Assessment of the Utilization of Different Peroxide Dispersion Media on the Controlled Degradation of Polypropylene

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ABSTRACT: A two-step investigation of polypropylene-controlled degradation was performed. First the controlled degradation of polypropylene was investigated by assessing the effects of using dicumyl peroxide (DCP) and 2,5-dimethyl-2,5-di(t-butylperoxy) hexane (DHBP) in different suspensions (neat, calcium carbonate, and organically modified montmorillonite). The second part of this research was performed according to a factorial design at two levels (2^2 experimental design) with center point, in which peroxide concentration and reaction time were studied. Polypropylene degradation was assessed by melt flow rate (MFR) and parallel plate rheometry. Results showed that DCP presented higher molar efficiency in polypropylene degradation reactions in relation to DHBP; likely due to radical recombination reactions. The results also indicate that clay may catalyze the recombination reactions of polypropylene radicals. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

The objective of chemical modification in polymers is to make these polymers fit for specific end applications. Chemical modifications include the controlled degradation of polypropylene as well as grafting or functionalization. The aim of controlled degradation is to reduce molecular weight, as well as to narrow molecular weight distribution, and hence facilitate processing.[1–3] The aim of grafting or functionalization, which involves introducing functional groups onto the polymer backbone, is to alter chain polarity to enable increased interaction between polymer and for instance reinforcing fillers.[3–7]

In both cases extruders are commonly used to promote the chemical reactions. The main reason for using extruders involves operational costs.[3,4,8] Extruders, especially twin screw extruders, are versatile mixing equipment that allows reactions in the melt without the use of solvents,[9] under different processing conditions, since temperature profiles and screws can be altered. In addition, side feeding of the material during extrusion and release of gaseous byproducts through degassing zones are also possible.[9,10] When used as reactor, this relatively common equipment requires little or no alteration in configuration.

The type of modification that can be accomplished in a polymer is intimately related to the existing functional groups in the polymer chain, or in the case of radical reactions, to the stability of the generated radicals.[11] With polypropylene, usually organic peroxides are used to initiate the chemical modification reactions. The RO-OR bonds of peroxide undergo homolytic cleavage and release RO• radicals that may function as primary radical sources initiating these reactions.[3,12]

The extent of chain scission during reactive processing depends on a balance between: (i) the shearing by the extruder screw; (ii) the thermooxidative degradation; and (iii) the amount of peroxide added to the system. The effect of peroxide is generally the most important factor and is hence the controlled variable to achieve the desired molecular weight reduction. The type of peroxide used may alter the types of parallel reaction and hence strongly affects the end result. In general, multifunctional organic peroxides, capable of generating mono or polyfunctional radicals, are used. Scorah et al.[13] reported that utilization of peroxides releasing bifunctional radicals promote chain extension reactions and are less efficient in the reduction of final molecular weight.

Proper distribution and dispersion of the peroxides in the molten mass increases their ability to reduce molecular weight, since

phase coalescence hinders contact between the peroxide and the polymer, inhibiting the chain scission promoting chemical reactions.[14] It is therefore recommended to incorporate the peroxide into carbonates or clays prior to addition to the polymer.[15]

When peroxide is added to the clay it may be adsorbed on the clay surface or enter the interlayer space where the cations are located. Shi et al.[12,16] proposed a peroxide incorporation process in the interlayer space in liquid medium which showed to be interesting for maleic anhydride grafting onto polypropylene. However, no investigations have been carried out in the field of controlled degradation. According to the authors, incorporation of peroxide into the interlayer space allows gradual addition of the peroxyl radicals into the medium by a diffusion process. Diffusion of the radicals from within the clay to the surface alters the reaction mechanisms, because reactivity becomes restricted to the interface between the clay and the polymer.

Despite the absence of functional groups, reactions on the polypropylene backbone can be accomplished by the generation of macroradicals, mainly through abstraction of tertiary hydrogens from the carbons sustaining the pending methyl groups.[12,16–18] The formed macroradicals are highly unstable and therefore very reactive and may react with other radicals or undergo stabilization by disproportionation.[12,16] The latter reactions lead to molecular weight reduction[17,18] and are known as β-scissions. These reactions are desirable in the controlled degradation of polypropylene, however highly undesirable in the grafting reactions of functional groups.

