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Selective functionalization of the ethylene rich phase of a heterophasic polypropylene

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Abstract

The purpose of the present work was to investigate the effect of the solubility parameters of various peroxides on the grafting level of maleic anhydride (MA) on the different phases of a heterophasic polypropylene (PP). In order to characterize the different phases, the material was separated by solvent extraction. The molecular structure of the different fractions was investigated by Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC). A qualitative comparison of the grafting levels was obtained by FTIR and quantified by titration. The degradation of the different phases was investigated by gel permeation chromatography (GPC). The investigation showed that both the degradation and the functionalization mainly occurred in the ethylene rich phase. A preferential attack of the free radicals at single tertiary hydrogens between ethylene units, or at the ends of a PP block, adjacent to one or multiple ethylene units, results in a selective functionalization of the ethylene rich copolymers, regardless of the solubility parameter or decomposition rate of the peroxides. These tertiary hydrogen atoms are not sterically protected by adjacent methyl groups, and are therefore more accessible to the generated free radicals and the bulky MA. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Heterophasic polypropylene; Maleic anhydride; Grafting

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1. Introduction

The functionalization of polypropylene (PP), either homopolymer or copolymer, by unsaturated polar groups has been widely investigated [1–9]. The increased polarity and reactivity of the various polymers can be utilized in different ways to improve the chemical or mechanical properties of the various polymers, blends or composites. The functionalization of heterophasic PP, is on the other hand almost not investigated in spite of the interesting properties these materials exhibit. The heterophasic polyolefins are an intimate blend of a highly crystalline homopolymeric matrix and a complex mixture of copolymers. The copolymers and the homopolymeric matrix are phase separated, where the mixture of copolymers is finely dispersed as rubber particles in the matrix. The rubber particles initiate delocalized energy absorption and reduce catastrophic brittle failure, resulting in an impact resistant material [10]. It has been shown that the copolymers have a wide variation in composition, ranging from amorphous ethylene–propylene rubbers, to crystallizable propylene–ethylene statistical copolymers, as well as block copolymers of various lengths [11–14].

The general and old beliefs have been that a PP-chain has been more susceptible for hydrogen abstraction, due to the abundant tertiary hydrogens, and therefore more susceptible to grafting than PE. These beliefs are based on experimental results from low molecular species and theoretical considerations based on kinetic data [15,16]. Experimental evidence on polyolefins shows that this is indeed not the case, and that an opposite kind of *selective functionalization* is observed. The grafting level of copolymers increase with ethylene content and lack of stereoregularity, indicating that the grafting reaction is sterically controlled [17–20]. Another explanation was also suggested, namely that the preferential grafting of the amorphous rubber phase of a heterophasic PP was due to an enrichment of the peroxide and monomer in the ethylene rich phase [21].

The purpose of this work was to determine if the selective grafting of the amorphous rubber of a heterophasic PP was due to an enrichment of peroxide in the ethylene rich phase and affected by the solubility of the peroxide in the different phases. In order to investigate the observed selectivity, a heterophasic PP was functionalized with maleic anhydride

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(MA) by means of a radical-initiated process. The effect of the peroxide on the grafting level of the different phases was investigated by using four different initiators with different solubility parameters and decomposition rates.

One of the main difficulties in working with a heterophasic material is the need for a complete separation of the different components in the matrix in order to characterize the material properly. Temperature rising elution fractionation (TREF) is an adequate technique, and is widely used in separating components on the basis of crystallinity [12–14,21,22]. The main problem with TREF is the limitations in the amount of sample possible to fractionate, as well as it is a very time consuming technique. Another technique is to fractionate polymers by solvent extraction, such as Soxhlet extraction. These techniques have also shown to be quite time consuming, as well as they have some difficulties in obtaining pure fractions [23,24]. This study utilizes a less know technique, based on solvent extraction, which is reported to be able to separate the homopolymeric isotactic PP from the complex mixture of copolymers [25,26]. The different fractions were characterized by FTIR and DSC to elucidate the molecular structure of the fractions. A qualitative comparison of the grafting levels was obtained by FTIR and quantified by titration. The degradation of the different phases was investigated with GPC. The results showed that the heterophasic PP could be separated in two major fractions, an amorphous and low crystalline ethylene rich phase and a highly isotactic PP phase. A third fraction was also identified, but was too small and inhomogenious for a proper characterization. The investigation verifies that both the degradation and the functionalization mainly occurs in the ethylene rich phase. The degradation and grafting level of the different fractions were not influenced by the solubility parameters of the peroxides, indicating that the selectivity are controlled by the structure and composition of the molecular backbone. The results are in that respect a support to the previous explanation that the selectivity is sterically controlled.

