

Grafting Itaconic Anhydride onto Polyethylene Using Extrusion

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Received 27 January 2009; accepted 27 November 2009

DOI 10.1002/app.31901

Published online 12 February 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Reactive extrusion was employed to graft itaconic anhydride (IA) onto polyethylene, using thermally induced peroxide decomposition. It was found that an increase in IA concentration lead to an increase in the degree of grafting (DOG), but only up to 6 wt % IA. Using di-cumyl peroxide (DCP) as the initiator resulted in a higher DOG compared to di-*tert*-butyl peroxide (DTBP) and required less reaction time to achieve the same DOG. However, raising the IA concentration also resulted in an increase in cross-linking. Increasing the initiator concentration from 0.2 to 2 wt % resulted in a higher DOG. However, 5 wt % initiator showed similar results compared to using 0.2 wt % due to termination by disproportionation,

which has been shown to be more prevalent at high initiator concentrations. Degradation was clearly observed by the inability to form a continuous extrudate during extrusion as well as discolouration. A residence time of more than 50 seconds, using DCP and 120 s for DTBP didn't offer any further increase in the DOG and also resulted in more pronounced degradation. Optimizing grafting is therefore a trade-off between maximal DOG and minimizing side reactions. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 3118–3126, 2010

Key words: copolymerization; cross-linking; degradation; extrusion; graft copolymers

INTRODUCTION

Increased environmental awareness has spurred development of products and processes that are more environmentally friendly. Many alternatives to synthetic polymers have been considered, such as polysaccharides, lipids polyesters and proteins, which can be extracted from plant or 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 utilizing 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 nonreactive in their native states.^{1–3} One solution is to functionalize the synthetic polymer to increase its reactivity towards bio-derived polymers.

Melt grafting functional monomers onto polyolefins is a well known area and a vast amount of work has been done in the area of grafting maleic anhydride onto polyethylene and polypropylene.^{4,5}

In the context of functionalising 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 certain anhydrides and maleimide-type chemical groups. These groups are, are also the best chemical reagents to react with amino acids, such as cystein and lysine.^{6,7} Monomers that have been used for grafting onto polyolefin include maleic anhydride (MAH),^{8–15} glycidyl methacrylate,¹⁶ citraconic anhydride,¹⁷ itaconic anhydride (IA)¹⁸ and itaconic acid,^{19–30} however, not all of these are reactive towards proteins.

Maleic anhydride (MAH) has been widely used as a monomer in modification reactions of polyolefins.^{14,31–37} MAH grafted polyolefins have shown great importance as compatibilizers in polymer modification, as adhesion promotes for polymers and as bonding agents for polymers and metals.³³ However, reaction with amino acid compounds resulted in unstable amide bonds that can easily be hydrolyzed below a pH of 5.²⁰ This makes it less suitable for further reactions with proteins.

On the other hand, IA is a harmful compared to MAH and can also be prepared from renewable sources.^{27,30} 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 (~ 70 °C).²⁰ IA can used for acetylating lysine, tyrosine and cystein.²⁰

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TABLE I
Summary of Materials Used

Material	Supplier	Boiling point (°C)	Melting point (°C)	Melt flow index (g/10 min)	Decomposition temperature (°C)	Solubility parameter (J cm ⁻³) ^{0.5}	Half life, t _{1/2} (min)	
							150 °C	200 °C
Linear low density polyethylene (LLDPE) (COTENE™ 3901)	ICO Polymers			4.0		16.1		
Itaconic anhydride (95%)	Sigma-Aldrich	114	66			14.6		
Di- <i>tert</i> -butyl peroxide (95%)	Sigma-Aldrich		-40		111	15.3	18	0.35
Di-cumyl peroxide (98%)	Sigma-Aldrich		39		130	17.4	9.2	0.25

The objective of this research was to explore reactive extrusion as a means to functionalize polyethylene using IA. Reactive extrusion has great prospect in modifying polyethylene compared to solution methods, as it can easily deal with highly viscous materials.³⁸ This study investigates the effect of initiator concentration, monomer concentration and residence time on the degree of grafting (DOG) of IA onto polyethylene, using free radical grafting.

