A PROCESS FOR MELT GRAFTING ITACONIC ANHYDRIDE ONTO POLYETHYLENE

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Dedication

To my family, for their love, support, encouragement and patience.

Abstract

Currently, extensive research in using bio-derived polymers is being done, highlighting the importance of sustainable, green polymeric materials. Some sustainable alternatives to synthetic polymers include lignin, starch, cellulose or blends of these with petroleum-based polymers.

In New Zealand, large quantities of animal derived proteins are available at very low cost, making it ideal as a sustainable alternative to petroleum-derived polymers. However, the processability of most proteins is very difficult, but can be improved by blending with synthetic polymers, such as polyolefins. To improve, the compatibility between these substances, a functional monomer could be grafted onto the polyolefin chain. Using an appropriate functional group, the polyolefin could then react with certain amino acids residues in the protein. Lysine and cystein are the two most appropriate amino acid residues because of their reactivity and stability at a wide pH range.

In this study, free radical grafting of itaconic anhydride (IA) onto polyethylene was investigated. IA was selected because it is capable of reacting with polyethylene and amino acid residues, such as lysine. The objective of the research was to identify and investigate the effect of reaction parameters on grafting. These were: residence time, temperature, initial monomer concentration as well as peroxide concentration and type. Grafting was characterized in terms of the degree of grafting (DOG), percentage reacted and the extent of side reactions.

The reaction temperature was taken above the melting point of the polyethylene, monomer and decomposition temperature of the initiator. It was found that above 160°C polymer degradation occurred, evident from sample discolouration. A higher degree of grafting can be achieved by increasing the initial monomer concentration up to a limiting concentration. The highest DOG achieved was about 1.2 mol IA per mol PE, using 2 wt% DCP. When using 2 wt % peroxide, the limiting concentration was found to be 6 wt% IA, above which no improvement in DOG was achieved. It was found that DCP is much more effective at grafting, compared to DTBP because DTBP is more prone to lead to side reactions than DCP.

It was found that a residence time of 168 seconds resulted in the highest DOG, corresponding to 4 extrusions in series. However, it was also found that an increase in residence time resulted in an increase in polymer degradation. The tensile strength of PE decreased after two extrusions when using DTBP, and three extrusions, when using DCP. Young's modulus decreased only slightly, while all samples showed a dramatic decrease in ductility, even after one extrusion. It was concluded that degradation had a more pronounced effect on mechanical properties than cross-linking, and residence time should therefore not exceed three extrusions in series, which corresponded to about 126 seconds.

It can be concluded that a high reaction temperature and high initiator concentration lead to a low degree of grafting, accompanied by high cross-linking and increased degradation. On the other hand, high monomer concentration and high residence time lead to a high degree of grafting.

Optimising grafting is therefore a trade off between maximal DOG and minimising side reactions such as cross-linking and degradation and optimal conditions do not necessarily correspond to a maximum DOG. Other factors, such as the use of additives to prevent degradation should also be investigated and may lead to different optimum conditions.

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1. Introduction

Synthetic polymers are man-made polymeric chains characterized by many excellent properties such as ease of moulding and low density. The awareness of the interconnectivity of global environmental factors, eco-efficiency and green chemistry with engineering, has spurred development of the next generation of materials, products and processes that are more environmentally friendly. Many alternatives to synthetic polymers have been considered. These include bio-derived polymers such as: polysaccharides, lipids polyesters and proteins, which can be extracted from plant and animal sources to be used as precursors to plastic materials.

In addition to fully bio-derived polymers, synthetic polymers may also be blended with bio-derived polymers to reduce the environmental impact of synthetic materials while utilising abundant natural resources. However, these kinds of blends are often incompatible. One solution to increase the compatibility is to graft these polymers onto each other. Unfortunately, synthetic polymers and the bio-derived polymers are often unreactive in their native states [1-3]. One solution is to functionalize the synthetic polymer in order to increase its reactivity towards bio-derived polymers.

As an agricultural country, New Zealand provides a wide range of bio-resources such as wool, proteins and lipids. In particular, bovine blood consists of a mixture of several proteins and is mostly a waste product from the dairy industry. In New Zealand, 211 million litres of blood is produced annually from cattle and sheep processing, which comprise 18 wt % proteins [4]. This makes it an ideal candidate as a bio-replacement for synthetics polymers, if appropriately processed.

The objective of this research was to explore reactive extrusion as a means to functionalize polyethylene in order for it to be reactive towards bovine blood proteins. Reactive extrusion has great prospect in modifying polyethylene compared to solution methods, as it can easily deal with highly viscous materials. With an appropriate functional group, polyethylene can be grafted to protein chains in order to improve the protein’s processability. However, in this study only the functionalization process of grafting itaconic anhydride onto linear low density polyethylene has been considered. Itaconic anhydride has been chosen as a monomer because of its lower price and less hazardous nature, compared to other monomers, such as maleic anhydride.

In this thesis, some available information regarding reactive extrusion will be discussed, focussed on improving the understanding of processes variables and how these can be manipulated to provide optimal functionalization.

Understanding reactive extrusion is fundamental to grafting and the specific objectives of this study were therefore:

- To understand current modification techniques of thermoplastics.
- To identify factors that may affect the modification techniques.
- Increase the knowledge and understanding of the process.
- Determine optimum process variables for melt grafting itaconic anhydride onto polyethylene.

An understanding of the entire process is required to improve the degree of grafting and consequently make the reaction reliable. In the modification of polymers, only thermoplastics will be discussed in this report and the modification process is limited to extrusion.

2. Reactive extrusion

In principle, extrusion comprises forcing a plastic or molten material through a shaped die by means of pressure [5]. Extrusion is widely used in the polymer, metal, food and ceramic industries. An extruder essentially consists of an Archimedean screw, fitted closely in a cylindrical barrel, with just sufficient clearance to allow its rotation. Solid polymer is fed at one end and the profiled molten extrudate emerges from the other side. The barrel is equipped with heating elements around the outside of the barrel, which provide the energy for melting the material. Inside the barrel, the polymer is melted and homogenized [5].

Extruders are typically used for pumping, mixing, solid conveying and metering [6]. Apart from its normal use, an extruder can also be used as a chemical reactor in the polymer industry. Before this can be discussed, a general description on the operation of a typical extruder is given below:

2.1 The extruder

An extruder is usually described by its diameter and length or the length to diameter ratio (L/D) (Figure 2-1). Typically, commercial extruders have a diameter of between 1.5 and 14 inches, with an L/D of about 24, 30 or 36 [6]. The maximum output rate of an extruder is roughly proportional to the barrel surface area. Longer extruders with higher L/D ratios, instead of larger diameters, is a cost effective way of increasing the barrel surface area for a higher output rate [6].

Generally, extruders are divided into two types, depending on the number of screws in the barrel:

- Single screw extruders
- Double screw extruders

2.1.1 Single screw extruders

A single screw extruder, as the name suggests, consist of a single screw tightly fitted within a barrel. The screw typically has one or two ‘flights’ spiralling along its length. The diameter at the outside of the flights is constant along the length to allow the close fit in the barrel. The core, however, is of varying diameter and so the spiralling channel varies in depth. In general, the channel depth decreases from feed end to die end, although there are variants for special purposes. A consequence of the decreasing channel depth is increasing pressure along the extruder, and this is what drives the melt through the die (Figure 2-1) [5; 6].

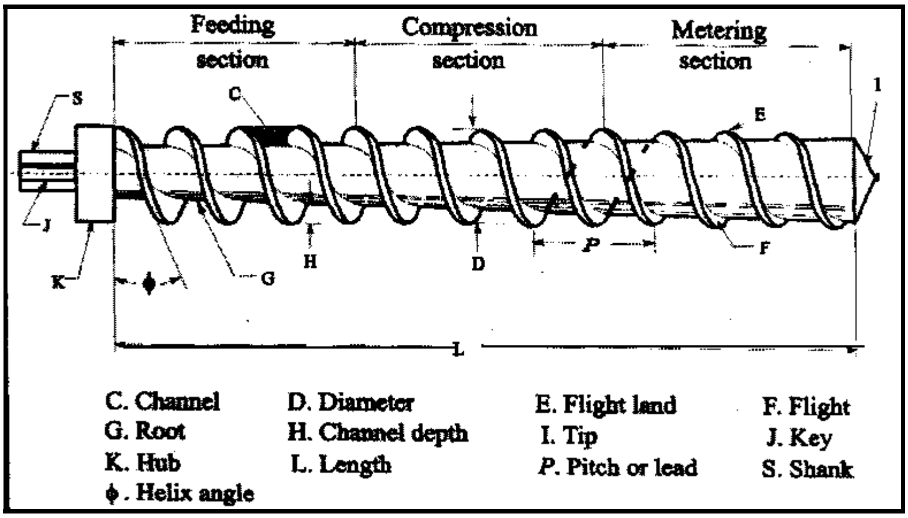


Figure 2-1: Sections and geometric features in a single screw extruder [5; 6].

This phenomenon makes the operation of this type of extruder dependent on frictional forces at the wall as well as on the properties of the polymer. As a consequence, single screw extruders are not generally considered to be suitable for reactive extrusion, especially when the difference between reagent viscosities is large. For example, at high revolutions per minutes (RPM), the material's radial velocity in the screw flight (Figure 2-1) differs substantially from the screw’s root towards the barrel. This contributes to shear and frictional heat build-up, as well as a non-uniform melt viscosity. The result is that the reagent and polymer do not disperse adequately, leading to poor reaction [7].

There are four sections in a typical extruder that will be discussed below (Figure 2-2):

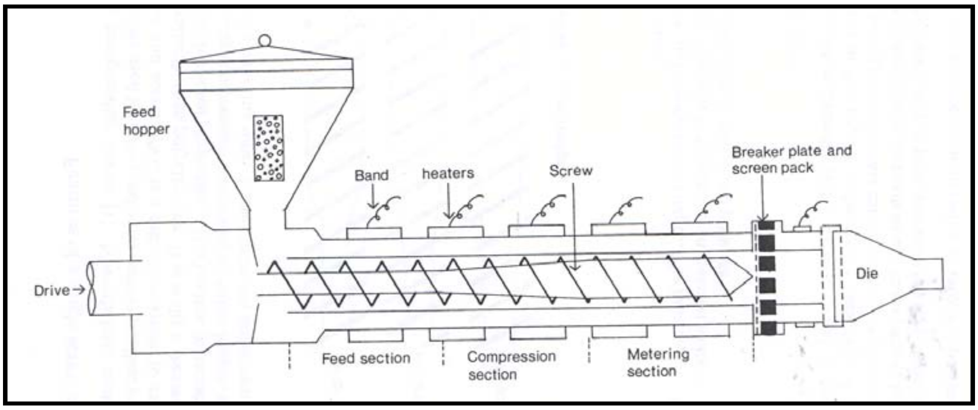


Figure 2-2: Main features of single screw extruder [5].

I Feed Zone

The function of the feed zone is to preheat the polymer and convey it to the subsequent zones. The screw depth is constant and the length of this zone is such as to ensure a correct feed rate. The correct feed rate varies with different types of polymers, as it is dependent on the viscosity of the melt.

II Compression zone

The compression zone is characterized by a decreasing channel depth and serves several functions: Firstly, it expels air trapped between the original granules and secondly, heat transfer from the heated barrel wall improves as the material thickness decreases. Thirdly, the material is compressed leading to an increase in density of the molten material [5].

Different screw designs are necessary for different types of polymer melting conditions. For a polymer that melts gradually like polyethylene, a screw as shown in Figure 2-3(b) is appropriate. However, if the polymer melts relatively sharply, e.g. nylon, a very short compression zone is used (Figure 2-3(a)).

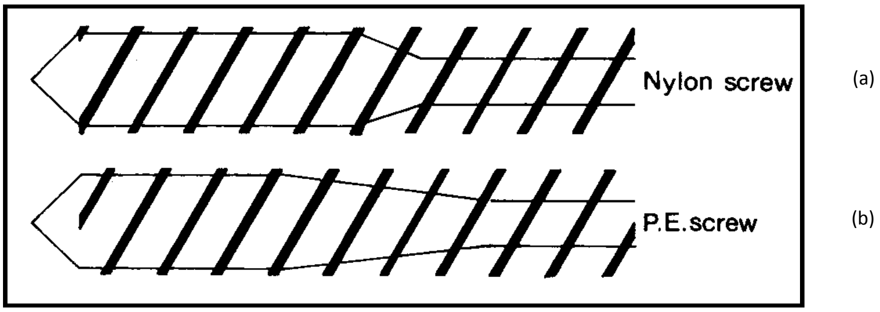


Figure 2-3: Variations in screw configuration [5].

III Metering zone

The function of the metering zone is to homogenize the melt in order to supply the die zone with a homogeneous material, at constant temperature [5].

IV The die zone

The die zone is located in the screen pack (Figure 2-2). The screen pack usually comprises a perforated steel plate, called a breaker plate, and a sieve pack, consisting of two or three layers of wire gauze upstream of the die. The breaker plate has three functions [5]:

- To sieve out extraneous material, e.g. dirt and foreign bodies.
- To allow pressure to develop by providing a resistance for the pumping action of the metering zone.

- To remove turning memory from the melt. Polymers are made up of long chain molecules, coiled and intertwined in melt, because of its visco-elastic behaviour. When the melt received a prolonged mechanical treatment, such as passage down the screw, appreciable chain alignment occurs. This manifests itself as tendency toward elastic recovery of this alignment as the preferred energetic configuration. Passage through the die is relatively short-lived, without sufficient time for the spiralled configuration to relax. The result is a tendency for the product to twist once it escapes the die and hardens [5].

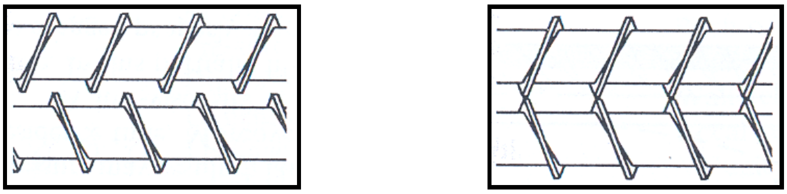
2.1.2 Twin screw extruders

In comparison, twin screw extruders typically results in more intense mixing. It has been shown that screw design will effect mixing and residence time. The development of recent twin screw extruders has gradually increased its importance in plastic compounding because of its superior mixing capabilities.

There are several types of twin screw extruders available in industry:

I Tangential twin screw extruder

This type of extruder can be pictured as two parallel single screw extruders. This extruder can be arranged with the flights either matched or staggered (Figures 2-4(a) and (b)). A staggered configuration results in enhanced mixing and low pressure build up.



(a) (b)

Figure 2-4:(a) staggered configuration, (b)matched configuration [8]

A matched configuration produces better pressure build up, but is at the cost of efficient mixing. The intermeshing cusps of the barrel are truncated for structural reasons to avoid weakness of feather edges. With the truncated section, incomplete sealing between barrel and screw occur resulting in back-mixing from one screw to another. This type of screw configuration can create twice the maximum flow, at the same discharge pressure, as single screw extruders [9].

II Intermeshing co-rotating twin screw extruders

In Figure 2-5, intermeshing co-rotating twin screw extruders are available in three types of configurations:

- single lobe
- double lobe
- triple lobe

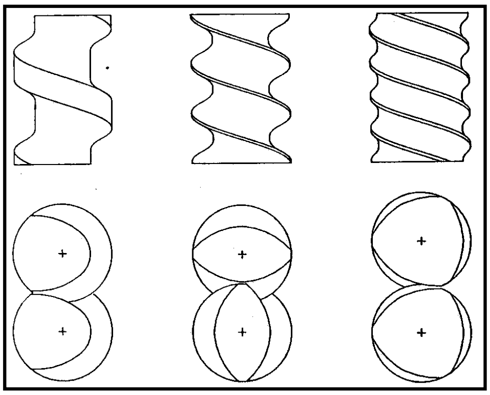


Figure 2-5: Single, double and triple lobes (from left to right) [6].

With an increasing number of lobes (Figure 2-5), the distance between screw axes has to increase and consequently, the maximum channel depth decreases. The result is that the maximum throughput, per screw rotation is decreased. Therefore, extruders with four or more lobes are not common because there are hardly any parallel planes close to each other in the geometry. Most commonly used are the double lobes, as it offers the largest reactive volume combined with minimum shear work input.

III Intermeshing counter rotating twin screw extruders

Intermeshing, counter rotating twin screw extruders often have a modular barrel and screw design and its multi-lobes designs (Figure 2-6) are similar to those of intermeshing co-rotating twin screw extruders [5]. As the polymer melt moves through the barrel, it is calendared by the action of the counter rotating screws in the calendaring section (Figure 2-6). When the screw channel is completely filled and compressed, the compressed polymer is locked within one screw chamber between two intermeshing points, and it is positively pushed forward along the screw channel by the intermeshing flight.

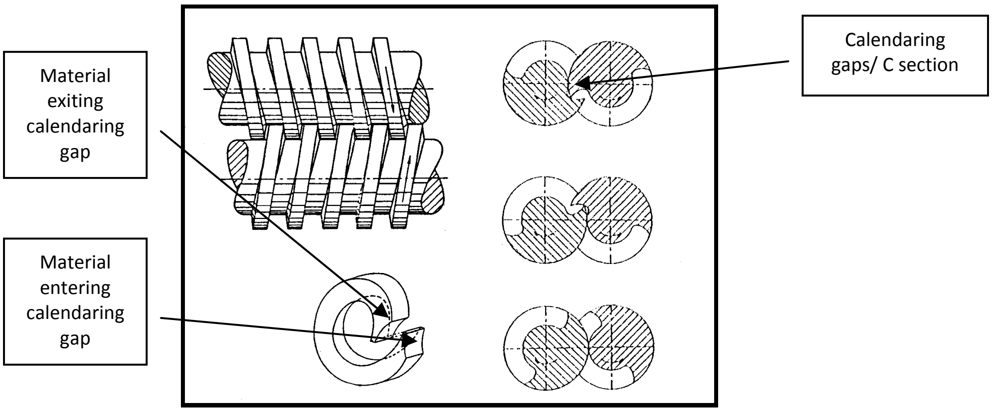


Figure 2-6: Intermeshing counter rotating twin crew extruder [6].