2. Experimental

2.1. Materials

The heterophasic PP was supplied by Targor, and had a total ethylene content of approximately 18 wt%, and a melt flow index of 4.2 g/10 min (230°C, 2.16 kg). The MA (99%, Merck-Schuchardt) and the peroxides (di-*tert*-butyl peroxide (DTBP), *tert*-butyl cumyl peroxide (TBCP), di-cumyl peroxide (DCP) and 2,5-Bis(*tert*-butylperoxy)2,5-dimethylhexane (DTBPH), Akzo Nobel) were used as received. So also heptane (puriss, Kebolab), xylene (puriss, Kebolab) and ethylene glycol monobutylether (99%, Kebolab) were used for extraction. Irganox 1010 was used to prevent thermal degradation during fractionation.

2.2. Functionalization

The heterophasic PP was functionalized using a Clextral BC 21, a 25 mm fully intermeshing, co-rotating twin screw extruder, with a L/D of 34:1. The extruder was equipped with K-tron Soder, LWF D56, loss in weight twin screw feeders, nitrogen flushing and vacuum venting. The functionalization was performed at a temperature profile of 180–220°C by adding peroxide, 0.5 mmol, based on active oxygen content, and 2.0 wt% MA. Similar runs without the addition of MA, were performed to evaluate the action of the peroxides alone.

2.3. Fractionation by solvent extraction [26]

The functionalized polymer was dissolved in boiling xylene and precipitated in cold acetone, to remove unreacted MA, and to convert the polymer pellets to powder form. Precipitated polymer powder (~12 g) was introduced in a glass reactor, and hot solvent (400 ml) was added under nitrogen blanket. The slurry was subjected to intensive stirring by vibromixing (30 min), before the solvent, along with dissolved polymer was drained. The extraction step was repeated with the same solvent (500 ml) to ensure complete extraction of the fraction. The remaining unextracted polymer was subjected to further extraction. The solvents were introduced in the following order and heated to the respective temperatures; heptane (98°C), ethylene glycol monobutylether (165°C) and xylene (137°C), resulting in three separated fractions. The fractions obtained by extraction with heptane and xylene, were recovered by evaporation of the solvent, while the ether-soluble fraction was precipitated in cold acetone. All solvents contained ~1.5 wt% Irganox 1010 to inhibit thermal degradation during fractionation.

2.4. Characterization of the separated fractions

The structure and grafting level of the different fractions were evaluated by Fourier transform infrared spectroscopy (FTIR) on a Bruker IFS 66v, using 200 scans and a resolution of 2 cm^{-1}. The FTIR spectroscopy was made on pressed films with a thickness of approximately 200 μm, and the spectra were normalized against film thickness. In order to reconvert hydrolysed succinic acid to succinic anhydride (SA), the films were heated in vacuum at 120°C for 24 h prior to FTIR analysis.

Determination of the MA content was done by titration after removing the unreacted MAH by dissolving the modified polymer in xylene and precipitating in acetone. The recovered polymer was filtered and dried. The recovered polymer (1 g) was dissolved in xylene and the solution was saturated with water and refluxed (1 h) to ensure complete opening of the anhydride ring. The hot solution was then titrated without cooling with 0.05 N ethanolic KOH, using Bromthymol blue as the indicator. Excess KOH was added and the deep blue color was back titrated

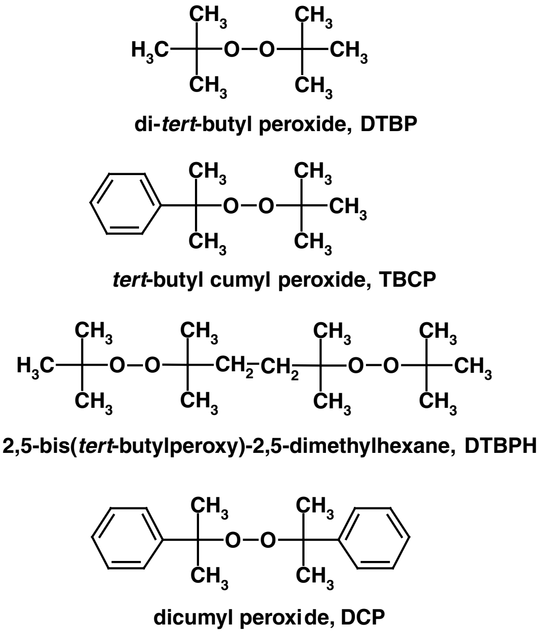


Fig. 1. Structure and annotation of the different peroxides.

to a yellow end point by the addition of 0.05 N isopropanolic HCl to the hot solution [27]. Unmodified polymer was also titrated and insignificant values were obtained.