EXPERIMENTAL

Materials

Materials used in this study are listed in Table I, along with their relevant properties.

Preparation

Several experiments were undertaken in this study and are summarized in Table II. The objective of the experimental work was to assess how variances in composition (% IA, % free radical initiator) and residence time affect the DOG as well as side reactions that may occur.

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. The material was compounded in a ThermoPrism TSE-16-TC twin-screw extruder using a flat temperature profile of 160°C and a screw speed of 65 rpm, unless otherwise stated.

Formulation parameters (Experiments 1–5)

It is well-known that the concentration of reagents will influence the grafting process.^{9,11–13,39} In these experiments the peroxide (0.2–5%) and monomer concentrations (0.2–10%) as well as the peroxide type (di-*tert*-butyl peroxide and di-cumyl peroxide) were varied.

Residence time

The residence time inside the reactor is a well-known parameter that will affect conversion. In these experiments, residence time in the extruder was increased up to 250 s by varying the number of extrusions performed in series. The formulations used were according to those specified in experiments 1 to 4 in Table II.

Characterization

The grafting process was assessed in terms of:

- The DOG (grams monomer reacted per gram polymer).
- Gel content or cross-linking (percentage insoluble polymer).
- Chemical properties.

TABLE II
Summary of Experimental Design

Experiment number	Peroxide type	Composition (wt %)		
		IA	PE	Peroxide
1	DTBP	0.2	99.6	0.2
		4	95.8	
		6	93.8	
		8	91.8	
		10	91.8	
2	DTBP	0.2	97.8	2
		4	94	
		6	92	
		8	90	
		10	89.8	
3	DCP	0.2	99.6	0.2
		4	95.8	
		6	93.8	
		8	91.8	
		10	89.8	
4	DCP	0.2	97.8	2
		4	94	
		6	92	
		8	90	
		10	88	
5	DTBP	0.6	94.4	5
		4	91	
		6	89	
		8	87	

The procedures followed are described in more detail below:

Reaction product purification

Purification of the graft copolymer is required before chemical titration. The purpose of purification is to remove unreacted monomer. Raw samples were boiled in xylene, precipitated using acetone and recovered using filtration. The precipitate was subsequently washed using fresh acetone and dried under vacuum at 60°C.^{9,12}

Chemical titration

Chemical titration of the polymer was done to measure the DOG as well as the % monomer reacted.^{9,12} Purified polymer was firstly dissolved in boiling xylene and a few drops of water were added to hydrolyse the anhydride functionality. Secondly, 0.05 M potassium hydroxide in methanol (KOH) was added to react with the hydrolysed anhydride. Using phenolphthalein as an indicator, samples were back titrated with 0.03 M trichloroacetic acid solution in xylene.

Gel content analysis

The gel content test method has been taken from the ASTM standard D2765-95. The rationale of doing the test is to measure the insoluble polymer fraction as a result of cross-linking. The soluble fraction was extracted using boiling xylene in a soxhlet extractor. A ratio of sample to solvent of 1 : 100 was used to ensure complete dissolution of the soluble fraction. Extraction is performed over 12 h, followed by drying.

Fourier transform 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 4 cm⁻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 by compressing homogeneous KBr/polymer blends to produce transparent discs. Discs were kept in desiccators to avoid exposure to humidity.