The calendaring action in intermeshing counter rotating twin screw extruders also generates high-pressures, pushing the two screws apart from each other. The calendaring action is minimized by using a large calendaring gap and the mixing function is primarily accomplished by kneading elements with multi-lobed designs, similar to intermeshing co-rotating twin screw extruders.

As discussed above, all types of extruders have their own benefits and weakness for processing. For example, it has been shown that screw rotational speed and geometry of the screw element, influenced chemical reactions during extrusion [10]. In another study, Zhu et. al. used three dimensional numerical simulations to study mixing mechanisms during reactive extrusion. They concluded that polymerization kinetics in the extruder is highly complex and even though plug flow is often assumed, the flow is much more complex [10]. Furthermore, B.Vergner et. al. [11], have found that reactive extrusion often involves problems when controlling a chemical reaction during conditions, such as high viscosity, high temperature, and short residence times. Understanding the fundamentals behind reactive extrusion is important for processes optimization, but is often done by trial and error [12].

2.1.3 Other factors affecting extrusion

Other factors that may influence the extrusion processes are feed conditions and heat transfer:

I Feed conditions

Feed conditions are not as crucial as other factors, and only indirectly affect the whole process.

A polymer feed is usually in the form of pallets that drop from a hopper through the feed throat into the barrel, containing the rotating screw (Figure 2-2). This occurs by gravity for most cases, especially for single screw extruders. However, some feeds such as sticky powders, tend to bridge inside the hopper and do not drop freely from the hopper into the screw by gravity [6]. This kind of problem therefore requires a forcing device to rectify it. A metered feeding device, such as a volumetric feeder, is used to control feed rate by avoiding the starved feeding mode in the extruder.

The feed throat, which is attached to the heated barrel, often becomes hot during the process. Feed materials, with a low melting point, tend to stick to the feed throat wall, and hence reduce the feeding rate may even block the feed throat. To overcome this problem, cooling water is typically used at the feed throat [6].

The feed rate is essentially dependent on the physical characteristics of the feed such as, the size, shape, bulk density and internal friction between the feed constituents [6]. Solid densities, external friction of material on metal surface, and the hopper design may also affect the feed rate. For example, when a feed material consists of several different types of materials, segregation may occur in the feed hopper. This is especially true when two different materials with the same shape, but different densities, or vice versa are fed simultaneously [6].

The feed hopper design as well as the feed throat is therefore important process parameters. However, in extrusion, the screw and barrel design are more important as these may directly contribute to the reaction mechanism during reactive extrusion.

Feed conditions are often neglected, but in reality, to reduce problems in the overall process, should be considered during design.

II Heat transfer

Heat transfer and thermal homogeneity are important considerations in reactive extrusion as careful control of the chemical reaction is required in order to achieve the desired product [8]. The rate of reaction is approximately doubled with every 10^{o}C increase in temperature, therefore making heat transfer an important consideration during reactive extrusion [8].

Reaction kinetics is sensitive to the bulk temperature, and a temperature distribution may affect selectivity and extent of reaction. Furthermore, overheating caused by heating elements should be avoided as it may degrade the product. Most reactive extrusion processes consist of multiple reaction stages, and it is therefore necessary to have a specific temperature profile along the axial direction of the extruder [9].

During reactor scale scale-up, range of factors need to be considered [6]. In a small scale extruder, the surface to volume ratio is quite consequential, and diminishes proportional to screw diameter. However, in a large production machine, this can be much lower than similar laboratory sized equipment. A stable temperature promises a consistent product and if heat transfer is very low, solidification of polymer product may occur and may cause the extruder to stop.

Xanthos [9] has stated that the simplest way to estimate heat transfer in an extruder is by assuming the extruder to be a cylinder with concentric layers. Even though it is logical, it is only applicable to single screw extruders. In large extruders, heat released in the middle of the screw needs to be transported over larger distances compared to small extruders, leading to larger radial temperature differences [9].

In addition, there are many other factors that need to considered concerning heat transfer [9]:-

- mechanical energy supplied by the rotation of the screw
- heat flow through the wall
- the heat of reaction

- mechanical energy that is partly used for pressure generation
- mechanical energy that is converted to heat by internal friction
- energy utilized to heat and melt the material.

Factors mentioned above are important as it can contribute to an increase in reaction temperature inside the extruder. For example, heat is generated due to friction between the polymer and the rotating screw, or heat may be generated during an exothermic reaction. This may lead to higher than expected temperatures inside the extruder and need to be carefully controlled.

In conclusion, feed conditions and heat transfer are important factors that contribute to adequate reaction conditions during extrusion. These factors are generally easily controlled during extrusion as they lead to the recognition of the extruder as a reactor of choice, especially in the polymer industry.

2.2 The extruder as a reactor

In order to better understand how an extruder can be used as a reactor, further discussion on the fundamentals of common reactors that are available in the processing industry is required. There are generally three types of reactors that are available:

2.2.1 Batch reactors

In a batch reactor (Figure 2-7 (a)), reactants are initially charged into a container, well mixed and left in the reactor for a certain time. The resultant mixture is then discharged as a product. In this kind of reactor, an agitator or mixer is used to homogenize the reactants. The wall of the reactor is typically insulated to control heat transfer [13].

2.2.2 Plug flow reactors (PFR)

Plug flow reactors are tubular in design (Figure 2-7 (b)), with reactant flowing in and out simultaneously. This type of reactor is characterized by the fact that flow of fluid through the reactor is orderly, with no fluid elements overtaking or mixing with any other elements ahead or behind [14]. This kind of reactor usually produces the highest conversion per reactor volume of any continuous flow reactor [15].

2.2.3 Continuous stir tank reactors (CSTR)

CSTR is a stirred tank-type reactor (Figure 2-7 (c)) where the reactants are introduced and products withdrawn simultaneously in a continuous manner. The contents is well mixed and uniform throughout and the exit stream has the same composition as the fluid within the reactor [14].

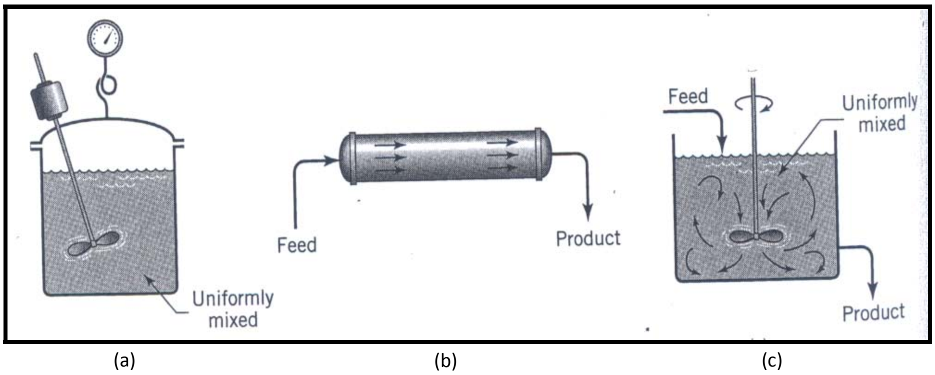


Figure 2-7: Type of reactors [14].

An extruder is almost the same as a PFR, being a tabular reactor and fluid moving from one end to another. Batch, normal PFR and CSTR reactors are rarely suitable for highly viscous media, and therefore reactive extrusion offers an attractive solution. It is the most suitable method to deal with viscous media and often requires very little purification processes. After the rapid improvement in reactive extrusion technology, the extruder is now an important reactor in several processes [8].

2.3 Typical reactive extrusion processes

Various reactions including polymerization, grafting, branching and functionalization can be performed successfully in an extruder. The economics of using extrusion for conducting chemical modifications or polymerization reactions have been shown to be an efficient way for low cost production and processing methods [16]. In Table 2-1, some advantages of reactive extrusion are listed [8]:

Table 2-1: Advantages of extrusion process vs. solution methods [8; 16]

Process	Extrusion	Solution Method
Occurrence	Continuous	Batch
Solvent	Small amount or no solvent are required	Large amounts of solvent required
Viscous media	Suitable	Less suitable
Residence time	Can be controlled by judicious screw design	Easily controlled

Generally, extruders have numerous advantages over conventional reactors that make them ideal for polymer modification and some polymerization processes. These include good mixing, reasonable heat transfer and good pumping abilities for high viscosity materials. One of the major advantages of reactive extrusion is the opportunity to perform reactions in the molten phase, therefore eliminating the need for a solvent and is therefore more environmentally friendly.

In order to better understand reactions performed in extruders, some aspects of extruder operation need to be discussed:

2.3.1 Extruder operation

When performing a reaction inside an extruder, the residence time and residence time distribution have a direct impact on the reaction. There are several factors that may contribute to residence time and residence time distribution, such as: screw speed and configuration, feed rate and barrel temperature. Residence time determines the extent of mixing and therefore will influence the extent and efficiency of the reaction during the extrusion process [17].

I Residence time

Residence time is effectively the average length of time material will remain in a reactor. By definition, the residence time is the amount of material in the reactor, divided by either the inflow or the outflow rate [14].

II Residence time distribution (RTD)

The residence time distribution (RTD) is a function that describes the distribution of times spent in the reactor by individual pockets of fluid and is used to characterize non-ideal mixing in the reactor [15]. In an ideal plug flow reactor, all atoms of material leaving the reactor have been inside for exactly the same amount of time, and it is similarly to a batch reactor. In other reactor types, the various atoms in the feed spend different times inside the reactor, hence a distribution of residence time [15]. For example, consider a CSTR: the feed introduced to the reactor at any given time becomes completely mixed with the material in the reactor. In other words, some atoms entering the CSTR leave almost immediately, because of the material being withdrawn from the reactor, while others may remain in the reactor almost indefinitely [15]. This could significantly affect reactor performance. RTD is also indicative of the type of mixing that occurs within the reactor and to the degree of deviation from ideal behaviour.

Measurement of RTD

RTD can be measured using two methods: pulse input or step input. A step input method has been chosen in this discussion as it is easily experimentally validated [15].

Step input

Using this method, RTD can be measured experimentally by using an inert tracer injected into the reactor at t = 0 (t, time). The tracer concentration at the outlet is then measured as a function of time. The tracer must be non-reactive and non-absorbing on reactor walls and internals. The tracer is usually coloured or radioactive to allow detection and quantification [14]. Figure 2-8(a) and Figure 2-8(b) show the time vs. concentration of the injection and step response, respectively.

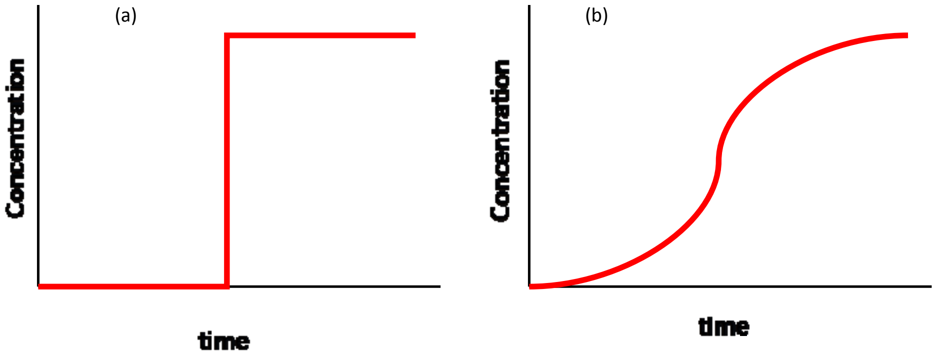


Figure 2-8: a) Step injection, b) Step response

Consider a constant rate of tracer addition to a feed that is initiated at time $t = 0$. C_o is initial tracer concentration in the feed, C_{step} is concentration of the tracer and C_{out} is the concentration at the exit. It is assumed that at time t = 0 the concentration of the tracer in the outlet would be zero.

The outlet concentration is conveniently normalized with respect to the initial tracer concentration in the feed to yield the F-curve (Figure 2-9). Furthermore, the exit age function (E(t), t^{-1}), is the time spent in the reactor by the flowing material (Figure 2-9) and is defined such that: $\int_0^\infty E(t)dt = 1$, assuming that after infinite time the exit concentration would be that of the tracer concentration.

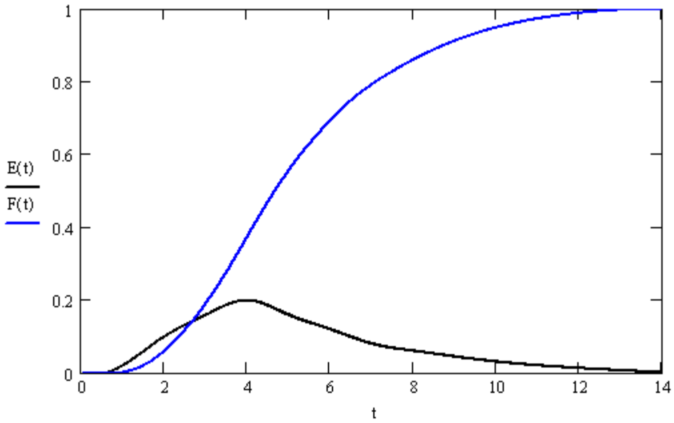


Figure 2-9: Graph of Exit age distribution (E_t) and normalized concentration function (F_t) vs. time.

The concentration at the exit can therefore be expressed as: [15]

$$C_{out}(t) = C_0 \int_0^t E(t)dt \qquad \text{(Equation 2-1)}$$

Dividing by C_0 yields:

$$\left(\frac{C_{out}(t)}{C_o}\right) = \int_0^t E(t)dt = F(t) \qquad \text{(Equation 2-2)}$$

Differentiation of Equation 2-2 will therefore yield the exit age function, $E(t)$:

$$E(t) = \frac{d}{dt}\left(\frac{C(t)}{C_0}\right) \qquad \text{(Equation 2-3)}$$

From the above equations, the mean residence time (τ) can be calculated and represents the average time a molecule spends in the extruder:

$$\tau = \int_0^\infty tE(t)dt = \int_0^1 tdF(t) \qquad \text{(Equation 2-4)}$$

The variance or dispersion around the mean, is another useful property, and is an indication of the degree of deviation from the assumption of ideal behaviour:

$$\sigma^2 = \int_0^\infty (t-\tau)^2 E(t)dt = \int_0^1 (t-\tau)^2 dF(t) \qquad \text{(Equation 2-5)}$$

For an ideal plug flow reactor, there should be no deviance from the mean. However, due to non-ideal mixing, some molecules remain in the reactor for either longer or shorter time, giving rise to a distribution of residence time.

2.3.2 Reactions performed in the extruder

I Grafting or functionalization

Grafting and functionalizing reactions will lead to a change in the chemical and physical properties of polymers, thereby increasing the industrial value [8]. Production of graft or functionalized polymers involves the reaction of polymer chains with monomers or mixtures of polymers with different monomers. In grafting reactions, short chains of monomers will link to the polymer backbone, while functionalization implies units of monomers chemically linking to the polymer. This will effectively render the polymer capable to reaction with other chemicals, reactive towards the functional group. In the grafting reaction, free radical initiators or ionizing radiation can be used to initiate the reaction [9].

II Inter-chain copolymerization

Inter-chain copolymerization occurs between two or more polymers to produce a copolymer [8; 9]. The reactions always involve the interchange or combination of reactive groups to form a graft or block-copolymer. Some examples of inter-chain copolymerization reactions performed in a extruder are summarized below:

Table 2-2: chemical processes for inter-chain copolymer formation in extruder reactor [9].

Type	Process	Type of polymer obtained
1	Chain recombination/cleavage	Block and random
2	End group 1st polymer + end group 2nd polymer	Block
3	End group of 1st polymer + pendant functionality of 2nd polymer	Graft
4	Pendant functionality if 1st polymer + pendant functionality of 2nd polymer Or	Graft
	Main chain of 1st polymer + main chain of 2nd polymer	Graft
5	Ionic bound formation	Graft

Random or block copolymers are usually formed through chain cleavage followed by recombination (Type 1, Table 2-2). Inter-chain polymerization typically involves combination of reactive groups of one polymer with reactive groups on a second polymer to form a block or graft copolymer. In contrast to graft reactions, there are no monomers involved, and the process run by intensively mixing of the melt of the two polymers in an extruder [9]. In the majority of cases, inter-chain copolymer formation involves combination of reactive groups of one polymer with reactive groups on a second polymer (types 2, 3, 4, 5, Table 2-2).

III Bulk copolymerization

In bulk polymerization, a new polymer is formed from a monomer or low molecular weight polymeric materials. The polymer that is formed is typically soluble in the monomer [9]. Because of the viscosity increase due to polymerisation, heat transfer may become a major factor to be considered during design.

IV Polymer degradation

This reaction type is always used to decrease the molecular mass of polymers to meet certain product specifications. The reaction is simply carried out by the addition of peroxides or by heat. Usually, longer chains have a bigger chance of being degraded and it accompanied by narrowing the molecular mass distribution [9].

V Branching and coupling

This reaction type involves the increase of molecular mass by coupling or branching different polymer chains through poly-functional coupling agents or condensing agents[9]. Suitable polymers should have end groups or side chains that are reactive towards the coupling agents used. Two different kinds of coupling agents are typically used:

Condensing agents are used to chain-extend polymers which have two different functionalities as end-groups. Usually, the condensing agent only reacts with one of the functional groups [9].

Coupling agents are always poly-functional and used to chain extent or branch polymers with either one or two different types of functionality as end groups [9].

3. Polymer modification

In the preparation of bio-derived resins, processability is often of major concern, especially when thermoplastic processing techniques are used. Plasticizers are often required, of which water is most common. Low molecular mass plasticizers often leach out during use and therefore limit their long term use in bio-derived resins. Alternatively, proteins and other natural polymers are often blended with synthetic polymers to improve its processability. In this case, the compatibility of the polymers is important as incompatible polymers lead to poor mechanical properties of the blend. Compatibility can be improved by grafting the polymers with groups that can render them compatible. Alternatively, by grafting the two polymers onto each other, the graft copolymer can act as a compatibilizer in the blend [3; 18] .

The broader context of this study is to produce blends of proteins and polyethylene, and means of compatibilizing these are explored. It is therefore important to understand how proteins and polyolefins can be modified in order for this to be possible.

3.1 Proteins and protein reactivity

Proteins are natural polymers, but are far more complex than most synthetic polymers, it can incorporate up to 20 different monomer units instead of only one or two. Most polymers are synthesized by polymerizing a mixture of monomers, producing a distribution of chain lengths. However, proteins are linear, unbranched and have a precise length and an exact sequence of amino acids.

