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# **New styrenic materials, a natural alternative to B in ABS**

ALBERT MARTÍ

Supervisor: Mark Foreman  
Examiner: Christian Ekberg

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ALBERT MARTÍ

Industrial Materials Recycling  
Department of Chemical and Biological Engineering  
Chalmers University of Technology

## **ABSTRACT**

Steps have been made towards a composite containing starch that can replace a plastic based totally on petroleum (ABS) within this project. The synthesis of composites from styrene, corn starch and myrcene and, the extrusion of a composite made of modified starch and high impact polystyrene has been studied. The syntheses of styrene / myrcene copolymers by solution and suspension polymerization have been studied. Selected materials have been subjected to mechanical testing. It has been found that the use of myrcene improved the mechanical properties of the polystyrene based plastic.

**KEYWORDS:** ABS, terpenes, composite, natural, plastic, polystyrene, starch.

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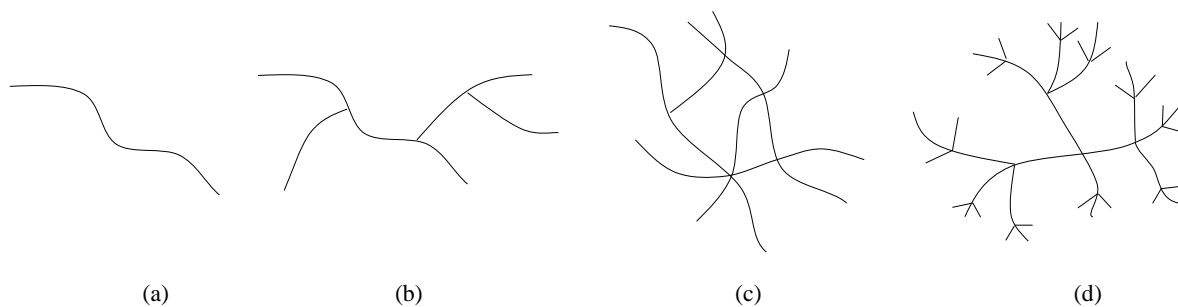
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# 1. Introduction

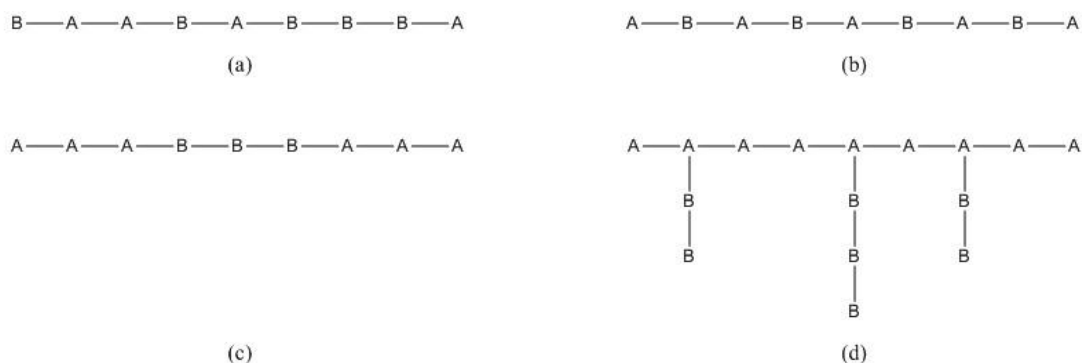
A polymer is a macromolecule composed of many repeating small units, or monomers, connected by covalent bonds. Monomers are joined end to end through chemical reactions with a process known as polymerization. The average number of monomer units in the polymeric chain is the degree of polymerization<sup>1</sup>.

Monomers can be connected in a variety of ways leading different molecular shapes. The simplest is the linear polymer in which the units are connected to each other in a linear sequence. An example of a linear polymer would be high density polyethylene (HDPE). An alternative to the linear polymer is a branched polymer. The side chains, or branches, can be long or short and are bounded to the main chain. When the branches become interconnected network structures form. Network polymers, also called cross-linked polymers, have three-dimensional structures in which each chain is connected to all others by a sequence of junction points or crosslinks<sup>2</sup>. One example of a cross-linked polymer would be an epoxy after curing with ammonia or a polyamine while a second example would be a polystyrene formed with divinylbenzene present. Polymers which have a tree-like shape arrangement of groups around a single point are known as dendrimers. One example of a dendrimer is poly(amidoamine)<sup>3</sup>.



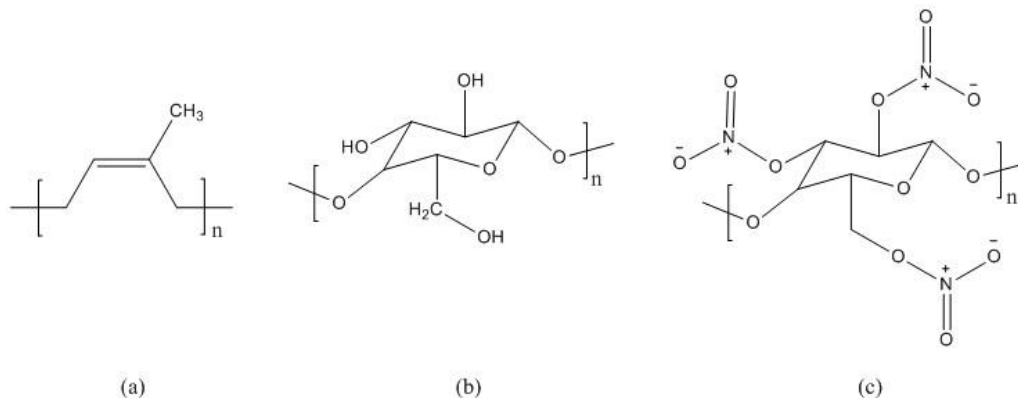
**Figure 1.** The shapes of (a) linear polymer, (b) branched polymer, (c) cross-linked polymer and (d) dendrimers.

A polymer which contains only a single type of repeat unit is defined as a homopolymer. Conversely, a copolymer is a polymer formed by two or more different monomers. Several types of copolymers can be identified depending on the arrangement of the monomers along the polymer chain. When the monomer distribution is arbitrary a random copolymer is obtained. On the other hand in an alternating copolymer the different monomers are arranged alternately along the polymer chain. A strong chemical driving force is needed to make an alternating copolymer. The most common alternating system is the strong electron donor-acceptor combination<sup>4</sup>. In a block copolymer the repeat units exist only in long sequences, or blocks, of the same type. Graft copolymers have the main chain composed of one individual polymer and the branches of another one<sup>1</sup>.

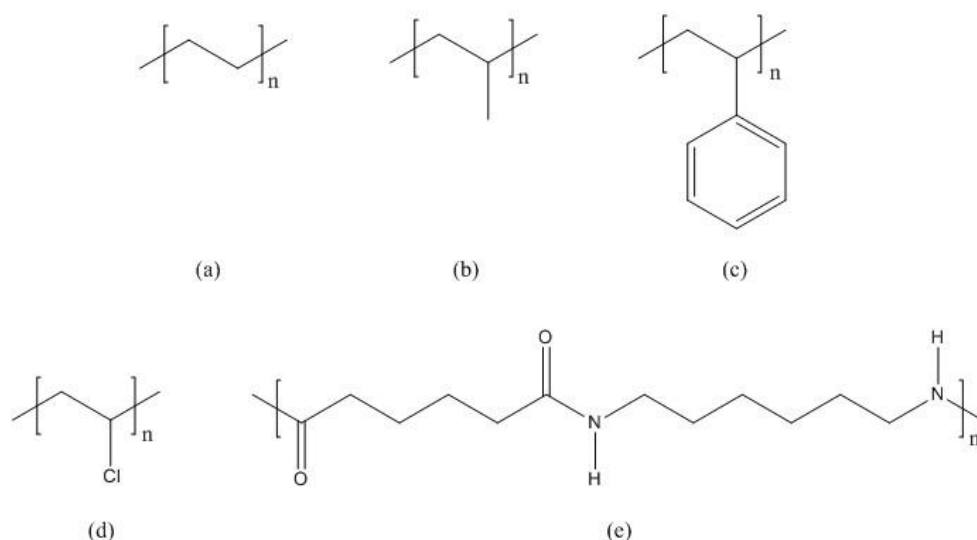


**Figure 2.** The arrangement of the monomers in a (a) random copolymer, (b) alternating copolymer, (c) block copolymer and (d) graft copolymer.

Polymers can be natural, semisynthetic and synthetic. Natural polymers include proteins, cellulose, wool or natural rubber (*cis*-poly(isoprene)). Semisynthetic polymers are obtained by the modification of natural polymers these include nitrocellulose, rayon and vulcanized rubber which are formed from cellulose, cellulose and natural rubber respectively. Synthetic polymers are obtained industrially. Examples include polystyrene (PS), polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC) and nylon 6, 6.



**Figure 3.** The repeating units of (a) *cis*-isoprene, (b) cellulose and (c) nitrocellulose

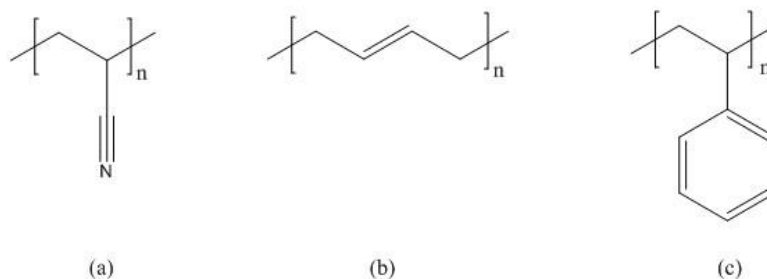


**Figure 4.** The repeating units of (a) HDPE, (b) PP, (c) PS, (d) PVC and (e) nylon 6, 6.

The materials commonly known as plastics are often mixtures of polymers with additives to form solids which can undergo plastic deformation, this allows them to be shaped and moulded. Plastics are often produced from crude oil and natural gas<sup>5</sup>. Depending on the molecular structure of plastics and, consequently, on their response to heating plastics can be classified in two main groups: thermoplastics and thermosets. Thermoplastics include polymers with linear or branched structure that can be melted to be reformed into new object<sup>6</sup>. Some examples are polystyrene (PS), polypropylene (PP) and polyethylene (PE). On the other hand thermosets are rigid polymer networks of high molecular weight. Thus, once formed they degrade rather than melt when they are heated at high temperatures. Examples of this group include Bakelite and most epoxy resins (EP)<sup>7</sup>.

The worldwide annual plastic production increased from 1.5 million tonnes in 1950 to 288 million tonnes in 2012. In the European Union's 27 Member States the plastics industry includes more than 62,000 companies with 1.4 million employees and it generated 26.6 billion euro in 2012<sup>8</sup>. This huge increase of the use of plastics can be justified by their useful properties such as lightness, cheapness and toughness, as well as the simplicity, versatility and rapidity of their processing operations. Plastics play a central role in life today. They are used in many applications such as packaging, building and construction, automotive, electrical and electronics and agriculture<sup>9</sup>. Although packaging is still the major application, high technology applications like aviation and automotive industry are gaining importance.

A commonly used plastic in automotive industry is acrylonitrile-butadiene-styrene thermoplastic (ABS). ABS consists of cross-linked polybutadiene rubber particles which are grafted with styrene-acrylonitrile copolymer (SAN) and embedded in a SAN matrix<sup>10</sup>. The acrylonitrile (A) increases the gloss of the plastic and its weather resistance, the butadiene (B) increases impact strength and the polystyrene (S) improves formability<sup>11</sup>. There are many variables in ABS production such as the rubber particle size and distribution, the amount of SAN grafted to the rubber, the styrene-acrylonitrile ratio and the cross-links density of the rubber. Through variation of these variables many different grades of ABS may be obtained such as high and low viscosity and impact resistance, flame-retardant, in which brominated additives plus antimony oxide are needed, non-flame retardant and glossy or matt grades<sup>10</sup>.



**Figure 5.** The chemical structure of ABS repeating units formed from the different monomers: (a) acrylonitrile, (b) butadiene and (c) styrene.

Some disadvantages of the use of plastics exist. Plastics are more difficult to recycle than traditional materials such as metals and glass because of the degradation of polymer chains<sup>12</sup>. Also their narrow span of densities makes it hard to separate some polymers by density<sup>6</sup>. However, metals, glass and paper have no value as fuels whereas plastics do. The increase of the use of plastics in packaging and agriculture has resulted in serious pollution problems on land and in the sea. Some plastic litter is so light weight that it can be carried by the wind and some plastic waste is able to float on the surface of water. These mobile plastic wastes are able to travel for long distances thus allowing an accumulation of plastic litter in environmentally sensitive areas such as the seashore<sup>12</sup>. Furthermore plastics are often produced from crude oil and natural gas which are non-renewable resources. Recent studies performed by U.S. Energy Information Administration (EIA) have shown that the world production peak for crude oil will be closer to the middle of the 21st century<sup>13</sup>. This prediction is in line with the estimation of the Organization of the Petroleum Exporting Countries (OPEC) which predicts that the world production peak for crude oil will be in approximately 40 years<sup>14</sup>. Therefore a total or partial replacement of petroleum based plastics with biomass based plastics could reduce the world's dependence on oil and offer a means of making plastic after the oil runs out.

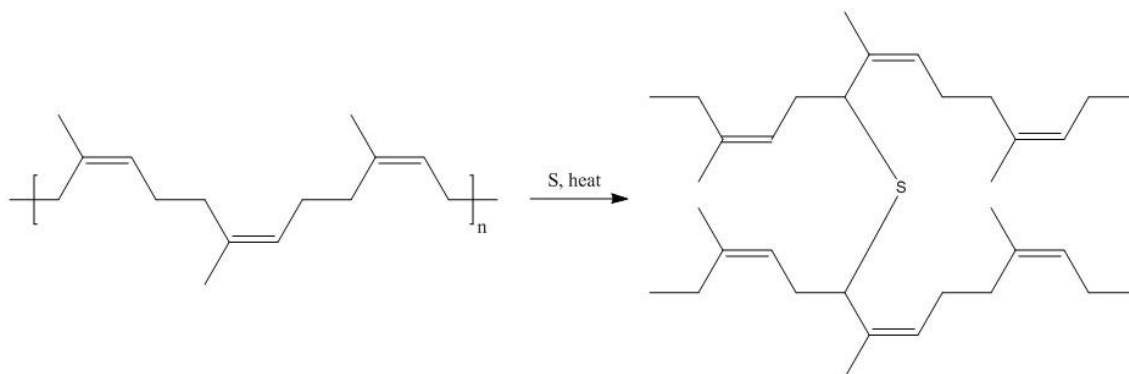
## **1.1. Objective**

The objective of this project is to synthesise a plant based composite that can replace oil based plastics such as ABS. In order to obtain a polymer with suitable mechanical properties two materials will be made and characterised. The first material synthesised was a hybrid plastic partially made from styrene which is a petroleum based compound and two natural compounds: corn starch and myrcene, a terpene that comes from plants such as parsley, hops and bay. The second material was made by extruding a blend of modified corn starch and high impact polystyrene.



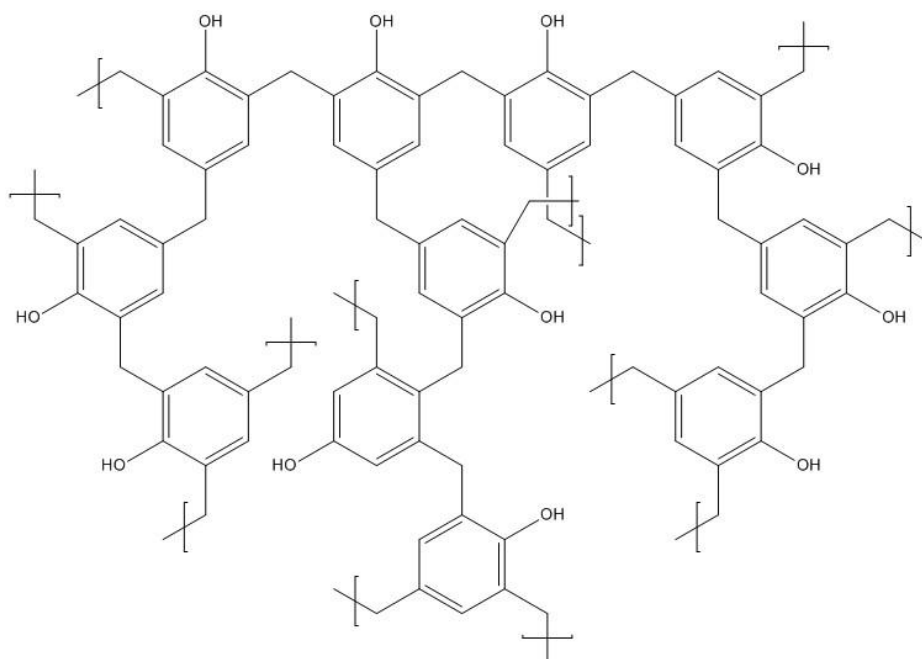
## 2. Background

The origin of modern plastics industry was in the nineteenth century when important discoveries concerning the modification of certain natural polymers were made. In 1839 Charles Goodyear found that the elastic properties of the natural rubber could be improved by heating with sulfur by a process known as vulcanizing<sup>15</sup>. Some of the first plastics products were made using a natural rubber (polyisoprene obtained from a tree) but it was found that chemical modification of this materials improved its mechanical and chemical properties.



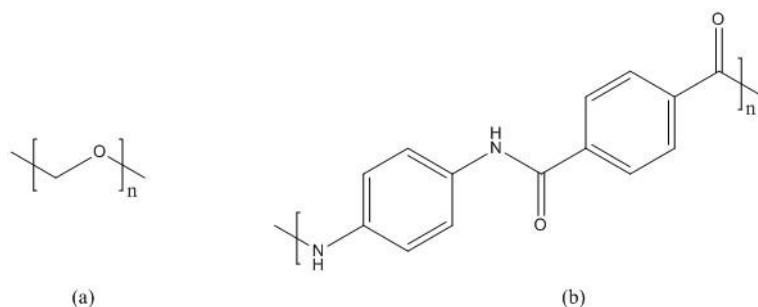
**Figure 6.** The vulcanizing reaction of natural rubber

In 1846 Friedrich Schönbein synthesised cellulose nitrate from cellulose. Highly nitrated cellulose, also called guncotton, is unstable to heat and is currently used widely as an energetic material. However, nitrocelluloses with far fewer nitrate groups per glucose unit can be moulded into different shapes by the application of heat and pressure. In 1868 John and Isaiah Hyaat synthesised a more easily processed material named celluloid from nitrocellulose by using camphor as a plasticiser<sup>1</sup>. Celluloid which was used as an ivory replacement and in photographic materials was the first widely used semisynthetic man-made plastic<sup>16</sup>. In 1909 Leo H. Baekeland discovered the thermoset Bakelite which is formed by reacting phenol with formaldehyde. Bakelite was the first synthetic plastic widely produced<sup>17</sup>. Bakelite was used in many different products including telephones, radios and electric guitars<sup>18</sup>.



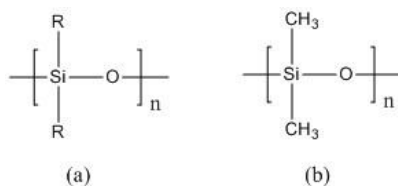
**Figure 7.** A representation of the molecular structure of Bakelite

Despite of these important discoveries there was a considerable lack of understanding of the nature of polymers. It was widely believed that polymers consisted of small joined molecules. The misconception was corrected by Staudinger in 1920. Staudinger stated that polymers were composed of very large molecules containing long sequences of simple chemical units linked together by covalent bonds. He also introduced the word macromolecule to describe polymers<sup>1</sup>. The experiments of Staudinger on the synthesis of polyoxymethylene (polyformaldehyde) and polystyrene and the studies of Carothers on the preparation of polyamides and polyesters in 1929 confirmed the hypothesis<sup>17</sup>. Staudinger concepts enabled a rational interpretation of the previous experiments and set up the bases of the modern polymer industry. In subsequent years a large number of synthetic polymers were produced for the first time on a large scale. These include polyethylene (PE), polystyrene (PS), poly(methyl methacrylate) (PMMA), polyvinyl chloride (PVC) or polytetrafluoroethylene (PTFE), as well as many others<sup>1</sup>. During the Second World War plastics played an important role, e.g. polyethylene as insulation in submarine and radar cables<sup>19</sup> or nylon in parachutes and B-29 bomber tires<sup>20</sup>. After the war plastics industry increased dramatically and a large number of new polymeric materials were produced and used in completely new applications such as silicone gel in breast implants (1962), produced by Dow-Corning (withdrawn from the market over 15 years ago)<sup>21</sup>, and Kevlar® that was developed by DuPont in 1965 for use in a range of products including bullet resistant vests<sup>22</sup>.



**Figure 8.** The repeating units of (a) polyoxymethylene (b) Kevlar

Silicones, which were first commercially produced in the 1940s by Dow Corning, are synthetic polymers whose main chain is made of alternating silicon and oxygen atoms. Typically, each silicon atom is also bounded to methyl groups but many other organic groups can be substituted for the methyl groups along the chain. The basic repeating unit of silicones is known as siloxane and the most common silicone is polydimethylsiloxane (PDMS). Silicones can be used in diverse fields and in numerous applications such as electrical insulation, adhesives, and waterproof coatings and in pharmaceutical and medical device<sup>23</sup>.

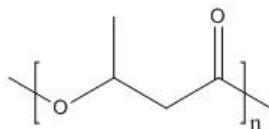


**Figure 9.** The repeating units of (a) siloxane and, if R is CH<sub>3</sub> (b) polydimethylsiloxane

During the last decade to face the problems of plastics accumulation in landfills and the running out of fossil fuels there has been a great effort to develop environmentally acceptable biodegradable polymers from renewable resources.

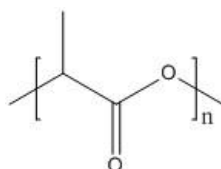
Biodegradable polymers are polymers in which the primary degradation mechanism is performed by the action of microorganisms such as bacteria, fungi and algae. They are degraded into biomass, carbon dioxide and methane<sup>24</sup>.

The search for environmentally acceptable biodegradable polymers based on renewable resources had already begun in the 1980s. The first widely produced fully biodegradable polymer was poly-(3-hydroxy-butyrate) (PHB), developed by microbial fermentation of sugar<sup>24</sup>. The development of a fully biodegradable polymer from renewable resources stimulated the search for other natural based biodegradable polymers.



**Figure 10.** The repeat unit of poly-(3-hydroxy-butyrate) (PHB)

Biodegradable polymers can be classified in two main groups: biopolyesters and agro-polymers. Among the biopolyesters poly(lactic acid) (PLA) is one of the most widely produced due to its relatively low cost and its mechanical properties which are similar to those of polyethylene terephthalate (PET)<sup>25</sup>. Poly(lactid acid) is mainly used in biomedical applications because of its biocompatibility with the human body, as well as in textile industry and packaging<sup>24, 25</sup>. In 2012 the total production volume of poly(lactid acid) was of 180 000 tones and it is expected that in 2017 it will be of 430 000 tones<sup>8</sup>. Thus, poly(lactid acid) based materials are becoming increasingly important.