The objective of this study was to analyze by means of rheological measurements how different media alter the stability of the macroradicals generated during the process, since the extent of chain scission may be affected by the way peroxide and macroradicals are distributed within the polymer bulk. The investigated dispersion media were organically modified montmorillonite and calcium carbonate.

MATERIALS

Samples were prepared with polypropylene homopolymer with melt flow rate of 2.89 ($\pm$0.78) g/10 min supplied by Quattor under trade name HP502H. Dicumyl peroxide (DCP) and 2,5-dimethyl-2,5-di(t-butylperoxy) hexane (DHBP) were used as degradation promoters. The latter is a liquid at room temperature, so utilization in the form of calcium carbonate suspension containing $\sim$ 47 wt % peroxide was also investigated. Peroxides were supplied by Archema under tradenames Luperox DC/SC (DCP), Luperox 101 (DHBP), and Luperox 101 XL (DHBP in CaCO$_3$).

Manipulation of DHBP was complicated, so it was solubilized in nujol at 10 wt % DHBP concentration. In addition to the solution in nujol, DHBP was incorporated in quaternary alkyl ammonium modified montmorillonite clay (Cloisite 20A, Southern). The same procedure was adopted using DCP. The investigated formulations are shown in Table I.

METHODS

Incorporation of Peroxides in Nanostructures
To prepare the peroxide/montmorillonite dispersion systems 4 g montmorillonite Cloisite 20A (MMT20) was added to 100 mL

Table I. Formulations Used to Assess the Effect of Different DCP Dispersion Systems on the Controlled Degradation of Polypropylene by Reactive Processing

Peroxide	Medium	Peroxide	Medium
DCP	None	DHPB	Nujol
	MMT20		CaCO3
	–		MMT20[a]

[a]MMT20: quarternary alkyl ammonium-modified montmorillonite clay (Cloisite 20A).

acetone and the system was left for 1 h in a closed ultrasound apparatus to avoid excessive evaporation of the solvent. After 1 h, 4 g peroxide dissolved in 10 mL acetone was added under stirring. Stirring was kept for 1 h 40 min. The material was then conditioned in Teflon vessels, dried in a vacuum oven at 40°C and subsequently conditioned in a desiccator. In addition to the dispersion systems a control sample with no peroxide was prepared.

X-ray Diffraction
X-ray diffraction patterns were obtained using a Philips X'PERT diffractometer equipped with a Cu source (wavelength 1.54 nm) operating at 40 kV and 40 mA. Scanning rate was 0.02° s^{-1} from $2\theta = 2°$ to 20° for montmorillonite clay samples and 2° to 40° for calcium carbonate samples to check for alteration in the characteristic diffraction peaks of the material after DHBP addition.

Reactive Processing
Assessment of the Different Peroxide Dispersion Media in the Controlled Degradation of Polypropylene. Polypropylene samples (35 g) were processed together with the peroxides under flowing nitrogen atmosphere (0.5 L min^{-1}) in a mixer equipped with roller 600 rotors coupled to a Reomix 600 Haake torque rheometer. The following conditions were used: temperature of 180°C, rotor frequency 50 rpm, 3 min melt time of the polymer and reaction time of 7 min. The investigated formulations are listed in Table II.

Assessment of Reaction Time and Peroxide Concentration on Controlled Polypropylene Degradation. Investigation on the effect of reaction time and peroxide concentration on the

Table II. Formulations Used for Investigating the Controlled Degradation of Polypropylene with Different Peroxides and Dispersion Media

Peroxide	Dispersion medium	C_{per} (phr)	$C_{p.eroxyl}$ (mmol)
DCP	None	0.05	12.9
		0.10	25.9
		0.15	38.8
DCP	MMT20	0.10	25.9
DHPB	Nujol	0.05	24.1
		0.10	48.2
		0.15	72.3
DHPB	CaCO$_3$	0.05	24.1
		0.10	48.2
		0.15	72.3
DHPB	MMT20	0.10	48.2

Table III. Formulations Used for Investigating the Effect of Reaction Time (t_r) and Peroxide Concentration (Cper) on the Controlled Degradation Reactions of Polypropylene in the Presence of Nanoparticles

Run	Codification		Level	
	t_r (min)	C_{per} (phr)	t_r (min)	C_{per} (phr)
1	+1	−1	15	0.5
2	−1	+1	7	1.5
3	+1	+1	15	1.5
4	−1	−1	7	0.5
5	0	0	11	1.0
6	0	0	11	1.0
7	0	0	11	1.0

controlled degradation of polypropylene was performed by means of a 2^2 experimental design with center point. The experimental design used is depicted in Table III. At this stage the controlled degradation of polypropylene was assessed by means of a parallel plate rheometer.