Amino acids are organic molecules possessing carboxyl and amino groups. Amino acid residues have a variety of chemical properties, mostly determined by the R-group, as defined in Figure 3-1.

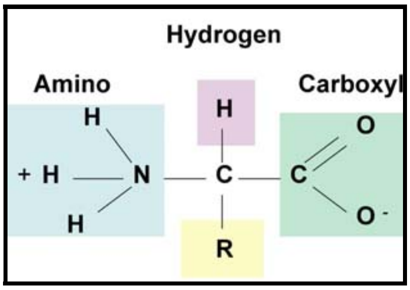
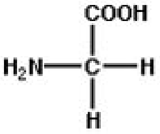
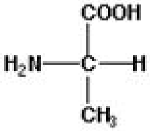
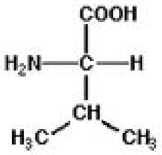
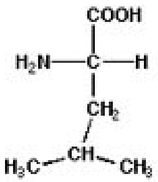
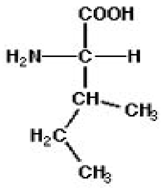
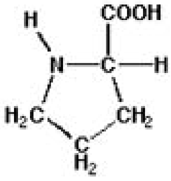
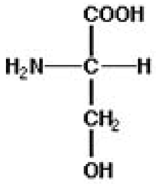
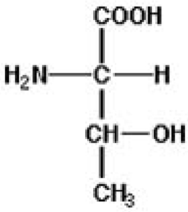
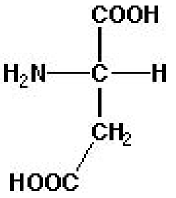
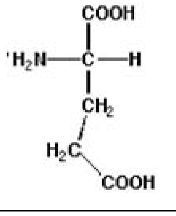


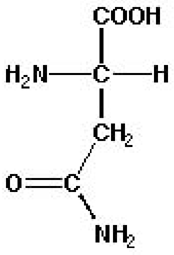
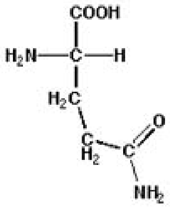
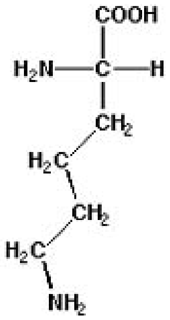
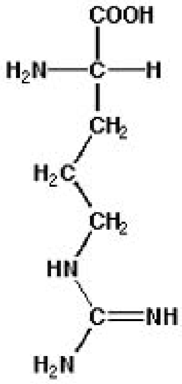
Figure 3-1: General formulation of amino acids [21].

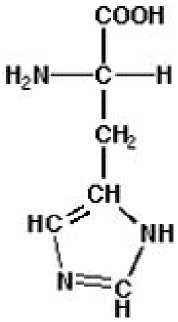
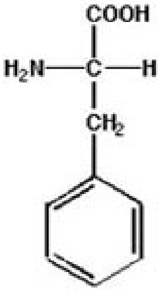
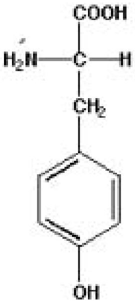
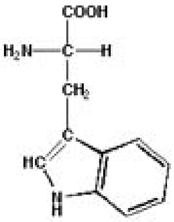
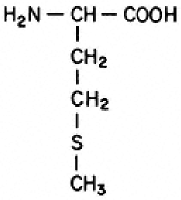
When combined in a single polymer molecule, the possible chemical properties are almost endless. The structure and properties of the 20 known amino acid residues are shown in the table below:

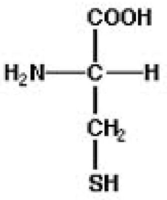
Table 3-1: Amino acid residues

Groups	Names	Structure	Discussion
	Glycine (Gly) (G)		Glycine is the simplest amino acids, with only a hydrogen atom as a side chain
Aliphatic	Alanine (Ala) (A)		These amino acids residues have no reactive groups on their side chains, only inert metyhlene and methyl groups; they have important properties, such as low interaction with water. They interact strongly with each other and with other non polar-atoms. This is one of the main factors in stabilizing the folded conformation of proteins [19].
	Valine (Val) (V)		
	Leucine (Leu) (L)		

	Isoleucine (Ile) (I)		
Cyclic	Proline (Pro) (P)		The side chain of proline is aliphatic like those of the proceeding amino acids, but with no functional groups. However, it is unique that it is bonded covalently to the nitrogen atom of the peptide backbone [19].
Hydroxyl	Serine (Ser) (S)		The side chain of Ser and Thr are small and aliphatic, except for the presence of a polar hydroxyl group on each. These hydroxyl groups are normally no more reactive chemically than ethanol, so there are a few chemical reactions in which they precipitate that are useful in protein chemistry. The only reaction that occurs readily is acetylation with acetyl chloride in aqueous trifluoroacetic acid [19].
	Threonine (Thr) (T)		
Acidic	Aspartic acid (Asp) (D)		The side chain of Asp and Glu differ only in having one and two methylene group respectively. The carboxyl group of Asp and Glu are normally no more reactive that are those of corresponding organic molecules such as acetic acid [19].
	Glutamic acid (Glu) (E)		

Amide	Asparagines (Asn) (N)		The Asn and Gln amide side chain do not ionize and are not chemically reactive. They are very polar, being both hydrogen donor and acceptors. The amide groups are labile at extremes pH and at high temperatures, and can deamidate to Asp and Glu residues [19].
	Glutamine (Gln) (Q)		
Basic	Lysine (Lys) (K)		The side chain of Lys is a hydrophobic chain of four methylene groups, capped by an amino group. Amino group of Lys residues readily undergo an acylation, alkylation, arylation and amidination reactions.
	Arginine (Arg) (R)		The Arg side chain consists of three non polar methylene groups and strongly basic guanido group at pKa about 12, guanido will ionize and resulting in the resonance of the Arg group thus may lead the Arg to protonated easily [19].

	Histidine (His) (H)		The imidazole side chains of His residue possess several special properties that make it extremely effective as a nucleophilic catalyst.
Aromatic	Phenylalanine (Phe) (F)		The aromatic ring of Phe residues is chemically comparable to benzene or toluene. It is non polar and is chemically reactive only under extreme conditions that are not applicable to proteins.
	Tyrosine (Tyr) (Y)		The hydroxyl group of the phenolic ring of Tyr residues makes this aromatics ring relatively reactive in electrophilic substitution reactions
	Trytophan (Trp) (W)		The indole side chain of Trp residues is the largest and the most fluorescent of the side chain of proteins. This amino acid also occurs least frequently [19].
Sulfur	Methionine (Met) (M)		The long side chain of Met residues is non polar and relatively unreactive and is the only unbranched non polar side chain of all amino acid. The sulfur atom is nucleophilic, but unlike other nucleophiles in proteins it cannot be protonated. Consequently it is most potent nucleophile in proteins at acidic pH [19].

	Cysteine (Cys) (C)		The thiol of group of Cys residues is the most reactive of any amino acid side chain. The Cys thiol usually ionizes at slightly alkaline pH it can react rapidly with alkyl halides, such as iodoacetate, methyl iodide to give stable alkyl derivatives [19].

Not all amino acids are capable of undergoing appropriate chemical reactions that would enable grafting with synthetic polymers. The most chemically reactive amino acids, lysine and cystein are discussed in Table 3-2.

Based on the reactivity of the amino acids discussed above, grafting functional groups for modifying synthetic polymers can be chosen. However, modification of synthetic polymers also depends on other parameters, discussed in the following section.

Table 3-2: Reagents that may be involved in the protein modification.

Amino acid residues	Reagent	Other components that may react	Description
Lysine	Acetic anhydride Citraconic anhydride	α-amino groups, tyrosine	Modification of lysine is easy compared to methionine and histidine. Reaction with anhydride group usually also affect other amino acid groups. Therefore, cystein and tyrosine may also be affected with if this kind of reagent is used [20; 21]. The lysine residue must be unprotonated to function as a satisfactory nucleophile, therefore an alkaline pH condition is required. Lysine readily undergoes a variety of acylation, alkylation, arylation and amidation reactions.
Cystein	N-ethylmaleimi-de Maleic anhydride	Lysine	One of the most powerful nucleophiles, and is the easiest amino aicd to be modified. The thiol group of cystein can also add across the double bond of N-ethylmaleimide or maleic anhydride [19].

3.2 Parameters affecting grafting

Functionalization is a reaction where a polymer is modified in the molten state by the addition of functional monomers. Modification is achieved when a functional monomer is attached to the polymer, resulting in structural and functional properties of the polymer changing.

With polyolefins, the reaction requires an initiator, which decomposes into free radicals that react with the polymer to form a reactive site on the polymer.

Grafting is a complex chemical reaction performed in the extruder and is influenced by many parameters. The most important parameters are listed below, and will be discussed further [8; 22]:

- Type of monomer
- Polyolefin characteristics
- Side reactions
- Co-agents or additives
- Temperature
- Mixing and feeding sequence
- Residence time
- Initiator
- Screw and extruder design (has been discussed in Section 2.1)

3.2.1 Monomer

In the context of functionalizing a synthetic polymer for further reaction with proteins, it is important that the selected functional group be reactive towards both the synthetic polymer and the protein. Polyolefins, such as polyethylene and polypropylene can be modified using some anhydrides and maleimide-type chemical groups. These groups, according to Lundblad [20; 21], are also the best chemical reagents to react with amino acids, such as cystein and lysine. Specifically, monomers that have been used for grafting onto polyolefins include maleic anhydride (MAH) [23-30], citraconic anhydride [31], itaconic anhydride [32] and itaconic acid. However, if the purpose of grafting is functionalization in order to enable reaction with proteins, only some of these can be used, and will be discussed below. Furthermore, in bovine blood, the percentage lysine (7.47 parts per protein) and cystein (1.68 parts per protein) are the highest, make it the most appropriate target amino acid residues for further reaction [33].

I Maleic anhydride

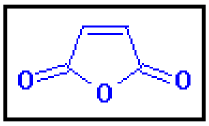


Figure 3-2: Molecular structure of maleic anhydride

Maleic anhydride (MAH) has been widely used as a monomer in modification reactions of polyolefins [8; 9] [29; 34-38]. The chemical structure of MAH is shown in Figure 3-2. MAH melts at 53°C and boils at 202°C.

Grafting MAH onto polyolefins has been shown to increase mechanical properties such as tensile strength and improved adhesion to metals [9]. Maleic anhydride also have great importance as a bonding agent in composite materials, where adhesion between fibres and polymer is important [9]. However, it has previously been shown that when MAH was reacted with amino compounds, the resulting amide bond was unstable and hydrolyzed easily below pH 5 [39]. This makes it less suitable for further reactions with proteins. Furthermore, maleic anhydride is highly volatile and is harmful to humans by attacking the skin, mucous membrane and eyes even at very low levels (>1ppm) [32].

II Itaconic anhydride

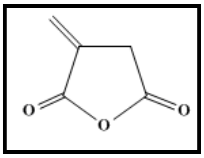


Figure 3-3: Molecular structure of itaconic anhydride

On the other hand, itaconic anhydride (IA) is less harmful [32] which makes processing much easier. It has a chemical structure similar to MAH and is shown in Figure 3-3. IA is melts at 66°C and decomposes above 114°C. It has been found that IA is extremely stable when reacted with proteins, between pH 1 and 12 and is also stable at high temperatures (approximately 70°C) [39]. Itaconic anhydride can used for acetylating lysine, tyrosine and cystein [39].

In a study by Vuorinen et. al., polyethylene (PE) was functionalized by grafting itaconic anhydride onto the main chain. The result was improved adhesion of PE to metal, in order to substitute traditional bitumen or coal tar enamel pipe coating [32]. It was postulated by the authors that grafting prior to the coating process will lead to improved strength, ductility, impact resistance, soil stress resistance, resistance to degradation and corrosion protection. These can only be achieved provided that PE is well bonded to the metal surface [32].

III Maleimide

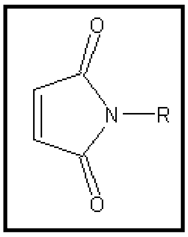


Figure 3-4: molecular structure of maleimide

A vast amount of literature is available regarding the modification of polymers using maleimide [40-45]. However, it has mainly been focussed on polyethylene glycol (PEG) modification, used in the bio-chemistry field [41].

Grafting PEG with this monomer, allows conjugation between sulfhydryl-containing amino acids, specifically peptides having cystein residues and the grafted polymer [41]. Maleimide reacts exclusively with the –SH group of cystein as opposed to other nucleophilic amino acids [43]. However, the number of free cystein groups in proteins is typically less compared to lysine [33], which may limit its use in the production of bio-derived resins. Furthermore, maleimide is very expensive, about $327.93 NZD per 25g (Sigma – Aldrich) and making it less attractive for use in the production of low cost bio-derived resins. Maleimide is also believed to be able to react with either polyethylene or polypropylene as it also contains a double bond on the ring structure. The reaction mechanism of this monomer could be similar to other monomers mentioned above.

3.2.2 Polymer type

There are several polymers that can be used for blending with proteins, but the requirement is that a suitable functional group should be able to be grafted onto that polymer. Some of the most commonly used polymers include polyethylene and polypropylene. For these polymers, degradation and cross-linking have always been an important consideration. Usually, degradation is more prominent for polypropylene (PP) and cross-linking for polyethylene (PE) [8]. Increasing the peroxide concentration and temperature would give rise to chain scission for (PP), cross-links for (PE) and generally a discoloration of the polymers. The most common monomer grafted onto these polymers is maleic anhydride (MAH) [24; 27; 32; 36; 46].

During processing, polymer molecules must flow, the ease of which is dependent on melt viscosity. Melt viscosity is proportional to molecular mass; at low molecular mass, polymer chains are free to flow, similar to single monomer units. When the critical molecular mass is reached, the melt viscosity increases rapidly, because as the chain length increases, chains begin to entangle and a network-like structure is formed, resulting in a increased resistance to flow [47; 48].

On the other hand, when temperature is increased during the melting, segmental movement is enhanced, facilitating stress decay due to chain disentanglement. Therefore, for higher molecular mass polymers, a temperature sufficiently above the softening point is required. .

The following polymers have characteristics that enables a suitable reaction temperature and ease of handling during processing [49]:

I Polyethylene (PE)

Polyethylene (PE) is of high commercial interest due to its characteristics such as availability, low cost and a wide range of physical and chemical properties. However, its use in polymer blends has been limited due to its non-polar character [50]. To overcome this deficiency, it can be functionalized with monomers, such as those mentioned above [50]. However, polymer degradation may occur in the presence of peroxides of oxygen. The major degradation mechanism is chain scission for HDPE and chain branching and cross-linking for LDPE. This could be avoided or reduced by the addition of stabilizers, such as primary anti-oxidants (hindered phenols) and hydro-peroxide-decomposing antioxidants (phosphites) [51].

II Polypropylene

As for polyethylene, polypropylene also requires modification in order to improve its compatibility with polar polymers [27; 28; 31; 36; 52-55]. The stereo-regularity of polypropylene (isotactic or atactic) has been shown to affect the degree of grafting [56; 57] and therefore it is important to select the most appropriate polypropylene type. During fuctionalization, polymer degradation may compete with grafting and should be carefully controlled.

3.2.3 Polymer degradation

Reactions at elevated temperature in the extruder may contribute to polymer degradation. Polymers are oxidized, partially degraded or cross-linked when processed in an air atmosphere, reducing the mechanical properties and the service-ability of the polymer [58].

The exposure of polymers to oxygen is characterized by an induction period during which the polymer does not show any obvious changes and there is no evidence of oxygen absorption (Figure 3-5). During this period, small amounts of hydro-peroxides (peroxide with hydrogen atom as the functional group) are formed and initiate subsequent rapid auto-oxidation of the polymer. Increasing the reaction temperature will also accelerate auto-oxidation [58].

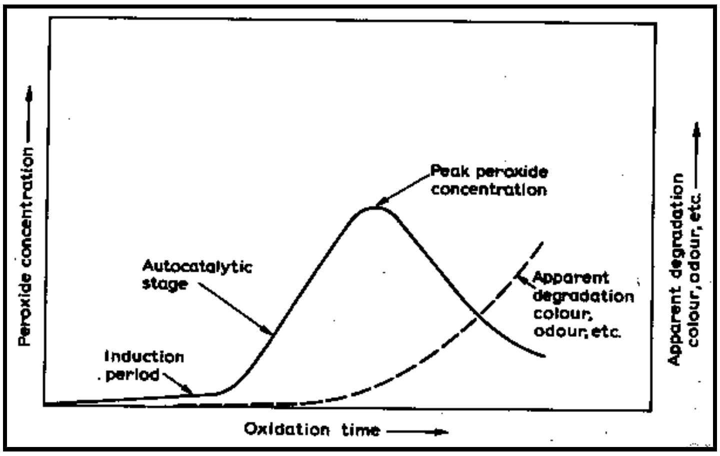


Figure 3-5: Schematic diagram of latent degradation, producing peroxide development and decay with undesirable colour and odour effect[58].

Oxidative degradation involves scission of the main polymer chains, leading to a decrease in molecular mass and the evolution of low molecular mass reaction products [58].

The process of polymer degradation is always accompanied by a parallel process of cross-linking which resulting in gel formation. Cross-linking depends on numerous factors, such as the structure of the macro-radicals, mixing, the presence of free radicals in oxygen and the concentration of the polymer [58].

In an oxygen free atmosphere, or in the presence of low concentrations of oxygen, cross-linking follows the reaction shown in Figure 3-6.

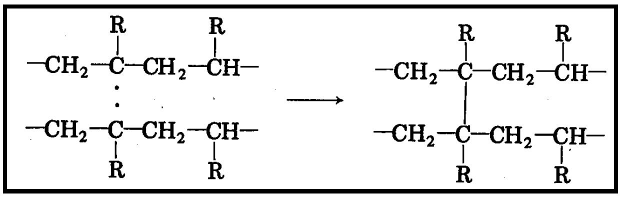


Figure 3-6: Cross-linking by macro-radicals [59].

In the presence of oxygen, oxy-radicals are produced and cross-linking may involve the formation of oxygen (Figure 3-7) or peroxide bridge (Figure 3-8).