**Figure 11.** The repeat unit of poly(lactic acid) (PLA)

Also some agro-polymers are renewable polymers which can be extracted from plants with ease. They include three main groups: polysaccharides, proteins and lipids. Polysaccharides are natural polymers which are formed by glucose units linked together in macromolecular chains. Some examples of polysaccharides include starch and cellulose<sup>25</sup>. Currently, starch-based composites are considered one of the most promising biopolymers due to their low cost and availability. Moreover starch based polymers biodegrade into sugars and organic acids which can be then used to manufacture many industrial chemicals thermoplastics, and biofuels. Also the structure of starch composites can be easily chemically modified allowing new functionalities in starch based composites<sup>26</sup>.

The starch industry is one of the largest manufacturing industries in the world. A range of companies over the world such as National Starch, Cargill-Dow, DuPont, Penford, CPC International, Global Starch, National Starch and Chemicals are leading producers of starch-based chemicals<sup>27</sup>.

Recently starch based bionanomaterials have emerged. Starch based bionanomaterials are mainly combinations of polystyrene matrix with nanofillers (e.g. silicates, carbon nanotubes, carbon black (CB), and cellulose) and starch nanocrystals<sup>25</sup>. These bionanocomposites have much better mechanical properties than starch based polymers used for packaging applications. Bionanocomposites are also of great interest in biomedicine and they are used in applications such as tissue engineering, bone replacement or repair, dental applications, and controlled drug delivery<sup>28</sup>.

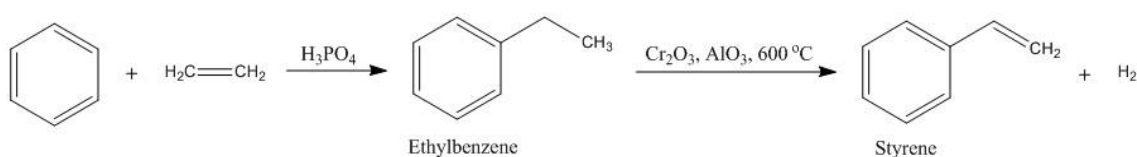
### 3. Theory

#### 3.1. Monomers and fillers

The organic monomers that were used to form the natural based composites in this project are: styrene and myrcene. Alternatively, corn starch and benzyl starch are used as fillers.

Styrene also known as vinyl benzene is the simplest alkenylbenzene. At room temperature pure styrene is a colourless liquid with a strong odour (boiling point: 145.2 °C, melting point: -30.6 °C, density at 20 °C: 0.9060 g·cm<sup>-3</sup>, vapour pressure at 20 °C: 670 Pa)<sup>29</sup>.

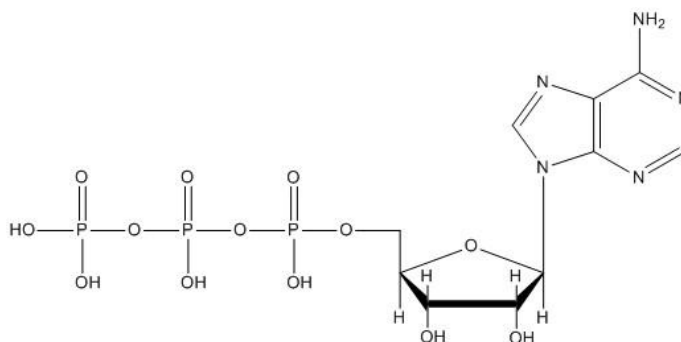
Styrene is mainly produced with a two-step process: alkylation of benzene followed by catalytic dehydrogenation of ethylbenzene. First, benzene is alkylated with ethylene over a solid catalyst to make ethylbenzene by a Friedel-Crafts reaction. In the second step ethylbenzene is dehydrogenated at high temperature (600 °C) in presence of a catalyst<sup>30, 31</sup>.



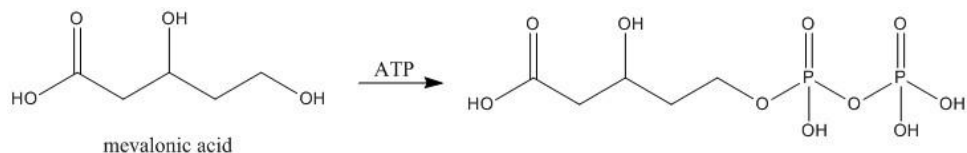
**Figure 12.** A common industrial preparation of styrene

Benzene and ethylene (ethene) are commonly obtained from petroleum and coal. Benzene and ethylene can be obtained from other processes. Benzene can be formed from alkanes (found in petroleum) by catalytic reforming and ethylene can be obtained from diesel fuel, naphtha and liquefied petroleum gas (LPG) by steam cracking<sup>32</sup>.

Myrcene is a terpene obtained from barberry wax and from oils of bay and verbena. Terpenes are volatile constituents of plants resins and essential oils. The essential oils are extracted from plants by distillation<sup>33</sup>. The main characteristic of the structure of terpenes is that their carbon skeleton can be divided into two or more isoprene units. This is known as the isoprene rule<sup>34</sup>. However recent research have shown that not isoprene but mevalonic acid is the true precursor of terpenes. Mevalonic acid is formed from three acetate units. To synthesise terpenes such as myrcene the pyrophosphorylation of the primary alcohol with ATP is carried out. Pyrophosphorylation involves the transfer of phosphate groups (PO<sub>4</sub><sup>3-</sup>) from ATP to mevalonic acid. The removal of these groups supplies the energy required to carry out the chemical reaction<sup>33</sup>.

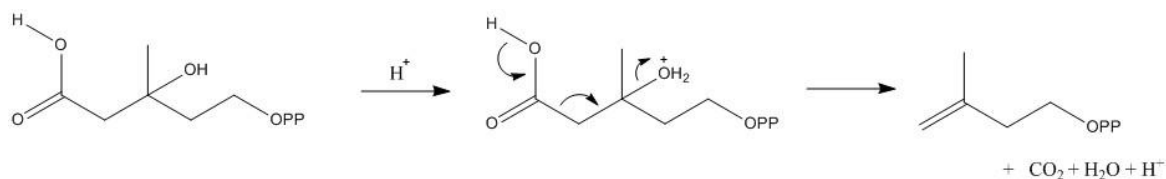


**Figure 13.** The molecular structure of adenosine triphosphate (ATP)

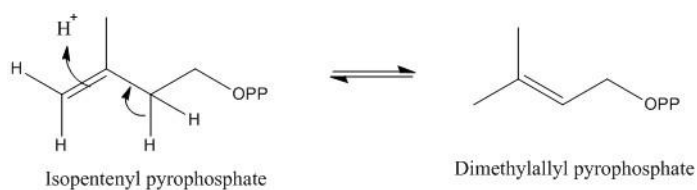


**Figure 14.** The pyrophosphorylation of mevalonic acid with ATP

In the next step mevalonic acid loses one carbon in  $\text{CO}_2$  form by elimination reaction to give a five carbon precursor. Isopentenyl pyrophosphate is in an equilibrium with dimethylallyl pyrophosphate by allylic proton transfer<sup>33</sup>.



**Figure 15.** The elimination reaction



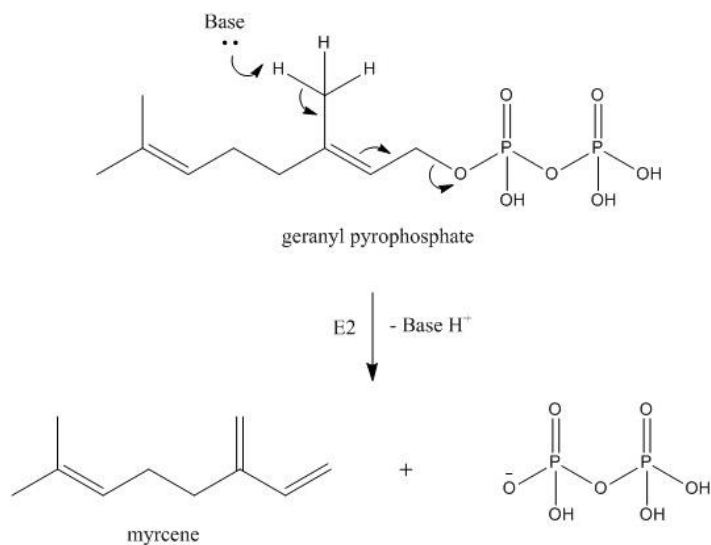
**Figure 16.** The allylic proton transfer equilibrium of mevalonic acid products

The two five carbons intermediates react with each other to produce geranyl pyrophosphate.



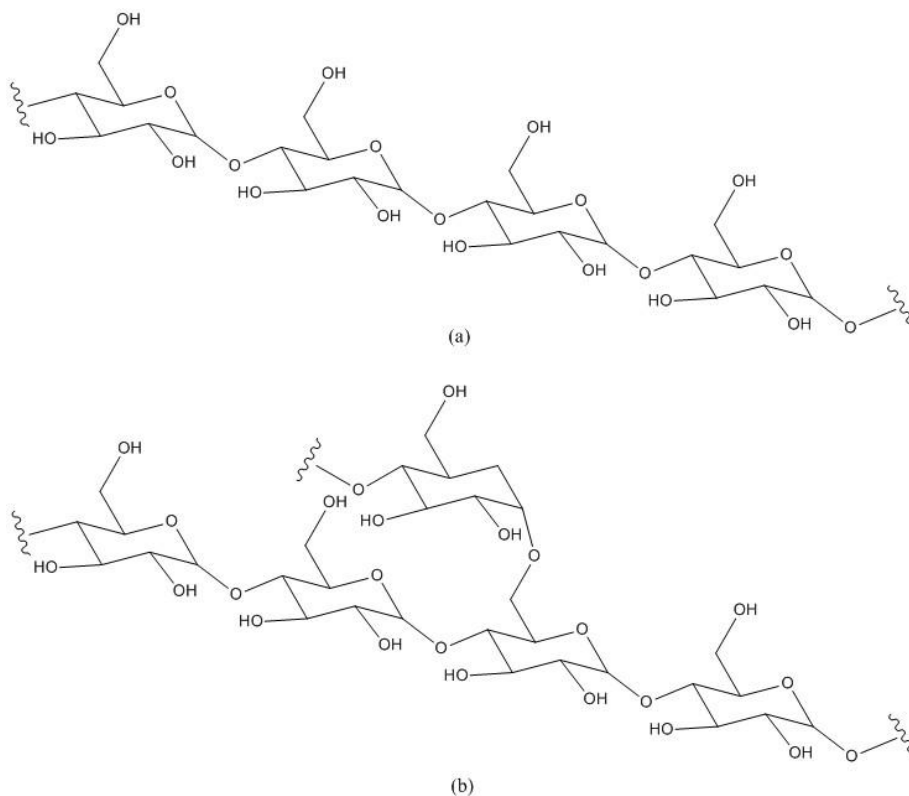
**Figure 17.** The formation of geranyl pyrophosphate

Geranyl pyrophosphate is the starting point for all terpenes with ten carbons, also known as diterpenes, such as myrcene. In particular myrcene can be produced by E2 elimination in presence of a base.



**Figure 18.** The synthesis of myrcene by E2 elimination from geranyl pyrophosphate

Starch is one of the most abundant polysaccharides in nature and it is produced by plants such as potato, corn and rice. Amylose and amylopectin are the two major components of starch. Amylose has a linear structure and is made principally of glucose units linked at 1 and 4 sites. On the other hand amylopectin is highly branched and is formed by glucose units linked at 1 and 4 sites and glucose units linked at 1 and 6 sites at the branch points.

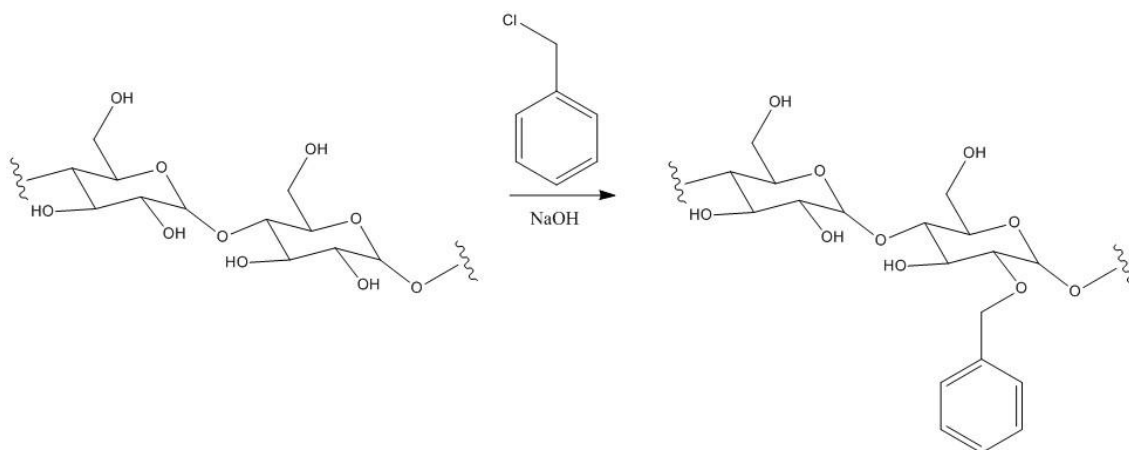


**Figure 19.** A short section of an amylose chain (a) and an amylopectin chain (b)

Different starches have different proportion of amylose and amylopectin in their structure. Corn starch was used in this project work, it is very branched because it has a high concentration of amylopectin whereas potato starch is almost completely linear (almost pure amylose)<sup>27</sup>.

Corn starch is obtained from the tissue that surrounds the embryo of the corn grain and refined by a wet milling process. At first, the corn is cleaned and soaked in steep water at 50 °C for 20 to 48 hours to extract soluble materials from the grain. The steep water contains small quantities of sulfur dioxide (SO<sub>2</sub>) to prevent the growth of bacteria and to facilitate the separation of starch and protein. When the steeping is finished the corn is milled. The steep water is concentrated by evaporation and used to produce animal feed products, while the grain is ground in an attrition mill to separate the germ from starch, hulls and gluten. Then water is added to the mill and a mixture of whole germs and macerated slurry is obtained. The slurry is added to a hydroclone separator to remove the corn germ from the mixture. The extracted germ is dried and sold for further processing into corn oil. The slurry is then ground a mill. After the grinding the hull particles are caught on screens, while the starch and gluten pass through. Next, the mixture of starch and gluten is separated by centrifugation. The gluten is dried and used in animal feed. Finally the starch is washed and dewatered and is either sold as corn starch or further processed into other products such as syrups and ethanol<sup>34,35</sup>. The largest producer of corn starch is the United States of America but this product is also produced in South America, Europe and Asia.

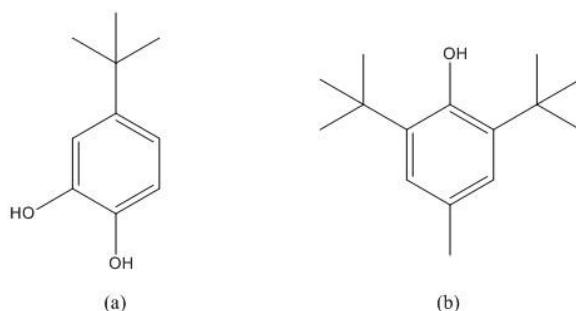
The other filler used in this project is benzyl starch. This benzyl starch was obtained by benzylation of corn starch in a sodium hydroxide solution. The alkylation agent used is benzyl chloride, an alkyl halide. In the reaction sodium hydroxide randomly deprotonates one of the three hydroxyl groups that are present in the glucose molecule. The alkoxide thus formed is alkylated in a S<sub>N</sub>2 reaction. An example benzylation reaction of an amylose starch is shown below.



**Figure 20.** The benzylation of pure amylose starch

The addition of the benzyl groups to corn starch was intended to increase the compatibility of starch with polystyrene-myrcene copolymer as the benzene rings in benzyl starch are able to interact with benzyl rings in polystyrene through  $\pi$ - $\pi$  effects<sup>36</sup>. Benzyl starch has been found by others to be compatible with polyurethanes formed from 4,4-Diphenylmethane diisocyanate (MDI)<sup>37</sup>.

Most of the monomers that are commercially distributed contain a stabilizer to prevent premature polymerization during the transport and storage of the monomers. An inhibitor is a substance that reacts with the free-radical active centre to produce species which are not capable of undergoing the polymerization reaction. 4-tert-butylcatechol is the inhibitor present in styrene and butylated hydroxytoluene (BHT) is present in the myrcene purchased from Aldrich. Therefore styrene and myrcene must be destabilized before carrying out the polymerization reactions



**Figure 21.** The molecular structures of (a) 4-tert-butylcatechol and (b) butylated hydroxytoluene (BHT) inhibitors

### 3.1.1. Destabilization of styrene

Styrene can be destabilized by extracting 4-tert-butylcatechol inhibitor from styrene with sodium hydroxide using gravity to separate the layers. This is an extraction of an organic acid where polystyrene is the organic phase and the aqueous phase is the solution of sodium hydroxide (2 M). According to the Nernst distribution law the distribution ratio  $D_{HA}$  can be defined. As only one chemical form of the protonated acid exists then  $K_D$  and  $D$  are the same:

$$HA(aq) \leftrightarrow HA(org) \quad D_{HA} = [K_{D,HA}] = \frac{[HA]_{org}}{[HA]_{aq}} \quad (1)$$

But if the organic acid dissociates in the aqueous phase the equation describing the distribution ratio becomes more complex:

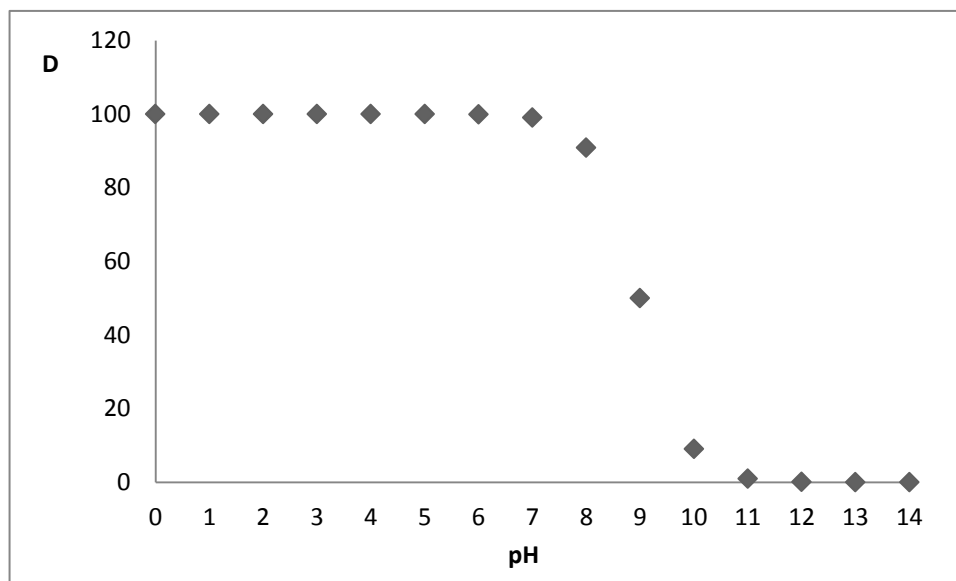
$$D_A = \frac{[HA]_{org}}{[HA] + K_a[H^+]} \quad \text{where} \quad K_a = \frac{[H^+][A^-]}{[HA]} \quad (2)$$

If equation (1) and (2) are combined the following equation is obtained<sup>38</sup>:

$$D_A = \frac{K_{D,HA}}{1 + \frac{K_a}{[H^+]}} \quad (3)$$



If arbitrary values of 100 for  $K_{D,HA}$  and 0 for  $K_{D,A}$  are assumed and when the  $pK_a$  is set at 9 (phenol relative to water)<sup>38</sup> the following graph of  $D_A$  versus pH can be plotted.



**Figure 22.** The distribution ratio of 4-tert-butylcatechol ( $pK_a = 9$ ) in different pH and with arbitrary values of  $K_D$  for the protonated and deprotonated forms of the compound

So a sodium hydroxide solution is shaken with the styrene and its inhibitor, the inhibitor is extracted into the aqueous layer. As it can be seen in figure 22, at alkaline pH the distribution ratio of 4-tert-butylcatechol is very small which means that the fraction of the inhibitor in the aqueous phase is large.

### 3.1.2. Destabilization of myrcene

Myrcene can be destabilized by separating myrcene from butylated hydroxytoluene by steam distillation. Steam distillation is a technique used to distill immiscible mixtures formed by an organic compound and water. The method is based on the fact that the total vapour pressure is the sum of the vapour pressures of each pure component which are independent of the other. As the liquids are not miscible the activities are independent of the mole ratio of the two liquids. Hence, when the sum of the individual vapour pressures equals the atmospheric pressure the mixture boils at a lower temperature than either of the pure liquids<sup>39</sup>.

As an example of this method a mixture of two components, water and aniline, can be considered. The vapour pressure as function of temperature of the components can be calculated with the Clausius-Clapeyron equation.

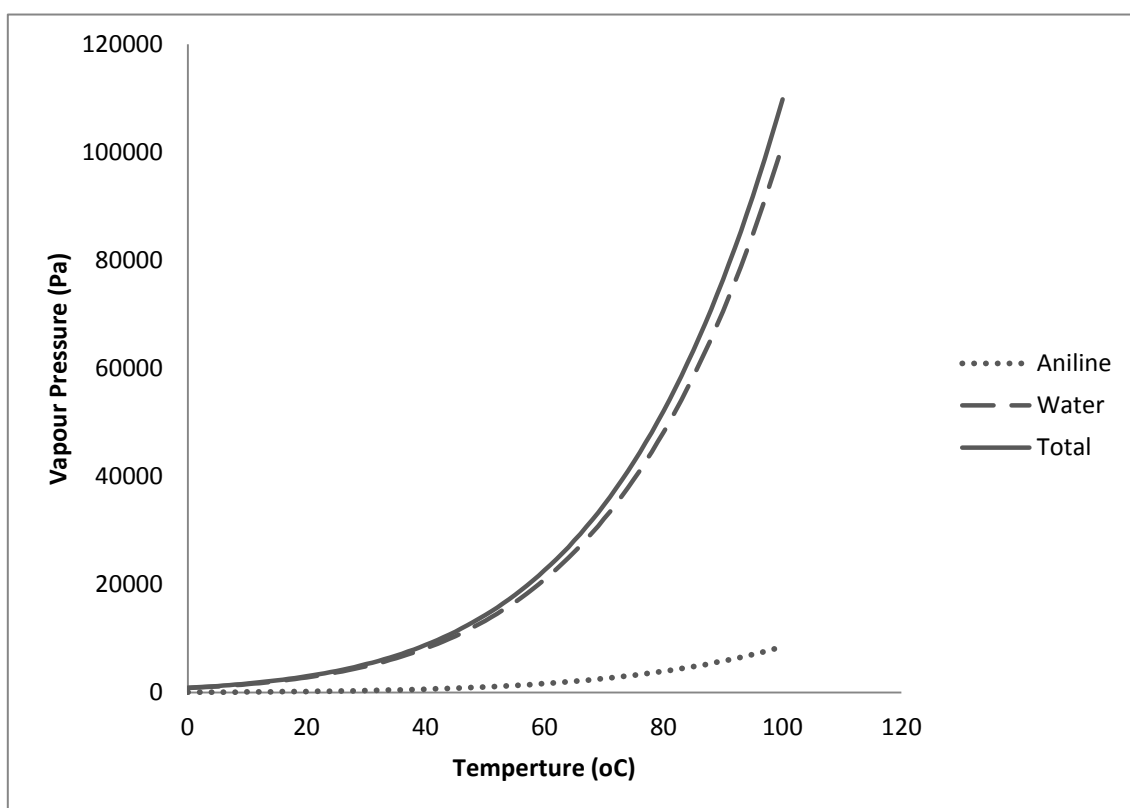
$$\ln \frac{P_2}{P_1} = \frac{L}{R} \cdot \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (4)$$

Where P is the vapour pressure, L is the  $\Delta H$  of vaporization, R is the specific gas constant and T is the temperature.