The thermal behavior of the fractions was investigated using a Differential scanning calorimeter (DSC), Perkin–Elmer 7 Series Thermal Analysis System. The sample (~1.5 mg) was subjected to the following temperature program; heating from 20 to 200°C at a rate of 10°C/min, holding at 200°C for 5 min, cooling to 20°C at 10°C/min, and finally recording the heating from 20 to 200°C at rate of 10°C/min.

The molecular weight and polydispersity of the different fractions were determined on a Polymer Labs PL-210 GPC, equipped with two Plgel 10 μm Mixed-B columns, a RI detector, three Viscoteck viscometers and a 15° and 90° Precision Detector light scattering system. The polymer was dissolved in 1,2,4-trichlorobenzene stabilized with 0.0125 wt% BHT and heated for 3 h at 150°C before collection of the data. The detector and column temperatures were set to 160°C. The flow rate was 1.0 ml/min. The instrument was calibrated against narrow standard polystyrene samples, and the molecular weights were obtained by universal calibration.

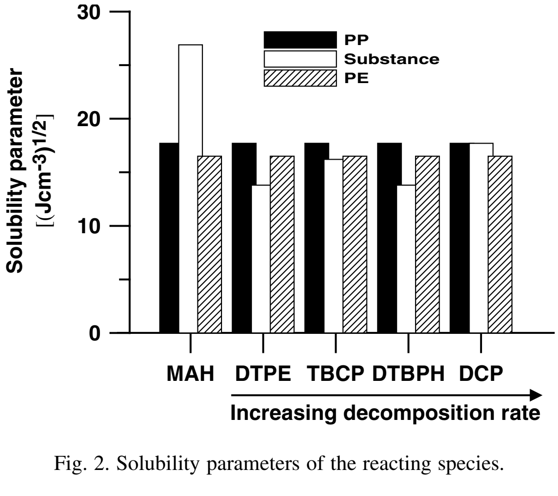


Fig. 2. Solubility parameters of the reacting species.

3. Results and discussion

3.1. Evaluation of the solubility of MAH and the different peroxides in the polymer

In order to investigate the effect of an enrichment of the peroxide in the amorphous phase, four different initiators were selected and their solubility parameters were compared to those of PE and PP. The structure and annotations of the different peroxides are given in Fig. 1.

The solubility parameters of PP, PE and MAH were obtained from literature data [28–31] and the solubility parameters of the different peroxides were calculated according to Small's group contribution method [30,32]. Such calculations on peroxides are previously reported to deviate less than 10% from experimental values [32], and are therefore found of sufficient accuracy for the following evaluation. A comparison of the solubility parameters of the components is given in Fig. 2.

The solubility parameter of MA indicates a very low solubility in either of the phases, and a phase separation is expected even at low MA concentrations. It is previously observed [32], that phase separation can take place at MA concentrations as low as 1–2 wt%, but that this value can be shifted to higher concentrations by more efficient mixing [2]. The solubility of MA is usually reported to be less than 3 wt% in molten polyolefins [33], but it is assumed that the MA will be completely soluble in both the PP and the ethylene rich phases at the given concentration and mixing conditions. If the solubility parameters of the peroxides are examined, a varying solubility of the different peroxides in the homopolymeric PP-phase and in the ethylene rich phase is expected. A comparison of the solubility parameters of the peroxides and the polyolefins, suggests that a peroxide like DTBP has a higher solubility in the ethylene rich copolymers than in the homopolymeric PP-phase, whereas an opposite distribution is anticipated for DCP.

3.2. Fractionation by solvent extraction

In order to investigate the effect of the various peroxides on the grafting level of the different phases it was necessary to fractionate the heterophasic PP. The main objective was to isolate the isotactic PP component. The fractionation was carried out as previously described, and three distinct fractions were obtained. The weight percentages of the different fractions are given in Fig. 3.

