurs.

Evolution curves for samples at 60 °C tend to plateau as the heating time is increased. The amount of oxygen containing functional groups in the soluble rubber are not being consumed in this process. Since we are limited with the soluble part and our resources are not able to detect the progression of degradation on the insoluble species, we cannot account for the functional groups present in them.

c. Correlation of IR analyses with the mechanistic processes of SBR thermal ageing

The formation of functional group in SBR is hardly seen in IR spectra mainly because of the abundance of C-H bonds in ratio with -C=O, -C-O and C-OH bonds. The formation of these bonds despite its quantity is still useful in determining the presence of important functional groups. For example, in Figure 3.29 where the absorbance at 1780 cm^{-1} which is the fingerprint region for carbonyls, particularly the aldehydic carbon, is observed to have a slow but steady formation as time of exposure is increased.

However, most low-resolution IR spectrometers are not able to correctly identify specific carbonyl groups as they overlap, creating a broad band on the fingerprint regions specific for C=O stretch. Confirmatory tests for $-CO_2H$ and -C=O are done in this study to differentiate the carbonyl groups as aldehydic and carboxylic.

9. Summary and Conclusions

Aerobic thermal remodelling is initiated when a macroradical is generated by an unknown mechanism. However, the detection of the end product can give a picture on how these mechanistic schemes work. The methods on the detection on four species, hydroperoxides, carbonyls, hydroxyls and carboxylic acids are investigated in this study. It was found that at lower temperature, the production of oxygen containing functional groups has a slower evolution until the molar mass starts to crosslink. The formation of oxidised species can be summarised as follows: hydroperoxides forms from the initation processes with oxygen molecules. The second one involves the initial oxidation producing the carbonyl groups which was detected by DNPH reactions. Finally the continuous autoxidation of the polymer melts lead to the formation of hydroxyl and carboxyl groups which were detected by the Steglich esterification method. Accumulation of carbonyl compounds and of polymers with masses below that of the original polymer are observed experimentally. High thermal lability of the O-O bond in dialkylperoxides produces pairs of macrolecular alkoxy radicals, resulting in radical chain branching and self-accelerating remodelling.

The analytical method in determining hydroperoxides, carbonyls, hydroxyls and carboxylic acids in oxidized rubbers has been verified by experimentation. The evolution of these oxygen-containing functional groups is dependent in temperature and time. The amount of heating in the presence of air increases the formation of functional groups. Understanding the limitations of reaction systems is important to see how macropolymer behaves ideally in certain chemical environments.

Concerning the DNPH Analysis: The hydrazone attachment can be done by reacting a chromophore in acidic environment. Experiments have shown that increasing the reaction temperature lowers the carbonyl detection and increases the formation of insoluble species. Triphenylphosphine (PPh_3) is shown to be an effective hydroperoxide scavenger on SBR melt. Hydroperoxides in the SBR do not react with DNPH thus the possibility of interferences is low to none.

Concerning Centrifugation and Shaking: The amount of peroxides in SBR have not been affected with the disturbance of the reaction system and dissolution. Hydroperoxides were not seen to proceed to homolytic cleavage when the reactions are shaken.

Concerning the Esterification Processes: Heating the solutions of Steglich esterification does not affect the chromophore yield however the reaction yield of soluble polymers decreases. The increased in temperature of the reaction promote crosslinking of the polymer melt in the solution.

Concerning Shearing and Application of Antioxidants: Shearing of rubber in the presence of air has been analysed to measure the amount of oxygen containing compounds. The addition of antioxidant TEMPO in rubber samples have shown the decrease in the formation of hydroperoxides and carbonyls. Under the aerobic condition, both thermal and mechanochemical remodeling generates fragments and cross-links. However, under shearing, only hydroperoxides are observed. However, fewer oxygenated species are observed in sheared SBR compared to thermally oxidised ones.

10. References

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Chapter IV

Conclusion and Recommendation

The thermal remodeling of SBR is an avenue to understand how polymer behaves in industrial set up. Being one of the most important synthetic materials produced globally, the SBR degradation is highly experimented by polymer scientists. Many researchers have developed methods in understanding the mechanistic schemes of the polymer oxidation however there is still no unified understanding how unsaturated polymers work in a thermally oxidized system. This work aimed to solve one area in SBR chemistry – detection of oxygen containing functional groups in degrading samples. As SBR is subjected to heat in the presence of air, remodeling is inevitable but observable. By understanding the evolution of the end products of degradation, we can have a picture of what is happening in the polymer systems. The importance of selecting the right temperature for this project is crucial for the detection of the desired functional groups. As the temperature of the degradation increases, the faster the conversion from soluble to insoluble product would become. Currently, there are no analytical tools available to understand the chemical components of SBR in its fully crosslinked form.

Concerning Induction Period: Induction period on degradation of polymers is observable at lower temperature. This allows us to understand how a polymer behaves when an external disturbance is applied. The induction periods of each analyses vary and has proven that not all functional groups are evolving at the same time. The lower the degrading temperature, the longer the induction period, thus separating the start of functional group evolution. Hydroperoxides have the shortest induction period followed by carbonyls, hydroxyl and carboxylic acids. The changes in the chemical properties of the SBR are attributed to the increasing of reaction time and temperature which is correlated with the mechanistic illustration of the degradation.

Concerning the DNPH Analyses: 2,4 dinitrophenylhydrazine is an effective reagent in determining the presence of carbonyl groups in polymer chains specifically aldehydes and ketones. In the experiment, SBR-hydrazones can be analysed at lower temperatures to prevent further unwanted kinetically driven reactions. Triphenylphosphine effectively quenched the hydroperoxides in the solution to prevent possible interferences.

Concerning the Diel-Alder Esterification: The attachment of chromophore on long polymer chain is an effective analytical tool in counting functional groups in solution. The reaction of anthracene on the oxidized rubber has been found to be selective and specific that allows us to calculate the amount of hydroxyl and carboxylic groups separately.

Concerning Crosslinking and Chain Scission: Thermal degradation of SBR produces highly reactive macroradicals that reacts to form different products. There are significant changes in the amount of soluble and insoluble materials observed between sample heated in air and inert atmosphere. In an inert environment, alkyl macroradicals are the only reactive species as opposed to an aerobic environment where the production of reactive hydroperoxides is observed. At lower temperatures, the induction period is much more observed in N_2 than in air.

Concerning the Effects of Shearing and Antioxidants (AO): Validated chemical detection of oxygen-containing species can be done on sheared and AO-treated samples. The addition of TEMPO on sheared melt was found to inhibit the production of functional groups. Further analyses on the sheared rubber are done to understand the kinetic parameters of the thermal degradation. Temperature of the shearing processes can also be increased to see the differences in the induction period and production of functional groups.

Understating the molecular mechanism of SBR can be beneficial in polymer industries as it gives insight on polymer degradation and stability. The ageing mechanism of SBR at lower temperatures is an avenue that has been neglected and could be of potential interest for future research. The consumption of rubbers in increasingly demanding industries calls for research in polymer stability to prevent excessive wastage that has a global environmental impact. Analysing the degradation of SBR in air can help develop new ways to improve the chemical integrity of rubber products on the market. The method of detection done in this project is a useful tool in detecting functional groups in rubbers, particularly the unsaturated ones that underwent chemical degradation.

Further work must be done on SBR oxidation to fully understand the complex mechanism of polymer degradation. The results from the experimentations corroborated to what is already known and can be useful in future methods to enhance detection. Avenues for other functional groups such as cyclic ethers, peresters, etc. are also considered.