Melt Flow Rate

Melt flow rate (MFR) tests were carried out according to ASTM D1238 in a CEAST MeltFlow Tester. Four automatically timed flow rate measurements were taken at temperature of 230°C and load of 2.16 kg.
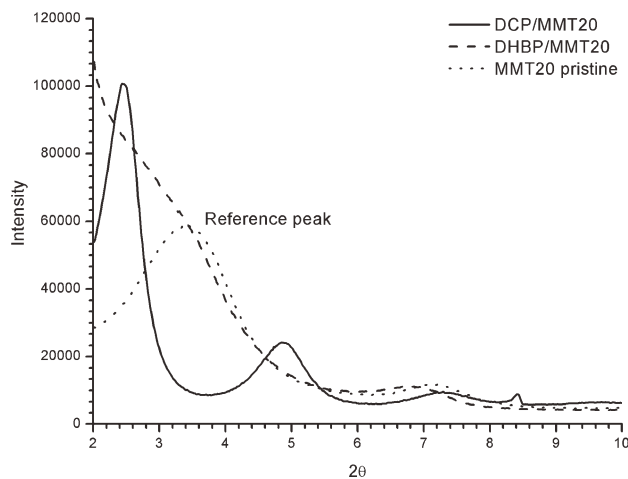
Parallel Plate Rheometry

Parallel plate rheometry was used to assess the reduction in molecular weight to study the effect of reaction time on the degradation of polypropylene. Viscosity at zero shear (η_0) was obtained in steady state by means of an ARES AGR2 rheometer. Test temperature was set at 180°C, shear rate varied from 0.01 to 1.00 s^{-1}. Data were collected at 10 s per point at 10 points per decade.

Scanning Electron Microscopy (SEM)

Strip specimens, cut from sheets pressed immediately after processing, were cryogenically fractured. The fractured surface was attacked with 7 wt %/v potassium permanganate solution in a 2 : 1 sulfuric and phosphoric acid (v/v) mixture for 1 h 20 min and subsequently washed with demineralized water. The degraded polypropylene samples were sputter coated with Au and analyzed

Figure 2. XRD of pure MMT and MMT recrystallized in the presence of peroxides DCP and DHBP.

by SEM. The PP degraded in the presence of MMT20 was analyzed in a Philips XL30 SEM_FEG equipment and the PP degraded in the presence of CaCO$_3$ was analyzed in a CS 3200LV Scanning Electron Microscope (Cambridge, UK).
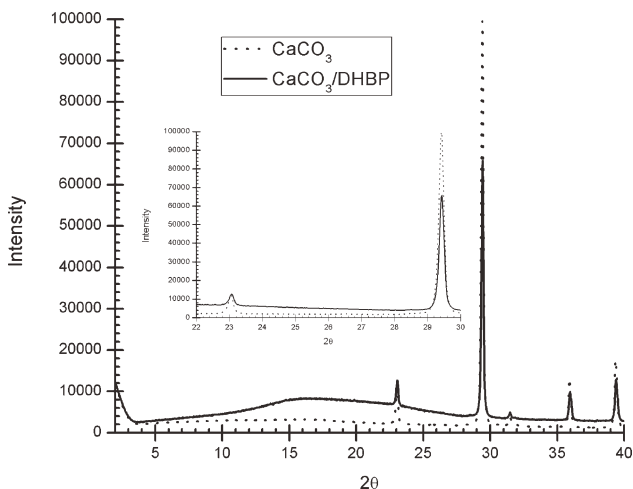
Transmission Electron Microscopy (TEM)

Ultra thin 45 nm specimens were cut using a REICHERT FCS cryomicrotome at −60°C on Cu grids. TEM analyses were carried out in a MET Phillips CM120 equipment at beam intensity of 20 kVA.

RESULTS AND DISCUSSION

Assessment of the Peroxide Incorporation in the Clays

Assessment of peroxide incorporation in the clays was done by means of X-ray diffraction (XRD). This technique allows verifying increase in crystalline plane spacing from the shifts in the 2θ values. Diffraction peak shift towards lower 2θ values indicate increase in crystalline plane spacing, suggesting incorporation of the peroxides into the clay structure.