The emphasis of the discussion will be on the PP and EPR

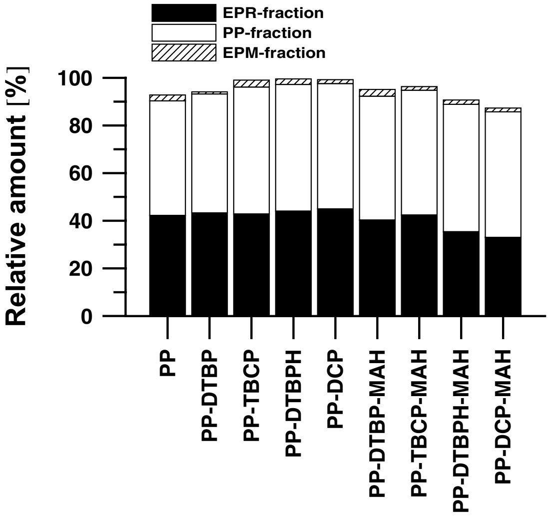


Fig. 3. Weight percentages of the separated fractions.

fraction since the EPM fraction was observed to be quite small and inhomogenous, and therefore difficult to characterize properly. The inhomogenous character of the EPM fraction was due to limitations in the fractionation apparatus, as well as crosslinking resulting in non-dissolvable polymer formed during the reactive extrusion. The somewhat less than 100% yield is due to mechanical loss in the fractionation apparatus as well as the above mentioned crosslinking.

3.3. Structural investigation of the fractionated samples

The thermal behavior of the raw material and the extent of the separation were investigated by DSC. The unfractionated raw material is compared with it's respective fractions in Fig. 4.

The DSC thermogram of the unfractionated material reveals two melting peaks, one characteristic of a highly crystalline isotactic PP fraction at 163°C and a second, smaller peak, characteristic of a semi-crystalline ethylene–propylene copolymer fraction at ~115°C. A more detailed information about the composition of the heterophasic material is obtained by looking at the thermograms of the fractionated material. The crystalline PP is identified by a sharp, single melting point at 163°C, but the ethylene–propylene copolymers is of a quite heterogenous character. The thermogram of the small EPM fraction shows two melting peaks, possibly a ethylene–propylene block copolymer consisting of a block with a low ethylene content ($T_m \sim 162$°C) and a block with a low propylene content ($T_m \sim 120$°C). The EPR fraction consists of several different components giving rise to multiple melting peaks of a very low crystalline character. The thermogram of the EPR fraction is magnified in Fig. 5, and at least five different melting peaks can be identified, indicating ethylene–propylene copolymers with various distribution of ethylene units.

Additional structural information, as well as an evaluation of the grafting level was obtained by examining the different fractions by FTIR. The FTIR spectra of the fractionated raw material are shown in Fig. 6.

The bands at 720 cm^{-1} and 730 cm^{-1} are characteristic of ethylenic structures, where the respective ethylene segments are of more than five methylene groups and of three methylene groups [34]. The quality of the fractionation is seen from the absence of absorbance of ethylenic units in the

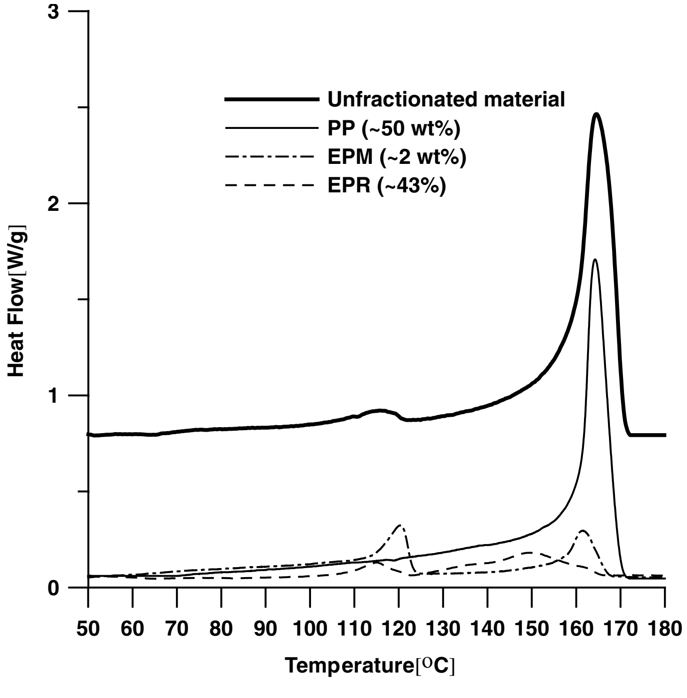


Fig. 4. DSC thermograms of the raw material and its separated fractions.