**Table 1.** The boiling point and the DeltaH of vaporization for each component<sup>40</sup>

Substance	Boiling Point at 760 mmHg (°C)	$\Delta H_{\text{vap}}$ (kJ·mol <sup>-1</sup> )
Water	100	40.7
Aniline	184	41.9
Gallium	2400	258
Mercury	357	59.11

The total vapour pressure and the vapour pressure of each component as function of temperature can be plotted.



**Figure 23.** The vapour pressure as a function of the temperature for every component and for the mixture

At 97.73 °C the sum of the individual vapour pressures equals the atmospheric pressure, hence the mixture boils. This only applies to pairs of immiscible liquids.

$$P_{\text{total}} = P_{\text{water}} + P_{\text{anyline}} = 93527.3 + 7797.7 = 101325 \quad (5)$$

Thus, by using this technique aniline can be distilled below 100 °C even though its boiling point is 184 °C.

The relative amount of aniline in the vapour phase, and hence the distillate, is directly proportional to the individual vapour pressures.

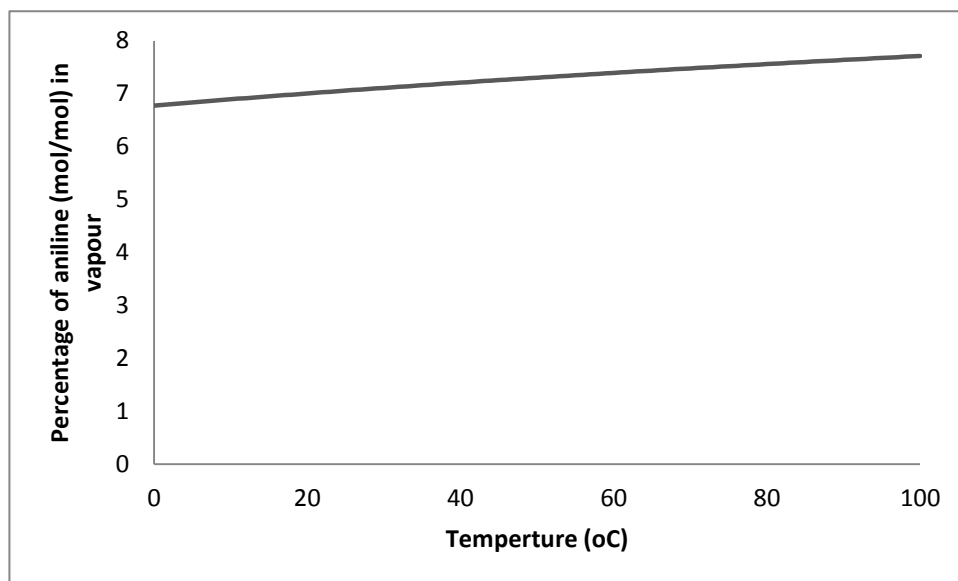


Figure 24. The percentage of aniline in the vapour phase

Another example that can be considered is a mixture of gallium and mercury. In this case unlike aniline and water both substances are fully miscible with each other. Assuming that the activity coefficients are all equal to 1 the total vapour pressure and the vapour pressure of a 1:1 (by moles) of mixture mercury and gallium can be calculated as a function of the temperature.

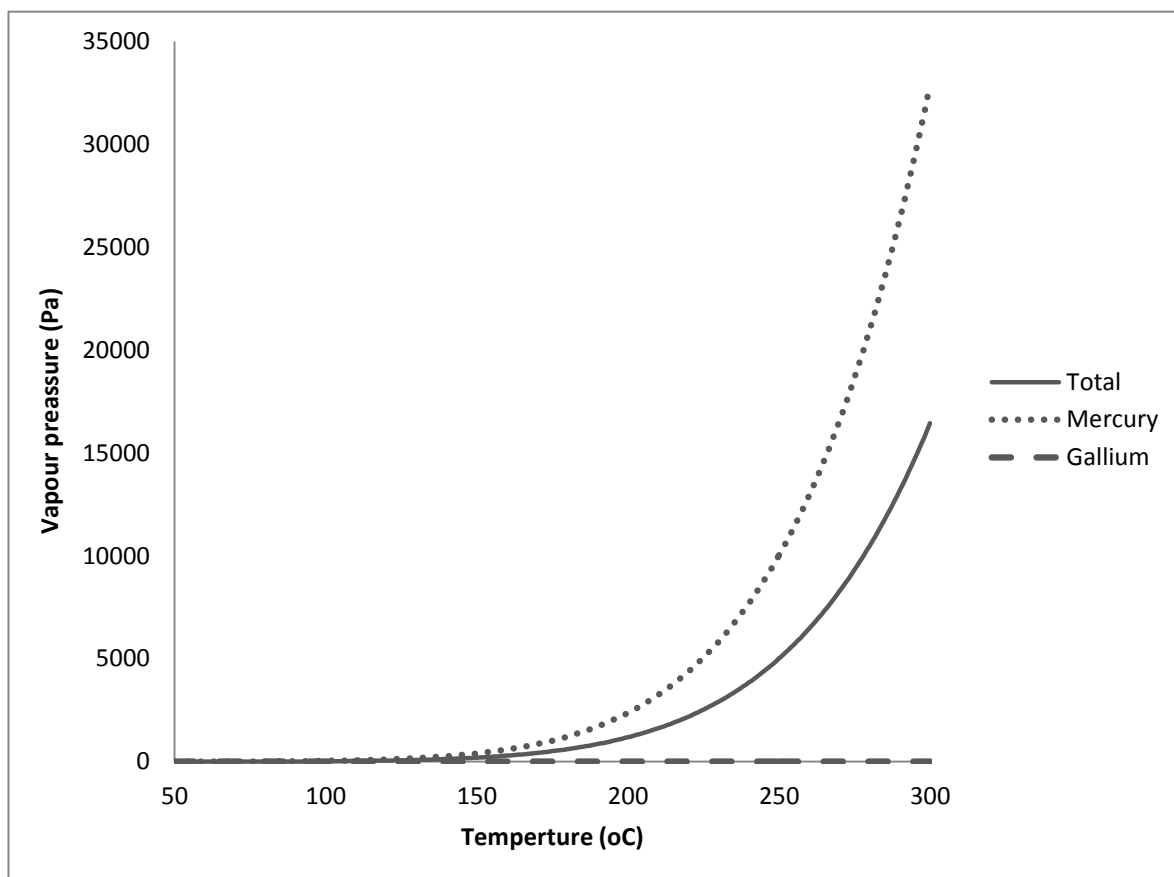
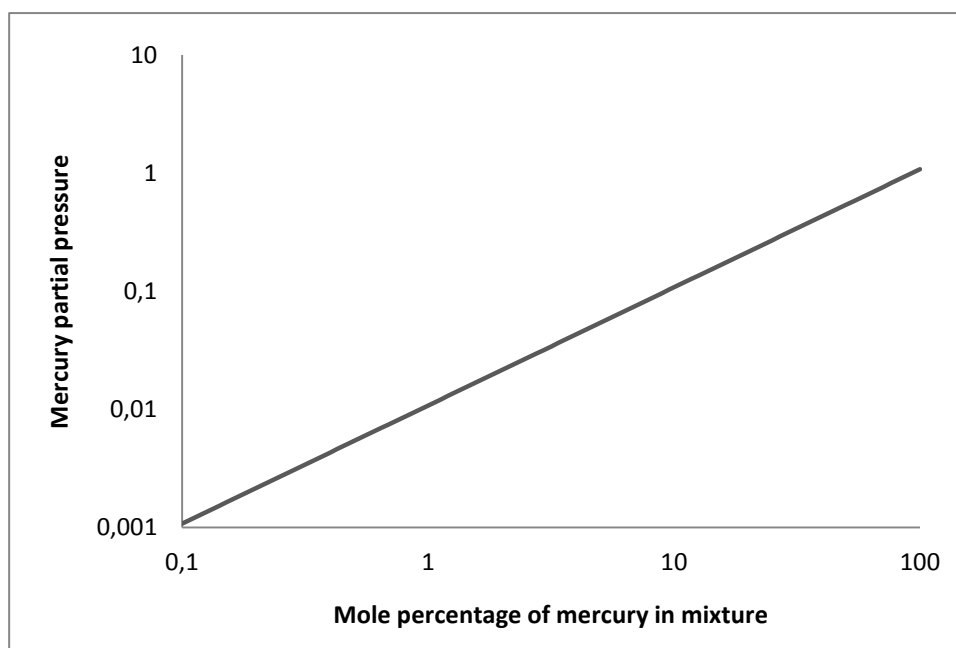


Figure 25. The vapour pressure of the two components as a function of the temperature (over the range 50 to 300°C)

The partial pressure of a component in a mixture is equal to the vapour pressure of the pure component at that temperature multiplied by its mole fraction in the liquid. This is known as the Raoult's Law and it only works for ideal mixtures.



**Figure 26.** The mercury partial pressure as a function of the mole percentage of mercury in the mixture

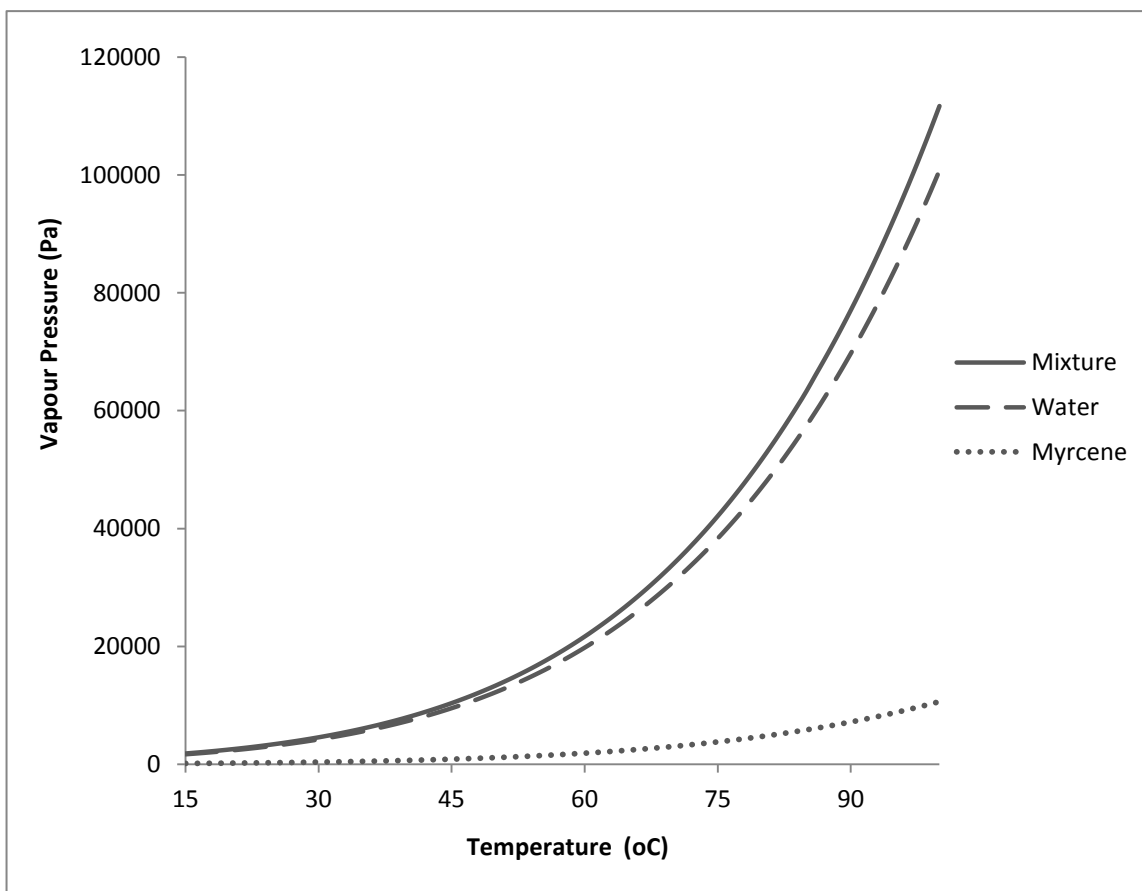
Thus, the addition of the gallium to the mercury lowers the vapour pressure of the mercury. This explains how the addition of zinc dust to the cracks in a mercury contaminated floor will lower the concentration of mercury in the air of the room.

The mixture that was to be steam distilled in this project has three components: water, myrcene and butylated hydroxytoluene (BHT) (boiling point: 265 °C<sup>40</sup>). As the vapour pressure of BHT it is so low it will be ignored in the equations that have been explained above.

**Table 2.** The boiling point and the DeltaH of vaporization for each component<sup>40</sup>

Substance	Boiling Point at 760 mmHg (°C)	$\Delta H_{\text{vap}}$ (kJ·mol <sup>-1</sup> )
Water	100	40.7
Myrcene	171	38.7

The total vapour pressure and the vapour pressure of each component as function of temperature can be plotted.



**Figure 27.** The vapour pressure as a function of the temperature for every component and for the mixture

At 97.4 °C the sum of the individual vapour pressures equals the atmospheric pressure, hence the mixture boils.

$$P_{\text{total}} = P_{\text{water}} + P_{\text{myrcene}} = 91712 + 9612 = 101325$$

The relative amounts of each component in the vapour phase, and hence the distillate, can be calculated. The amount in moles of each component in the vapour phase is directly proportional to their individual vapour pressures:

$$\frac{\text{no. of moles of myrcene}}{\text{no. of moles of water}} = \frac{9612}{91712} = 0.105$$

Therefore the distillate contains 0.105 mole myrcene per mole of water. Translated into weight, the distillate contains 14.3 g myrcene per 18 g of water, or *circa* 45% myrcene by weight. Thus, by using this technique myrcene can be separated from butylated hydroxytoluene and any polymeric impurities by distillation below 100 °C even though its boiling point is 171 °C.

After carrying out the steam distillation of myrcene, water and remaining traces of BHT are removed from myrcene by using the same method as that used for styrene.

### 3.2. Plant-based materials synthesis

Three plant-based materials were synthesised: a polystyrene-myrcene copolymer, a polystyrene-myrcene-corn starch composite and a polystyrene-myrcene-benzyl starch composite. In all cases the chemical reaction is a free radical chain-growth polymerization reaction. In chain-growth addition polymerization there is a series of reactions each of which consumes a reactive species and produces another similar species. Therefore each individual step requires the reactive species formed in the previous one. The reactive species can be free radicals, cations, or anions<sup>41</sup>. In the polymerization reactions of the three plant-based materials the reactive particle involved is a free-radical. Free radicals have the advantage of being very mobile in most solvents as they are often weakly bonded (solvated) to the solvent.

In addition to the general class of the synthesis reaction (addition vs condensation) the reaction conditions determine the polymer structure and, consequently, the polymer properties. For example the same monomer in an emulsion polymerization can form very fine particles while larger particles are formed in suspension polymerizations.

The same monomer can react in two different addition reactions to form different products. For example the conversion of ethylene (ethane) into polyethylene. The high pressure free radical polymerization of ethylene produces side branched polyethylene. On the other hand ethylene polymerized with Zeigler-Natta catalyst (a non radical process) is very linear. The branched polyethylene also known as low density polyethylene (LDPE) is flexible, is a good electrical isolator and has a low tensile strength. It is used to make plastic film wrap, cables, bags and plastic items that need to be moulded. Linear polyethylene also known as high density polyethylene (HDPE) is stronger and more resistant to chemicals than low density polyethylene and it is mainly used for items requiring blow moulding techniques, such as toys, automobile parts and bottles<sup>7</sup>. Thus, LDPE and HDPE are completely different polymers even while they are formed from the same monomer.

Two other important related factors that must be considered during polymer synthesis are viscosity and heat dissipation. Polymer melts and polymer solutions have a very high viscosity because of the shape and length of their molecular chains. During the polymers synthesis the viscosity of the reaction mixture increases greatly. This can cause difficulties in pumping, stirring and heat dissipation. Heat dissipation is crucial as nearly all chain growth polymerizations are strongly exothermic and polymers are poor conductors of heat. Inefficient removal of heat can lead to an autoacceleration and to a fast increase of the temperature. The autoacceleration of the polymerization reaction is known as the gel effect. The gel effect is consequence of the increase in viscosity of the reaction mixture due to the formation of polymer molecules that slow termination reactions. (The gel effect will be discussed later in great detail).

The gel effect can be avoided by carrying out the polymerization reaction at low conversions as gel effect occurs at intermediate or high degrees of conversion<sup>42</sup>. Alternatively the monomer can be diluted in a solvent which reduces the increase of viscosity.

There are many different methods to perform free-radical polymerization. In this project work the polystyrene-myrcene copolymer will be synthesised by the solution polymerization method and the polystyrene-myrcene-corn starch composite and a polystyrene-myrcene-benzyl starch composite will be synthesised by the suspension polymerization method.

The solution polymerization method is characterised by the addition of a solvent to the reaction mixture to reduce the viscosity and facilitate heat dissipation reducing the risk of autoacceleration. However this solvent addition has some disadvantages. The rate and degree of polymerization are reduced as the monomer concentration is decreased. Also the solvent has to be carefully chosen as it can lead to a further reduction in the degree of polymerization.

Furthermore, the polymer obtained has to be separated from the mixture by either evaporation of the solvent or precipitation of the polymer by adding the solution to an excess of non-solvent. For these reasons solution polymerization is only used in industry to produce polymers that later on will be used in solution<sup>43</sup>. Some examples include surface coatings and industrial glues.

Another way to solve the viscosity and heat dissipation problems is the suspension polymerization method. In this method the reaction mixture is suspended as small droplets in an inert non-solvent medium. Each droplet acts as a small bulk reactor and it is suspended by agitation and by dispersing agent such a surfactant or inert solid. The high surface area of the droplets and the low viscosity of the aqueous continuous phase allows good heat dissipation which helps to keep the rate of reaction under control despite the autoacceleration. The product is obtained in the form of beads (typically 0.1-2 mm diameter) and can be easily separated by filtration. This polymerization method is widely used on an industry scale to produce polystyrene, polyvinylchloride and poly(methyl methacrylate)<sup>43</sup>.

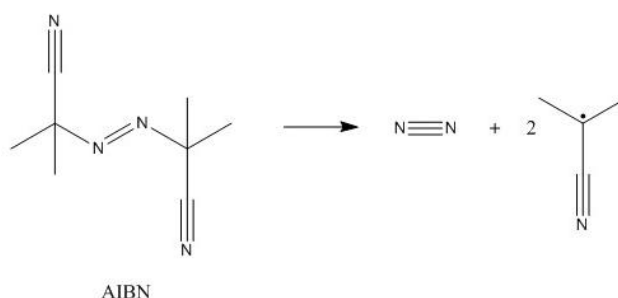
In the case of the production of the polystyrene-myrcene-corn starch composite corn starch rather than being incorporated into the solid polymer it acts as a dispersing agent during the suspension polymerization method and as a filler of the final composite.

In the polystyrene-myrcene-benzyl starch composite production the benzyl starch is also used as a dispersing agent and as a filler. The benzyl starch is less hydrophilic than untreated starch. As the benzene rings in benzyl starch interact with benzyl rings in styrene and polystyrene through  $\pi$ - $\pi$  effects the styrene is more able to wet the benzyl starch. Hence, it was expected that the benzyl starch will form a solid which is more compatible with polystyrene-myrcene copolymer than untreated corn starch<sup>36</sup>.

As explained above the three plant-based materials synthesised are formed by a free-radical polymerization reactions in which the monomers were converted into polymers. This polymerization mechanism can be divided in three main steps: initiation, where the free radicals are formed, propagation, where the products are evolved, and termination, when the active centres are deactivated.

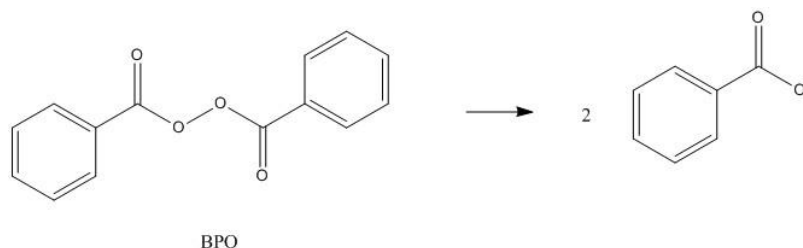
### 3.2.1.1. Initiation

Initiation is the first step of the free-radical polymerization mechanism. In this step free radicals are formed by the decomposition of an initiator. The initiator used was AIBN (2,2'-Azobis(2-methylpropionitrile)) which is a thermal initiator and one of the most important azo compounds. AIBN breaks down to form two free radicals as shown in the reaction below<sup>44</sup>.



**Figure 28.** The thermal decomposition of AIBN

Another substance that is commonly used as an initiator is benzoyl peroxide (BPO). Benzoyl peroxide is also a thermal initiator and it decomposes as follows<sup>44</sup>:



**Figure 29.** The thermal decomposition of BPO

However, in this project AIBN is used instead of benzoyl peroxide because benzoyl peroxide is explosive. It can ignite at temperatures above 80 °C and it is also sensitive to shock and friction<sup>45</sup>. The storage and use of explosives in industrial materials recycling is forbidden as it would violate the radioactivity license of nuclear chemistry.

The decomposition of AIBN follows a first order rate law because at a given temperature and in a given solvent the reaction rate depends linearly only on the AIBN concentration.

$$\text{Reaction Rate} = -\frac{d[\text{AIBN}]}{dt} = k \cdot [\text{AIBN}] \quad (6)$$

The reaction rate has units of moles per time and  $k$  is the rate constant ( $\text{time}^{-1}$ ). Moreover the time required for half of the quantity of AIBN to be decomposed ( $t_{1/2}$ ) can be calculated with the following equation for a first order reaction:

$$t_{1/2} = \frac{\ln 2}{k} \quad (7)$$

Using the Arrhenius equation, the exponential decay law, and decomposition rate ( $k_d$ ) data obtained at different temperatures the amount of AIBN is required for the polymerization reaction at a different temperature and total reaction time can be predicted.