RESULTS AND DISCUSSION

Formulation parameters

Two types of peroxides, namely di-*tert*-butyl peroxide (DTBP) and di-cumyl peroxide (DCP) were tested using a flat temperature profile of 160°C

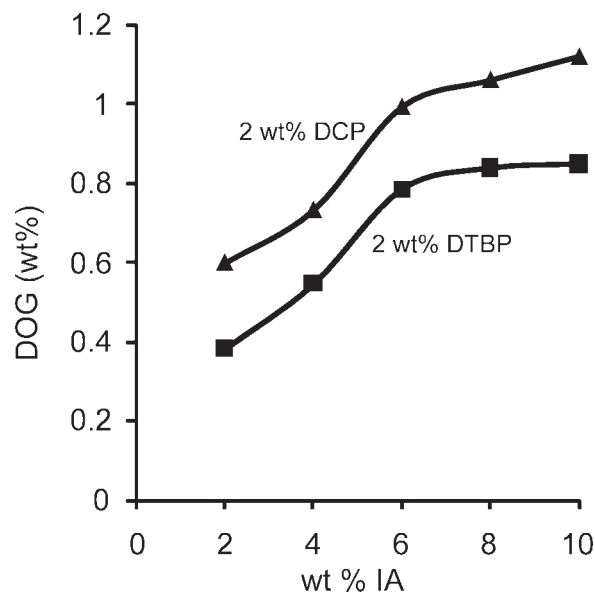


Figure 1 The effect of monomer concentration on the DOG at 2 wt % peroxide.

throughout the extruder. The results obtained are shown in Figure 1.

From Figure 1 it can be seen that increasing the IA concentration leads to an increase in DOG up to 6 wt % IA, for DTBP and an apparent 10 wt % IA for DCP. It has previously been shown for MAH systems that an increase in MA concentration typically intensifies hydrogen abstraction from the PE backbone and therefore increase the DOG.^{35,40} However it is clearly shown, that above 6 wt % IA, the DOG almost plateaus. At low IA concentration, initiator dissociation leads to a high concentration of polyethylene radicals. This reaction is followed by a cross-linking or disproportioning reaction. It was shown that using 2 wt % peroxide and 0.6 wt % 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. However, high monomer concentration may lead to the formation of many other polyethylene and IA radicals.⁴¹ This lead to either homopolymerisation or grafting, hence the plateau at higher monomer concentrations.

It was also found that the DOG was higher using DCP compared to DTBP. The half life of DTBP is longer than DCP, and may therefore not be completely utilized during the reaction.⁴⁰ DCP has also been shown to be more effective in the introduction of long chain branches in linear PE compared to DTBP.⁴²

The half life of DCP is shorter than DTBP, consequently, under experimental conditions, DBTP will decompose slower, yielding lower concentrations of initiator radicals, resulting in a lower DOG.¹⁴ In

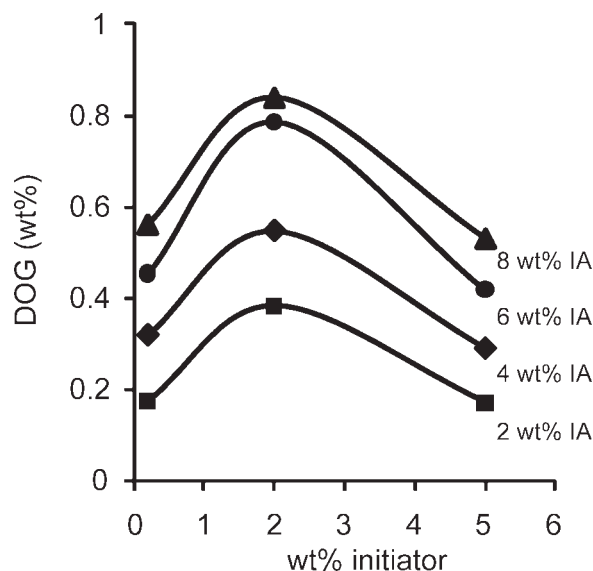


Figure 2 Graph of IA wt % concentration vs. DOG at different peroxide concentrations.

addition, it has been shown that because DTBP has a higher volatility and a lower decomposition temperature, it results in more radical species, such as: $\bullet\text{OC}(\text{CH}_3)_3$ and $\bullet\text{CH}_3$.²⁶ Consequently, more polyethylene macro-radicals can be formed early in the extruder's feed zone, before the mixture being completely homogenized. These radicals are preferably recombined with each other, leading to a high yield of cross-linked polymer and a low DOG.