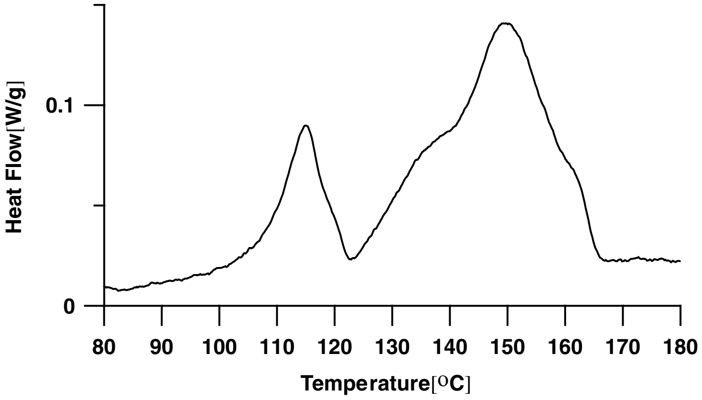


Fig. 5. Magnification of the DSC thermogram of the EPR fraction.

spectra of the PP fraction, although weak ethylenic bands are detected. The existence of these weak bands probably stems from short ethylene blocks and single insertions of ethylene units inside a propylene chain, since no crystalline melting peaks from PE is found in the DSC thermogram of this fraction. Specific absorption bands related to the critical length of isotactic PP sequences is also found, and sequence lengths of at least 5 PP units is observed at 975 cm^{-1}, 11–12 units at 998 cm^{-1} and 13–15 units at 841 cm^{-1} [34]. The change in the ratio of the bands at 1167 cm^{-1} and 1156 cm^{-1} is also influenced by the tacticity of the PP segments [21]. The characteristics of the different spectra confirm the interpretation of the DSC thermograms. The somewhat confusing band at 1740 cm^{-1} is due to absorption from the antioxidants used during the fractionation. The PP fractions lack this absorption band since these fractions were collected by precipitation and washing in cold acetone.

3.4. Selectivity

The extent of the grafting reaction is evaluated by FTIR in Fig. 7.

The absorption from the carbonyl stretching bands from the SA is seen at 1790 cm^{-1} and 1865 cm^{-1}. The total grafted MA content of the material was determined by titration to be between 0.35–0.45 wt%. Only a weak absorption is detected in the PP fraction, in contrast to the strong absorption found in the EPR fraction. A comparison of the FTIR spectra of the materials functionalized with DTBPH and DCP, which have approximately the same decomposition rate, reveals that the solubility parameter of the peroxide is of no significance. Both peroxides give rise to the same selective functionalization, although the DCP should by solubility aspects give a higher grafting level in the PP-phase. In order to determine, whether various diffusion rates

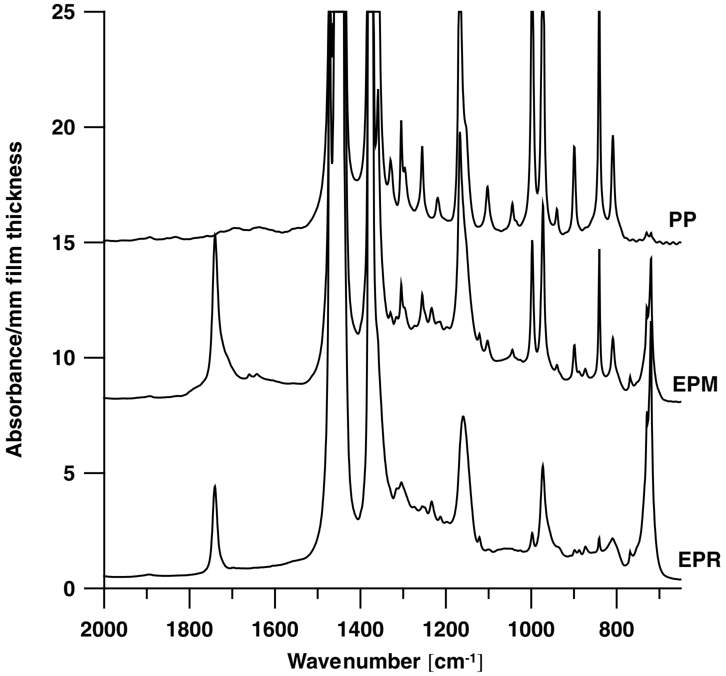


Fig. 6. FTIR spectra of the fractions of the raw material.