**Table 3.** The decomposition rates for AIBN at different temperatures with Benzene as a solvent<sup>46</sup>.

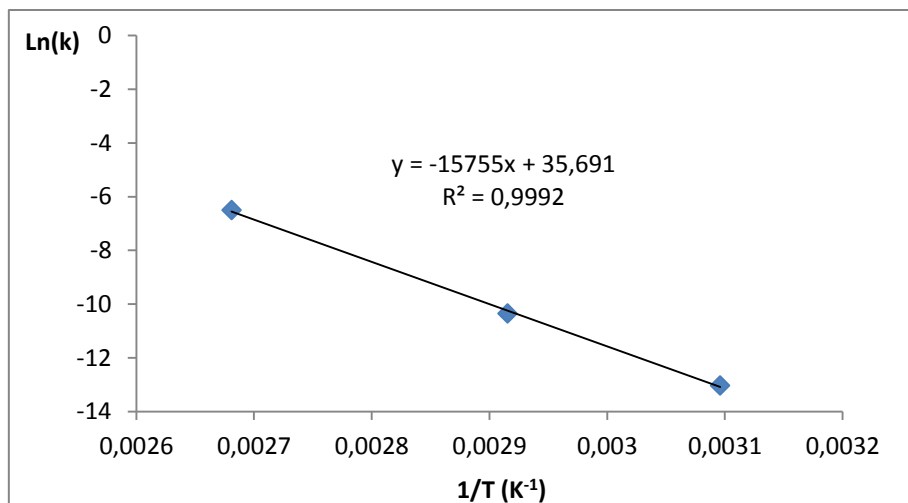
Temperature (°C)	Decomposition rate ( $k_d$ ) ( $\text{s}^{-1}$ )
50	$2.09 \cdot 10^{-6}$
60	$8.45 \cdot 10^{-6}$
70	$3.17 \cdot 10^{-5}$

Using a semi-logarithmic graph the Arrhenius equation can be used to make a prediction of the decomposition rate at a new temperature.

$$k(T) = A \cdot \exp\left(\frac{-E_a}{R \cdot T}\right); \quad \text{then } \ln(k) = \ln(A) - \frac{E_a}{R \cdot T} \cdot \left(\frac{1}{T}\right) \quad (8)$$

Where  $A$  is a pre-exponential factor,  $E_a$  is the activation energy,  $R$  is the universal gas constant and  $T$  is the temperature (K). It is important to note that if the solvent is changed then both the activation energy and the pre-exponential factor can change.





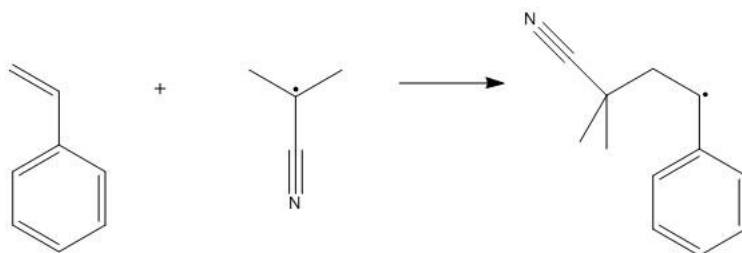
**Figure 30.** The Arrhenius equation

Once the decomposition rate is known the exponential decay law can be applied to determine how much AIBN is left after a desired reaction time or, equally, how much AIBN has been consumed.

$$N(t) = N_0 \cdot \exp(-k \cdot t) \quad (9)$$

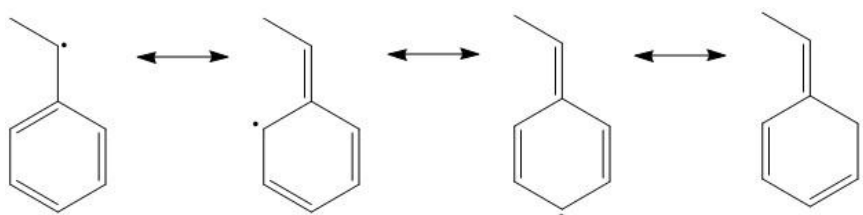
Where  $N$  is the quantity of AIBN at reaction time  $t$ ,  $N_0$  is the initial quantity of AIBN and  $k$  is the decomposition rate ( $\text{time}^{-1}$ ).

When then initiator has been decomposed the free radicals generated are added either to the double bonds of styrene or myrcene monomers. The reaction of styrene with the 2-cyanoprop-2-yl radical is shown below.



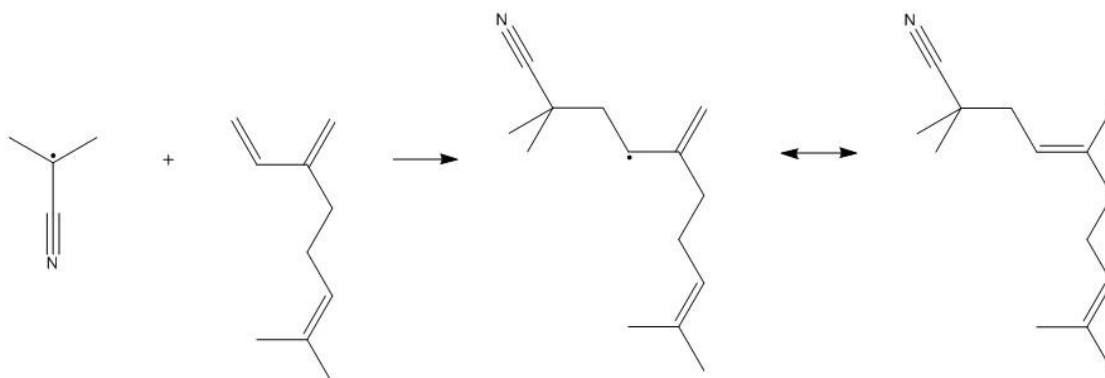
**Figure 31.** The initiation step of styrene

The reason why this styrene free radical, rather than the other possible radical, is formed is because it is stabilized by resonance as shown in the figure below.

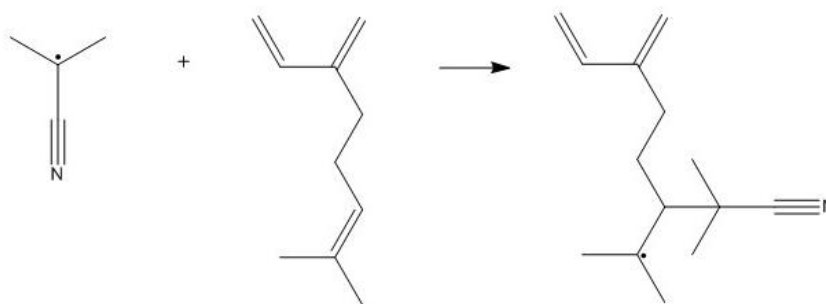


**Figure 32.** The free radical stabilization by resonance of Styrene

Myrcene monomers, as well as styrene monomers, have more than one double bond so different free radicals can be formed. However, in reality only the free radical formation reaction of myrcene shown in figure 34 occurs. This is because the free radical formed with this reaction is more stable than the one produced with the reaction of figure 35 as it is stabilized by resonance.



**Figure 33.** The Initiation step of myrcene

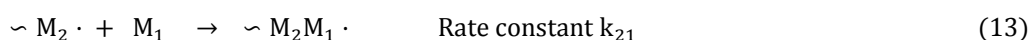
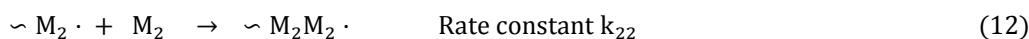
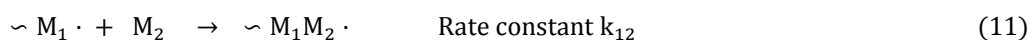
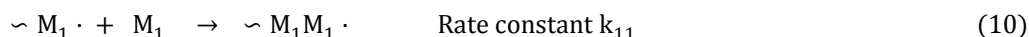


**Figure 34.** The Formation of the less stable myrcene free radical

### 3.2.1.2. Propagation

The next stage of the free-radical polymerization mechanism is propagation. In chain-propagating steps styrene and myrcene growing radicals are continuously added to the monomers generating larger free radicals. Consequently the macromolecular radical increases its size. The addition of the free radicals depends on the relative concentration and the relative reactivity of the monomers.

To quantify the relative reactivity of styrene and myrcene the reactivity ratios are used. The monomers reactivity ratios  $r_1$  and  $r_2$ , for any monomer pair are the ratios of the rate constants of different propagation reactions as defined<sup>47</sup> by



$$r_1 = \frac{k_{11}}{k_{12}} \quad (14)$$

$$r_2 = \frac{k_{22}}{k_{21}} \quad (15)$$

~ M· represents a polymer chain ending in a radical derived from monomer M·.

In the table below the reactivity ratios for styrene and isoprene couple are given<sup>47</sup>. Due to the lack of data for myrcene, isoprene is used as a surrogate. This assumption was made as myrcene and isoprene are both 3-alkyl butadienes.

**Table 4.** The reactivity ratios for three couples at 50 °C

M <sub>1</sub>	M <sub>2</sub>	r <sub>1</sub>	r <sub>2</sub>
Isoprene	Styrene	7.6	0.14
Styrene	Maleic anhydride	0.04	0.015
Ethylene	Tetrafluoroethylene	0,61	0,024

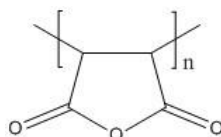
As it can be seen in the table above for isoprene-styrene couple the reactivity ratio r<sub>1</sub> is quite high while the reactivity ratio r<sub>2</sub> is very small. Thus, k<sub>11</sub> is much higher than k<sub>12</sub> and k<sub>21</sub> is much higher than k<sub>22</sub>. Then, from the propagation reactions it can be noticed that myrcene monomers are more likely to be added to the polymer chain than styrene monomers.

By using the reactivity ratios the relationship between the composition of a copolymer and the composition of the initial monomer mixture can be determined by

$$\frac{dm_1}{dm_2} = \frac{M_1 (r_1 M_1 + M_2)}{M_2 (r_2 M_2 + M_1)} \quad (16)$$

Where m<sub>1</sub> and m<sub>2</sub> are the moles of monomer 1 and 2 entering the copolymer, M<sub>1</sub> and M<sub>2</sub> are the moles of monomer 1 and 2 in the monomer mixture, and r<sub>1</sub> and r<sub>2</sub> are the monomers reactivity ratios<sup>48</sup>.

The reactivity ratios can also be used as a guide to the type of copolymer structure which is likely to be formed in the polymerization reaction. When the product of the reactivity ratios (r<sub>1</sub>·r<sub>2</sub>) is close to zero the formation of an alternating polymer is favoured whereas when the product is close to one a statistically random copolymer is preferably formed<sup>4</sup>. The product of reactivity ratios can be greater than one. As an example the monomer reactivity ratios product for styrene-maleic anhydride copolymer, which is a well-known alternating copolymer, is 6·10<sup>-4</sup>. On the other hand (r<sub>1</sub>·r<sub>2</sub>) for myrcene-styrene copolymer is 1.064 which is close to one.



**Figure 35.** The repeating unit formed from maleic anhydride

Another example of mixture of monomers which has a strong tendency to form an alternating polymer is polyethylene-tetrafluoroethylene. The product of their reactivity ratios is 0.015 which is close to zero.

One commonly used empirical scheme for monomer reactivity ratios prediction is the Q-e scheme. In the Q-e scheme, developed by Alfrey and Price, two important factors that influence are the relative reactivity of the monomers and the polarization of the radical<sup>4</sup>. In the Q-e scheme the monomer reactivity ratios are given by the following equations<sup>4</sup>:

$$r_1 = \frac{Q_1}{Q_2} \cdot \exp[-e_1 \cdot (e_1 - e_2)] \quad (17)$$

$$r_2 = \frac{Q_2}{Q_1} \cdot \exp[-e_2 \cdot (e_2 - e_1)] \quad (18)$$

Where Q is a measure of the monomer reactivity and  $e_1$  and  $e_2$  quantify the polarization characteristics of the radical and the reactive monomer, respectively.

Q and e are empirical parameters that are calculated using the results from kinetics experiments; styrene has been defined as having a Q value of 1 and e value of -0.8<sup>4</sup>. In the table 5 the values of Q and e are given for styrene, isoprene, maleic anhydride and isobutyl vinyl ether.

**Table 5.** The Q and e values for styrene, isoprene, maleic anhydride and isobutyl vinyl ether<sup>49</sup>

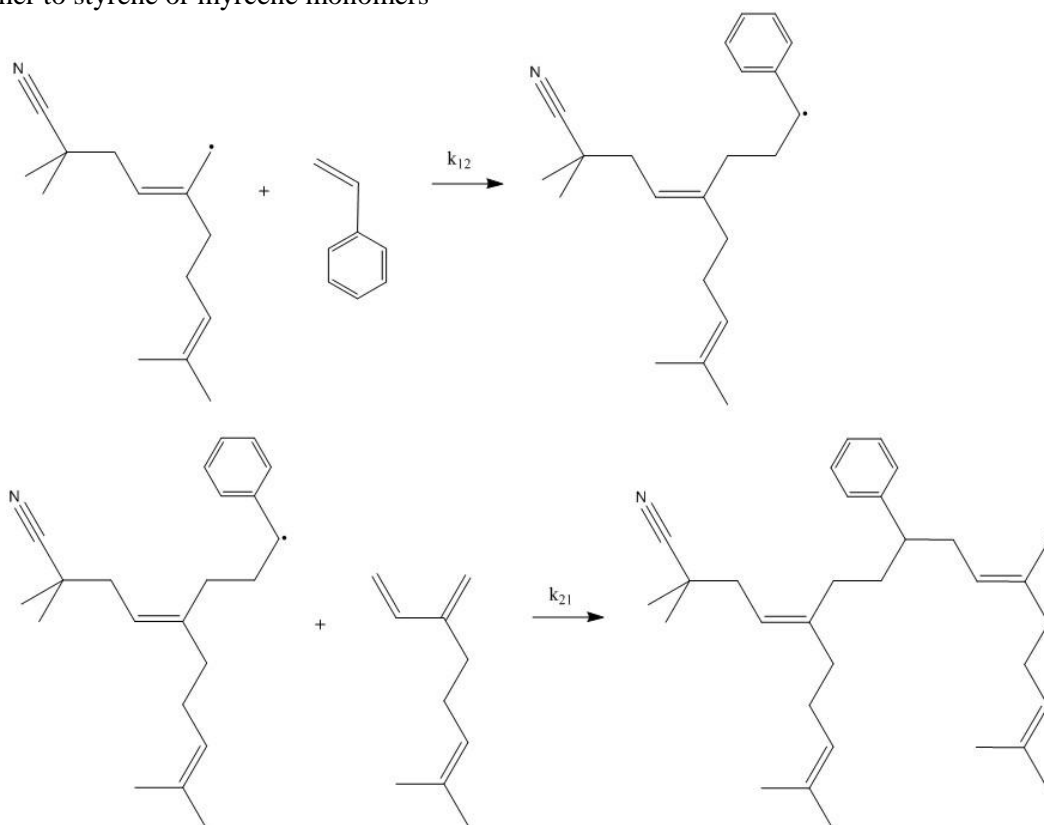
Monomers	Q	e
Styrene	1	-0.8
Isoprene	3.33	-1.22
Maleic anhydride	0.23	2.25
Isobutyl vinyl ether	0.023	-1.77

The electronic effects are described by the e values. Electron poor free radicals such as those which contain carbonyl groups, cyanide or ester groups have high e values, while electron rich free radicals such as those which contain ether groups have lower values. For example maleic anhydride which contains two carbonyl groups has a high e value whereas isobutyl vinyl ether which contains an ether group has a low e value.

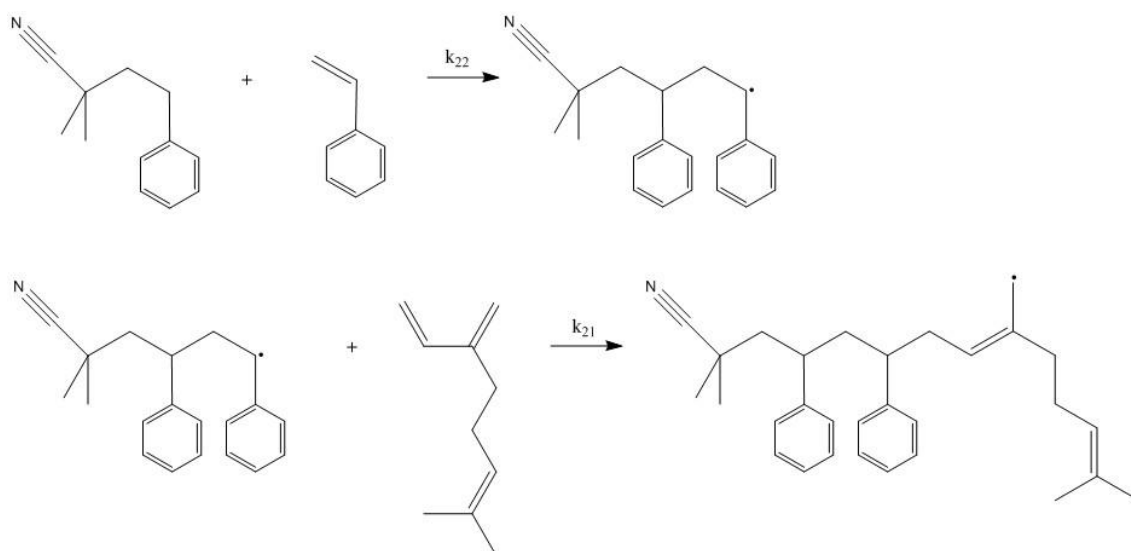
The Q-e scheme can also be used as a qualitative tool to predict copolymer structure. It has been determined that monomers with similar Q and e values will tend to form statistically random copolymers with the same proportion of incorporated monomers as in the feed, while when the Q values are similar but e values are high and of opposite sign the alternating copolymer is formed. As it can be seen in the table above styrene and isoprene have similar e values. On the other hand styrene and maleic anhydride, an alternating copolymer, have e values of opposite signs.

Therefore, according to the reactivity ratios product for myrcene-styrene copolymer as well as Q-e scheme it can be reasonably assumed that polystyrene-myrcene copolymer synthesised is a statistically random copolymer.

In the chain-propagating steps the free radicals formed during chain-initiating steps are added either to styrene or myrcene monomers



**Figure 36.** The first and second steps of propagation from a myrcene free radical formed in the initiation step



**Figure 37.** The first and second steps of propagation from a styrene free radical formed in the initiating step

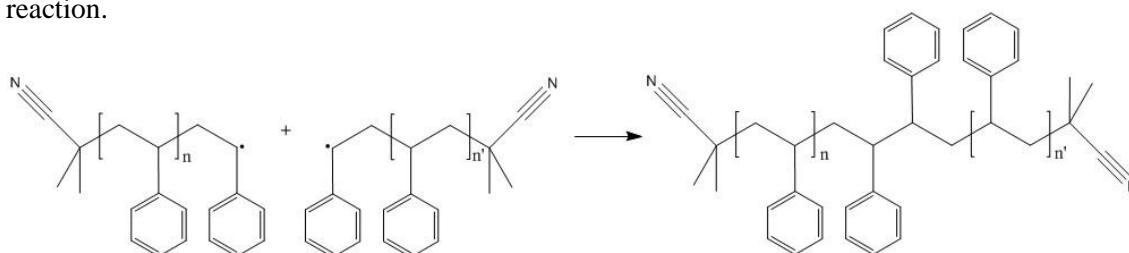
During propagation steps successive additions of a large number of monomer molecules occur. In each addition step the consumption of a free radical is accompanied by the formation of a new larger free radical. The time required for each propagation step typically is of the order of a millisecond. Thus, several thousand additions can take place within a few seconds. Propagation continues until the termination stage is reached.

### 3.2.1.3. Termination

The last step of the polymerization reaction is termination. In this stage the active centres are deactivated and the growth of the polymer chain is terminated.

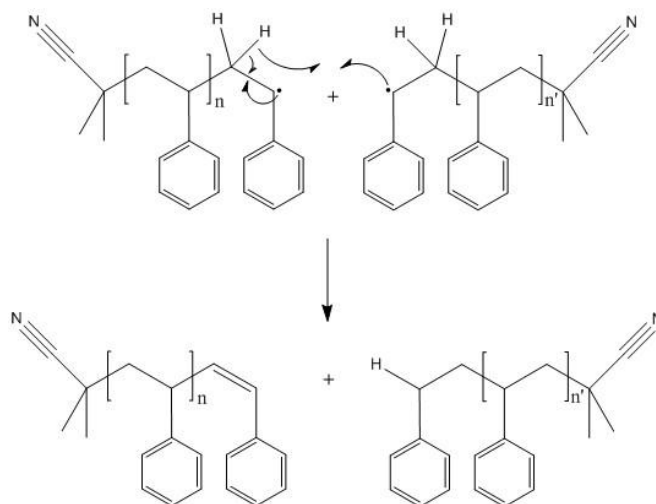
During this stage a phenomenon known as the gel effect can occur. The gel effect consists of the autoacceleration of the rate of the polymerization reaction. It is consequence of the increase in viscosity of the reaction mixture due to the formation of polymer molecules that slow termination reactions. This increase of viscosity can cause difficulties in heat dissipation which can lead to a fast increase of the temperature as nearly all chain growth polymerizations are strongly exothermic and polymers are bad heat conductors. The gel effect can be avoided by carrying out the polymerization reaction at low conversions as gel effect occurs at intermediate or high degrees of conversion<sup>42</sup>.

The two common mechanisms of termination are combination and disproportionation of two free radicals. In a combination reaction two growing free radicals join together by a covalent bond to form a large polymer molecule. As an example consider the polystyrene combination reaction.



**Figure 38.** The combination reaction of two polystyrene radicals

Alternatively, in a disproportionation reaction a hydrogen atom is abstracted from one growing free radical by another. As a result two polymer molecules, one with a terminal saturated group and one with a terminal unsaturated group, are formed.



**Figure 39.** The disproportionation reaction of radicals

As it can be noticed in the reactions above the polymer chains formed by disproportionation have initiator fragments at only one end while combination yields polymer molecules with initiator fragments at both ends.

During the polymerization some other reactions that can cause premature termination occur. The most important is chain transfer. In chain transfer an atom or other group is transferred

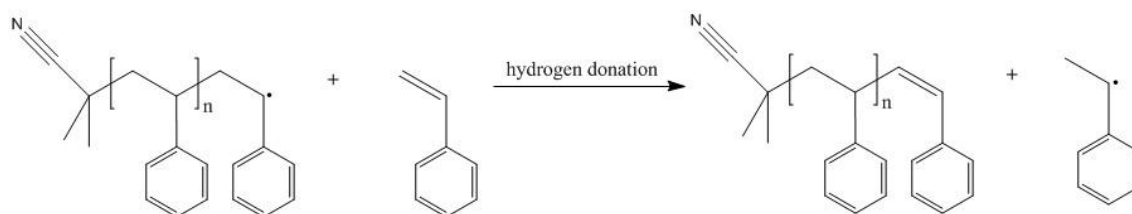
from a compound present in the reaction mixture to the growing chain of the polymer causing the premature termination<sup>50</sup>. These radical transfer reactions can be represented as



Where XA can be monomer, initiator, solvent, or other substance and X is the atom or group transferred.