Initiator concentration is among the most important parameters affecting grafting. From Figure 2 it can be seen that the DOG increased with increasing monomer concentration. The graph also shows that the DOG is at a maximum when the peroxide concentration is 2 wt %. Theoretically, higher peroxide concentrations should result in a higher DOG. At higher peroxide concentrations, more radicals will form and consequently, more radicals are available for reaction, leading to a higher DOG.^{13,41} However, above 2 wt % peroxide, severe cross-linking may occur. Cross-linking is mainly caused by combination of PE-IA \bullet radicals with PE \bullet radicals. 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 % IA) 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. 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 and consequently mechanical property reduction.¹³

From Figure 3 it can be seen that 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 earlier. Also, DTBP resulted in higher cross-linking compared to DCP, which is consistent to what was discussed earlier.

Residence time

The effect of prolonged residence time on the DOG is shown in Figures 4 and 5 when using DTBP and DCP at various concentrations. The residence time was increased by performing multiple extrusions in series. Each extrusion had an average residence time of about 50 seconds.

From Figure 4(A) it can be seen that the DOG 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 4(B), 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 shorter half life than DTBP, therefore requiring less reaction time. DCP is less prone to induce decomposition than DTBP, making the DOG of IA onto PE using DCP slightly higher compared to using DTBP.⁴⁰ However, in both cases, increasing IA resulted in a higher DOG. Furthermore, for both peroxides, 6 wt % IA seemed optimal, since above that, no significant increase in grafting was observed.

It was therefore concluded that when using DTBP, a longer residence time is required to reach similar

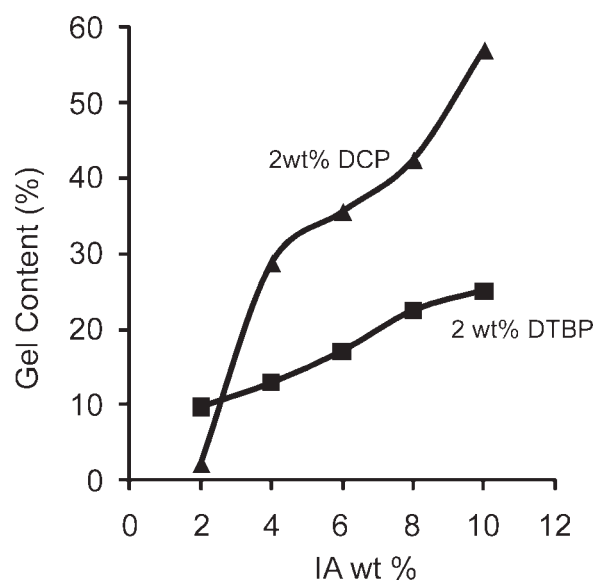


Figure 3 Gel content as a function of IA concentration at different initiators used.