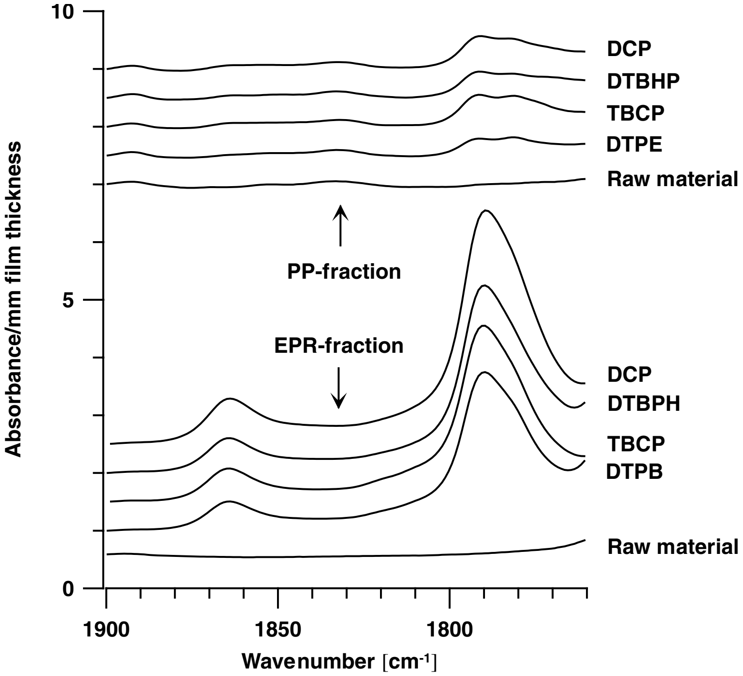


Fig. 7. Comparison of the FTIR spectra of the PP and EPR fractions of the raw material and the materials functionalized with various peroxides.

have an influence, a comparison between two peroxides with equal solubility parameters, but different decomposition rates should be of relevance. DTBP and DTBPH have according to Small's group contribution method solubility parameters of equal size, but have a significant difference in decomposition rate. The decomposition rate of DTBPH is more than twice of that of DTBP at 200°C. If the diffusion rate is of importance for the selectivity, a higher grafting level of the PP phase is expected in the case of DTBPH, since this peroxide would have less time to diffuse through the PP matrix and reach the dispersed EPR phase before it decomposes and initiates the grafting reaction. No such increase in grafting level is observed in the PP phase without a corresponding increase of the grafting level of the EPR phase, and the effect of different diffusion rates on the selectivity is therefore neglected. A qualitative comparison of the different FTIR spectra of the reactive extrusion with different initiators shows that no significant difference in selectivity is observed, indicating that neither differences in solubility or diffusion rates play an important role in the explanation for the selective functionalization.

When discussing the selectivity of the grafting reaction, also the nature of the free radical is of importance. Although there exist several side reactions and by products following the decomposition of the different peroxides, three main radicals are responsible for the abstraction of hydrogens. The methyl and butoxy radical are the main active species from the decomposition of DTBP and DTBPH, while DCP and TBCP also generate 2-phenylisopropoxy radical. If we evaluate the reactivity of these radicals by comparing the respective hydrogen bond dissociation energies of their precursors, we find their reactivity in the order $CH_3^{\cdot} \approx (CH_3)_3CO^{\cdot} < C_6H_5(CH_3)_2CO^{\cdot}$ [15]. A higher reactivity of the radical corresponds to a less discriminating radical behavior, resulting in a faster hydrogen atom abstraction. This fact can possibly be a part of the explanation of the higher grafting level of both the EPR and PP phases in the reactive extrusion with DCP and TBCP as initators. No effect of the somewhat higher "bulkyness" of the 2-phenylisopropoxy radical is seen on the selectivity.