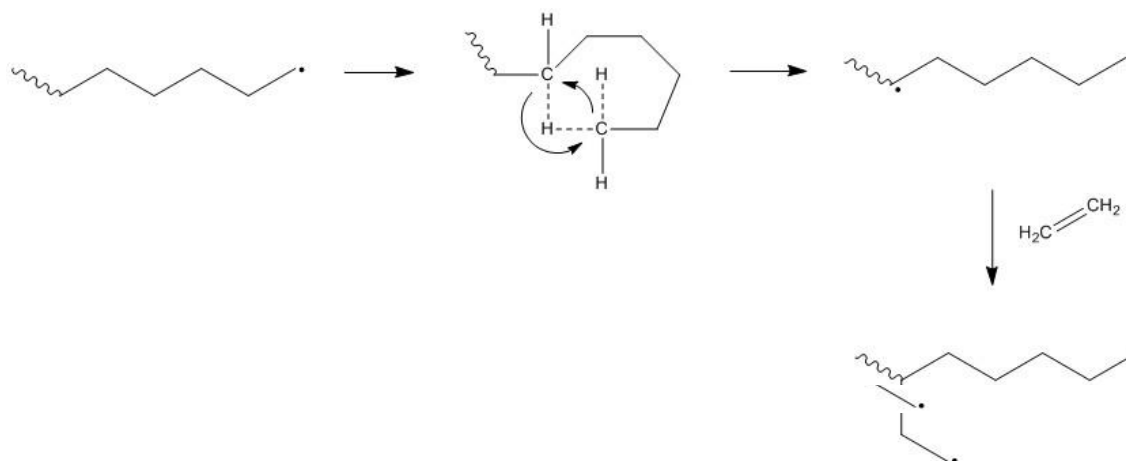
As it can be seen in the reaction above the product of chain transfer is an inert polymer molecule and, often, a new free radical capable of starting the growth of a new chain. As a result the length of the polymer chains is decreased<sup>50</sup>.

An example of transfer of a hydrogen atom between a growing chain of polystyrene and a polystyrene monomer is presented below.



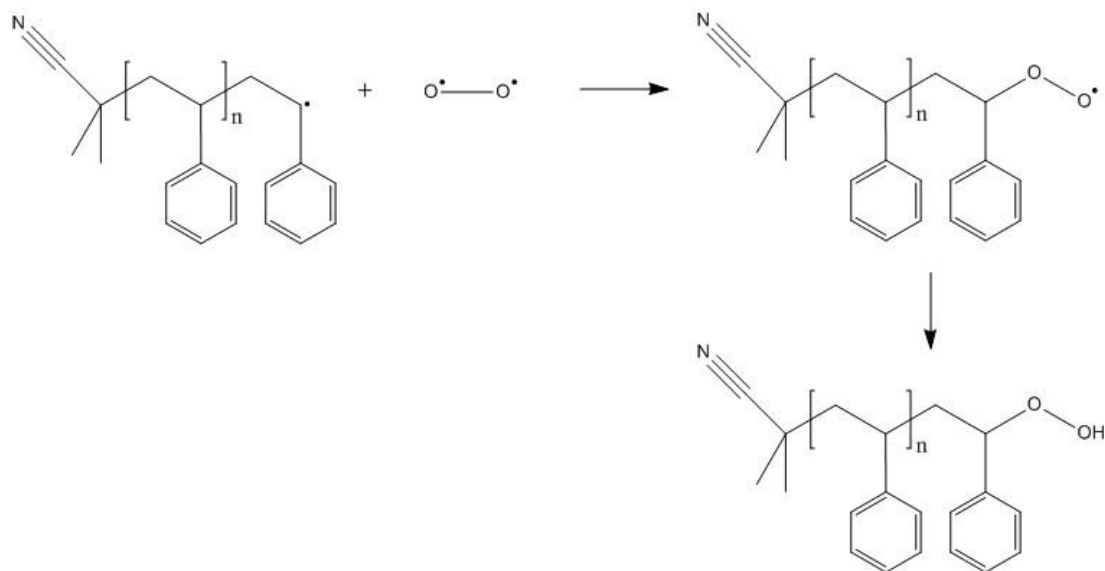
**Figure 40.** The hydrogen transfer between a growing chain of polystyrene and a polystyrene monomer

Another example is low density polyethylene synthesis (LDPE), where the radical transfers to a carbon near the final atom. As a result the side chains of LDPE are generated. This intermolecular transfer process is also termed backbiting. The figure below illustrates this process. Backbiting has a significant influence on the structure, and hence, the properties of the final polymer<sup>50</sup>.



**Figure 41.** The mechanism of backbiting in LDPE synthesis

The presence of oxygen during the polymerization process can also cause the premature termination. Oxygen binds to carbon centred radicals and form non radical products thus stopping the reaction<sup>50</sup>. To avoid oxygen inhibition many polymerization reactions are performed in an inert atmosphere of nitrogen gas. The reaction by which the oxygen terminates a growing chain of polystyrene is shown below.



**Figure 42.** The reaction of oxygen inhibition of a polystyrene growing chain

While peroxy compounds can decompose to form radicals the net effect of the oxygen is to greatly reduce the radical concentration in the reaction mixture.

### 3.2.2. Extrusion of a benzyl starch-high impact polystyrene blend

After the synthesis of three different plant based materials a benzyl starch-high impact polystyrene blend was extruded.

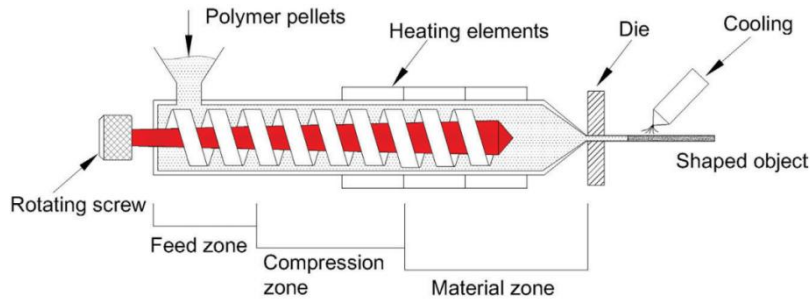
The high impact polystyrene (HIPS) is a multiphase material formed by a continuous rigid polystyrene phase together with disperse rubber particles, typically polybutadiene<sup>51</sup>. As in the case of ABS the rubber phase increases the impact strength of the material and makes HIPS tougher solid than pure<sup>52</sup>. High impact polystyrene is used in several applications in which impact resistance, machinability, and low cost are required. These include packaging, toys and computers cases.

In a normal extrusion process the polymer, typically in pellet form, is fed into the extruder cylinder through the hopper. The pellets are supplied to the screw which rotates within a heated cylinder, or barrel. Pellets move forward along the barrel between the flights of the screw and the hot walls of the cylinder. As pellets move along the barrel they melt due to the heat delivered by the heating elements. The melted polymer is squeezed at high pressure by the screw into the die. The shape and size of the die determines the dimensions of the profile of the plastic strip or thread which comes out of the extruder. This extruded plastic is normally hot; after it emerges from the die it rapidly cools which helps to maintain the profile of the extruded matter. Finally the product formed is cut or rolled.

Typically an extruder can be divided into three distinct zones: the feed zone, the compression zone and the material zone. The feed zone, where no heating takes place, is the one that receives the polymer pellets. In the compression zone the material is melted and pressurised. Finally in



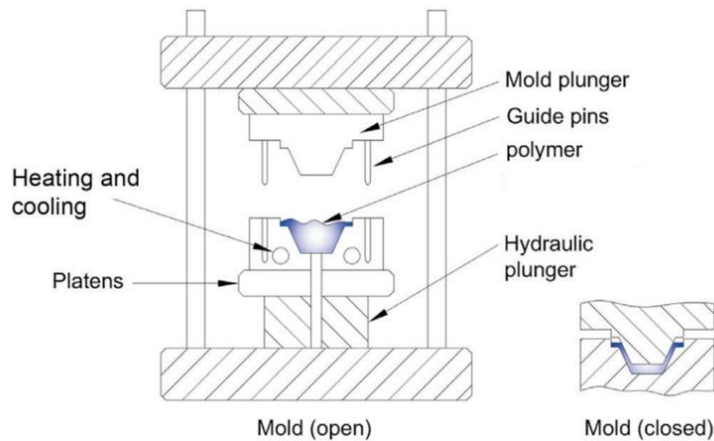
the material zone is a constant flow rate is imparted to the melt polymer<sup>9, 54</sup>. A picture of a regular extruder is shown below.



**Figure 43.** A typical single screw extruder and die<sup>54</sup>

In this project an extruder used to mix benzyl starch and high impact polystyrene is an extruder (AEV 330, Brabender Technologie). In this case a specific shape of the profile of the plastic strip or thread which comes out of the extruder is not required. Instead, the profile is ground into powder to, later on, press plates.

Another commonly used method for polymer processing is compression moulding. The mould used in this processing method is in two parts, the lower half which usually contains a cavity and the upper half which has a projection that matches the shaped cavity when the mould is closed. During the process the polymer material is placed in the open mould cavity. Then upper part is lowered and the polymer is compressed; it is simultaneously heated by the heated mould. When the mould is closed the hot polymer flows and fills the mould completely. After holding the two halves of the mould together the mould is opened and the part removed<sup>9, 54</sup>.



**Figure 44.** The production of objects by compression molding<sup>49</sup>

In this project the machine used to make the polymers plates is (TP 200, Fontune Holland). The mould used is rectangular and has a cavity of 0.5 mm deep.

In addition to the extrusion and compression moulding methods there are other methods used for polymer processing which are not discussed in this project such as injection moulding, blow moulding and the bubble blown method<sup>9, 54</sup>.

### 3.3. Methods

#### 3.3.1. Proton nuclear magnetic resonance spectroscopy ( $^1\text{H}$ NMR)

Nuclear magnetic resonance (NMR) spectroscopy is a versatile analytical tool widely used to identify individual compounds and to determine the structure of most organic molecules. Protons (spin= $1/2$ ) are a commonly used nuclide in nuclear magnetic spectroscopy.

Atomic nuclei possessing angular moment or spin have an associated magnetic moment.  $^1\text{H}$  NMR is based on the fact that without an external applied magnetic field the nuclei have a random orientation. However when an external magnetic field is applied the nuclei become aligned either with ( $\alpha$  orientation) or against ( $\beta$  orientation) the external magnetic field. The  $\alpha$  orientation is lower in energy; therefore more nuclei are aligned with the field than against the field. In  $^1\text{H}$  NMR technique energy is supplied in the form of electromagnetic radiation to pump the excess  $\alpha$  oriented nuclei into the  $\beta$  state. The resonance is detected and converted into the peaks of the  $^1\text{H}$  NMR spectrum<sup>55, 56</sup>. In  $^1\text{H}$  NMR spectrum the signal intensity is plotted versus the chemical shift ( $\delta$ ). The chemical shift is defined by the difference of the frequency of the resonance expressed to that of the standard compound. For both proton and carbon MNR the methyl resonance of tetramethylsilane (TMS) is used as the standard. The chemical shift is expressed in parts per million (ppm) thus making it independent of the field strength<sup>56</sup>.

$$\delta \text{ (ppm)} = \frac{\text{peak position in Hz (relative to TMS)}}{\text{spectrometer frequency in MHz}} \quad (20)$$

Once  $^1\text{H}$  NMR spectrum is obtained the following information can be extracted. The peak positions, which depend on chemical environment, provide information about the different types of hydrogens present in the molecule. The peak area, which depends on the number of contributing nuclei, provides information about the relative number of hydrogen atoms in a given environment. Moreover the fine structure of peak gives information about the presence of hydrogen neighbours a hydrogen has. This is due to the fact that the magnetic field of one nucleus has an effect on others. This effect which is expressed through bonds is known as coupling. The number of lines is normally that can be seen is given by

$$\text{Number of lines} = 2n \cdot I + 1 \quad (21)$$

Where  $I$  is the nuclear spin and  $n$  is the number of nuclei. More than one coupling can occur to a given nuclei<sup>56</sup>.

#### 3.3.2. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is analytical technique used to determinate the thermal stabilities of materials and the size of any thermally induced mass change by monitoring the weight change of a sample as a function of temperature or time when it is heated. The sample is subjected to a controlled temperature program in a controlled atmosphere which can be air or an inert atmosphere<sup>57, 58</sup>.

In a TGA experiment the sample, placed in a pan, is hung from a recording thermobalance which continuously measures its weight change as function of the temperature. The pan is placed in a furnace and is heated or cooled during the experiment. The variation of the temperature of the furnace chamber and of the temperature near the sample is measured by a thermocouple. A sample is normally within flowing gas which maintains a constant environment for the sample. This gas may be inert or a reactive gas that flows over the sample and exits through an exhaust. In many cases a TGA experiment is performed using a linear

temperature ramp. It is common to choose a final temperature far in excess of the last temperature induced change to ensure that all chemical reactions are completed at the end of the run<sup>58</sup>.

In TGA curves the temperature at which the material undergoes thermal degradation beginning ( $T_0$ ) and the amount of inert residue remaining are provided ( $M_{res}$ ). Commonly TGA experiments can be used to determine the water or volatile solvent content of a sample<sup>57</sup>.

### 3.3.3. Uniaxial tension test

The uniaxial tension test is a widely used test for evaluating materials. In this test the sample of the material is gripped at the two ends by a test machine. Then a uniaxial load, a load which is applied in only one direction, is applied by the machine, resulting in the gradual elongation and eventual fracture of the sample.

The axial load and the change of the length of the sample are monitored and recorded. From the data recorded several important mechanical properties of a material can be determined. These include elastic deformation properties, such as Young's modulus and Poisson's ratio, yield strength and ultimate tensile strength and ductility properties, such as elongation and reduction in area<sup>59, 60</sup>.

Typically the tensile test specimen has two shoulders from which the sample is gripped and a reduced gauge section in between over which measurements are made. The cross sectional area of the gauge section is reduced to be sure that deformation and failure are localized in this region. Tensile test specimens are often standardized according to the ISO or ASTM organizations. The specimens used in this project are standardized according to ISO 527-5A<sup>60</sup>.



**Figure 45.** A standardized tensile test specimen of a copolymer of benzyl starch with 50 % (w/w) HIPS

The primary output from a tensile test is the load, the tensile force that acts on the sample, as a function of the increase in gauge length, or elongation. As the load and the elongation depend on the dimensions of the sample they are normalized with respect to specimen dimensions. Thus, engineering stress ( $s$ ), or nominal stress, and engineering strain ( $e$ ), or nominal strain, are defined

$$s = \frac{F}{A_0} \quad (22)$$

Where  $F$  is the tensile load and  $A_0$  is the initial cross-sectional area of the gauge section.

$$e = \frac{\Delta L}{L_0} = \frac{L - L_0}{L_0} \quad (23)$$

Where  $L_0$  is the initial gauge length and  $\Delta L$  is the nominal change in length.

Another possible way to work with data that is independent of the sample dimensions is to define the true stress and the true strain. True stress ( $\sigma$ ) uses the instantaneous area of the specimen at any given point, as opposed to the initial area that uses nominal stress<sup>60</sup>.

$$\sigma = \frac{F}{A_i} \quad (24)$$

Where  $F$  is the tensile load and  $A_i$  is the instantaneous cross-sectional area of the gauge section. Assuming material volume remains constant true strain ( $\epsilon$ ), or logarithm strain, is defined as

$$\epsilon = \int_{L_0}^{L_i} \frac{dL}{L} = \ln\left(\frac{L_i}{L_0}\right) \quad (25)$$

Where  $L_0$  is the initial gauge length and  $L_i$  is the instantaneous gauge length.

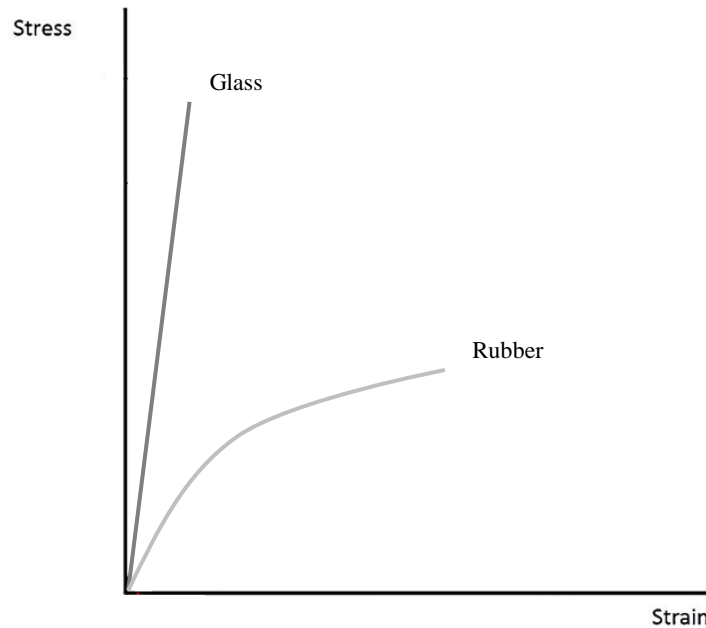
True and nominal values are related by the following expressions<sup>60</sup>

$$\sigma = s \cdot (1 + e) \quad (26)$$

$$\epsilon = \ln(1 + e) \quad (27)$$

The differences between using true and nominal stress and strain are very small at very low strains. Nominal stress and nominal strain are more commonly used during uniaxial tension test. Thus, all mechanical properties explained below are based on nominal stress and nominal strain<sup>60</sup>.

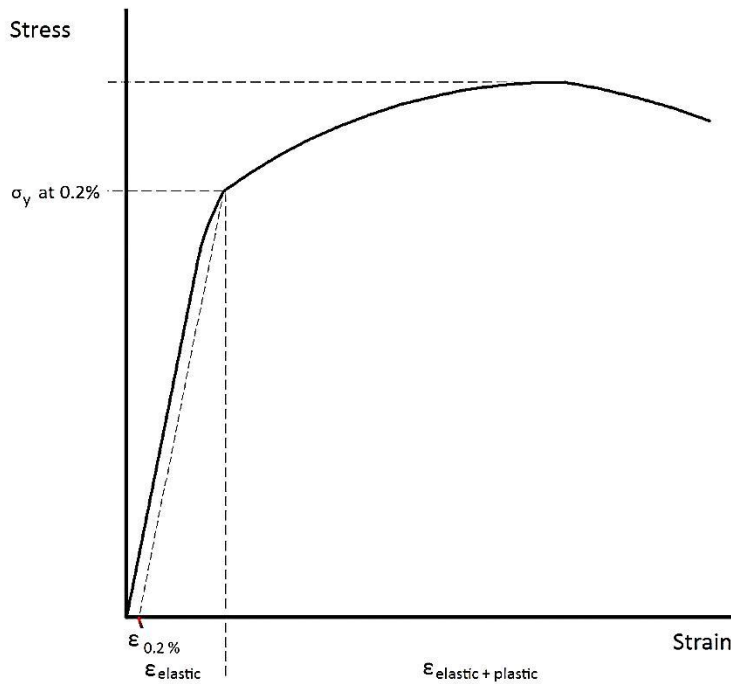
The resulting curve stress versus strain is independent of specimen dimensions. From the stress-strain curve several important mechanical properties can be determined. In figure 47 a typical stress-strain curve for a rubber and glass materials is shown.



**Figure 46.** A typical stress strain curves for rubber and glass materials

In general rubber materials have no linear range. Alternatively, glasses at room temperature often have only an elastic range.

A stress-strain curve for an elastic-plastic material is shown below.



**Figure 47.** A typical stress-strain curve for a plastic-elastic material

In the curve two different sections can be differentiated: the elastic region and the plastic region. The initial portion of the curve is the elastic region. In this region the deformation is elastic which means that the deformation is reversible. In the elastic deformation when the force is no longer applied, the sample fully recovers its initial dimensions. In this region the strain is proportional to the applied stress. The slope of this region is referred to as modulus of Young (E). The Young's modulus is a basic intrinsic physical property of all materials that measures the resistance of a material to elastic deformation when stress is applied. It can be determined as the ratio of the applied stress on a sample to the strain produced<sup>60</sup>.

$$E = \frac{s}{e} \tag{28}$$

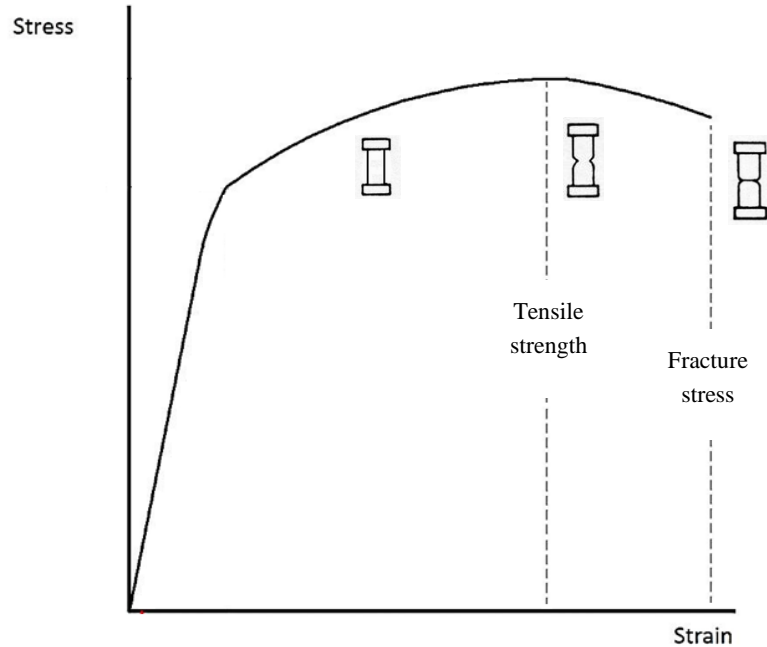
Another mechanical property that can be determined in the elastic range is the Poisson's ratio. The Poisson's ratio ( $\nu$ ) is the ratio of lateral contraction strain to axial strain in the direction of the applied load.

$$\nu = -\frac{e_y}{e_x} \tag{29}$$

Where x is the direction of the applied load in the tensile test.

As the stress rises the stress-strain behaviour ceases to be linear. This region is defined as the plastic region at which the deformation of the sample is irreversible. The stress value at which the plastic deformation is initiated is defined as the yield stress ( $\sigma_y$ ) of the material. However, most materials do not exhibit the presence of this yielding point on the stress-strain curve.

Therefore the yield stress is usually defined as the stress at which the plastic strain is 0.2 %. Beyond the yield point there is elastic and plastic deformation<sup>60</sup>. Tensile strength (TS) is the highest value of stress. Tensile strength often implies the end of uniform elongation and the start of localized necking<sup>60</sup>.



**Figure 48.** Necking in a Stress-strain curve for curve for a plastic-elastic material

Moreover the ability of a material to deform plastically without fracturing, or ductility, can be studied. The most common way to determine the ductility of a material is by calculating the percent elongation at break, which is defined simply as

$$\% \text{ El} = \frac{(L_f - L_0)}{L_0} \cdot 100 \quad (30)$$

Where  $L_0$  is the initial gauge length and  $L_f$  is the length of the gauge section at fracture.

Ductility can also be estimated by calculating the percent reduction of area. It is defined as

$$\% \text{ RA} = \frac{(A_0 - A_f)}{A_0} \cdot 100 \quad (31)$$

Where  $A_0$  is the initial cross-sectional area of the gauge section and  $A_f$  is the cross-sectional area at fracture<sup>60</sup>.