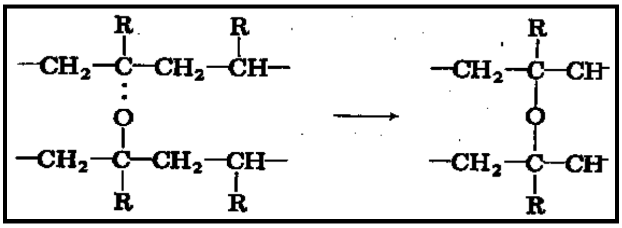


Figure 3-7 :Cross-linking resulting from oxygen bridging [59].

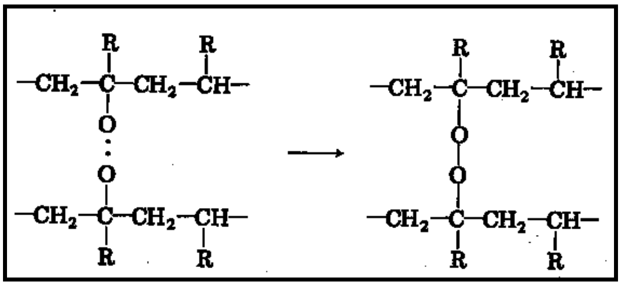


Figure 3-8: Cross-linking resulting from peroxide bridging [59].

However, it is has been found that oxidation of polyethylene at high temperatures leads to a higher degree of grafting, when using MAH as monomer [35]. Porejko et. al. [60] had similar findings when they compared grafting under inert conditions with an oxygen containing atmosphere, using MAH and benzoyl peroxide as initiator.

3.2.4 Additives

A lot of research has been done to reduce polymer degradation during polymer modification. One method of reducing degradation is by using co-agents or additives during extrusion [61-63]. In a study by Yang et al.[61], styrene was added while grafting glycidyl methacrylate (GMA) onto PE, which lead to an increase in the degree of grafting as well as gel content (degree of cross linking). However, when paraffin or oleic acid was added, the degree of grafting was increased, while gel content was decreased.

According to S.Al-Malaika [62], addition of trimethylol propane triacrylate (tris) while grafting 3,5-ditert-butyl-4-hydroxyl benzyl acrylate (DBBA) to polypropylene resulted in 50% increase in grafting. It has also has been found that adding neodymium oxide may lead to an increase in degree of grafting of MAH onto PP, along with a simultaneous decrease in gel content [24].

3.2.5 Temperature

Grafting is mostly an exothermic process, requiring adequate cooling to maintain reaction conditions. In the extruder, temperature is controlled by heating elements along the barrel. Temperature control in extruders is usually good compared to solution methods because in solution methods heat transfer is dependant on the efficiency of heat removal from the reactor wall, or by cooling coils. In an extruder, polymer is conveyed along the screw, resulting in a large surface area available for heat transfer.

Generally, in modification reactions, higher processing temperatures favour polyolefin degradation, reduce initiator half life, modify the reaction rate and changes reaction specifity [22].

3.2.6 Mixing and feeding sequence

Mixing during extrusion occurs in three ways: distributive mixing, dispersive mixing and shear refining. In addition, preliminary mixing of feed stock may also be important. Reagents may be premixed in a batch mixer to ensure homogenization. Two types of mixers are commonly used in reactive extrusion, namely: static mixers and dynamic mixers[6].

Static mixers are used to improve distributive mixing and temperature uniformity of the melt in a radial direction. It is mostly used in conjunction with single screw extruders between the screw and the die [6].

Dynamic mixers have at least one moving part attached to the screw. Dynamic mixers provide better distributive and dispersive mixing compared to static mixers, but requires a higher pressure drop [6].

According to B.Jurkowski [64], the homogeneity of a reactive blend can be improved by using a dynamic mixer and a higher degree of grafting can be obtained compared to using a static mixer. Grafting reactions are usually considered multi-component reactions and diffusion during the reaction is often limited. Therefore allowing enough time for sufficient mixing is very important.

It was found that, during melt grafting of 3-isopropenyl-α-α-dimethylbenzene isocyanate (TMI) with polypropylene and styrene as comonomer, varying the feeding sequence also changed the degree of grafting [63]. In that study, it was found that by dividing the reagents into three equal lots resulted in better grafting as opposed to feeding all the reagents together in one step. It was concluded that the reason for this is that, every additional batch charged to the mixer lead to a proportional increase in TMI's grafting yield, as if the batches were started with previously TMI-modified PP.

Similarly, H.Nazockdast [38], also varied the feeding sequence of PE, MAH and DCP prior to melt grafting. It was found that by first feeding the polymer and monomer and allowing it to melt, and then introducing the peroxide, maximal grafting was obtained [38]. This is most likely due to DCP having a greater reactivity towards MA compared to PE. The result is that when all components are introduced simultaneously, side reactions are more prominent. Likewise, in a study by Hu et. al., it was found that when a given amount of peroxide was divided into several fractions and subsequently added to the grafting system, at different time intervals, the monomer grafting yields was higher and chain scission was less severe compared to adding the peroxide all at once [65].

Generally, by ensuring that the initiator only decomposes after both monomer and polymer have been well mixed, will result in higher degrees of grafting. As mentioned earlier, grafting typically competes with homopolymerization, which is exacerbated when the rate of homopolymerization is fast. Good mixing is therefore required to provide a large surface area between the reagents.

3.2.7 Initiator

The role of the initiator is to activate the polymer by transferring a radical formed from decomposition on to the polymer chain. When choosing an initiator, the following factors should be considered [22; 24]:

- Initiator concentration
- Thermal decomposition temperature
- Initiator solubility

I Initiator concentration

The effect of initiator concentration has been studied by H.Nazockdast [38]. In that study, the effect of peroxide concentration was correlated with the melt flow index (MFI) of the grafted polymer. Their results showed that the degree of grafting (DOG) initially increased with increasing initiator concentration, but reached a plateau at intermediate concentrations (Figure 3-9). This can be attributed to the limited solubility of monomer in polymer [38]. When the concentration MAH exceeds the saturation point, phase separation may occur, leading to the peroxide being absorbed in the separated MAH phase due to its greater miscibility in monomer. This resulted in less peroxide being available for reaction [66].

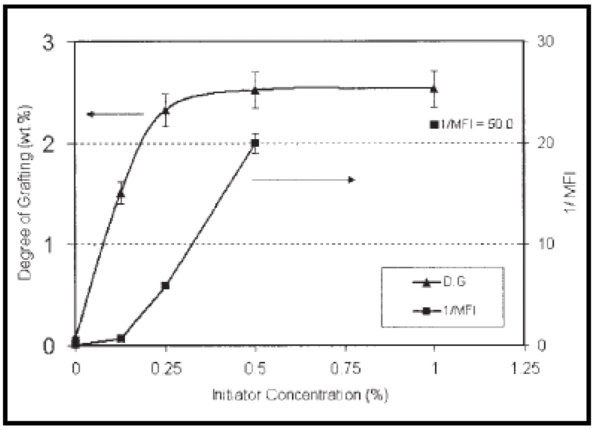


Figure 3-9: Study on the effects of initiator concentration on DOG and MFI [38].

II Thermal decomposition temperature

The thermal decomposition of peroxides also plays a role in the over all grafting reaction mechanism. The rate of thermal decomposition of the initiator is dependent on the substituent (the pendant group attached to the initiator). The rate of decomposition increases when the pendant group changes from a primary alkyl, secondary alkyl or tertiary alkyl [67]. It has been shown that the stability of the radical is dependent on the nucloephilicity of the pendant groups as well as stearic hindrances [67].

Ideally, decomposition should result from uni-molecular homolysis of the relatively weak O-O bond. However, there are always some undesired rearrangement and non-radical decomposition that complicate the kinetics of radical generation and thus reduce the initiator efficiency. For example, benzoyl peroxide (BPO) may give rise to the formation of one benzoyloxy radical, one phenyl radical and one carbon dioxide molecule when β-scission occurs [67].

III Initiator solubility

The solubility of the peroxide is important, especially in the liquid phase. Upon decomposition, free radicals will diffuse into the molten polymer phase and initiate grafting. When the initiator is in the liquid phase, two radials are formed that exist side by side at any point in time. These are surrounded by solvent molecules creating a "cage" around the pair of formed radicals; this is commonly referred to as the 'cage effect'[68]. Polyolefins are semi-crystalline polymers, and therefore low molecular mass substances penetrate and diffuse preferably in the amorphous phase. Each radical or radical pair is surrounded by segments of the macromolecules. Since the segments in the amorphous phase are not packed as tightly as crystalline phase, diffusion occurs more easily [68]. Therefore, combined with the high molecular mass of polymers, the rate of diffusion of the peroxide radical will be much lower in the polymer phase. This leads to a high probability of free radical pairs recombining inside the polymer cage. This cage effect contributes towards a low grafting degree of monomer onto the polymer.

In conclusion, there are several common rules of thumb that have been discussed for optimizing the grafting reaction. It has been shown that there is a maximum ratio between monomer and initiator required to optimize grafting and to avoid side reactions, such as cross linking (for polyethylene) and chain scission (for polypropylene). From the above discussion, it can be concluded that reactive extrusion is well suited for the modification of polymers, because of the advantages offered by extrusion. However, controlling the process to optimise the main grafting reaction is difficult as reactions such as homopolymerization often becomes a competitor in reactive extrusion.

3.3 Reaction mechanism of grafting anhydrides onto polyolefins.

Grafting an anhydride onto a polyolefin follows the same reaction mechanism as general free radical polymerization. An anhydride contains an unsaturated bond that can be used in a free radical reaction to enable grafting. Free radicals are independently existing species which possess an unpaired electron and normally are highly reactive with short lifetimes. During free radical polymerization, each polymer molecule grows by the addition of a monomer to a terminal free radical active site known as the active centre. After every addition of a monomer, the active centre is transferred to the newly-created chain [69]. The common steps in polymerization involve three stages, which are:

Initiation. This stage involves the creation of the free radical active centre and usually takes place in two steps. Firstly, the formation of the free radicals from an initiator and secondly, is the addition of one of these free radicals to a monomer or polymer [69]. The peroxide can decompose either by homolytic scission or single electron transfer.

Propagation. This process involves the growth of the polymer chain by rapid sequential addition of monomers to the reactive centre [69].

Termination. This stage the growth of the polymer chain is terminated. The two most common mechanism of termination is combination and disproportionation. Combination involves the coupling together of two growing chains to form a single polymer molecule. Alternatively, disproportionation occurs when a hydrogen atom is abstracted from one growing chain, thus resulting in the formation of two polymer molecules, one with a saturated end group and one with an unsaturated end group [69] .

There are many possibilities by which grafting can occur during extrusion, but no definite reaction mechanism has been proposed. However, most findings are very similar and will be discussed further.

Dean Shi et. al. [65] had proposed a simplified free radical grafting process, and is shown in Figure 3-10. In this diagram there are three main reactions: homo-polymerisation, chain scission and monomer grafting. All of these compete among each other and is dependent on process conditions, as described earlier. Disproportionation is most commonly known as chain scission whereby the polymer chain will be cut resulting in the degradation of the polymer. The first two reactions are considered undesirable, with grafting the main reaction. A more comprehensive mechanism is shown in Figure 3-11 [35].

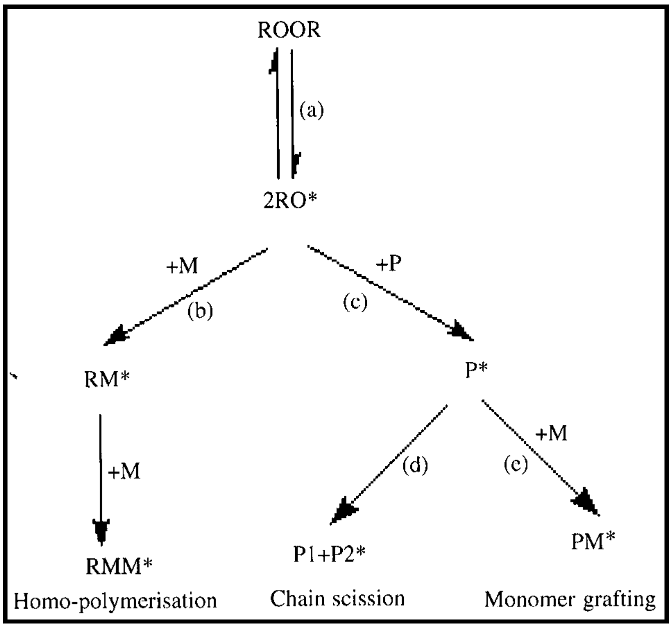


Figure 3-10: A simplified scheme of the free radical grafting process [65].

In the reaction described above, maleic anhydride was used as monomer and was grafted onto polyethylene in solution. During heating in a solution of maleic anhydride and radical initiator, in an air atmosphere, the formation of macro-radicals of polyethylene may be due to two reactions:

Chain transfer from radicals formed by the decomposition of the initiator or from growing chains of poly (maleic anhydride).

The decomposition of peroxide groups formed during the oxidation of polyethylene.

In Figure 3-11, the peroxide firstly decomposes, resulting in a free radical (step (1)). Then, initiation takes place, where the unstable peroxide tends to abstract a hydrogen atom from the polymer backbone, making the polymer unstable. The unstable polymer is then involved in propagation and reacts with maleic anhydride at the double bond in the maleic anhydride ring.

The process stops when all of the monomer is consumed. Unfortunately, other side reactions such as termination (step (5)) may also occur. Termination involves disproportionation and cross-linking of the polymer. Cross-linking occurs within the polymer or with the MAH monomer.

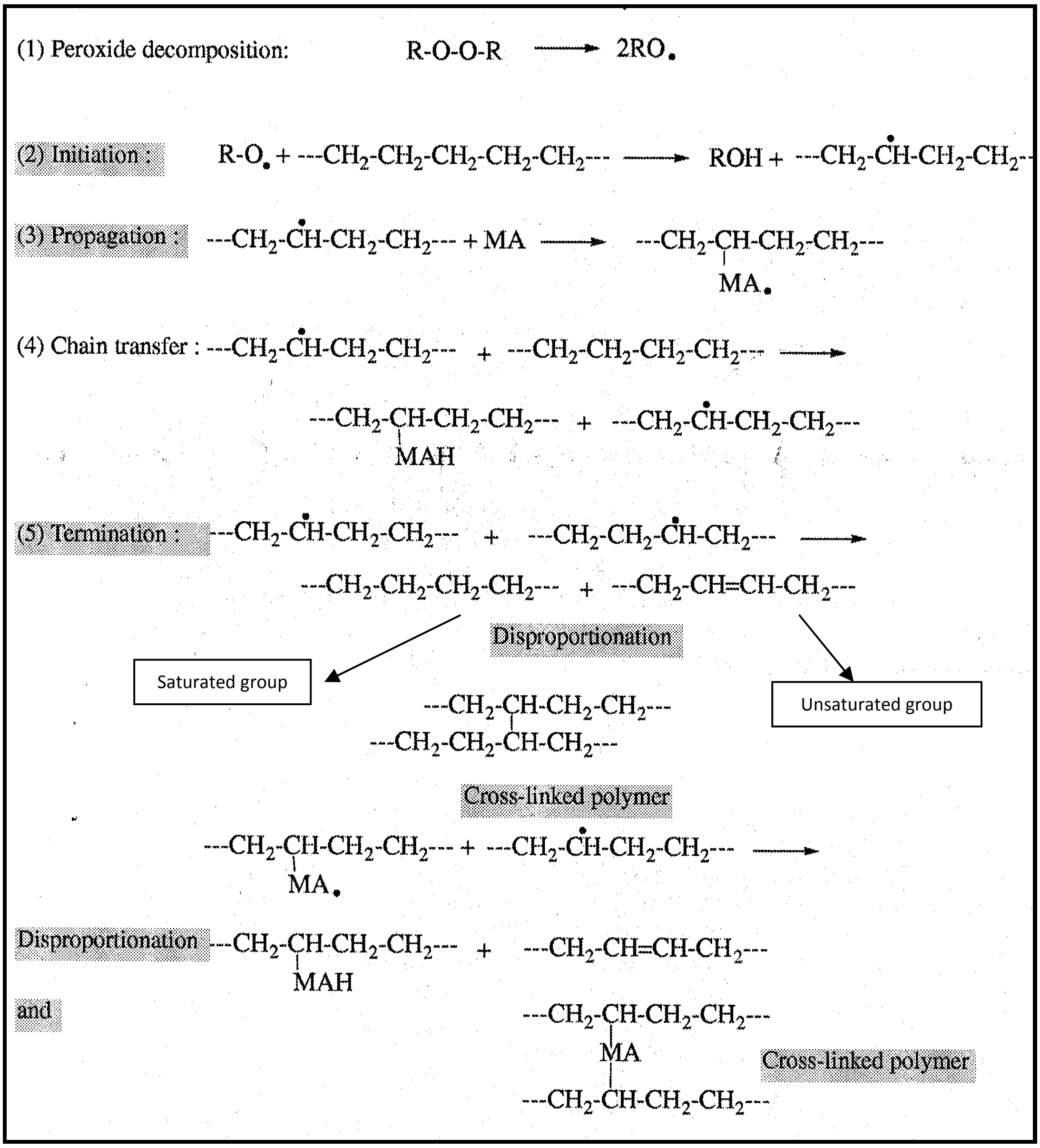


Figure 3-11: The reaction mechanism of maleic anhydride onto polyethylene[35].