The remaining explanation given by several others suggests that sterical hindrance is the controlling mechanism, although no direct evidence was provided. [17–20]. Through an investigation of the fate of the ethylenic units inside the PP chains, before and after peroxide treatment and after functionalization this explanation is substantiated. A magnification of the area of interest in FTIR, along with the molecular environment resulting in these absorption bands is magnified in Fig. 8.

These bands result from the methylene rocking vibrations in which all of the methylene groups rock in phase [35]. Single and multiple insertions of ethylene units result in two different bands, at $\sim 730\ \mathrm{cm}^{-1}$ and $\sim 720\ \mathrm{cm}^{-1}$, respectively. The peroxide treatment reduces the intensity of the absorption from the "in phase" rocking of the methylene units, indicating that the concentration of ethylene units in the PP fraction has been reduced. This reduction can be explained by a chain scission at PP units next to ethylenic segments, and a separation of the broken chains during the fractionation.

A further insight of the origin of the selectivity can be found by investigating the action of the peroxide on the degradation of the different fractions. The effect of peroxide

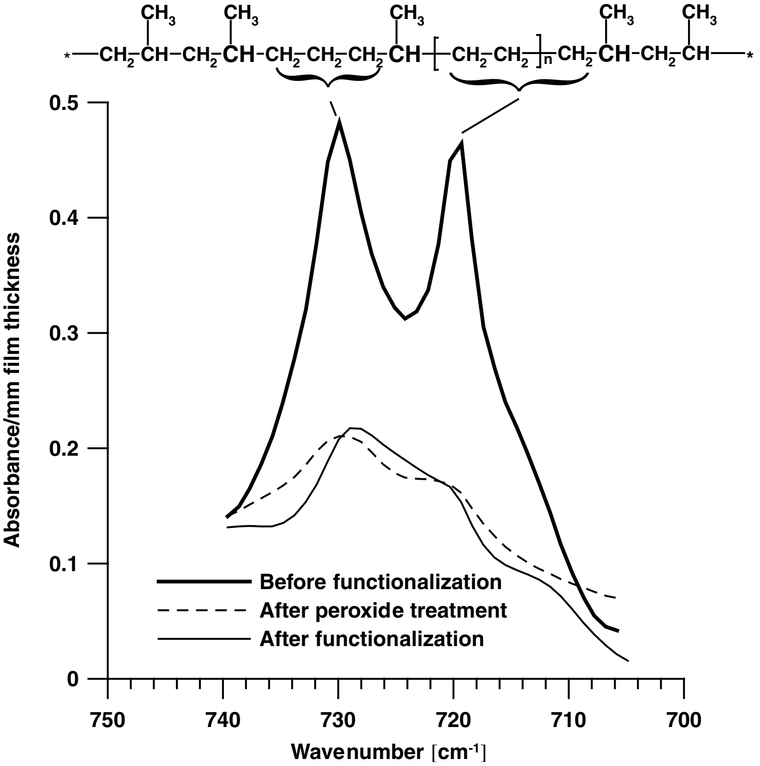


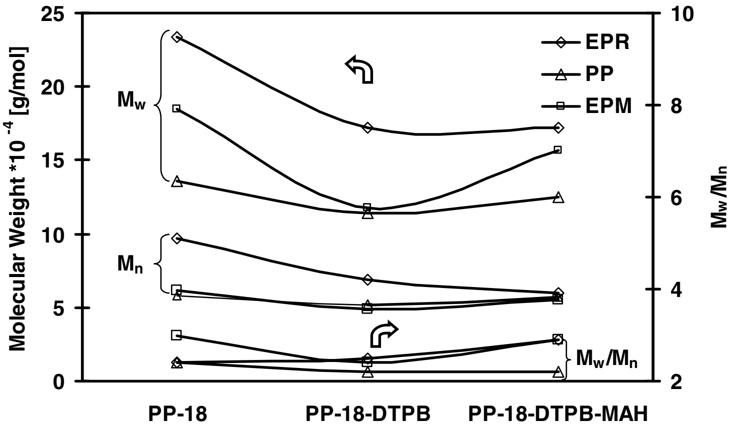
Fig. 8. FTIR spectra of the ethylenic absorption in the PP fraction before and after functionalization with di-*tert*-butyl peroxide as initator.

treatment and grafting on the molecular weight is shown in Fig. 9.