Figure 1 contains diffractograms of nonrecrystallized MMT20 clay and a control sample that had been submitted to lamella

Figure 1. XRD of pure MMT20 and recrystallized in acetone.
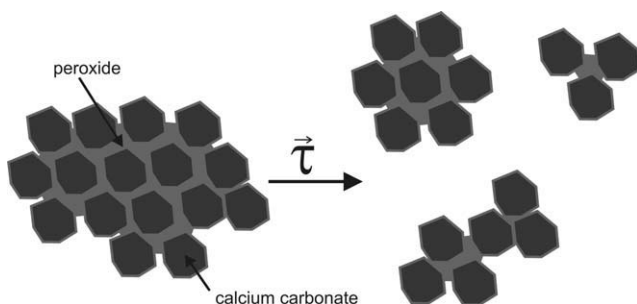
Figure 3. X-ray diffractograms of pure calcium carbonate and of DHBP in calcium carbonate.
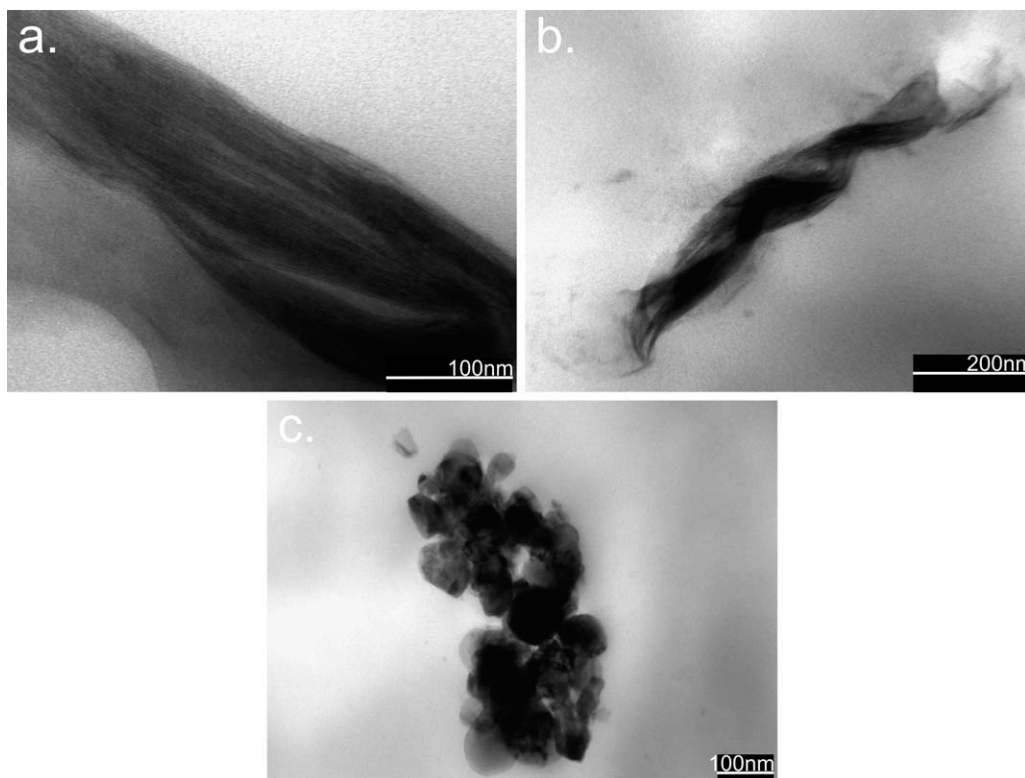
Figure 4. Transmission electronic microscopy of fillers into polypropylene: (a) lamellar structure (tactoids) of montmorillonite into nondegraded polypropylene; (b) detail of montmorillonite tactotoids into degraded polypropylene with DCP; (c) calcium carbonate particles into degraded polypropylene with DHBP.

spacing in acetone in the absence of peroxide. No alterations were observed in the diffraction peaks and it could be assumed that recrystallization of the clay in acetone does not cause modification in clay crystalline conformation. Therefore, any alteration in interlayer spacing may be related to the incorporation of peroxide molecules in this region.