Some other mechanical properties which are not discussed in this project can be determined with tensile test such as the shear modulus, elastic limit, proportional limit, as well as many others.

#### **4. Hypotheses tested**

1. It is possible to form a plastic from styrene, corn starch and myrcene with suitable mechanical properties that can replace oil based plastics such as ABS.
2. The solid formed from the reaction of starch with benzyl chloride is more suitable for forming a composite with polystyrene than untreated starch.
3. It is possible to obtain a material with mechanical properties similar to those of ABS by extruding a benzyl starch-high impact polystyrene blend.

## 5. Materials

Styrene (Reagent Plus S4972-1 L with 4-tert-butylcatechol as stabilizer,  $\geq 99\%$ ) and myrcene (M100005-100 mL with 1000 ppm of butylated hydroxytoluene (BHT) as stabilizer) were provided by Aldrich. AIBN (98%) was provided by ACROS. Corn starch was purchased from a local supermarket {Majsstärkelse (Maizena<sup>TM</sup>) from Unilever}.

All the other organic reagents were purchased from either Aldrich or ACROS. Inorganic reagents were purchased from either Aldrich or British Drug Houses (BDH).



## 6. Methods

In this section the experimental procedure followed during the laboratory experiments is explained in detail. Furthermore the design and the methodology followed during the test are described.

### 6.1. Experimental procedure

In order to obtain a plant based composite similar to ABS the following laboratory experiments were carried out. All organic chemistry and polymer chemistry experiments were performed while wearing eye protection and a lab coat. When the hands needed to be protected nitrile rubber surgical gloves were worn

#### 6.1.1. Destabilization of styrene

As it has been mentioned in the section 3 purchased styrene contained a free radical inhibitor: 4-tert-butylcatechol. Therefore styrene must be destabilized before carrying out the polymerization reaction.

The 4-tert-butylcatechol inhibitor was removed from styrene by separating it with sodium hydroxide using a separation funnel. To do it the following procedure was used. Styrene (50 ml) and aqueous 2M sodium hydroxide (50 ml) were added to a 500 ml separation funnel. The separation funnel was shaken to mix the two liquids, after allowing the mixture to settle a yellowish organic phase and a red aqueous phase were seen.

This is because phenols and catechols tend to form coloured quinones on exposure to oxygen when in alkaline media. While a copper catalyst makes the reaction go faster, it will happen without a catalyst<sup>61</sup>. Then the aqueous phase was removed via the tap at the bottom of the funnel and more of sodium hydroxide solution (50 ml) was added before shaking again. The process was repeated several times until the aqueous phase was no longer red or pink. Finally the styrene was washed with water to remove the sodium hydroxide remaining until the pH of the aqueous layer was between 5 and 7. The pH was measured with a pH-indicator paper (Merck Millipore International, pH 1-10 universal indicator). Unwanted destabilized styrene was added to the non-halogenated solvent waste.



**Figure 49.** The first shaking of styrene with sodium hydroxide to remove its inhibitor (4-tert-butylcatechol )

### **6.1.2. Destabilization of myrcene**

Purchased myrcene contained butylated hydroxytoluene as an inhibitor. Therefore myrcene, as well as styrene, must be destabilized before carrying out the polymerization reaction.

#### **6.1.2.1. Method 1**

Based on what was known about the destabilization of styrene the same method was tried for myrcene. An attempt was made to remove butylated hydroxytoluene inhibitor from myrcene by separating myrcene with sodium hydroxide by using gravity to separate the two liquids. It was intended myrcene (5 ml) and aqueous 2M sodium hydroxide (5 ml) were added to a 100 ml separation funnel. Then the aqueous phase had to be removed via the tap and sodium hydroxide solution (5 ml) had to be added again. The process should have been repeated several times until the aqueous phase was no longer coloured. Finally the myrcene had to be washed with water to remove the remaining sodium hydroxide until the pH of the aqueous solution was between 5 and 7.

However when the separation funnel was shaken the formation of an emulsion was seen. Something increased the stability of the emulsion by decreasing the surface tension between the two liquids; this is an example of the third phase problem. Therefore it was impossible to remove the aqueous phase from the viscous milky white mixture. Finally the destabilization of myrcene by this method was rejected.

#### **6.1.2.2. Method 2**

The second attempt that was tried was the removal of butylated hydroxytoluene (BHT) from myrcene by separating myrcene with sodium hydroxide by centrifugation. To do it myrcene (1 ml) and aqueous 2M sodium hydroxide (1 ml) were added to a 3.5 ml glass tube. Once the glass tube was shaken the formation of a viscous milky white mixture was seen. To break the emulsion the glass tube was put in a centrifuge (Labofuge 200, Heraeus) during 5 minutes at 500 rpm. After the centrifugation two different colourless phases were seen. The lightest phase (myrcene) was then removed with 1 ml pipet (Starstedt) and added to another 3.5 ml glass tube with aqueous 2M sodium hydroxide (1 ml). Finally the same process was carried out three times more to remove as much inhibitor as possible. Unwanted destabilized myrcene was added to the non-halogenated solvent waste.

Although the inhibitor extraction appeared to have worked, further results indicated that a large amount of the stabilizer was still present in myrcene. Hence, another destabilization method was tried.

#### **6.1.2.3. Method 3**

The last method that was evaluated for the destabilization of myrcene was the removal of butylated hydroxytoluene from myrcene by steam distillation. First of all water (500 ml) was added to a 1 L three necked round bottom flask (two B19 sidenecks and a central neck of B29). To this a still head joined to a Liebig condenser (B19, 200 mm active length) was attached. The condenser was connected to a refrigerated circulator (Julabo F25, DPC) with water at 5 °C as a coolant. The three necked flask was then heated electrically with a heating mantle. As soon as the sum of the individual vapour pressures of water and myrcene was equal to the atmospheric pressure (760 mmHg) water and myrcene were co-distilled. The distillate (water and myrcene without inhibitor) was collected in a separation funnel with a distillation adapter. During this process water was continuously added to the three necked flask. Finally the two immiscible layers of distilled water and myrcene were separated using a separation funnel.

### 6.1.3. Synthesis of a polystyrene-myrcene copolymer by solution polymerization

Once styrene and myrcene were destabilized the polymerization of a styrene-myrcene copolymer was performed. The first polymerization method tried was solution polymerization.

The destabilized myrcene-styrene mixture (40 ml) was placed in a 250 ml two-neck round bottom flask (central neck of B24 and sideneck of B19), to this toluene (100 ml) and AIBN (200 mg) of were added. The reaction flask which was placed in an oil bath was equipped with a Liebig condenser (B19, 200 mm active length) connected to a refrigerated circulator (Julabo F25, DPC) delivering water at 5 °C as a coolant. The reaction mixture was stirred at 500 rpm with a magnetic stirrer (RTC Basic, IKA) and the flask was flushed with nitrogen gas for 30 minutes to remove oxygen. After 30 minutes the sideneck on the flask was sealed and the oil bath set to a 120 °C. When the solution started to boil the stirring rate was decreased to 300 rpm. The reaction mixture was allowed to boil under reflux (24 hours).

After 24 hours boiling the reaction mixture was added to an agitated (300 rpm) 500 ml beaker filled with ethanol (300 ml). Immediately the precipitation of a soft white polymer was seen. The precipitate was stirred (300 rpm) (10 minutes). After this time the ethanol was removed by decanting and added to the non-halogenated solvent waste. The solid remaining was dissolved in a small volume of toluene. The beaker was covered with aluminium foil and it was left with stirring (2 hours). The polymer solution was added carefully to an agitated (600 rpm) 1 L spherical flask with flat bottom flask containing ethanol (1 L). As in the first precipitation immediately the appearance of a soft white polymer was seen. Then it was left with agitation (3 hours). Later on the precipitate was separated from the liquid (mainly ethanol with some toluene) by filtration. The spherical flask with flat bottom was washed several times to be sure that the entire polymer was removed from the flask. A filter paper (circle 90 mm grade Ø, Whatmman), a Büchner funnel and a 2 L Büchner flask were used to collect the polymer. The filtrated solid was allowed to dry in air 30 minutes. After 30 minutes it was transferred to a jar and allowed to dry for 1 week.

The myrcene used in this polymerization was destabilized using sodium hydroxide and the emulsion broken by centrifugation.

In the table below the amounts of the chemical reagents added as well as the reaction times are detailed.

**Table 6.** The reaction conditions of solution polymerization for different composition polystyrene-myrcene copolymers

Synthesised polymer	Styrene (ml)	Myrcene (ml)	AIBN (g)	Reaction time (h)
Pure polystyrene	40.0	0.0	0.2950	22
Polystyrene 1 % (v/v) myrcene	39.6	0.4	0.2002	21
Polystyrene 2 % (v/v) myrcene	39.2	0.8	0.1993	19
Polystyrene 5 % (v/v) myrcene	38.0	2.0	0.2016	19
Polystyrene 10 % (v/v) myrcene	36.0	4.0	0.2017	21
Polystyrene 20 % (v/v) myrcene	28.8	7.2	0.1992	20
Pure myrcene	0.0	10.0	0.0693	24

### 6.1.4. Synthesis of a corn starch-polystyrene-myrcene composite by suspension polymerization

The second polymerization method tried was suspension polymerization. The destabilized styrene and water (500 ml) were placed in a 1 L ground glass flange flask with an inside flange

diameter of 100 mm. To this AIBN (800 mg) was added. The reaction flask was stirred using an overhead stirrer (OST basic, Yellowline) and a movable Teflon stirrer blade. The stir blade used was a segment of a circle of radius 67 mm and angle of the chord of 108°. Meanwhile the reaction mixture was being agitated at 300 rpm a Liebig condenser (B19, 200 mm active length) was fitted to one of the sidenecks of the reaction flask. After that the destabilized myrcene was added. The mixture (40 ml) was stirred for a couple of minutes, then corn starch (10 g of 87 %) was added and the flask was flushed with nitrogen gas for 1 hour. Thereupon the reaction mixture was stirred under reflux at 50 °C for 60 hours.

Later the precipitate was separated from the liquid by filtration. A filter paper (circles 90 mm grade Ø, Whatmman), a Büchner funnel and a 2 L Büchner flask were used. Then the composite was dried in air for 30 minutes. After 30 minutes it was transferred to a jar and allowed to dry for 1 week.

This experimental method was first tried with styrene containing 5 % (v/v) myrcene destabilized by centrifugation at 60 °C and using a 1 L three necked round bottom flask (two B19 sidenecks and a central neck of B29) as a reaction flask. However with these conditions only viscous oil could have been obtained.

The second attempt that was tried was the suspension polymerization of styrene 5 % (v/v) myrcene destabilized by steam distillation at 60 °C and using a 1 L three necked round bottom flask as a reaction flask. Nevertheless, in this case only a hard lump of polymer could have been obtained. This made extremely difficult the removal of the polymer from the flask.

Therefore, finally, the suspension polymerization was carried out with myrcene destabilized by steam distillation in a 1 L ground glass flange flask, at 50 °C as it has been explained in the procedure above.

In the table 7 and 8 below all the amounts of the chemical reagents added as well as the reaction conditions are specified for all the suspension polymerization tried.

**Table 7.** The reaction conditions of suspension polymerization for different experiments of starch-PS 5% (v/v) myrcene composite

Attempt	T (°C)	Styrene (ml)	Myrcene (ml)	AIBM (g)	Corn starch (g)	Reaction time (h)
1	60	38.0	2.0	0.2015	0.4200	72
2	60	38.0	2.0	0.5006	0.4080	70
3	40	38.0	2.0	0.8515	10.1276	74

**Table 8.** The reaction conditions of suspension polymerization for corn starch-PS 10% (v/v) myrcene composite

T (°C)	Styrene (ml)	Myrcene (ml)	AIBM (g)	Corn starch (g)	Reaction time (h)
40	36.0	4.0	0.8378	10.0057	74

The cleaning of the 1 L three necked round bottom flask was performed by oxidation of the polymer remaining on the glass with potassium permanganate (KMnO<sub>4</sub>). Potassium permanganate tends to attack organic compounds at the benzylic sites; it converts alkyl chains into carboxylic acids. Thus it is likely to digest polystyrene into benzoic acid. To do so potassium permanganate and water (500 ml) were added to the 1 L three necked round bottom flask which was placed in an oil bath. The flask which had Allihn condenser fitted to the central neck was heated under reflux with magnetic stirring (3 hours). After this time the liquid was poured from the flask. Afterwards the flask was filled with diluted sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and

was placed into an ultrasonic bath (2 hours). Finally the solid was removed from the flask easily with the aid of a spatula.

#### 6.1.5. Benzylation of corn starch

Corn starch (57.24 g of a 81 % grade) was added to the 1 L ground glass flange flask (containing already water {500 ml}). The reaction flask was then stirred using an overhead stirrer (Yellowline OST basic) and a movable Teflon stirrer blade. The stir blade used was a segment of a circle of radius 67 mm and angle of the chord of 108°. Meanwhile the reaction mixture was being agitated at 800 rpm a Liebig condenser (B19, 200 mm active length) was fitted to one of the sidenecks of the reaction flask. The condenser was connected to a refrigerator circulator (Julabo F25, DPC) which was set to deliver water at 5 °C. Because of the corrosive nature of hot concentrated sodium hydroxide solution towards borosilicate glass it is important to use a PTFE sleeve between all ground glass joints or to use vacuum tap grease to prevent the surfaces sticking together.

A solution of sodium hydroxide was prepared by adding sodium hydroxide (87 g) to water (160 ml). The sodium hydroxide solution was added drop wise over 15 minutes from a 250 ml dropping funnel to a stirred (300 rpm) of corn starch in water (500 ml) at 40 °C. The stirring rate was increased to 700 rpm before benzyl chloride (110 ml) was added drop wise over 15 minutes to the reaction flask. At this point the starch started to separate from the water because it was becoming hydrophobic. Then the reaction mixture was boiled under reflux (2 hours) with stirring at 300 rpm at 110 °C.

After being allowed to cool (*circa* 1 hour) the solid product obtained was transferred to a 1 L beaker full of water. Then the solid was cut up into small pieces with a pair of scissors and it was let in water overnight. Twice per day the solid was regularly cut up with scissors and the water of the beaker was changed. As the days passed by the solid became harder as the sodium hydroxide remaining was being gradually removed.

When the pH of the water measured with a pH-indicator paper (Merck Millipore International, pH 1-10 universal indicator) was between 5 and 7 the water was removed and benzyl starch was ground with a pestle and sieved. Then it was collected by filtration again using a filter paper (circle 90 mm grade Ø, Whatmman), a Büchner funnel and a 2 L Büchner flask. Afterwards the filtrated solid was placed in a 1 L beaker full of water all night long. Later benzyl starch was collected again by filtration and placed in a desiccator with silica gel as a drying agent to dry. Then the solid was dried to a constant mass before the benzyl starch was placed in a vacuum oven at 30 °C for further drying.

#### 6.1.6. Synthesis of a benzyl starch-polystyrene-myrcene composite by suspension polymerization

The same method described in section 6.1.4 was followed for the suspension polymerization of a benzyl starch-polystyrene 10 % (v/v) myrcene composite. However in this case instead of adding corn starch (10 g) to the reaction mixture the equivalent benzyl starch (15.5575 g) was added. In the table 9 the amounts of the chemical reagents added as well as the reaction conditions are specified.

**Table 9.** The reaction conditions of suspension polymerization for benzyl starch PS 10% (v/v) myrcene composite

T (°C)	Styrene (ml)	Myrcene (ml)	AIBM (g)	Benzyl starch (g)	Reaction time (h)
40	36.0	4.0	0.8484	15.5868	73

### **6.1.7. Extrusion of a benzyl starch-high impact polystyrene blend**

After the synthesis of three different plant based composites two benzyl starch-high impact polystyrene blends were extruded. The high impact polystyrene used was (Polystyrol 454 C, BASF) and the mixtures were extruded with an extruder (AEV 330, Brabender Technologie).

The two blends were a 20% (w/w) benzyl starch HIPS and benzyl starch 50% (w/w) HIPS. In both cases the total mass of the mixture was 45 g and the temperature of the extruder was set at 135 °C. The procedure followed in the two extrusions is explained below.

The powdered benzyl starch and high impact polystyrene in pellet form were added to the extruder chamber. The screw rotation rate was set at 0.06 rpm (3 minutes) to melt and mix the two components. After that the screw rotation rate was increased to 50 rpm (5 minutes) to facilitate the mixing process. Then the mixture was allowed to cool for (2 minutes) and removed from the extruder with the aid of a spatula. Finally the product obtained was ground into powder to make plates.

## **6.2. Performed tests**

### **6.2.1. Proton nuclear magnetic resonance spectroscopy (<sup>1</sup>H NMR)**

To determine if some myrcene had been incorporated into the polystyrene in the styrene-myrcene solution copolymerization a proton nuclear magnetic resonance spectroscopy was performed.

Pure polystyrene and polystyrene 1, 2, 5, and 10 % (v/v) myrcene copolymers were tested. The samples were prepared by dissolving the polymers (0.03 g) in chloroform-d (CDCl<sub>3</sub>) (1 ml). The solutions were then transferred to a 5 mm outside diameter glass tubes of 25 mm in length specially made for <sup>1</sup>H NMR spectroscopy. Finally the samples were analysed and the <sup>1</sup>H NMR spectrums were obtained.

### **6.2.2. Thermogravimetric analysis (TGA)**

To determine if the synthesised benzyl starch could be pressed into plates and mixed and extruded with high impact polystyrene a thermogravimetric analysis was performed. (TGA 7/DX, PerkinElmer) was used. The test was performed in two different controlled atmospheres: air and nitrogen gas. The samples were placed in a standardised aluminium pan (PerkinElmer) and hanged from a recording thermobalance. In both cases the initial temperature of the sample was 25 °C, the temperature increase rate of 10 °C per minute and the gas flow was 20 ml per minute. The test was performed up to 550 °C. The sample was held 1 minute at the initial and the final temperature. All data were collected and analysed with Pyris software.

### **6.2.3. Uniaxial tension test**

To determinate the mechanical properties of the synthesised corn starch based polymers uniaxial tension test was carry out. To make the tension test specimens it was necessary to make polymer plates first.

Corn starch based polymers plates were made with a (TP 200, Fontune Holland) hotpressing machine. First the mould was filled with the powdered polymer and placed above a metal sheet. The volume of the mould had been previously measured to know how many grams of polymer had to be put to fill the mould completely. Once the mould was filled it was covered by another metal plaque and placed into the machine. The temperature was set at 135 °C. The polymer was

heated during at 135 °C (3 minutes). After that it was pressed with a pressure of 100 kN (*circa* 10 tons force) during 5 minutes. Finally the resulting polymer plate was allowed to cool for 3 more minutes.

After making the polymer plates the tension test specimens were made. The equipment used was (EP-08, Elastocon AB). The mould used to make the tension test specimens was standardized according to ISO 527-5A.

Finally the uniaxial tension test was carried out by using a (BZ 2.5/TN 1S, Zwick) machine. The test speed was set at 1% of the initial length per minute and the pre-load at 1 N. Five samples of each material were tested. In all cases the length, thickness and width of the gauge section were measured. The sample was gripped at the two ends by the test machine paying attention that the specimen axis had to be properly aligned with the applied load.

## 7. Results and discussion

### 7.1. Destabilization of the monomers

The styrene and myrcene purchased were destabilized to remove their stabilizers that could inhibit the polymerization reaction. As it has been previously explained styrene was destabilized by extracting 4-tert-butylcatechol inhibitor from styrene with sodium hydroxide by using gravity to separate the two liquids. After that an attempt was made to use the same method for myrcene. However, in this case, an emulsion was formed making the extraction impossible to carry out. The formation of an emulsion can be explained by the large concentration of inhibitor that myrcene contains. Myrcene contains approximately 1000 ppm of BHT whereas styrene only contains 50 ppm of its inhibitor. What happens is that BHT loses a proton and acts as a surfactant. BHT lowers then the surface tension between the two liquids, sodium hydroxide (NaOH) and styrene, causing the droplet size to become smaller. This leads to a stable emulsion forming. Thus, the destabilization of myrcene by using simple separation of the organic from aqueous phases by gravity was dismissed as being ineffective.

The second attempt that was tried was the removal of butylated hydroxytoluene (BHT) from myrcene using sodium hydroxide in which the emulsion was broken using centrifugation. Although apparently the inhibitor extraction worked, when the polymerization reactions were carried out only a little amount of polymer was obtained. Therefore it was thought that this could be caused by a large amount of some impurity being present in the reaction mixture, also this second method will be difficult to increase in scale. Hence, myrcene was destabilized by steam distillation, this method was found to be successful.

### 7.2. Synthesis of polystyrene-myrcene copolymer by solution polymerization

The solution polymerization method was carried out for pure styrene, pure myrcene and five different composition styrene-myrcene copolymers. The myrcene used in this polymerization was destabilized by shaking with sodium hydroxide solution before centrifugation.

In the table below the amount of polymer that was obtained in each polymerization reaction is detailed.

**Table 10.** The amount of polymer obtained in each polymerization reaction

Synthesised polymer	Amount of polymer obtained (g)
Pure polystyrene	35.48
Polystyrene 1 % (v/v) myrcene	23.61
Polystyrene 2 % (v/v) myrcene	15.84
Polystyrene 5 % (v/v) myrcene	16.04
Polystyrene 10 % (v/v) myrcene	19.79
Polystyrene 20 % (v/v) myrcene	-
Pure myrcene	-

As it can be seen in the table above from the 40 ml of the initial reaction mixture only a little amount of polymer was obtained. This could be caused by a large amount of inhibitor of myrcene present in the reaction mixture. That also could explain why the amount of pure polystyrene obtained is much higher than the amount of copolymers obtained.

In the polymerization reactions of polystyrene 20 % (v/v) myrcene copolymer and pure myrcene only a low amount of a soft polymer soaked in toluene could be obtained. This might also be caused by a trace of BHT present in the reaction mixture that partly inhibited the polymerization



reaction. Also during the filtration of the polymer the filtrate was a milky white liquid. Thus, an alternative explanation could be that the myrcene made the polymer product more soluble in ethanol, leading to a loss of product.

### 7.2.1. $^1\text{H}$ NMR results

To determine if some myrcene had been incorporated into the copolymer a proton nuclear magnetic resonance  $^1\text{H}$  NMR was performed.  $^1\text{H}$  NMR was done for pure polystyrene and polystyrene 1, 2, 5, and 10 % (v/v) myrcene copolymers. To discuss the results a  $^1\text{H}$  NMR spectrum for pure polystyrene and polystyrene 10 % (v/v) myrcene copolymer is attached below. All other  $^1\text{H}$  NMR spectrums are shown in Appendix A.