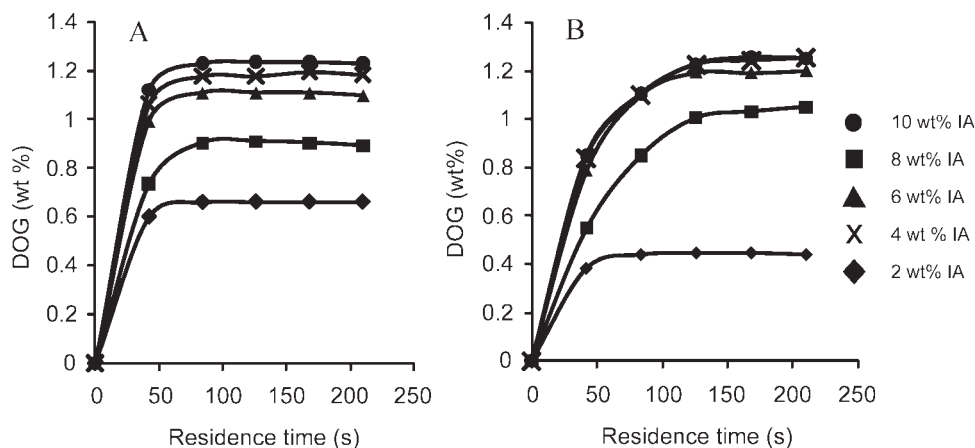


Figure 4 Graph of residence time vs. DOG using 2 wt % (A) DCP or (B) DTBP.

DOG compared to DCP. It would therefore be more efficient to use DCP in a commercial environment. This furthermore, as shown earlier, that DCP generally leads to higher degrees of grafting, further supporting its use as the preferred initiator.

In Figure 5, the effect of residence time on the DOG is shown, 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 s 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 initiator concentration, more polyethylene radicals are formed, leading to the higher degree of grafting. However, using lower initiator concentrations, requires less reaction time to reach the maximum DOG, all be it lower. Final process design would therefore be a trade off between higher DOG and shorter reaction times.

The lack of grafting at longer residence time would suggest either a lack of monomer or initiator.

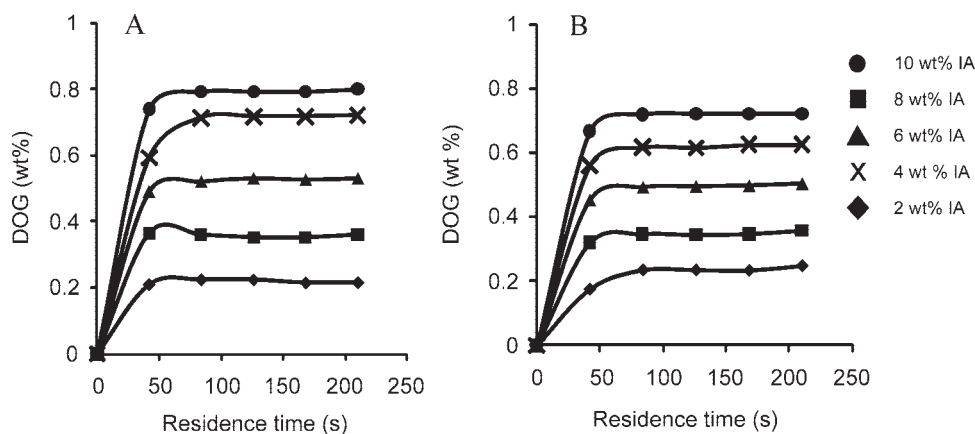


Figure 5 Graph of residence time vs. DOG using 0.2 wt % of (A) DCP or (B) DTBP.

Considering the excess monomer used, and the DOG achieved, one can conclude that in either case the initiator would have been mostly consumed after the second extrusion pass. Initiator consumption could be a result of either grafting or side reactions, as further explained in light of the reaction kinetics.

Reaction kinetics

Several studies have proposed reaction mechanisms for grafting monomers to polyolefins and it now well known.^{5,43} In general terms, it is well known that:

- Initiator decomposes into free radicals,
- The free radicals may be consumed by dismutation reactions or
- Initiate grafting,
- Initiate homopolymerisation of the monomer,
- Cause chain scission (degradation) or
- Cause cross-linking.