Figure 2 presents the diffractograms of clays recrystallized in the presence of peroxides. XRD analysis of the clays recrystallized in the presence of peroxides shows that modification occurred in the interlayer spacing, likely due to the incorporation of the peroxides in the structures. For the DHBP/MMT20 system, the characteristic peak of MMT20 disappeared, indicating that the interlayer spacing may have been too large to be captured by

the equipment. For the DCP/MMT20 system the diffraction peaks were shifted to lower values, indicating intercalated peroxide structure.

On the basis of the XRD results we concluded that incorporation of DCP into the interlayer space of the clay occurred satisfactorily with the developed methodology. It was hence assumed that the mechanism proposed by Shi et al.[12,16] also holds for

Figure 5. Mechanism proposed to influence of shear stress in peroxide diffusion through calcium carbonate aggregates during processing.
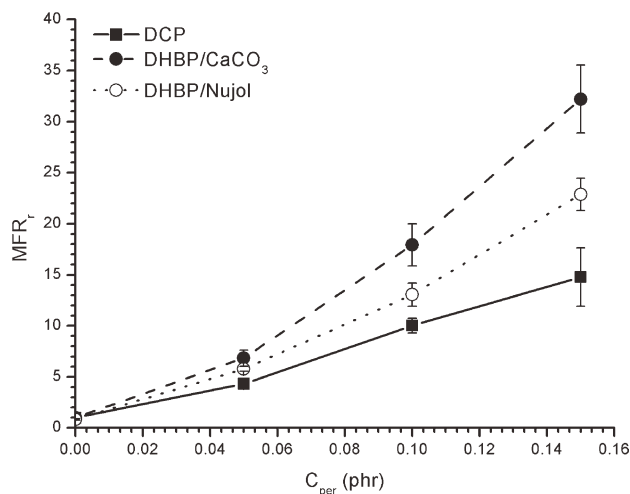
Figure 6. MFR_r of polypropylene as a function of mass of the peroxide added to the system.
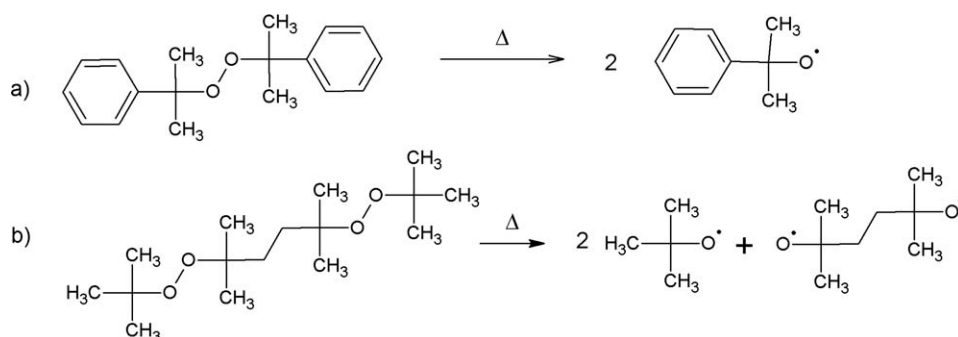
Figure 7. Thermal cleavage reactions of DCP (a) and DHBP (b).

this system, i.e., addition of peroxyl radicals in the medium likely occurs by diffusion.

According to Shi et al.,[12,16] when peroxides are inserted into the clay, radical addition in the medium is altered. Furthermore, Bettini and Agnelli[5,19] reported chemical modification levels similar to those obtained by former authors utilizing peroxides suspended in calcium carbonate. Therefore, it was decided to check whether calcium carbonate would act in a similar manner. The investigation was carried out by means of XRD, comparing pure calcium carbonate and a DHBP/CaCO$_3$ suspension. In the study only DHBP was used, because up to the present no company has been encountered in Brazil that commercializes DCP in calcium carbonate.

Unlike montmorillonite, calcium carbonate does not have a lamellar structure. Thus, peroxide will likely enter the interstitial spacings of the crystal, altering the lattice parameters. Analysis of CaCO$_3$ diffractograms, in the presence and absence of DHBP (Figure 3), reveals that no alteration took place in the lattice parameters. It can therefore be assumed that DHBP has been adsorbed on the calcium carbonate crystals which are prone to form clusters.

TEM images (Figure 4) reveal the difference between the calcium carbonate and montmorillonite particles. Figure 4(a) shows the lamellar structure of montmorillonite in polypropylene matrix and Figure 4(b) exhibits the montmorillonite clay in DCP degraded polypropylene; where it can be seen that even after processing there was no alteration in the clay dispersion. Clusters of calcium carbonate can be seen in Figure 4(c).