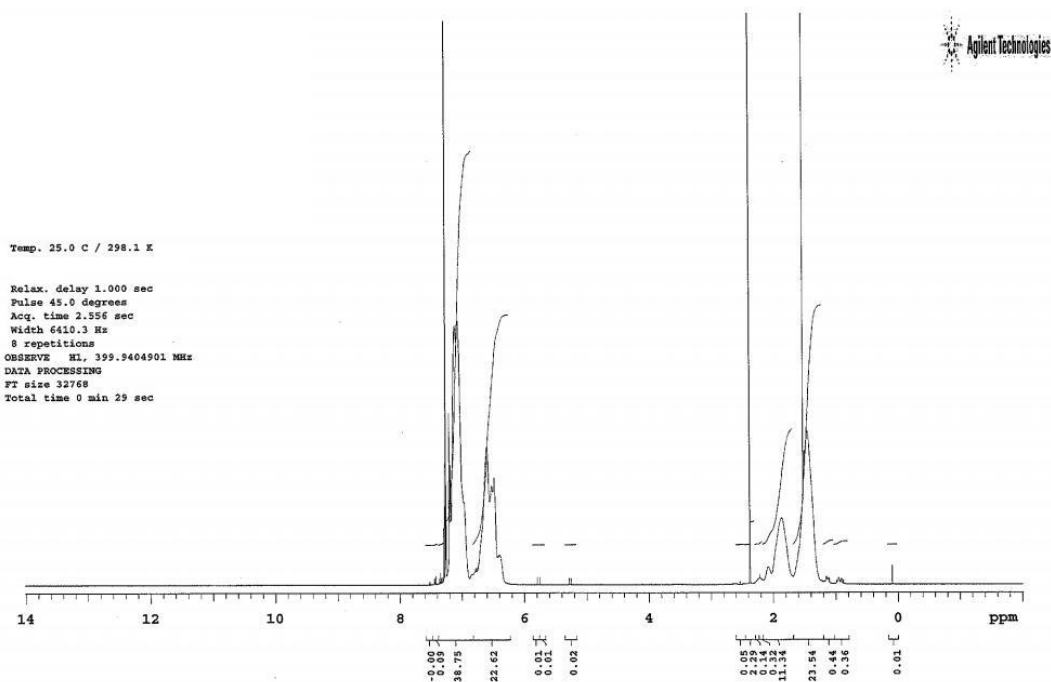


Figure 50. The  $^1\text{H}$  NMR spectrum of pure polystyrene

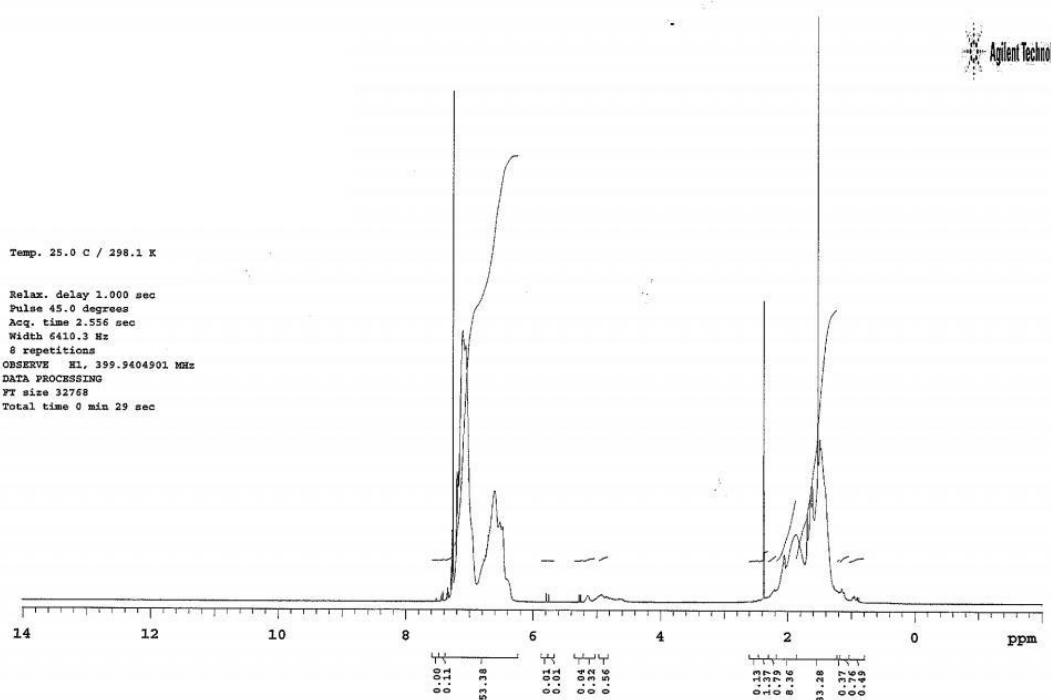


Figure 51. The  $^1\text{H}$  NMR spectrum of polystyrene 10 % (v/v) myrcene copolymer

As it can be observed in the  $^1\text{H}$  NMR spectrum of pure polystyrene there are two main peaks. The peak between 1 and 2.4 ppm corresponds to the alkyl groups, of polystyrene whereas the peak between 6 and 8 ppm corresponds to the benzene rings.

If the two  $^1\text{H}$  NMR spectrum are compared it can be seen that in the  $^1\text{H}$  NMR spectrum of polystyrene 10 % (v/v) myrcene copolymer a new peak has appeared at approximately 5 ppm. This new peak corresponds to the double bounds of myrcene. Moreover the peak between 1 and 2.4 ppm is quite different due to the methyl groups of myrcene. Therefore, it can be concluded that there is some myrcene incorporation. However the peak intensity is quite low. Thus, it may be possible that polymyrcene is partially soluble in ethanol. Hence, some myrcene containing polymer could be lost in the filtration process.

### **7.3. Uniaxial tension test of solution polymerization copolymers**

After determining that myrcene had incorporated into the copolymers they were pressed to make plates. Although it was possible to make the polymer plates it was impossible to obtain samples suitable for mechanical testing due to their brittle nature. Another polymerization method (suspension) was then employed. One of the reasons for using the suspension method is that it is impossible for an ethanol soluble polymyrcene to be lost from the product. Even if the myrcene reacts much faster than the styrene and forms a homopolymer which is mixed with the other homopolymer (polystyrene) then the polymyrcene could still improve the properties of the plastic.

### **7.4. Synthesis of a corn starch-polystyrene-myrcene composite by suspension polymerization**

As it has been explained at section 4.1.4 this method was first performed with styrene containing 5 % (v/v) myrcene destabilized by centrifugation at 60 °C and using a 1 L three necked round bottom flask as a reaction flask. However with these conditions only viscous oil could have been obtained. To increase the purity of the myrcene used it was decided to destabilise myrcene by steam distillation.

The second attempt that was tried was the suspension polymerization of styrene containing 5 % (v/v) myrcene destabilized by steam distillation at 60 °C and using a 1 L three necked round bottom flask as a reaction flask. While a polymerisation formed a solid product we were dismayed to find that the product was in the form of a single lump which was about the size of a man's fist. The formation of a hard lump was reasoned to be due to the myrcene lowering the glass temperature of the mixture of styrene and polystyrene forming a glue like blob during the polymerization which then turned solid as the glass temperature rose as the styrene was converted. The glass temperature is that at which the material changes from a hard and relatively brittle state into a molten or rubber-like state. It was decided to run the reaction at a lower temperature and use more starch to decrease the size of the droplets. The change of the polymerization reaction's temperature increased the amount of initiator required to carry out the process. As a third measure to prevent a similar debacle the reaction flask was changed from one with a B29 joint to a flange flask (opening *circa* 100 mm internal diameter) to enable the removal of the product even in the event of a single lump forming.

In suspension polymerisation it is sometimes necessary to adjust several parameters to get the reaction to form small pellets. The method was carried out with myrcene destabilized by steam distillation in a 1 L ground glass flange flask, at 50 °C. In the table below the amount of polymer that was obtained in each polymerization reaction is detailed.

**Table 11.** The amount of polymer obtained in each polymerization reaction

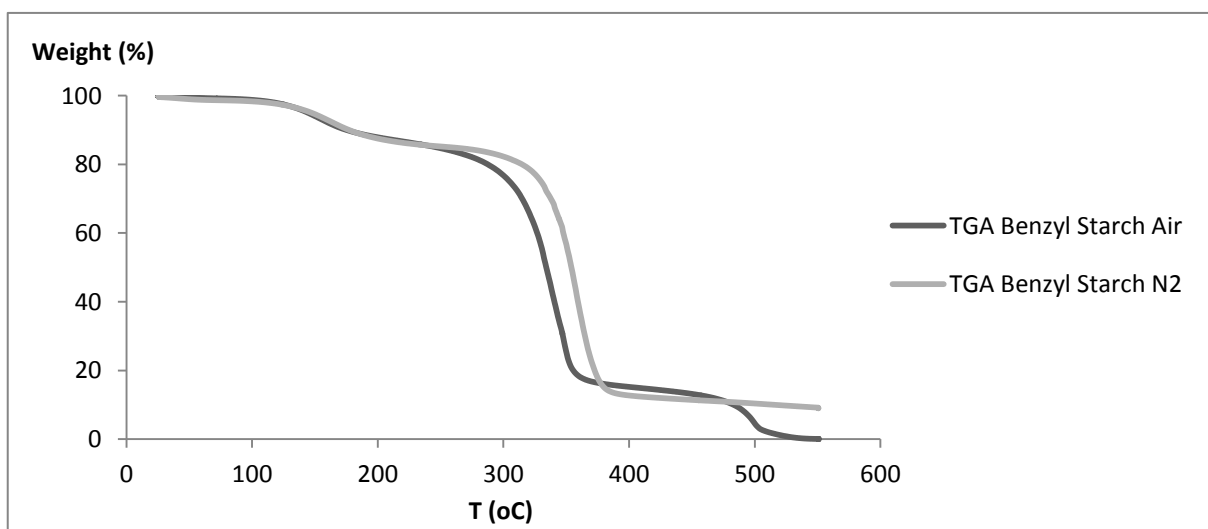
Synthesised polymer	Amount of polymer obtained (g)
Corn starch-polystyrene 5% (v/v) myrcene	31
Corn starch-polystyrene 10% (v/v) myrcene	42

## 7.5. Benzylation of corn starch

Benzyl starch was obtained from the benzylation of corn starch with benzyl chloride. After that to be able to determinate if the synthesised benzyl starch could be pressed into plates and mixed and extruded with high impact polystyrene a thermogravimetric analysis was performed.

### 7.5.1. Thermogravimetric analysis (TGA)

The thermogravimetric analysis of the synthesised benzyl starch in air and in nitrogen gas gave similar results below 300 °C.



**Figure 52.** The TGA results for benzyl starch in air and in nitrogen gas with a sample initial temperature of 25°C and a temperature rate of 10 °C/min

As it can be observed in figure the above in both cases the first weight decrease happens between 100 °C and 150 °C. This decrease may correspond to the evaporation of the water remaining in the sample. The most important decrease takes place around 300 °C for benzyl starch in air and around 340 °C for benzyl starch in nitrogen gas. These may be caused due to simple dehydration of  $C_6H_{10}O_5$  units to  $C_6$ . This would be a 44 % mass loss. However the mass loss looks bigger.

The sample exposed to nitrogen atmosphere was not fully burned whereas the one exposed to air was. This is reasonable as it is easier for the sample to burn in an atmosphere which contains oxygen than in an inert atmosphere.

In the end it was concluded that benzyl starch can be pressed into plates because its thermal decomposition happens above 135 °C which is the maximum temperature reached in the polymer plates pressing. Therefore benzyl starch will not decompose during the polymer plates pressing.

### **7.6. Synthesis of a benzyl starch-polystyrene-myrcene composite by suspension polymerization**

The synthesis of a benzyl starch-styrene 20 % (v/v) myrcene composite by suspension polymerization was done guided by the results obtained from the synthesis of a corn starch-styrene-myrcene composite by suspension polymerization. The myrcene used was destabilised by steam distillation, the reaction's temperature was set at 50 °C and the reaction flask used was a 1 L ground glass flange flask. 75 g of benzyl starch-polystyrene 20% (v/v) myrcene were obtained.

### **7.7. Uniaxial tension tests of the materials made by suspension polymerization and by extrusion**

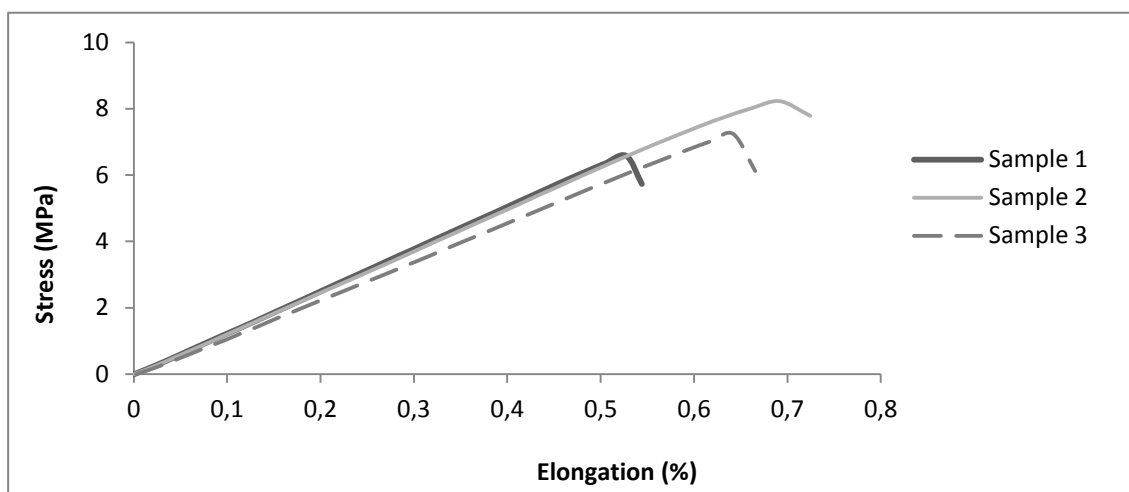
Uniaxial tension tests were made to determinate and compare the mechanical properties of composites synthesised by suspension polymerization and extruded blends. In order to do so, first polymer plates were pressed. Four different polymer plates were pressed: benzyl starch-20% (w/w) HIPS, benzyl starch-50% (w/w) HIPS, corn starch-polystyrene 10% (v/v) myrcene and benzyl starch polystyrene 20% (v/v) myrcene. However the plate of benzyl starch polystyrene 20% (v/v) myrcene that was obtained was not homogenous. This can be seen in the image below.



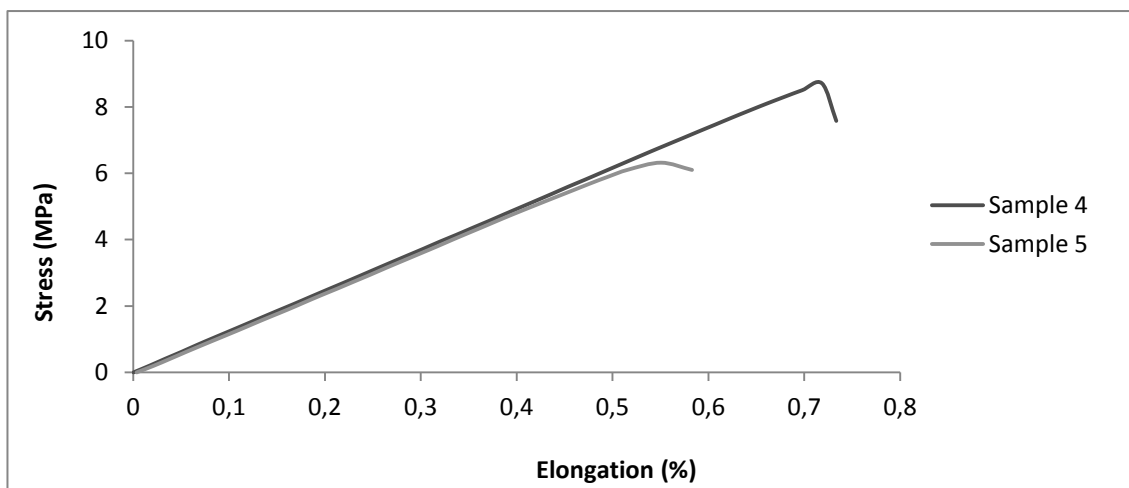
**Figure 53.** A picture of the plate of benzyl starch polystyrene 20% (v/v) myrcene composite

Hence, it was not possible to test this material and, in the end, only the other three materials were tested. In particular, five samples of each material were tested. Then, from the measured load as a function of the increase in gauge length, or elongation, the stress-strain curves were plotted.

The stress-strain curves of corn starch-polystyrene 10% (v/v) myrcene samples are shown below as an example. All other stress-strain curves are shown in Appendix B.



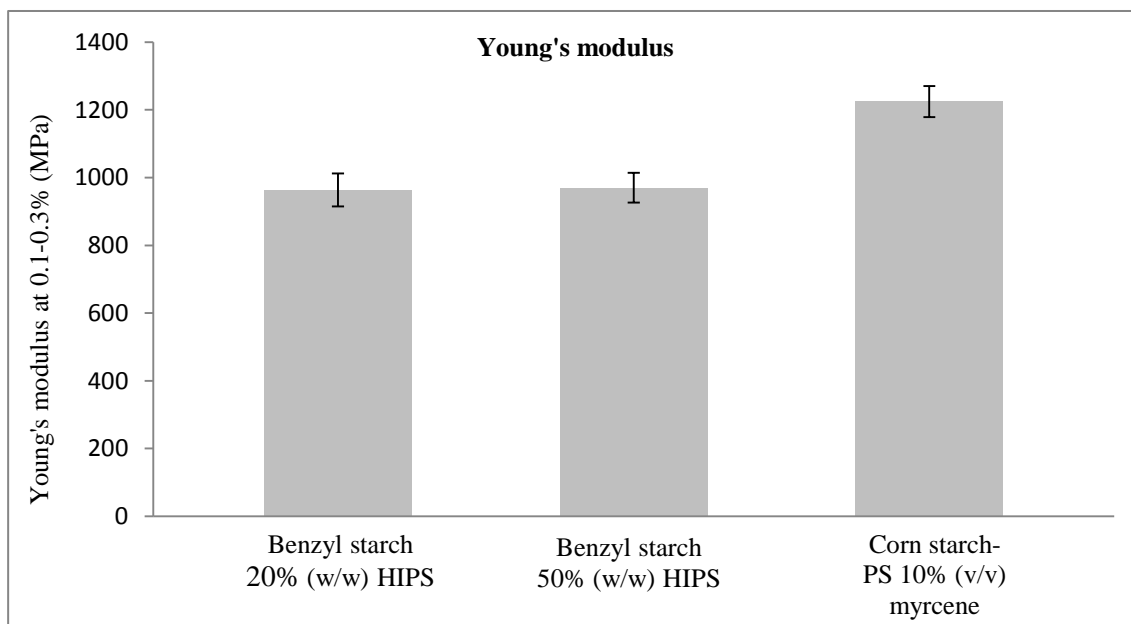
**Figure 54.** The stress-strain curve for the samples 1, 2 and 3 of corn starch-polystyrene 10% (v/v) myrcene composite



**Figure 55.** The stress-strain curve for the samples 4 and 5 of corn starch-polystyrene 10% (v/v) myrcene composite

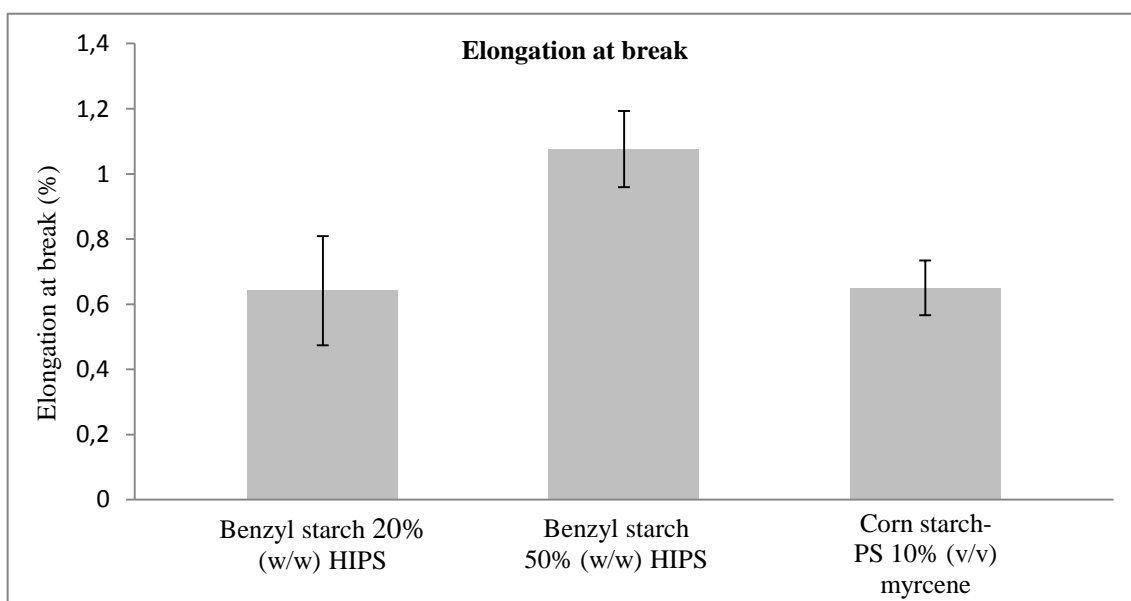
The stress-strain curves that can be seen above, as well as stress-strain curves that are shown in Appendix B, are typical curves of a brittle material. As it can be observed in the curves the five samples break at extremely low strains and they do not show plastic deformation. There is no yielding point, thus the ultimate strength and the breaking strength are the same and the material can fail suddenly without much warning. Moreover the area under the curves is quite low. Hence, the material is only capable to absorb small quantities of energy before failure (128.5 to 170.31 kJ).

To further characterize the three composites Young's modulus, elongation at break and tensile strength were determined. Young's modulus (E) of the each material was calculated as the Young's modulus average of the five samples tested. Young's modulus of each sample was calculated as the slope of the elastic region between 0.1 and 0.3 % elongation of the stress-strain curve. In the figure below the Young's modulus (E) of the each material as well as the standard deviation are detailed.



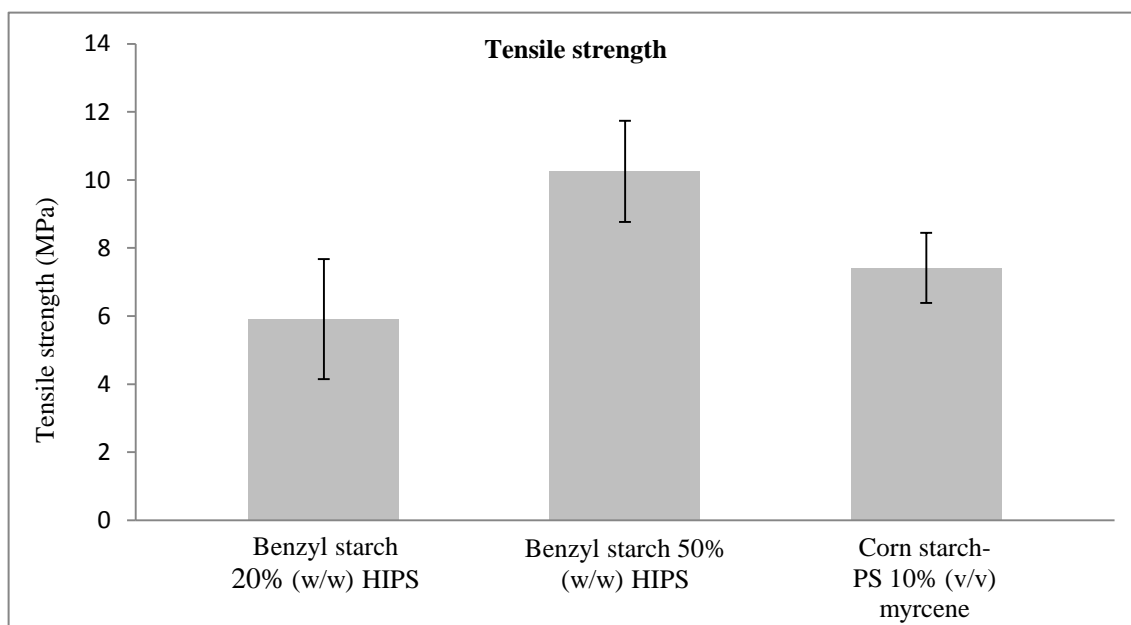
**Figure 56.** The Young's modulus of the three synthesised materials

The elongation at break of each material was calculated as the average of the elongation at break of the five samples tested. Elongation at break of each sample was calculated according to the equation (30).