The effect of the ethylene content on the degradation is quite significant, since a substantial degree of degradation is observed in the two copolymeric fractions, while the PP fraction is only affected to a minor degree. The effect is most evident on the M_w, since the high molecular weight molecules have the highest probability of chain degradation. A comparison between the different peroxides on the degradation of the EPR and PP phase is given in Fig. 10.

Again, the solubility parameter of the peroxides is of no influence, but an increasing degradation along with increasing decomposition rate is observed. This effect is possibly due to a generation of a different amount of free radicals, due to the differences in decomposition rate or various volatility of the different peroxides and a consequent loss of initiator. In any case the same effect as in Fig. 9 is seen, namely that the PP fraction is almost not effected, while a severe degradation of the EPR phase is observed.

The results from the FTIR spectra and the data from GPC



$\delta_{DTPE} < \delta_{PE} << \delta_{PP}$

Fig. 9. Effect of peroxide treatment and functionalization in the molecular weights of the fractionated samples.

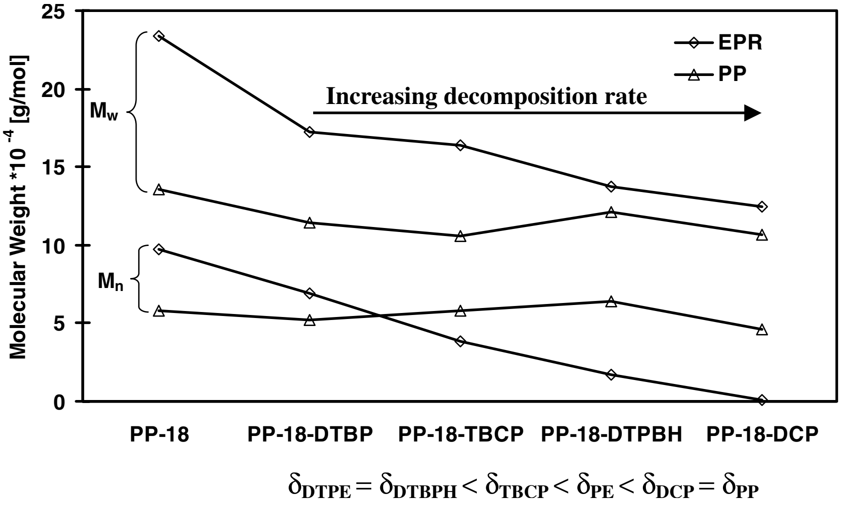


Fig. 10. Comparison of the relative change on molecular weight of the fractionated samples, and the effect of decomposition rate and solubility parameter of the different peroxides.

indicate that the hydrogen abstraction preferentially occurs on the ethylene rich copolymers. If we take into account that the hydrogen abstraction increases in the order primary < secondary < tertiary hydrogens atoms, a reasonable explanation for our results is that the attack by the peroxides preferentially occurs at single tertiary hydrogens between ethylene units, or at the ends of a polypropylene block, adjacent to one or multiple ethylene units. The most accessible hydrogen atoms are highlighted in Fig. 8. These tertiary hydrogen atoms are not sterically protected by adjacent methyl groups, and are therefore more accessible to the free radicals and the bulky MA. A chain scission at the end of a polypropylene block will then promote a PP fraction with a lesser ethylene content, as observed in the FTIR spectra of the peroxide treated and functionalized material. This explanation is also coherent with the observations that it is the EPR fractions that experience the highest degree of grafting, while the PP fractions are almost ungrafted and not degraded. Another effect that may contribute to the preferential grafting of the ethylene rich sequences is the fact that a large amount of helical sections of the isotactic PP chain still persist in the melt [36]. This chain conformation makes the tertiary hydrogens even more sterically protected and the attack by radicals and monomers more difficult.

4. Conclusions

The complex composition of a heterophasic PP has been illustrated through a fractionation of the material into three distinct components. The two major components consisted of a highly isotactic PP homopolymer and a very low crystalline ethylene–propylene copolymer, with a irregular distribution of ethylene units. A third, minor component was also identified, possibly a ethylene–propylene block copolymer. A preferential attack of different peroxides at single tertiary hydrogens between ethylene units, or at the ends of a polypropylene block, adjacent to one or multiple ethylene units, results in a selective functionalization of the ethylene rich copolymers, regardless of the solubility parameter or decomposition rate of the peroxides. These tertiary hydrogen atoms are not sterically protected by neighboring methyl groups, and are therefore more accessible to the peroxide and the bulky MA.

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