Some authors have also refined the reaction kinetics scheme specifically for MAH^{32,24,44,24} and are shown as follows:

Thermal decomposition of the initiator : $I \xrightarrow{k_d} 2R \bullet$

Radical attack onto polymer : $R \bullet + P \xrightarrow{k_{tr}} RH + P \bullet$

Initiation of grafting : $P \bullet + M \xrightarrow{k_g} PM \bullet$

Reaction with impurities : $P \bullet + I_m \xrightarrow{k_{i1}} PI_m$
 $PM \bullet + I_m \xrightarrow{k_{i2}} PMI_m$

Termination : $P \bullet + P' \bullet \xrightarrow{k_t} P + P'$
 $PM \bullet + P' \bullet \xrightarrow{k_t} PM + P'$
 $PM \bullet + PM' \bullet \xrightarrow{k_t} PM + PM'$

Cha and White²⁴ have shown that the kinetic equations based on this scheme can be simplified to that shown in eq. (1), assuming steady state production and consumption for various radical species and $f = \frac{[P \bullet]}{[PM \bullet]}$. Homopolymerization of IA is not expected since the reaction is carried out well above the ceiling temperature (90°C²⁹).

$$-\frac{d}{dt}[M] = \frac{k_g}{1+f} \cdot \sqrt{\frac{2k_d}{k_t}} \left\{ 1 - \frac{k_{im}[I_m]}{\sqrt{8k_d k_t [I]}} \right\} [I]^{1/2} [M] \quad (1)$$

$$\frac{d}{dt}[M] = k_{overall} [I]^{1/2} [M]$$

In eq. (1), k_{i1} and k_{i2} have been lumped into a single term, k_{im} .

Cha and White²⁴ have estimated reaction constants for MAH grafted polypropylene, initiated by 2,5-dimethyl-2,5-bis-(*t*-butylperoxy) (DBHA) or 2,5-dimethyl-2,5-bis-(*t*-butylperoxy) hexane (DBHY). They have found that the constant $\frac{k_g}{1+f} \cdot \sqrt{\frac{1}{k_t}}$ was 0.011 and 0.061 (L/mole-sec)^{1/2} for DBHA and DBHY respectively. In addition, based on extrusion conditions employed in their study, $\frac{k_{im}[I_m]}{\sqrt{8k_d k_t}}$ was estimated to be ~ 0.1 L/mol.

Considering the IA grafting system of this study, a plot of initial monomer concentration vs initial reaction rate produced a straight line, as shown in Figure 6. The initial rate of reaction can be calculated from the rate data in Figure 5. The slope of this line represents the combined rate constants as described in eq. (1), using a constant initial initiator concentration of 0.2 wt %. Knowing that $k_d = 109 \text{ s}^{-1}$ and $k_d = 194.8 \text{ s}^{-1}$ for DCP and DTBP respectively, $k_{overall}$ for the IA system was estimated to be 0.21 and 0.14 (mol/L)^{3/2}, which is in the same order of magnitude than that estimated by Cha and White for MAH. However, the value is greatly dependant on the assumed value for initiator decomposition efficiency and the extent of side reactions ($\frac{k_{im}[I_m]}{\sqrt{8k_d k_t}}$). It is well known that the initiator decomposition efficiency is

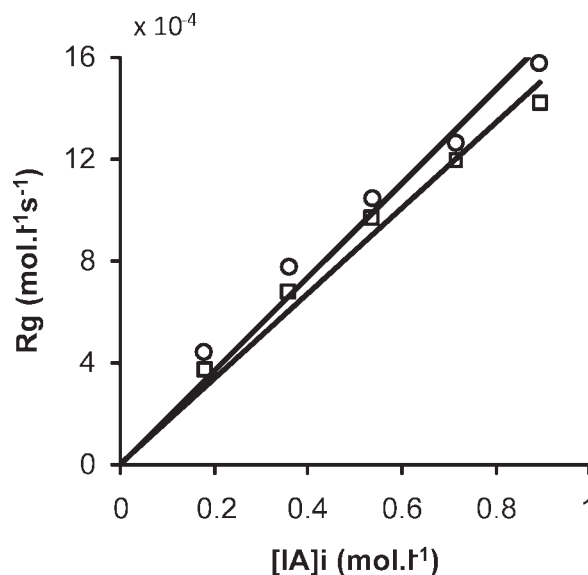


Figure 6 Comparison of the initial rate of reaction (R_g) using DCP (○) and DTBP (□) using an initial initiator concentration of 0.2 wt %.