4. Characterization

As highlighted in the previous section, performing melt grafting in an extruder involves several reactions in competition with each other. These were: grafting, degradation and cross-linking. Characterization of the reaction products is therefore essential and properties that should be tested for are:

- The degree of grafting and identification of grafted functionalities
- The gel content or degree of cross-linking
- Rheological properties of the product
- Mechanical properties of the product

4.1 Degree of grafting (DOG)

The degree of grafting is defined as the number of moles monomer grafted sample mass. Quantification of the DOG is made difficult by the small number of grafted monomers with respect to the number of polyolefin repeat units in the polymer chain. The DOG can easily be as low as 0.1% and is typically in the range 0.5 to 2%. This corresponds to only about one to five functional monomer units per polymer molecule, if the polymer's molecular mass is in the range M_n = 20000-40000 g/mol. A further complication is the low solubility of most polyolefins, in particular convectional PP and PE, in most solvents. The degree of grafting is typically determined by two methods:

4.1.1 Chemical method

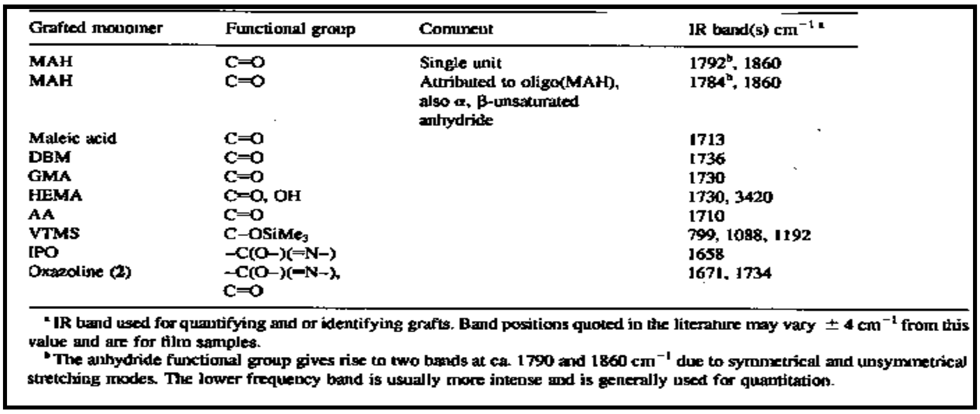
The chemical method is a titration method, and has been widely used for determining the DOG of MAH onto PE and PP [24; 27; 36; 50]. The polymer is firstly purified from unreacted monomer by dissolving the polymer in boiling xylene followed by precipitation by acetone. The grafted anhydride groups are then converted to the corresponding dicarboxylic acid by heating under reflux in water saturated xylene. The acid is then neutralised by treating the hot solution with an excess of ethanolic potassium hydroxide solution (KOH). This solution is then back titrated with acid hydrochloric (HCL) and the DOG is then calculated [22]. The exact method followed in this research is described in detail in the experimental section.

4.1.2 FTIR spectroscopy

FTIR spectroscopy can be used for identifying and quantifying functional groups. For quantitative work, FTIR spectra are generally measured on melt pressed films. The procedure involves determining the intensity of a band due to the particular functionality relative to a band that can be attributed to the polymer backbone. A calibration curve, based on a standard containing a known concentration of groups is then necessary to convert the intensity data to concentration [22]. In Table 4-1 the infrared band positions for grafted functionalities, derived from common monomers, are shown [22].

In addition, FTIR is also used to identify reaction products from side reactions, such as degradation.

Table 4-1: Principal infrared absorption bands of modified polyolefins [22].



Grafted monomer	Functional group	Comment	IR band(s) cm^{-1} [a]
MAH	C=O	Single unit	1792[b], 1860
MAH	C=O	Attributed to oligo(MAH), also α, β-unsaturated anhydride	1784[b], 1860
Maleic acid	C=O		1713
DBM	C=O		1736
GMA	C=O		1730
HEMA	C=O, OH		1730, 3420
AA	C=O		1710
VTMS	$C-OSiMe_3$		799, 1088, 1192
IPO	–C(O–)(=N–)		1658
Oxazoline (2)	–C(O–)(=N–), C=O		1671, 1734

[a] IR band used for quantifying and or identifying grafts. Band positions quoted in the literature may vary ± 4 cm^{-1} from this value and are for film samples.

[b] The anhydride functional group gives rise to two bands at ca. 1790 and 1860 cm^{-1} due to symmetrical and unsymmetrical stretching modes. The lower frequency band is usually more intense and is generally used for quantitation.

4.2 Gel content analysis

Gel content analysis is a test undertaken to measure the insoluble fraction produced by polymer cross-linking. Gel content can be determined by extraction with a solvent, such as xylene or decahydronaphthalene and is well described by ASTM standard 2765-95.

It is well known that cross-linking of polyethylene (PE) causes in structural changes resulting in many changes in its mechanical and chemical properties. According to Kampouris [70], the density of linear density PE decreased continuously with decreasing gel content. This behaviour resulted from network formation leading to a reduction in crystallinity.

4.3 Rheological properties of the products

The rheological properties of polymers are often influenced by grafting and side reactions associated with grafting. The easiest method that describes the viscosity of polymer melts is the Melt Flow Index (MFI). The MFI of a polymer melt is the mass of molten polymer that would flow through a predetermined size die, over a certain time.

It was previously shown that the MFI of grafted LLDPE decreased rapidly with increasing peroxide concentration because cross-linking is favoured at these conditions, leading to a higher molecular mass [56]. On the other hand, if modification resulted in chain scission, the MFI decreased [28].

4.4 Mechanical properties

The mechanical properties of grafted polymers are likely to change due to the introduction of a functional group on the polymer backbone. The most common mechanical properties likely to be influenced by grafting and the side reactions accompanying grafting are:

- Young modulus
- The tensile strength
- Elongation at break

4.4.1 Young's modulus

Typically the Young's modulus of a polymer is dependent on molecular mass. At high molecular mass, more force is required to align polymer chains because of chain entanglement. Degradation and cross-linking may therefore have opposing effects on modulus, since degradation reduces molecular mass and cross-linking reduces mobility [71]. Depending on the extent of each of these side reactions, either a reduction or an increase in modulus can be expected.

4.4.2 Tensile strength

The degree of inter-molecular bonding between polymer molecules influences the strength of the polymer. In the crystalline region, chains are closely packed due to strong intermolecular bonds. Typically, the tensile strength of polymers increase with increasing crystallinity [72]. When functional groups are grafted onto the polymer main chain, it may disrupt the ability of the chains to pack closely into a crystalline structure, leading to a reduction in crystallinity and hence reduced strength.

4.4.3 Elongation at break

Elongation at break is a measure of the ductility of a polymer material. If the polymer were slightly cross-linked, the elongation at break will increase because of higher chain interaction. On the other hand, chain mobility will be limited at high cross-link densities, resulting in a more brittle material. If the molecular weight of the polymer is reduced due to chain scission during grafting, the elongation at break will also decrease [51]. This is because more chain ends are present at lower molecular masses.

5. Experimental Methods

This chapter provides details of the materials and equipment used in this research and discusses several parameters that have been investigated.

5.1 Materials used

5.1.1 Polymer

In this research, only one type of polymer was used, namely linear low density polyethylene (LLDPE) and is often referred to as polyethylene (PE).

Table 5-1:Polyethylene data

Type of polymer	**Linear low density polyethylene (LLDPE)**
Manufacturer	ICO Polymers
Manufacturer code	COTENE ™ 3901
Density, ρ	0.905 g/cm^3
Melt flow index (MFI) (g/10min)	4.0

5.1.2 Monomer

There is only one type of monomer used in this research namely, itaconic anhydride (IA) with its specifications shown in Table 5-2.

Table 5-2: Monomer specification

Monomer	**Itaconic anhydride 95%**
Manufacturer	Sigma Aldrich
Manufacturer code	259926
Molecular weight	112.09 AMU
Boiling point (BP) (^{o} C)	114.0
Melting point (MP) (^{o} C)	66
Appearance	Colourless , fine crystal

5.1.3 Peroxide initiators

Two types of peroxides were used in this research for comparative purposes. The important properties of these peroxides are listed in Table 5-3.

Table 5-3: Table of peroxide properties

Peroxide	Di-tert-Butyl peroxide (95%)	Di-cumyl peroxide (98%)
Manufacturer	Fluka, Sigma - Aldrich	Sigma Aldrich
Molecular mass	146.23 AMU	270.37 AMU
Density, ρ	0.794 g/mL	1.56g/mL

5.1.4 Solvents

The following solvents were used in this study: acetone (Univar, 99.5%), xylene (Univar, 98.5%), methanol (Scharlau, HPLC grade 99.98%), ethanol (Univar, 99.5%) and water (distilled). All the solvents used were AR-grade.

5.2 List of Equipment used

5.2.1 Extruder

A tangential, intermeshing counter rotating extruder (Thermo PRISM TSE-16-TC) was used, with the following specifications (Figure 5-1 and Figure 5-2):

- Twin bore diameter: 16 mm
- Screw diameter: 15.6 mm
- Channel depth: 3.3 mm

- Barrel length: 384 mm
- Max. Screw speed: 500rpm
- Max. Operating pressure: 100bar

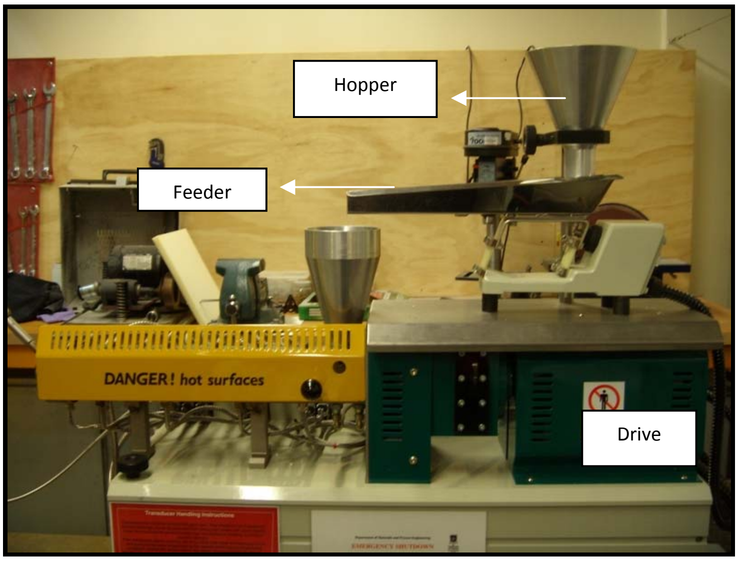


Figure 5-1: The extruder

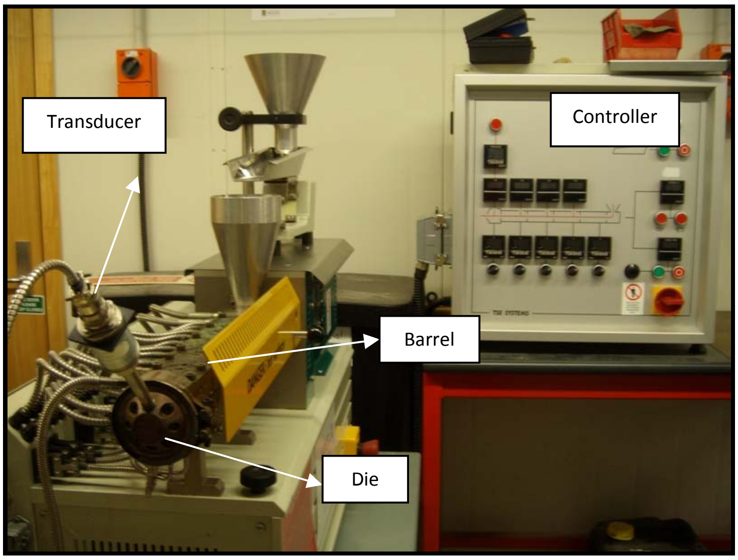


Figure 5-2: Front view of extruder

5.2.2 Injection moulding

Injection moulding was used in this research for making tensile test pieces, as specified by ASTM D- 638. A BOY 15 S GmbH injection moulders was used (Figure 5-3).

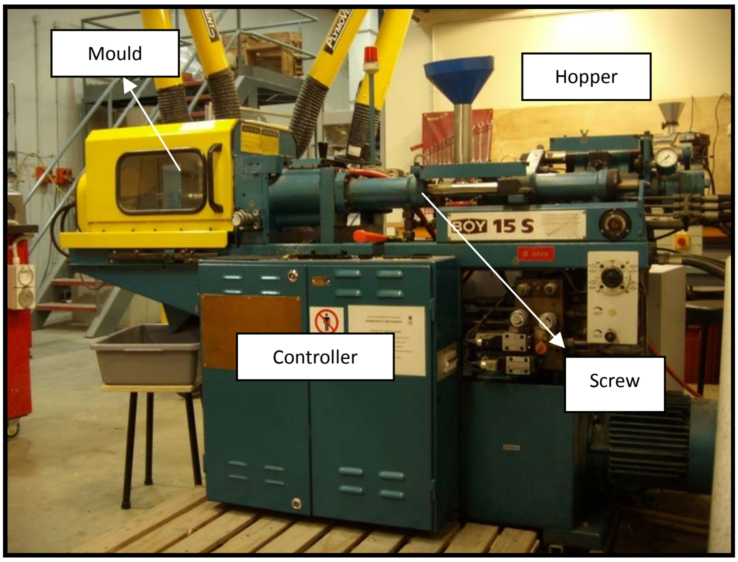


Figure 5-3: Injection moulder BOY 15S

5.2.3 Tensile testing

The tensile test machine used in this research was an INSTRON 4204 (Figure 5-4). It is a computer controlled electro-mechanical testing system capable of performing a variety of tests based on tension and compression. The load frame is a tension/compression type employing a moving (screw-driven) crosshead. The sample is being hold with wedge grips. It is rated for forces up to 50 kN, crosshead speeds 5-500 millimetres (mm) per minute and crosshead travel of up to 1.170 meters. The system is controlled from the control panel and a computer. The computer provides automated control, data acquisition and analysis.

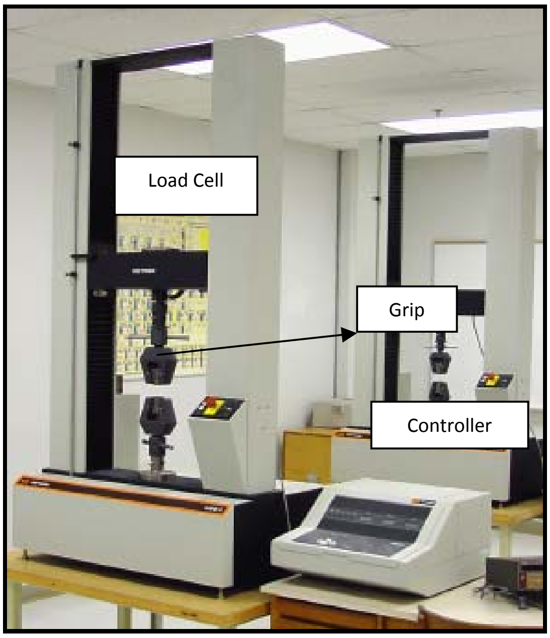


Figure 5-4: Tensile test machine INSTRON 4204

5.3 Experimental design

The main parameters investigated that may influence grafting were:

5.3.1 Residence time

Prior to the execution of the research, one experiment on extruder characterization was carried out. The experiment was done to study the effect of the screw speed on the residence time in the extruder.

Using a step change of calcium carbonate ($CaCO_3$) (ρ =2.8 g/cm^3) concentration in the feed, the outlet concentration of $CaCO_3$ could be measured. Linear low density polyethylene (PE) (ρ= 0.905 g/cm^3) was used as base polymer. A mixture of 40 wt% of $CaCO_3$ and 60 wt% polyethylene was premixed, and used as tracer feed.

The experiment was repeated at three different speeds, namely 60 rpm, 65 rpm and 70 rpm, starting with pure PE as feed. After the tracer feed was introduced, extrudate was sampled every 20 s.

The concentration of $CaCO_3$ was obtained indirectly by measuring density. Knowing composition and mass of each sample, the volume could be measured using Archimedes' principle, which allowed the calculation of the density. The concentration of $CaCO_3$ could then be calculated using Equation 5.1.

$$\frac{1}{\rho} = \left(\frac{x}{\rho_{CaCO3}}\right) + \left(\frac{1-x}{\rho_{PE}}\right) \qquad \text{(Equation 5-1)}$$

Specifics regarding the residence time experiment are shown in Table 5-4.

Table 5-4: Table of experiment of different screw speed.

Experiment #	**Sample ID**	**Composition (wt %)**		**Screw speed**
		PE	$CaCO_3$	
1	A B C	40	60	60 65 70

Historically, extruders have been treated as normal plug flow reactors [6; 8; 9], although actual extruder behaviour is more complicated. The residence time and residence time distribution were measured to investigate their effect on the degree of grafting and product properties. Average residence time was controlled by multiple extrusions in series, until the desired average residence time was achieved.

5.3.2 Temperature (experiment 2A*)*

The purpose of this experiment was to investigate the effect of temperature on the degree of grafting. A mixture of itaconic anhydride

(IA), polyethylene and di-tert-butyl peroxide (DTBP) was reacted at 160°C and 180°C. These temperatures were selected to be above the melting temperature of the polymer and the decomposition temperature of the peroxide, but low enough to minimise degradation, as mentioned in literature [23; 32; 73]. This experiment was carried out according to formulation 2A, listed in Table 5-5.

5.3.3 Monomer concentration (experiments 4 and 6)

It is well known that the initial concentration of reagents will influence the grafting process [24-28; 30; 32; 34; 37; 38; 50; 52; 57; 74-76]. A range of compositions were tested, at constant initiator concentration, to determine optimal monomer feed concentration for grafting. In these experiments, various initial monomer concentrations were tested, according to Table 5-5, experiments 4 and 6.

5.3.4 Peroxide type and concentrations (experiments 3-7)

Two types of peroxides were used to compare their effectiveness during grafting, namely di-tert-butyl peroxide and di-cumyl peroxide. Both of these peroxides were chosen because of their availability and cost.

Details regarding the formulations used in each experiment are listed in Table 5-5.

Table 5-5: Experimental design.

Experiment Number	Sample ID	Peroxide type	Composition (wt %)		
			IA	PE	Peroxide
2	A	DTBP	0.77	99.03	0.2
3	A	DTBP	0.2	99.6	0.2
	B		4	95.8	
	C		6	93.8	
	D		8	91.0	
	E		10	19.8	
4	A	DTBP	0.2	97.8	2
	B		4	94	
	C		6	92	
	D		8	90	
5	A	DCP	0.2	99.6	0.2
	B		4	95.8	
	C		6	93.8	
	D		8	91.8	
	E		10	89.8	
6	A	DCP	0.2	97.8	2
	B		4	94	
	C		6	92	
	D		8	90	
	E		10	88	
7	A	DTBP	0.6	93	5
	B		4	91	
	C		6	89	
	D		8	87	

A screw speed of 65 rpm and reaction temperature of 160^{o}C were maintained in all experiments, unless otherwise stated.