**Figure 57.** The elongation at break of the three synthesised materials

Another mechanical property that can be determined is the tensile strength (TS). Tensile strength at break is the highest value of stress.



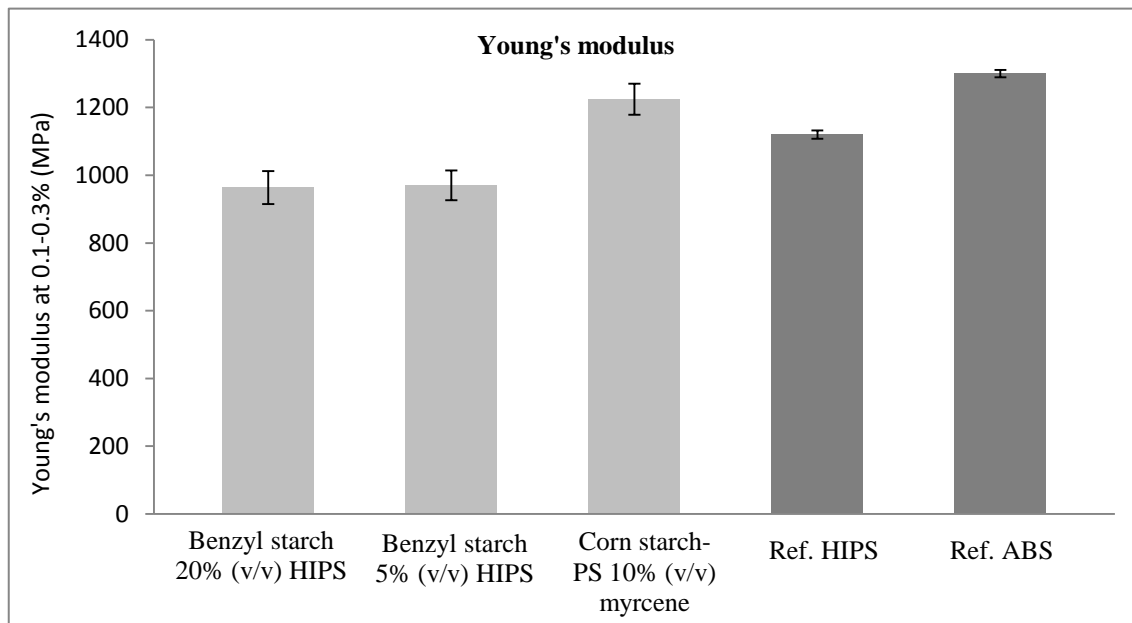
**Figure 58.** The tensile strength of the three synthesised materials

As it can be seen in figure 57 Young's modulus of corn starch-polystyrene 10% (v/v) myrcene composite is higher than Young's modulus of the other two composites. The higher the Young's modulus is the more stiff an object or substance is. Thus, corn starch-polystyrene 10% (v/v) myrcene composite is more rigid and stiff than the other two materials.

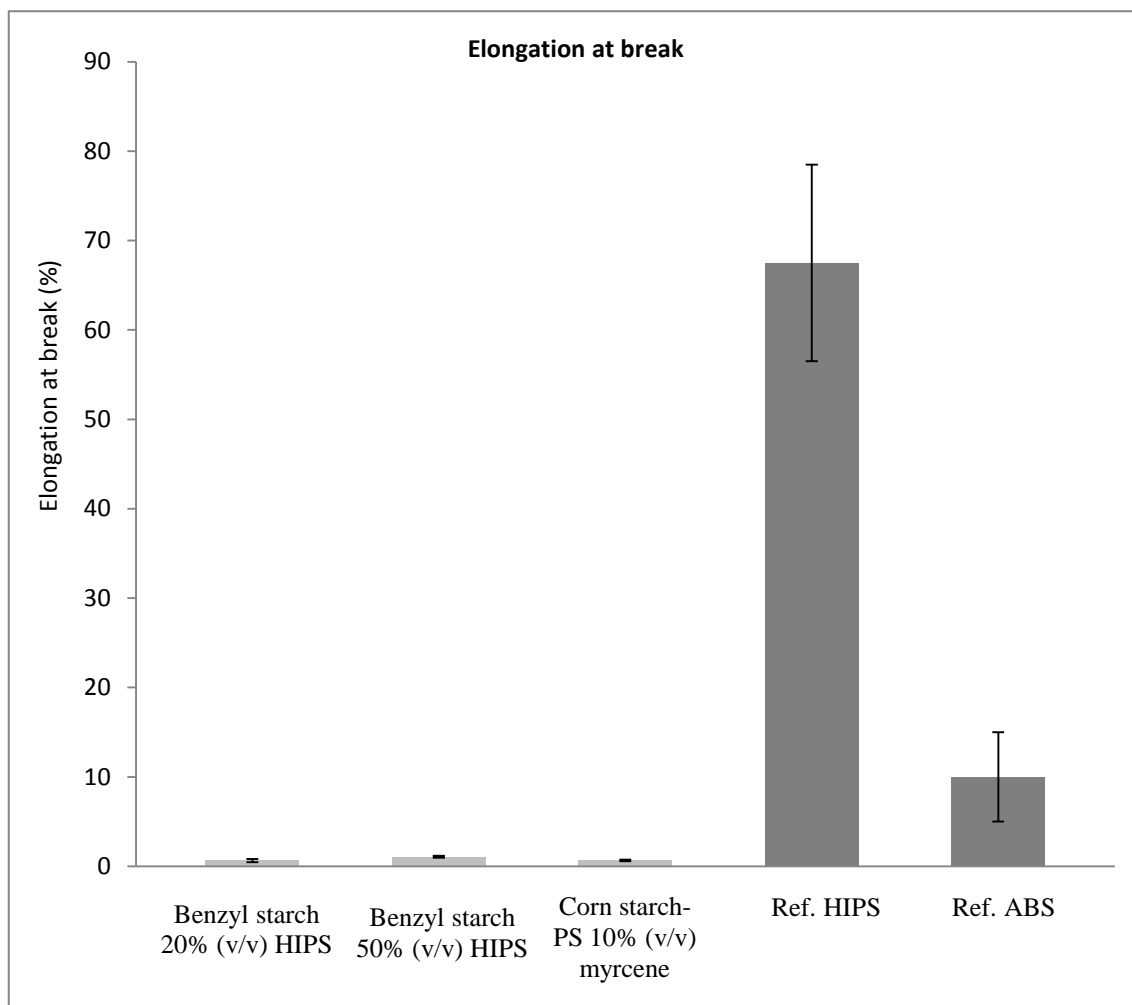
On the other hand in figure 58 it can be seen that benzyl starch 50% (w/w) HIPS breaks at higher elongation than the other two materials. Nevertheless, as it has been observed in stress-strain curves, elongation at break of the three polymers is low. Thus, the three materials are very fragile and do not deform plastically without fracturing. As fragile materials they are only capable to absorb little quantities of energy before failure.

Moreover in figure 59 it can be observed that benzyl starch 50% (w/w) HIPS can withstand higher stresses than the other two composites before the failure.

To be able to determine the effect of HIPS in benzyl starch composites and to compare the mechanical properties of the synthesised materials to those of virgin HIPS and ABS the tensile test results of HIPS V180 and ABS V180 obtained by S. Tostar and E. Stenvall in the study of the influence of extrusion conditions on mechanical and thermal properties of virgin and recycled PP, HIPS, ABS and their ternary blends are used<sup>62</sup>.



**Figure 59.** The Young's modulus of the synthesized materials, reference HIPS and ABS<sup>61</sup>



**Figure 60.** The elongation at break of the synthesised materials, reference ABS and HIPS<sup>56</sup>



From Young's modulus, elongation at break and tensile strength results the influence of HIPS in benzyl starch-HIPS composites can be determined. As it can be seen in figures 60 and 61 the percentage of HIPS in the composite does not affect the resistance to elastic deformation. However, it does increase elongation at break. This is due to the dispersed rubber phase in the brittle polystyrene matrix that increases the toughness of the composite. When HIPS is subjected under stress the formation of multiple crazes around the rubber particles is promoted. These crazes act as precursors to fracture and failure and as a form of energy-absorbing mechanism which results in a toughness improvement<sup>52</sup>. As a result elongation at break is also increased.

Moreover from the plots above it can be seen that the mechanical properties of the materials are far from those of ABS. Although Young's modulus is quite similar, the elongation at break of ABS is much higher than the elongation at break of the synthesised materials. Thus, despite the improvements of mechanical properties that can be achieved by incorporating HIPS in the materials, they have still low strength and are too brittle to replace ABS. Therefore, further research should be carried out in order to obtain a more ductile material.

## 8. Conclusions

It was seen that the synthesis of polystyrene-myrcene-starch composites by solution polymerization and suspension polymerization methods follows a free-radical polymerization mechanism. It was reasoned by looking at the reactivity ratios that the obtained polymer is a random copolymer.

It was found that the amount of stabilizer in the initial monomers has a great influence in the destabilization step. Large concentration of myrcene inhibitor lowered the surface tension of the raffinate and the extract in the decantation method causing the droplet size to become smaller. This led to a stable emulsion forming. Thus, myrcene had to be destabilized by steam distillation.

It was possible to modify corn starch using benzyl chloride by treating the starch with sodium hydroxide and heating. It was reasoned that benzene rings in benzyl starch are able to interact with benzyl rings in polystyrene through  $\pi$ - $\pi$  effects. Hence, benzyl chloride formed a solid which is more compatible with polystyrene-myrcene composite than corn starch.

After that it was observed that polystyrene-myrcene copolymers synthesised by solution polymerization were too brittle to for mechanical characterization. Alternatively polystyrene-myrcene-starch composites made by suspension polymerization, as well as the extruded benzyl starch-HIPS composites, could be mechanical tested.

Then mechanical properties of benzyl starch-20% (w/w) HIPS, benzyl starch-50% (w/w) HIPS, corn starch-polystyrene 10% (v/v) myrcene were studied. From the uniaxial tension test it was determined that these materials were also quite brittle as they broke at low strains and didn't show any plastic deformation. The corn starch-polystyrene 10% (v/v) myrcene composite was found to be more rigid and stiff than the other two composites as it had a higher Young's modulus. Alternatively, the benzyl starch 50% (w/w) HIPS broke at higher elongation than the other two materials.

Furthermore the influence of HIPS in benzyl starch-HIPS composites was studied. It was found that the fraction of HIPS in the composite increases the elongation at break but not the Young's modulus. It was reasoned that it is caused by the rubber phase dispersed in the brittle polystyrene matrix that promotes the formation of crazes which act as a form of energy-absorbing mechanism. Finally, when comparing the mechanical properties of the ABS and the composites, it was concluded that the materials had low strength and were too brittle to replace a plastic such as ABS.

While it has not been able to make a bioplastic that can be used on a large scale, the fact that it was able to do mechanical testing does suggest that a progress has been made in comparison to the solids made in the Winter of 2012<sup>36</sup> (the solids were so brittle that it was impossible to make the tensile test specimens).

Further research is required to synthesise a plant based composite with suitable mechanical properties. Starch based nanomaterials are a good starting point to achieve this goal as it has been found that they have much better mechanical properties than the starch based polymers.

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## 11. List of abbreviations

ABS	Acrylonitrile butadiene styrene
AIBN	2,2'-Azobis(2-methylpropionitrile)
ASTM	American Society for Testing and Materials
ATP	Adenosine triphosphate
BHT	Butylated hydroxytoluene
BPO	Benzyl Peroxide
CB	Carbon black
CDCl <sub>3</sub>	Chloroform-d
CO <sub>2</sub>	Carbon dioxide
Cr <sub>2</sub> O <sub>3</sub>	Chromium (III) oxide
EIA	Energy Information Administration
EP	Epoxy resins
H	Hydrogen
HDPE	High density polyethylene
HIPS	High impact polystyrene
<sup>1</sup> H NMR	Proton nuclear magnetic resonance
H <sub>2</sub> SO <sub>4</sub>	Sulfuric acid
ISO	International Organization for Standardization
KMnO <sub>4</sub>	Potassium permanganate
LDPE	Low density polyethylene
LPG	Liquefied petroleum gas
NaOH	Sodium Hydroxide
OPEC	Organization of the Petroleum Exporting Countries
PE	Polyethylene
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinyl chloride
PTFE	Polytetrafluoroethylene
PHB	Poly-(3-hydroxy-butyrate)
PLA	Poly(lactic acid)
PET	Polyethylene terephthalate
PMMA	Poly(methyl methacrylate)
PO <sub>4</sub> <sup>3-</sup>	Phosphate group
SAN	Styrene acrylonitrile resin
SO <sub>2</sub>	Sulfur dioxide



TMS	Tetramethylsilane
TGA	Thermogravimetric analysis
TS	Tensile strength
US	United States

## 12. Appendices

### Appendix A

Summary of the  $^1\text{H}$  NMR spectrums of polystyrene 1 and 5 % (v/v) myrcene copolymers.

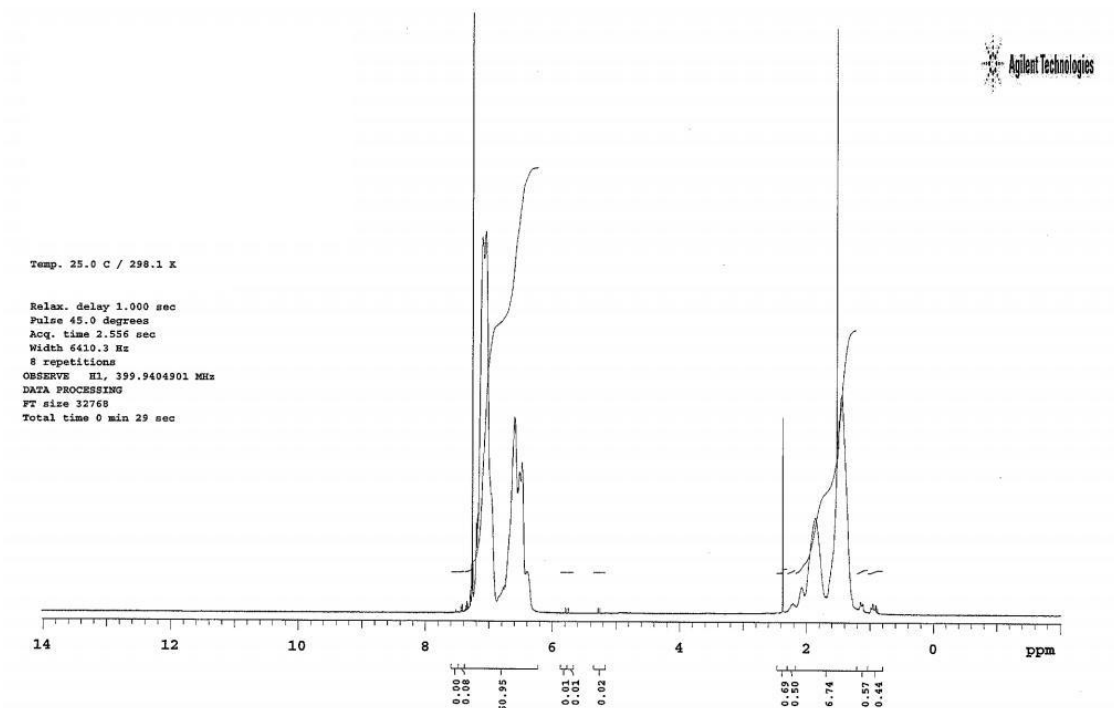


Figure A. The  $^1\text{H}$  NMR spectrum of polystyrene 1 % (v/v) myrcene copolymer

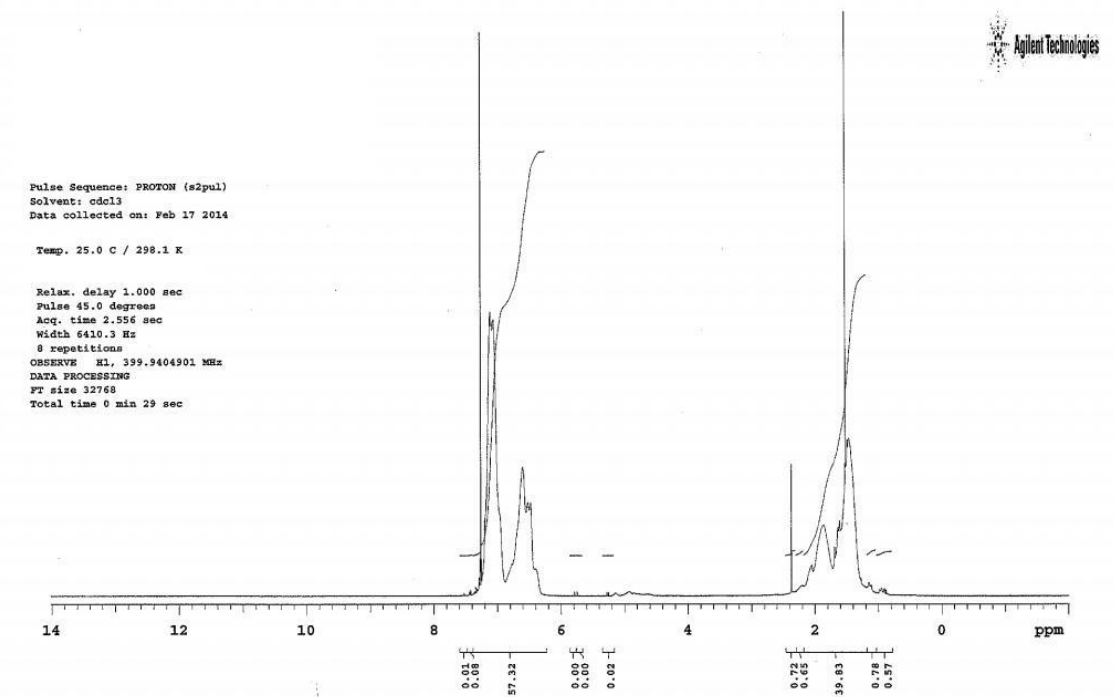


Figure B. The  $^1\text{H}$  NMR spectrum of polystyrene 5 % (v/v) myrcene copolymer

## Appendix B

Summary of the tensile test curves (five samples per material) with a test speed of 1% of the initial length per minute and a pre-load of 1 N.

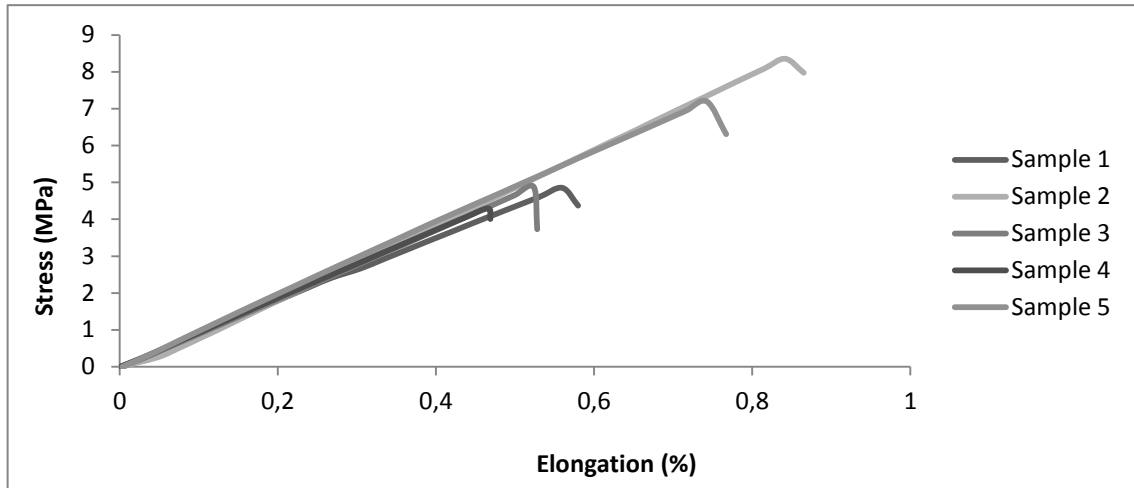


Figure C. The stress-strain curve for five samples of benzyl starch- 20% (v/v) HIPS copolymer

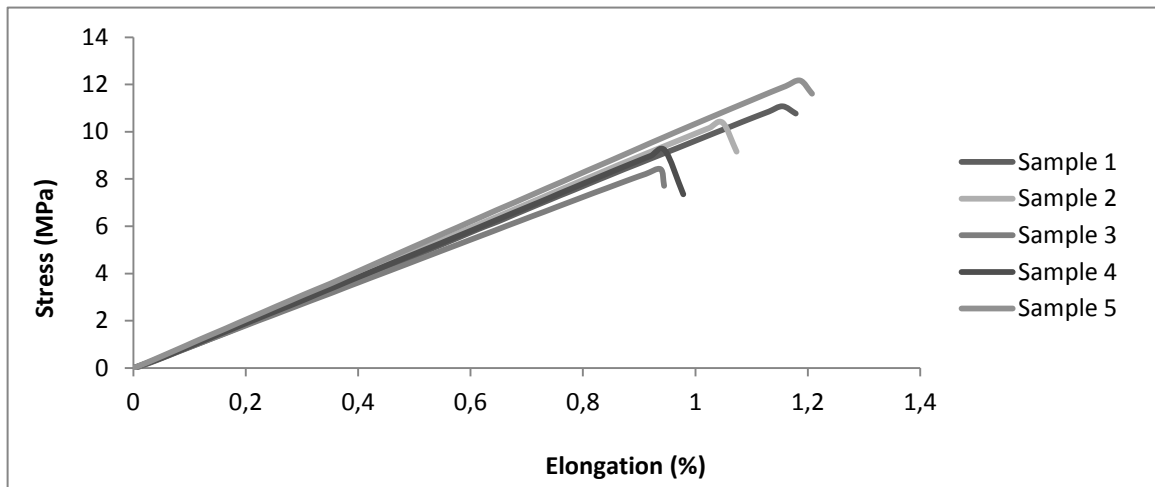


Figure D. The stress-strain curve for five samples of benzyl starch- 50% (w/w) HIPS copolymer