greatly influenced by factors such viscosity of the reaction mixture and may vary by an order of magnitude between systems.⁴³

From eq. (1), it is clear that the overall reaction constant will be influenced by the initiator decomposition rate (k_d), its efficiency and the extent of side reactions with impurities (k_{im}). Initiator decomposition in turn is influenced by reaction temperature and other processing variables. During extrusion the reaction mixture may only reach the set temperature slowly (measured temperature profile was within 5°C of set point), leading to much slower than expected rate of initiator decomposition. Impurities, such as free radical scavengers may also greatly affect the overall rate of reaction in the extruder. All of these not accounted for in eq. (1).

Juggling solely on the data presented in Figures 4 and 5, one would expect the initiators to have a very short half life, where in fact, both DCP and DTBP have half lives of several hundred seconds at 160°C. One could therefore only conclude that side reactions such as inefficient initiator decomposition, cross-linking and the influence of free impurities were the main influence of the observed reaction behavior.

Chemical structure

The physical properties of polymeric systems depend, in the first instance, on the chemical constituents and the configuration of the macromolecules. 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 IA was indeed grafted and to assess the structure

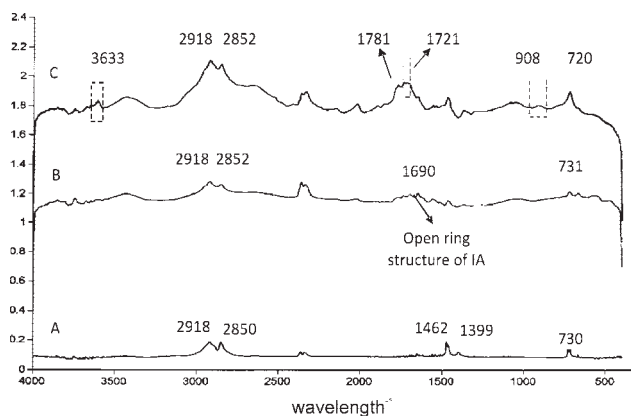


Figure 7 FTIR spectra for (A) pure LLDPE, (B) hydrolysed IA grafted LLDPE, and (C) IA grafted LLDPE.

of the grafted molecule. Figure 7(A) is used as a reference for pure LLDPE in the FTIR analysis.

In Figure 7(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 IA) in the polymer backbone after grafting.⁴⁶ This indicated that IA was grafted, and that anhydride hydrolysis has occurred.

In Figure 7(C), the spectrum of grafted itaconic anhydride (PE-g-IA) is shown. It can be seen that the peak at 1690 cm^{-1} , as mentioned earlier, has been eliminated, but a new peak at 1781 cm^{-1} can be observed. This peak is indicative of the anhydride group grafted onto the polymer backbone. It can therefore be concluded that the grafting has indeed occurred and that the grafted monomer is still in the anhydride form.

Thermal degradation

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.⁴⁷ It has been shown that thermal degradation of polymers can occur via side group elimination, random scission and depolymerization. For polyethylene, thermal degradation mostly occurs via a free radical mechanism, leading to random chain scission and cross-linking.⁴⁸

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 discoloration occurred after extrusion, which is often indicative of degradation. Samples were extruded five times and test pieces were injection molded 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 later.