All chemicals were used as received from the manufacture, with no further purification done. Samples were first weighed and then thoroughly mixed in a laboratory mixer for about 4-5 minutes until the mixture of polymer, monomer and initiator were uniform.

5.4 Analysis

In order to characterise the process of grafting, several measurements had to be made. It was determined that the most important measurements were:

- the degree of grafting
- percentage reacted
- gel content
- mechanical properties
- chemical properties

The procedures followed are described in more detail below:

5.4.1 Reaction product purification

Purification of the graft copolymer is required prior to chemical titration. The purpose of purification is to remove unreacted monomer from the sample taken.

Several grams of the raw samples were taken and boiled with xylene for 0.5 hours. The polymer is precipitated using acetone, directly from the hot solution. The polymer is recovered using filtration. The precipitate is subsequently washed repeatedly using fresh acetone and dried under vacuum at 60°C until constant weight is achieved [24; 27].

5.4.2 Chemical Titration

Chemical titration of the polymer was done to measure the degree of grafting as well as the % monomer reacted [24; 27].

One gram of purified polymer was taken and dissolved in 100 ml of boiling xylene. A few drops of water were added to hydrolyze the anhydride functionality. Secondly, 10 mL of 0.05 M potassium hydroxide in methanol (KOH) was added. A drop of 1 % of phenolphthalein as indicator was added and the samples were back titrated with 0.03 M trichloroacetic acid solution in xylene. The titrations were stopped when the colour remained constant for 30 seconds.

Knowing that 10ml of KOH was added and the concentration was 0.05 gmol/L, 5 x 10^{-4} g mol KOH was present initially, given as a.

Knowing the volume acid consumed during the titration, given as $b\,(liter)$, with, constant acid concentration of 0.03 (mol/L) (given as c) is used, the mol acid reacted can be calculated as:

$$Acid\,volume, b(L)\,x\left[acid, c\right](\frac{gmol}{L}) = gmol\,acid, d \qquad \text{(Equation 5-2)}$$

In the reaction, one mol of acid will react with one mol KOH, therefore:

$$gmol\,acid, d = gmol\;\;KOH\,reacted, e \qquad \text{(Equation 5-3)}$$

Knowing that one mole of IA will react with two mole KOH,

$$Mol\;of\;\;IA\,onto\;PE = \left(\frac{a-e}{2}\right)(mol) \qquad \text{(Equation 5-4)}$$

$$Degree\,of\;\;grafting = \left(\frac{mol\;\;IA\,onto\;PE\;x\,M_w IA}{Sample\;mass(g)}\right)x100 \qquad \text{(Equation 5-5)}$$

Where $M_w = molecular\;mass\;of\;\;IA(\frac{g}{mol})$.

With the same data as above, the percentage monomer reacted can also be calculated, using Equation 5-7:

$$Mol\ IA\ present\ initially = \left(\frac{wt\ \%IA\ \ x\ sample\ mass}{M_w} \right) \quad \text{(Equation 5-6)}$$

$$\%\,reacted = \left(\frac{mol\ of\ \ IA\ onto\ PE}{mol\ IA\ present\ initially} \right) x100\ \% \quad \text{(Equation 5-7)}$$

5.4.3 Gel content analysis

The gel content test method has been taken from the ASTM standard D2765-95, entitled 'Determination of Gel Content and Swell Ratio of Cross-linked Ethylene Plastic'[77]. The rational of doing the test is to measure the gel content (insoluble fraction) produced in polyethylene as a result of cross-linking and is determined by extraction with xylene. Samples were put in a pouch and immersed in the xylene in a soxhlet extractor (Figure 5-5). A ratio of sample to solvent of 1:100 was used to ensure complete dissolution of the soluble fraction. Extraction is performed over 12 hours, followed by drying. Calculation of the gel content analysis is as follows:

$$Gel\,content\,\% = \frac{M_{\mathrm{Residual}} - (M_{total} - M_{Polymer})}{M_{Polymer}} x100 \quad \text{(Equation 5-8)}$$

Where:

$M_{Polymer} = Mass\,of\ \ polymer\,before\,extraction\,(g)$
$M_{total} = Mass\,of\ \ polymer\,and\ \ filter\ \ paper\,(g)$
$M_{\mathrm{Residual}} = Mass\,of\ \ polymer\,and\ \ filter\ \ paper\,after\,extraction\,(g)$

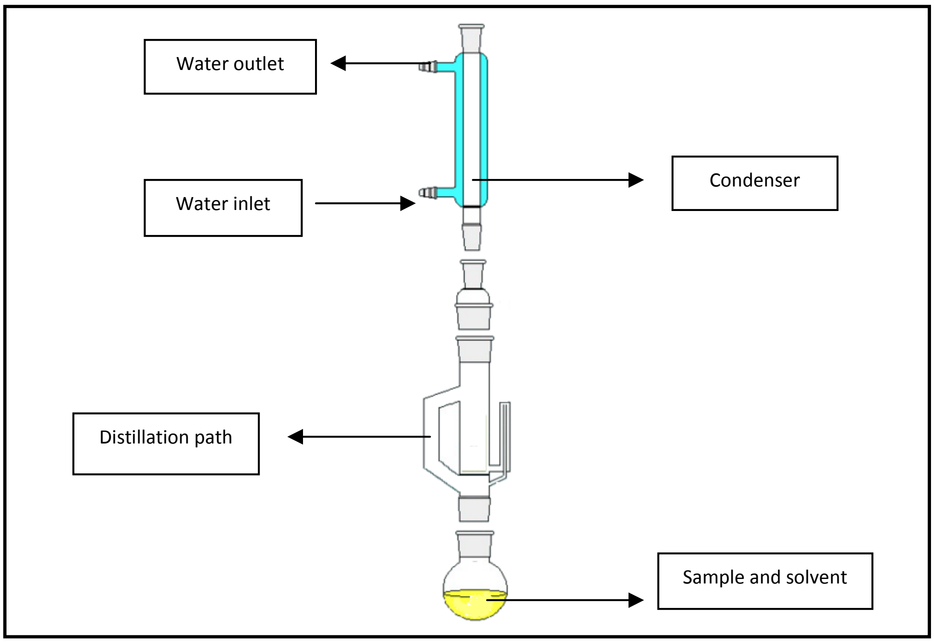


Figure 5-5: Soxhlet Extractor [78].

5.4.4 Fourier transforms infrared spectroscopy (FTIR)

FTIR analysis was performed using a Bio-Rad FTS40A. FTIR operated using a single beam of neon laser infrared spectrometer with resolution 4cm^{-1} and 30 scans per spectrum. Dry air was supplied to make sure the optics were in proper working order and to pulse the interferometer. Samples were prepared using a KBr disc method. Samples were intimately mixed with powder KBr and pressed at 10,000 – 15,000 psi to produce transparent discs. Discs were kept in desiccators to avoid exposure to humidity.

5.4.5 Tensile testing

Tensile testing was used to quantify the effect of degradation on the polymer. Samples were tested using the tensile equipment, as described earlier. Small test pieces were prepared using injection moulding to conform to ASTM standard D 638-01 [79]. Test were performed using a load cell of 5kN and a cross-head speed of 50mm/min. Five measurements were taken for each sample to ensure statistical significance.

6. Results and discussion

Several factors may affect the grafting reaction of itaconic anhydride (IA) onto polyethylene and will be discussed and compared in this section. The results are expressed in terms of the degree of grafting and percentage IA reacted. The degree of grafting (DOG) is the number of moles IA grafted per sample mass and the percentage IA reacted is the number of moles IA grafted onto PE per mol IA present initially.

6.1 Extruder characterization

It is well known that the degree of grafting and the extent of reaction are dependent of the reaction time. In an extruder, the residence time and residence time distribution is influenced by parameters, such as screw speed and viscosity. In order to characterize the extruder used in this study, experiments were under taken to measure the residence time distribution as a function of and screw speed using linear low density polyethylene.

By using a step change in feed concentration, the residence time distribution was measured, using $CaCO_3$ as tracer. Theoretically, with an increase in screw speed, the average residence time will decrease and the degree of dispersion around the mean should also decrease. In Figure 6-1 the effect of screw speed on the outlet concentration of $CaCO_3$ over time, using 40 wt% $CaCO_3$ in PE is shown. From the graph, it can be seen that at high screw speed (70rpm) the concentration of $CaCO_3$ reached a plateau after 80s while at low screw speed (60rpm) the plateau was reached after 160s.

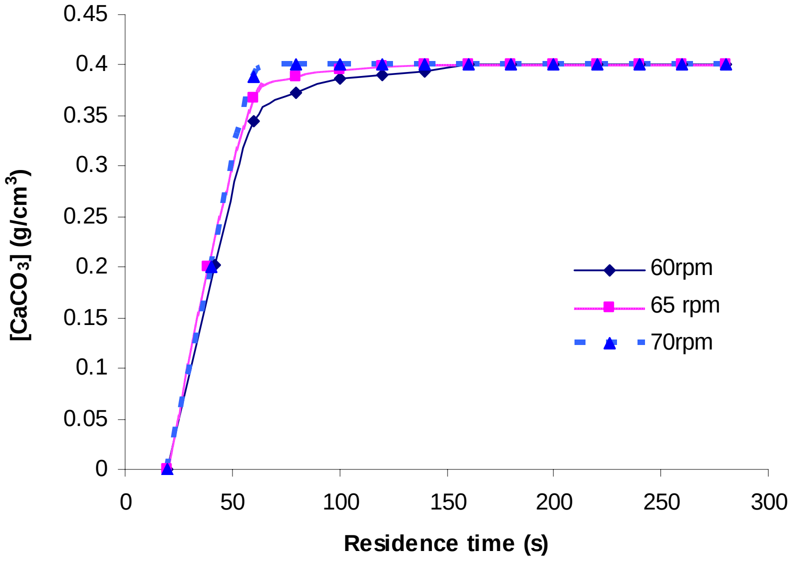


Figure 6-1: Graph of residence time (s) vs. [$CaCO_3$]

The data presented above enabled calculation of the normalised concentration vs. time graph (Figure 6-2), called the F-curve or normalised exit age [14].

From this data, the average residence time (τ) can be calculated according to Equation 6-1.

$$\tau = \int_0^1 t dF(t) = \int_0^\infty t \frac{dF(t)}{dt} dt \qquad \text{(Equation 6-1)}$$

The average residence time can also be seen as the area below the curve shown in the Figure 6-2. The Average residence times for the various screw speeds tested are listed in Table 6-1. Also shown in the table, is the degree of dispersion around the mean, as calculated from Equation 6-2:

$$\sigma^2 = \int_0^1 (t-\tau)^2 dF(t) = \int_0^\infty (t-\tau)^2 \frac{dF(t)}{dt} dt` \qquad \text{(Equation 6-2)}$$

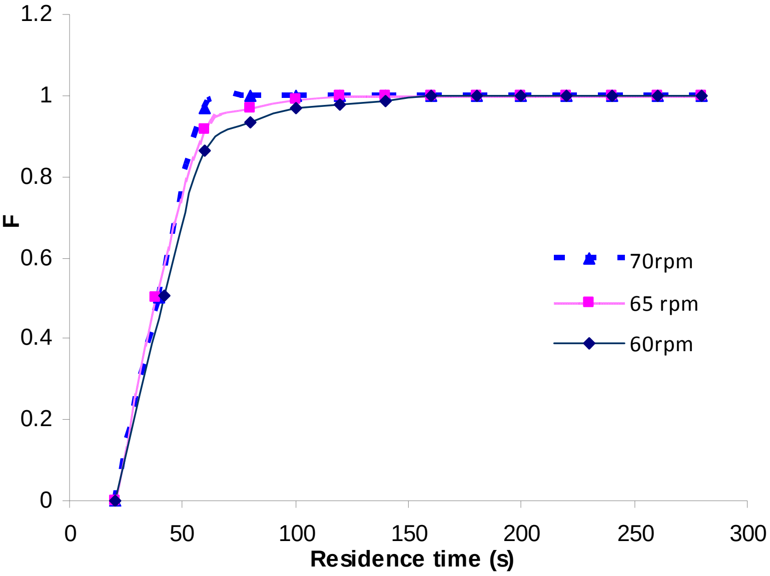


Figure 6-2: Graph of normalised exit age vs. time (s)

Table 6-1: Average residence times at different screw speeds

RPM	**Average residence time (τ)**	**Degree of dispersion (σ^2) (s^2)**
60	46 s	23.4
65	42 s	17.5
75	40 s	11.2

As expected, the average residence time decreased with increasing screw speed. A narrow range of RPMs was tested because it long residence times are required for sufficient mixing and therefore, higher screw speeds was not considered. The dispersion around the mean also decreased with increasing screw speed.

6.2 Temperature profile

It was previously shown that the temperature at which the reaction is carried out has an effect on the DOG and percentage IA reacted. In this study, a flat temperature profile of either 160°C or 180°C was used across all heating zones in the extruder. A blend 0.77wt% IA, 99.03 wt% PE and 0.2 wt% DTBP were used, in this experiment as it was believed that a high degree of grafting could be achieved under these conditions, as previously described by Vourinen et al [32].

Furthermore, the temperature was selected to be above the ceiling temperature of IA polymerization (90 °C) in order to avoid homopolymerization [80]. The temperature should also be high enough for the polymer and monomer to melt, and should be above the peroxide decomposition temperature. The melting temperature for PE and IA is 83°C and 66°C respectively.

The screw speed was maintained at 65rpm, which according to earlier experimentation translates to an average residence time of 42 seconds. The purpose of this experiment was to investigate the effect of temperature on the degree of grafting and the results are shown in Table 6-2.

Table 6-2: Effect of temperature on the DOG and % reacted.

Temperature	180 °C	160 °C
DOG	0.2904	0.3285
% reacted	0.3771	0.4267

It can be seen that the degree of grafting (DOG) at 160°C is slightly higher compared to 180°C. By increasing the temperature the half life of the peroxide is reduced, hence the rate of radical generation is increased.

Higher temperatures may also lead to increased chain scission. Besides that, higher temperature can attribute to the greater peroxide evaporation and a higher probability of the occurrence a disproportionation reaction [66]. It was therefore concluded that 160°C is more appropriate for grafting.

6.3 Effect of initial monomer concentration on the degree of grafting.

In this experiment, two types of peroxides were used, namely di-tert-butyl peroxide (DTBP) and di-cumyl peroxide (DCP). The purpose of this experiment was to investigate the effect of initial monomer concentration and peroxide type on the degree of grafting and percentage reacted. All samples were homogenized prior to extrusion, according to the experimental plan discussed earlier. The screw speed was maintained at 65 rpm with a flat temperature profile of 160°C. The peroxide concentration was maintained at 2 wt% for all samples tested. The results obtained shown in Figure 6-3.

From the Figure 6-3 it can be seen that increasing the IA concentration leads to an increase in DOG up to 6 wt% IA, for DTBP and 10 wt% IA for DCP. According to Aghjeh [38], an increase in IA concentration typically leads to an increase in the IA-excimer formation [38] (refer to discussion below), which intensifies hydrogen abstraction from the PE backbone and therefore increase the DOG [22]. However it is clearly shown, that above 6 wt% IA, the DOG almost plateaus. This can be attributed to the limited solubility of IA in PE [38]. When the concentration IA exceeds the saturation point, phase separation may occur, leading to the peroxide being absorbed in the separated IA phase due to its greater miscibility in IA. This resulted in less peroxide being available for reaction.

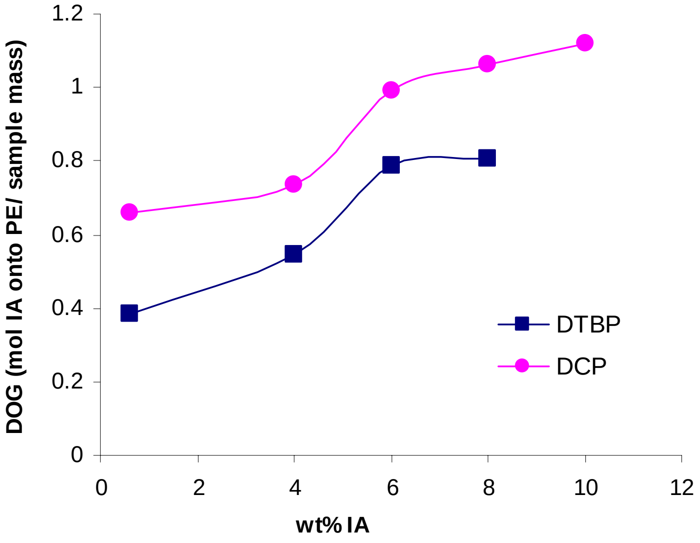


Figure 6-3: The effect of monomer concentration on the DOG at 2 wt% peroxide.

Two specific mechanisms can be distinguished regarding the effect of monomer concentration on the DOG [8]. These mechanisms were proposed mainly for work done on maleic anhydride grafting [8; 66]. However, it can be expected that itaconic anhydride will have the same reaction mechanism, since both anhydrides have similar molecular structures (Chapter 3, Section 3.2.1).