Tensile strength

From Figure 8, it can be seen that when using DCP and DTBP, the tensile strength decreased slightly 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 in his work on maleic acid grafted PE.⁴⁷

Young's modulus

From Figure 8, 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

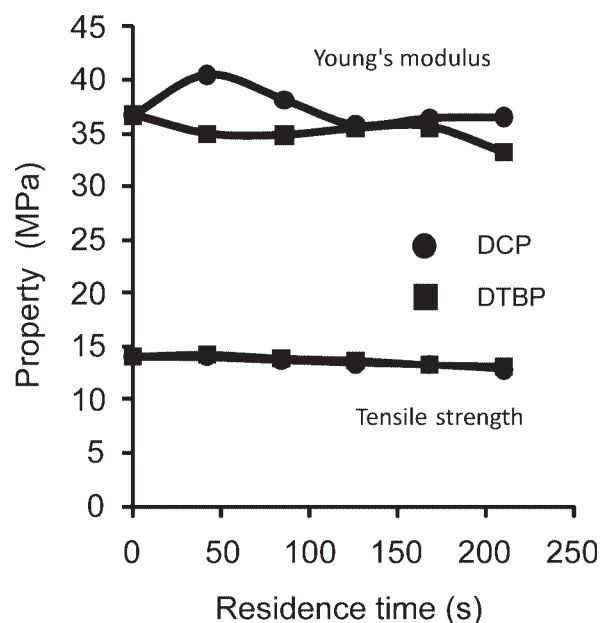


Figure 8 Graph illustrating the influence of residence time on the tensile strength and Young's modulus of IA grafted PE.

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.

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 9.

From Figure 9, 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 color change after each extrusion. It was

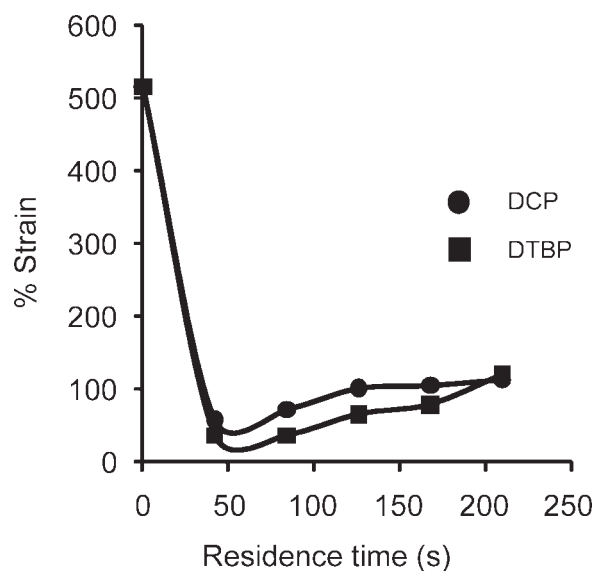


Figure 9 Graph illustrating the influence of residence time on the percentage strain of IA grafted PE.

TABLE III
Main Absorption of Polyethylene in the IR Region and their Assignment

Band (cm^{-1})	Assignment
908	Polyethylene unsaturation peak ⁴⁹
1721	Carbonyl band ⁵⁰
3633	Hydroxyl band ⁵⁰

observed that with increasing number of extrusion cycles (reaction time) specimens were getting darker, taken as indicative of greater degradation. FTIR also revealed some degradation peaks at three points, shown with the dotted boxes in Figure 7(C). The significance of each of peaks is summarized in Table III.

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.

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

CONCLUSIONS

It was concluded that under the conditions tested, IA was successfully grafted onto PE using a peroxide initiator. The resulting functional group was found to be in the anhydride form, as apposed to the hydrolysed carboxylic acid form.

Melt grafting required a reaction temperature above the melting temperature of the PE ($T_m = 86^\circ\text{C}$) and IA ($T_m = 66^\circ\text{C}$) and the decomposition temperature of the initiator. It was concluded that a higher DOG 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.

At 2 wt % initiator, DCP required 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 s 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 s reaction time to reach a maximum DOG.

It was concluded that insufficient residence time lead to a low DOG. To this extent, 168 s resulted in the highest DOG, corresponding to four extrusions in series. However, it was also found that an increase in residence time resulted in an increase in polymer degradation.

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