6.3.1 At low concentration

At low IA concentration, initiator dissociation leads to a high concentration of polyethylene radicals that can react directly with IA. This reaction is followed by a cross-linking or disproportioning reaction. It was shown that using 2 wt% peroxide and 0.6wt% IA, the DOG was low. At low IA concentration, the probability of IA being in close proximity to macro-radicals, at the moment of their formation is low, leading to an increased probability of chain scission. (A schematic representation of this mechanism can be found in Chapter 3, Figure 3-12.

$$PE - IA^{*} + PE - IA \rightarrow PE - IA_{saturated} + PE - IA_{unsaturated}$$
$$PE - IA^{*} + PE \rightarrow PE - IA + PE^{*}$$
$$PE - IA^{*} + PE \rightarrow PE - IA - PE$$

As an alternative to chain scission, polyethylene radicals may also combine with each other, resulting in cross-linking:

$$PE^{*} + PE^{*} \rightarrow PE - PE$$

6.3.2 At high concentration

At higher concentrations of itaconic anhydride, a relatively high amount of excimers will be formed:

$$2IA \xrightarrow{RooR} [{}^{*}IA^{+\,-}IA^{*}]$$
$$IA^{+\,-}IA^{*} \rightarrow IA^{*} + [{}^{*}IA^{*}]^{*}\,(IA_{triplet})$$
$$[{}^{*}IA^{*}]^{*}\,(IA_{triplet}) + IA \rightarrow {}^{*}IA^{+\,-}IA^{*}$$

Many other reactions may follow, that do not lead to grafting:

$$PE + [{}^{*}IA^{+\,-}IA^{*}] \rightarrow PE^{*} + [IA^{+\,-}IA^{*}]$$
$$PE^{*} + [{}^{*}IA^{+\,-}IA^{*}] \rightarrow PE - IA^{+\,-}IA^{*}$$
$$[{}^{*}IA^{*}]^{*} + IA \rightarrow [{}^{*}IA^{+\,-}IA^{*}]$$

If the concentration of initiator is sufficiently high, itaconic anhydride can also homopolymerize before being grafted onto polyethylene.

$$[{}^{*}IA^{+\,-}IA^{*}] \rightarrow IA - IA^{*} \xrightarrow{IA} [IA^{+\,-}IA^{*}] + IA^{*} \rightarrow IA - IA^{+\,-}IA^{*} \rightarrow IA - IA - IA^{*}$$
$$PE^{*} +_{n} IA^{*} \rightarrow PE - (IA)_{n}$$

However, this mechanism (production of excimers) may also lead to the formation of many polyethylene and itaconic anhydride radicals, thereby increasing the probability of grafting with an increasing itaconic anhydride concentration [8].

It was also found that the degree of grafting was higher using DCP than compared to DTBP. According to literature [73], DCP has a higher solubility in PE compared to DTBP. In addition, the half life of DTBP is longer than DCP, and may therefore not be completely utilized during the reaction[22]. DCP has also been shown to be more effective in the introduction of long chain branches in linear PE compared to DTBP [56]. Some typical properties of DCP and DTBP are shown in Table 6-3.

Table 6-3: Structure and properties of initiators used in the grafting experiments [81].

Initiator	Radicals Formed		$t_{½}$ at			Decomposition temperature (°C)	Melting Temp (°C)	Physical form
			100°C	150°C	200°C			
Di-tert-butyl peroxide	Tert-butoxy	methyl	2600	18	0.35	111	-40	liquid
Dicumyl peroxide	Cumlyl oxy	methyl	890	9.2	0.25	130	39	solid

From the table, it can be seen that the half life ($t_{1/2}$) of DCP is lower than DTBP, consequently, under experimental conditions, DBTP will decompose slower, yielding lower concentrations of initiator radicals. This resulting in a lower degree of grafting [29]. In addition, it has been shown by B.Jurkowski et al [73] that, because DTBP has a higher volatility and a lower decomposition temperature, it results in more radical species, such as: $\bullet OC(CH_3)_3$ and $\bullet CH_3$. Therefore, more polyethylene macro-radicals can be formed early in the extruder's feed zone, prior to the mixture before being completely homogenized. Therefore, these radicals are preferably recombined with each other, leading to a high yield of cross-linked polymer and a low degree of grafting

6.4 Effect of residence time on the degree of grafting.

An extruder can typically be treated as a normal plug flow reactor, although it is usually slightly more complicated [6; 8; 9]. In this section, the effect to prolonged residence time on the degree of grafting was investigated. In Figure 6-4 and 6-5, the results when using DTBP and DCP, at various concentrations, are shown for residence times up to 210 seconds. The residence time was increased by performing multiple extrusions in series.

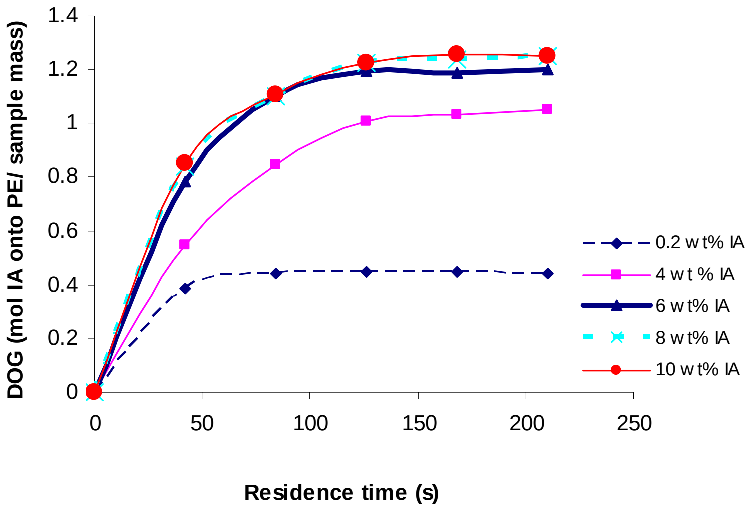


Figure 6-4: Graph of residence time vs. DOG using 2wt % DTPB

From Figure 6-4, it can be seen that the degree of grafting gradually increases and reaches a plateau after about 125 seconds, when using more than 4 wt% IA and DTBP as initiator. On the other hand, from Figure 6-5, it can be seen that, when using DCP, the DOG quickly plateaus after about 50 seconds, irrespective of the percentage IA used. This is because DCP has a higher solubility and shorter half life than DTBP, therefore requiring less reaction time. These results are in agreement with that of W.Jiang et al [23]. According to G. Moad [67], DCP is more prone to induce decomposition than DTBP, making the degree of grafting of IA onto PE using DCP slightly higher compared to using DTBP. However, in both cases, increasing IA resulted in a higher degree of grafting. Furthermore, for both peroxides, 6 wt% IA seemed optimal, since above that, no significant increase in grafting was observed.

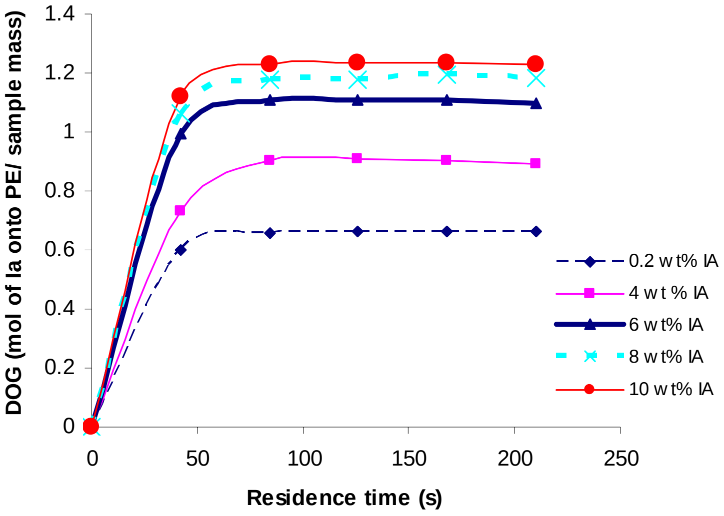


Figure 6-5: Graph of residence time vs. DOG using 2wt % DCP

It was therefore concluded that when using DTBP, a longer residence time is required to reach similar DOG compared to DCP. It would therefore be more efficient to use DCP in a commercial environment. Furthermore, it was shown earlier, that DCP generally leads to higher degrees of grafting, further supporting its use as the preferred initiator.

In Figures 6-6 and 6-7, the effect of residence time on the DOG is shown, when using 0.2 wt % initiator. It can be seen that, at low monomer concentration, the difference between DTBP and DCP is less prominent. It was found that the DOG plateaus after about 80 seconds using either DTBP or DCP as initiator. In both cases, the DOG is lower than compared to using 2 wt % IA, and DTBP resulted in slightly lower DOG compared to DCP, which is consistent with earlier experiments.

The reason for this observation is that at higher peroxide concentration, more polyethylene radicals are formed, leading to the higher degree of grating. However, using lower initiator concentrations, requires less reaction time to reach the maximum degree of grafting, all be it lower. Final process design would therefore be a trade off between higher DOG and shorter reaction times.

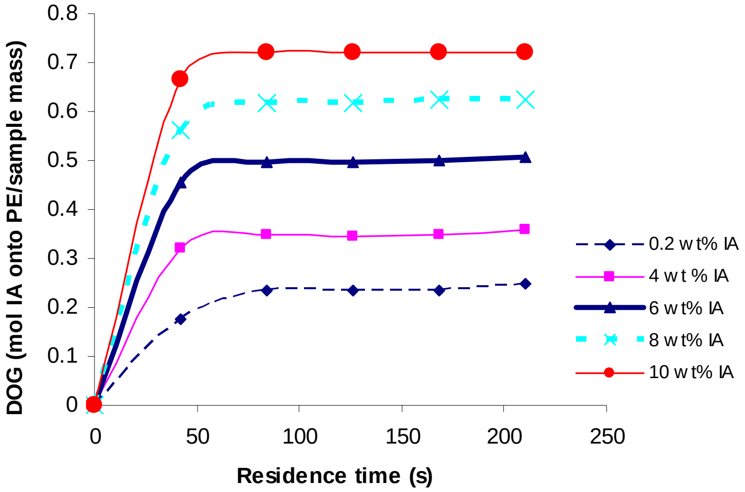


Figure 6-6: Graph of residence time vs. DOG using 0.2wt% of DTBP

In summary, concerning the effect of residence time on the DOG, the following conclusions were reached:

- When using 2 wt% initiator, DCP requires less time to reach a maximum DOG compared to DTBP and the maximum DOG with DCP is also higher.
- Using 2 wt% DCP required 80 seconds reaction time, compared to 125 seconds, when using DTBP.

- When using 0.2 wt % initiator, the difference between using DTBP and DCP is that DCP leads to only a slightly higher DOG. At this peroxide concentration both systems required about 80 seconds reaction time to reach a maximum DOG.

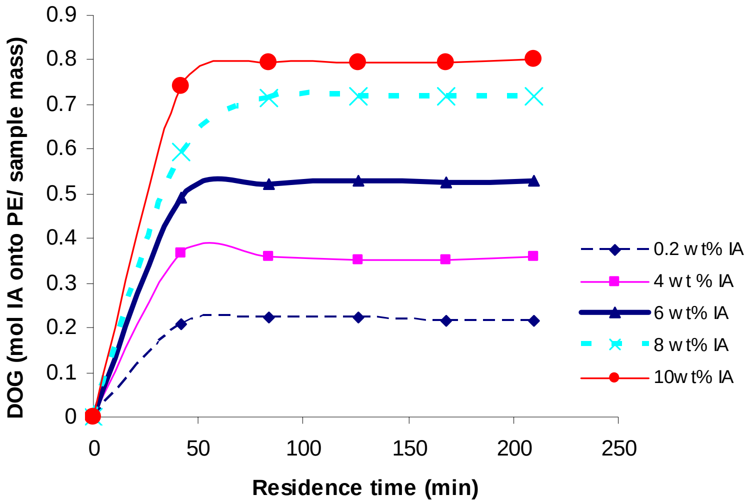


Figure 6-7: Graph of residence time vs. DOG using 0.2wt% DCP

The observations regarding the effect of initiator concentration prompted further experimentation, and are discussed below:

6.5 Effect of initiator concentration

As grafting is a free radical reaction, the effect of initiator concentration is among the most important parameters affecting grafting. In this section, the effect of DTBP concentration on the DOG was investigated. It was shown in previous sections that DCP is more effective than DTBP, but both show similar trends. The results of experiments performed at concentrations between 0.2 and 5 wt% DTBP are shown in Figure 6-8.

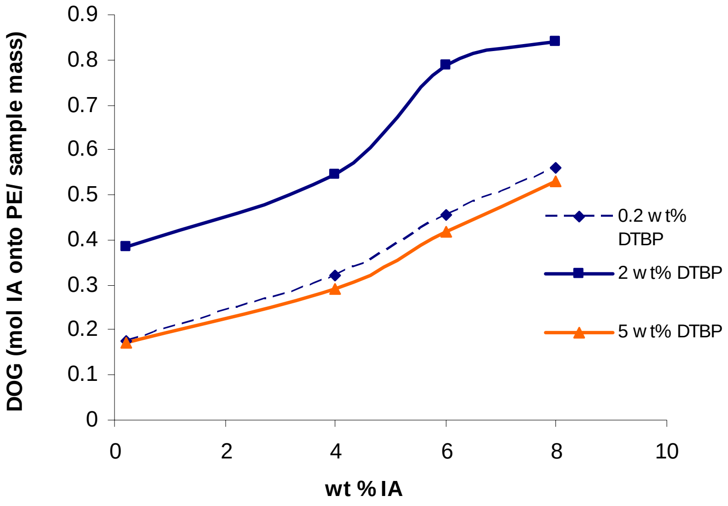


Figure 6-8: Graph of IA wt% concentration vs. DOG

From Figure 6-8, it can be seen that at as the monomer concentration increased, the degree of grafting increased as well. The graph also shows that the degree of grafting is higher when the peroxide concentration is raised from 0.2 to 2 wt%. Theoretically, higher peroxide concentrations should results in a higher degree of grafting [8]. This has been shown for a maleic anhydride/ polypropylene system by Bettini et. al. [28]. At higher peroxide concentrations, more radicals will form and consequently, more radicals are available for reaction, leading to a higher degree of grafting [28].

However, above 2 wt% peroxide, severe cross-linking may occur. Cross-linking is mainly caused by combination of PE-IA* radicals with PE* radicals:

$$PE - IA^* + PE^* \rightarrow PE - IA - PE$$

This was clearly shown in the experimental work when 5 wt% DTBP was used. It was found that the pressure in the extruder increased, indicative of a viscosity increase, most likely due to cross-linking.

In addition, it was found that at a very low concentration of monomer (0.2 wt % itaconic anhydride) and 5 wt% DTBP, a continuous extrudate could not be formed and that it was easily breakable. The reduction in mechanical properties of the extrudate is most likely due to a chain scission process, leading to polymer degradation. It has previously been shown that excessive amounts of peroxide may lead to polymer degradation, and cross-linking [28]. At lower monomer concentration, there will be a lower probability of monomer molecules being at close proximity to macro-radicals at the time of formation, increasing the probability of chain scission [28] .

6.6 Cross-linking

Gel content analysis is a method to determine cross-linking as a result of reactive extrusion. After 12 hours of being immersed in xylene, samples were dried in a vacuum oven until constant weight. The results are presented in Figure 6-9 and expressed as a percentage.

From the graph it can be seen that at as the monomer concentration was increased the degree of cross-linking also increased. By increasing the monomer concentration, cross-linking and disproportionation are promoted, as discussed in Section 3.3. Also, DTBP resulted in higher cross-linking compared to DCP, which is consistent to what was discussed earlier.

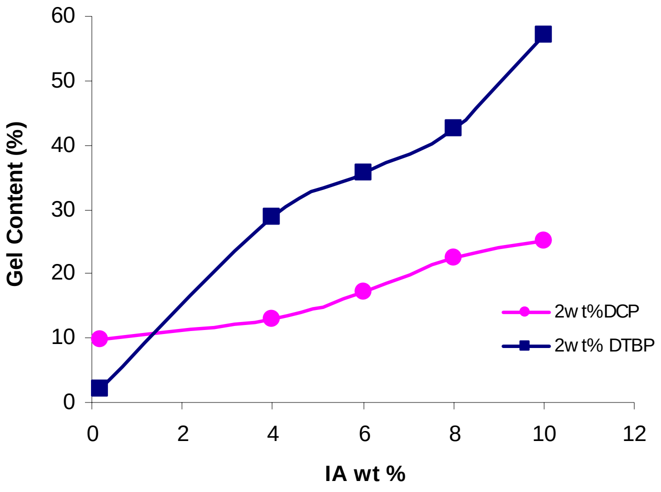


Figure 6-9: Graph of gel content as a function of IA concentration.

6.7 Material characterization

The degree of grafting, percentage reacted and degree of cross-linking are all properties influenced by process variables. However, it is also important to consider the effect process variables have on the mechanical properties of the product. In this section, the actual occurrence of grafting is firstly confirmed using FTIR analysis and then the effect of grafting on the polymer's mechanical properties is investigated.

6.7.1 Chemical structure

The physical properties of polymeric systems depend, in the first instance, on the chemical constituents and the configuration of the macromolecules. Many spectroscopic techniques are available nowadays to access the chemical structure of materials. FTIR-spectroscopy is perhaps on of the most widely used techniques due to its versatility in determining composition, conformation and crystallinity [82].

Under certain conditions, IA can be hydrolyzed, leading to ring opening, rendering it unable for further reaction with proteins. The objective of this section was therefore to use FTIR analysis to confirm that itaconic anhydride was indeed grafted and to asses the structure of the grafted molecule.

Prior to testing, KBr discs were prepared by micronizing the polymer and mixing it with potassium bromate. Several methods of preparing samples for FTIR have been tested, but preparation of samples as KBr discs gave the best absorption peaks. Casting films from solution is one of the best methods in FTIR, but good film thickness is crucial and difficult to obtain with PE.

Table 6-4 list the most important absorption peaks of pure polyethylene, according to literature. Linear low density polyethylene, as used in this study, was also analysed using FTIR, and the absorption spectrum is shown in Figure 6-10(a).

Table 6-4: Main absorption of polyethylene in the IR region and their assignment

Band (cm^{-1})	Assignment
2918	CH_2 asymmetric stretching
2850	
1462	Bending deformation
730-720	Rocking deformation

In Figure 6-10(b) the absorption spectrum of grafted PE is shown, after water was added to the sample while dissolved in xylene. This would ensure that any anhydride would be hydrolysed to the corresponding carboxylic acid. It can be seen from the figure that an additional absorption peak appeared at 1690 cm^{-1}, which is indicative of the occurrence of a carboxylic acid structure (from the itaconic anhydride) in the polymer backbone after grafting [83]. This indicated that itaconic anhydride was grafted, and that anhydride hydrolysis has occurred.

In Figure 6-10(c), the spectrum of grafted itaconic anhydride (PE-g-IA) is shown. It can bee seen that the peak at 1690 cm^{-1}, as mentioned above, has been eliminated, but a new peak at 1781cm^{-1} can be observed. This peak is indicative of the anhydride group grafted onto the polymer backbone. This is in agreement with other work [28; 29].

It can therefore be concluded that the grafting has indeed occurred and that the grafted monomer is still in the anhydride form.

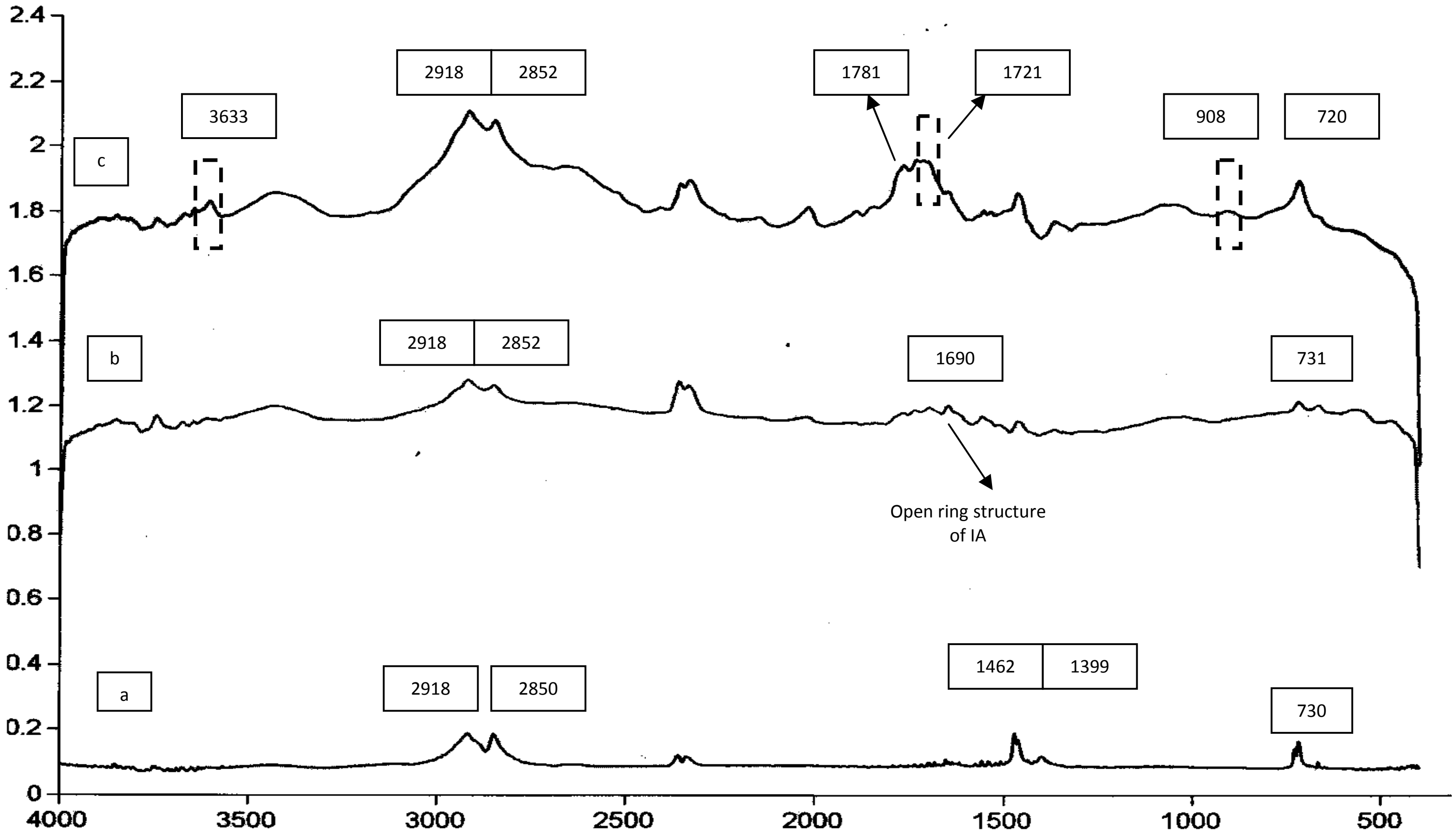


Figure 6-10: FTIR analysis of three different samples, Pure Polyethylene (a), Grafted IA with open ring (b), Grafted IA onto Polyethylene (c)

6.7.2 Mechanical properties

Polymers are prone to degradation during exposure to high temperatures for a prolonged period of time. Mechanical properties, such as tensile strength, Young's modulus and ductility of the sample are related to the extent of degradation. It has previously been shown that by increasing the processing time, a decrease in tensile modulus, tensile strength and ductility was observed [72].

DTBP and DCP initiators were tested for their effect on mechanical property degradation after varying reaction times. It was observed from previous experiments that significant discolouration occurred after extrusion, which is often indicative of degradation. Samples were extruded 5 times and test pieces were injection moulded after each extrusion. Three reactions may occur during extrusion: grafting (main reaction), chain scission and cross-linking (side reactions). These three reactions affect the mechanical properties of the modified polymers and will be discussed as below.

I Tensile strength

From Figure 6-11, it can be seen that when using DCP and DTBP, the tensile strength decreased with increasing reaction time. The reduction of the tensile strength is mainly due to chain scission becoming more severe over time. Cross-linking also increased with increasing reaction time, which is expected to increase tensile strength. However, the effect of chain scission was shown to be the overriding effect. Therefore, if grafting disrupts crystallinity, a reduction in tensile strength can be expected. Similar results was observed by Chodak I, in his work on maleic acid grafted PE [84].

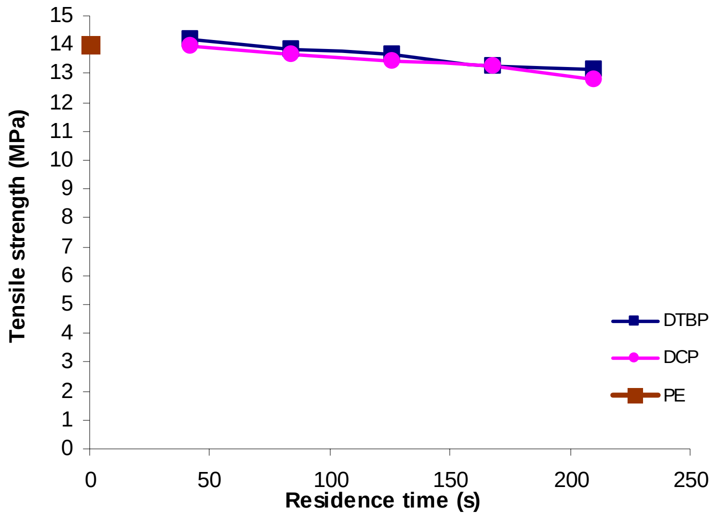


Figure 6-11: Graph of tensile strength vs. residence time of 2 wt % peroxide and 4 wt % IA

II Young's modulus

From Figure 6-12, it can be seen that the Young's modulus remained relatively constant with increasing reaction time for the both peroxides used. Modulus is typically less affected by a reduction in chain length, especially above the critical chain length of the polymer in question. Cross-linking, on the other hand is expected to lead to an increase in modulus, in the absence of chain scission. The relative small change in modulus is therefore indicative of the two reactions leading to opposite results.

III Ductility (elongation at break)

Ductility is a measure of the degree of plastic deformation that has been sustained at fracture. Ductility may be expressed quantitatively as either percent elongation or as percent reduction in area. In this study, the ductility of the polymer will be presented as percentage elongation at break. The effect of residence time on the ductility of the polymers is shown in Figure 6-13.

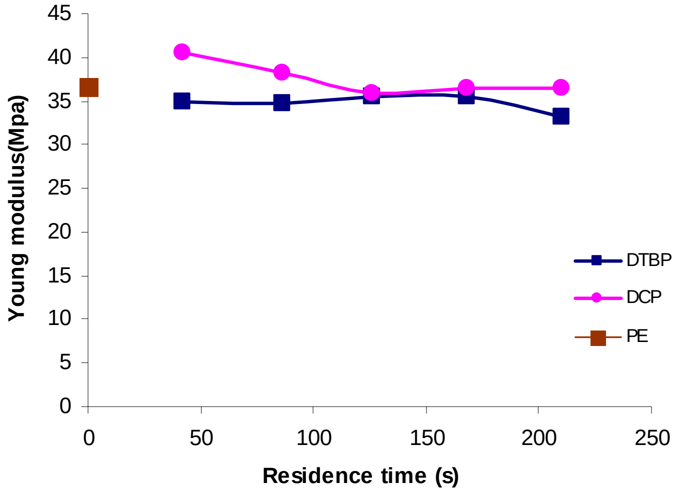


Figure 6-12: Graph of Young modulus vs. residence time (s) of 2 wt % peroxide and 4 wt % IA.

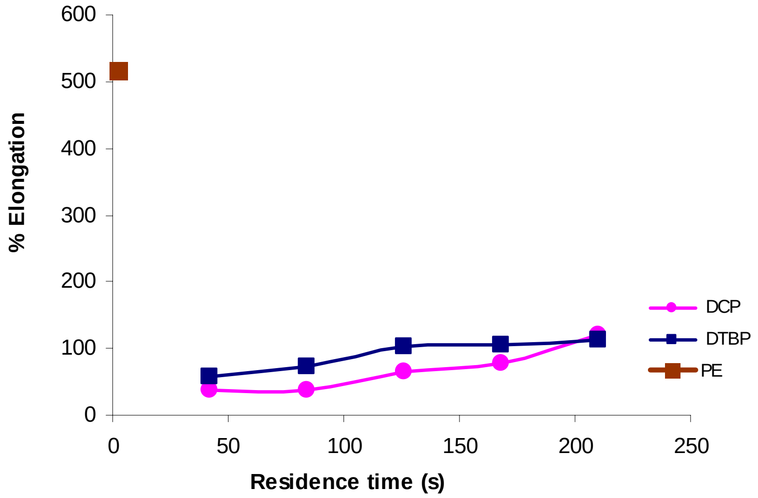


Figure 6-13: Effect of residence time on the elongation at break of 2 wt % peroxide and 4 wt % IA.

From Figure 6-13, it can be seen that the ductility of the samples decreased significantly after the first extrusion, where after it increased slightly with increasing residence time. DTBP resulted in slightly higher elongation at break values after the first four extrusions. Side reactions, like cross-linking, lead to reduced chain mobility, thereby reducing possible chain extension, hence lower elongation.

When the change in mechanical properties is compared to the data observed regarding gel content analysis, it can be seen that DTBP-samples had a higher gel content compared to DCP-samples. Higher gel content should result in lower elongation, but the reverse is observed here. It can therefore be concluded that degradation was the overriding effect causing the change in mechanical properties, despite cross-linking.

Evidence of degradation was further supported by a gradual colour change after each extrusion. It was observed that with increasing number of extrusion cycles (reaction time) specimens were getting darker, taken as indicative of greater degradation. Figure 6-14 shows the colour change due to the degradation of the polymer, using DTBP (Figure 6-14(b)) and DCP (Figure 6-14)(a)) as the peroxide initiator.

FTIR also revealed some degradation peaks at three points, shown with the dotted boxes in Figure 6-10 (c). The significance of each of peaks is summarized in Table 6-5:

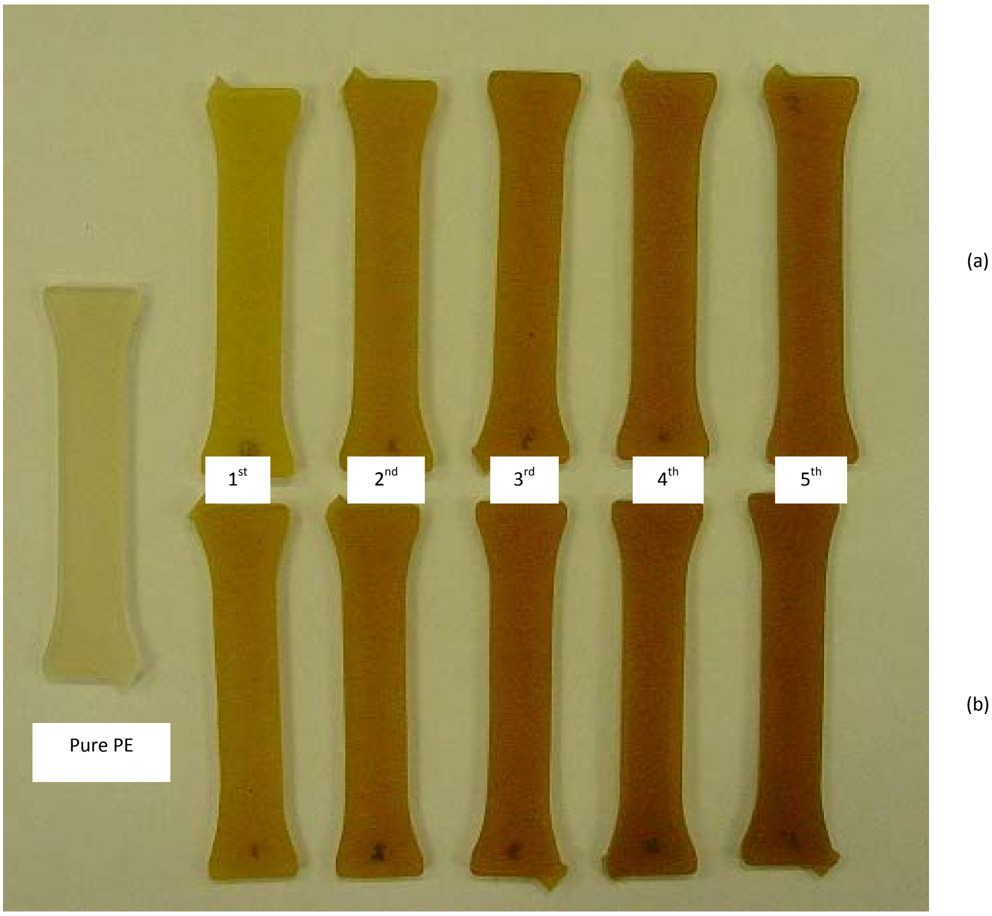


Figure 6-14: Colour changes of the polymer (a) DCP, (b) DTBP with an increment of residence time(1st cycle-5th cycle of extrusion)

Table 6-5: Main absorption of polyethylene in the IR region and their assignment

Band (cm^{-1})	Assignment
908	Polyethylene unsaturation peak [85]
1721	Carbonyl band [86]
3633	Hydroxyl band [86]

The peaks observed in the degradation of the polyethylene are similar to other work, where carbonyl and hydroxyl bands were observed due to the thermal decomposition (oxidation) of polyethylene.

FTIR analysis revealed that for both types of peroxides, chain scission of PE occurred.

In light of all the results discussed, it can therefore be concluded that DCP is more effective an initiator because:

- It leads to higher DOG compared to DTBP at all levels monomer and initiator tested.
- The degradation of mechanical properties is less when DCP is used due to the lower occurrence of cross-linking in the DCP-initiated samples.

7. Conclusions and recommendations

Reactive extrusion is an excellent method when dealing with highly viscous materials. Low residence time and less solvent required for purification are contributing to the cost effectiveness of the use of reactive extrusion as opposed to solvent methods. The main difference between reactive extrusion and solution methods is that the reaction is carried out in the molten state during extrusion.

In this study, modification of polyethylene, using itaconic anhydride was investigated. The objective of the experimental work was to identify and study the most important factors that affect melt grafting and also to optimize the process to achieve high degree of grafting and minimal side reactions.

Itaconic anhydride was selected as monomer because of its stability at a wide pH range (from pH 1 to 12) and it is also less hazardous compared to other kinds of anhydrides, such as maleic anhydride.

From literature, many factors were identified that influence grafting; these were: screw design, polymer type, initiator type and concentration, temperature, mixing efficiency, residence time as well as additives used. It was found that most of these factors are interrelated as to their effect on the DOG and side reactions.

In this study, it was shown using FTIR, that grafting IA onto PE using a peroxide initiator did occur and the functional group is in the anhydride form, as apposed to the hydrolyzed carboxylic acid form.

Melt grafting requires a reaction temperature above the melting temperature of the PE (T_m = 86 ^oC) and IA (T_m = 66 ^oC) and the decomposition temperature of the initiator. It further shown that higher reaction temperatures resulted in an increase in the occurrence of side reactions. It was found that above 160 °C severe polymer degradation occurred, evident from sample discolouration. It was concluded that a higher degree of grafting can be achieved by increasing the initial monomer concentration, up to a limiting concentration. When using 2 wt % peroxide, the limiting concentration was found to be 6 wt% IA and above this point no improvement in DOG was achieved. Increasing the initial monomer concentration was also shown to increase cross-linking with an evident from an increase in gel content. Cross-linking may lead in reducing processability of the polymer.

It was found that DCP is much more effective at grafting, compared to DTBP because DTBP is more prone to induce side reactions. Furthermore, it was shown that the initiator concentration also had a pronounced effect on melt grafting. High initiator concentrations lead to increase polymer degradation, while at very low concentration, the probability of grafting is reduced, further promoting the more likely chain scission reaction. Therefore, from this investigation, 2 wt % initiator was found to be optimal.

It was found that insufficient residence time lead to a low degree of grafting. To this extent, 168 seconds resulted in the highest DOG, corresponding to 4 extrusions in series. However, it was also found that an increase in residence time resulted in an increase in polymer degradation. This was evident from a severe decrease in tensile strength of PE after two extrusions, when using DTBP and three extrusions, when using DCP. Young's modulus decreased only slightly, while all samples shown a dramatic decrease in ductility, even after one extrusion. It was concluded that degradation had a more pronounced effect on mechanical properties than cross-linking and residence time should therefore not exceed three extrusions in series, which corresponded to about 126 seconds.

Degradation was further confirmed using FTIR, evident from absorption peaks at 3633, 1721 and 908 cm^{-1}. Those peaks were observed due to the thermal degradation of the polyethylene.

The effect of the process conditions, as discussed can be summarized, in Table 7-1.

Table 7-1:Effects of the reaction parameters onto the grafting degree

Parameter	**Condition**	**Degree of grafting (DOG)**	**Gel content (%)**	**Degradation**
Temperature	High Low	Low High	High Low	High Low
Initial monomer concentration	High Low	High Low	High Low	High Low
Initiator concentration	High Low	Low High	High Low	High [a] Low
Residence time	Long Short	High Low	Low Low	High Low

[a] condition apply to low initial monomer concentration

It is recommended that further work is required to study the effect of other factors, such as additives that prevent side reactions. Quantifying grafting, cross-linking and degradation kinetics may also assist in further understanding and optimization residence time and reaction temperature. Additional characterization techniques, such as melt flow index, molecular mass distribution, rheological and thermal properties of the grafted polymer may also assist in selecting more appropriate reaction conditions, leading to an optimised product.

8. References

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