The diffusion process in montmorillonite clay occurs in the region between the silicate layers, whereas in calcium carbonate it likely occurs in the region between the cluster particles. As clusters of calcium carbonate may be broken by the action of shear forces applied during processing, its ability to gradually add peroxide to the polymer melt is reduced with respect to montmorillonite; addition of peroxide to the medium is strongly affected by the dispersion of carbonate, since the carbonate particles adsorb the peroxide. Figure 5 contains a simplified scheme of the diffusive mechanism caused by peroxide adsorption by the calcium carbonate particles. When cluster size is reduced, the amount of peroxide retained inside the particles decreases and addition of peroxide retained on the surface of the particles will depend on CaCO$_3$ distribution.

Polypropylene Degradation in the Presence of Peroxide with Different Dispersion Media

The reduction in polypropylene molecular weight was assessed by melt flow rate. The melt flow rate is an indirect measurement of viscosity and is inversely proportional to polymer molecular weight. It was however observed that both nujol and montmorillonite increase polypropylene MFR, likely due to lubrication of the chains by nujol oil and by MMT20 clay consisting of very fine particles with hydrocarbonate-like chains from the modifier. Therefore, two polypropylene standards were prepared: one containing equivalent concentrations of montmorillonite and the other containing nujol. Relative MFR (MFR$_r$) values were calculated by the following equation:

$$MFR_r = \frac{MFR_{sample}}{MFR_{standard}}$$

MFR$_r$ results are shown in Figure 6. DHBP is seen to present superior efficiency in reducing PP molecular weight in relation to DCP. This improved efficiency might be related to the improved dispersion of peroxide in the medium due to the chemical similarity between DHBP and PP. This improved dispersion might allow initiation of the chain scission reactions in other regions of the melt. Utilization of calcium carbonate as
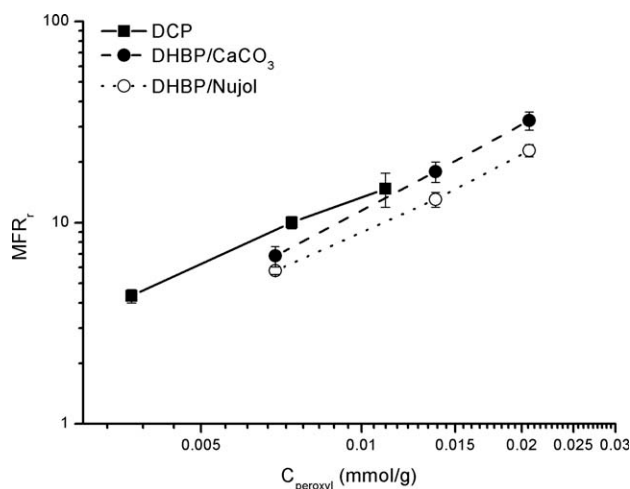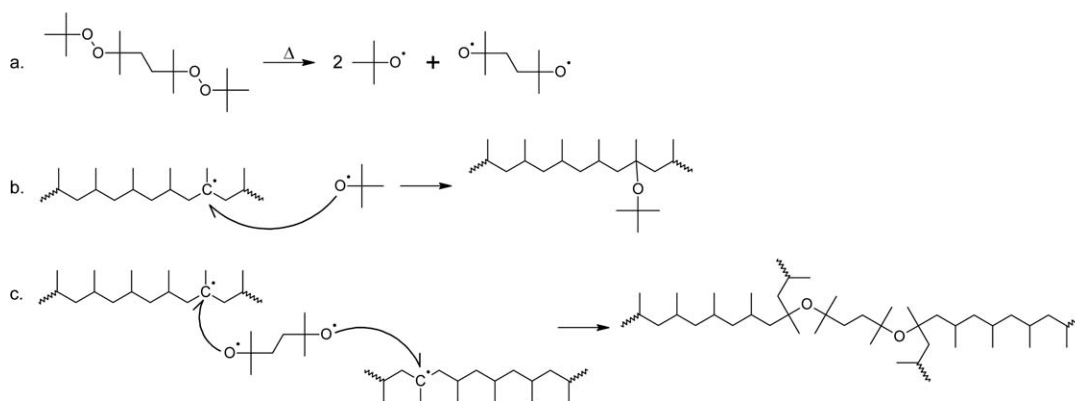

Figure 8. MFR$_r$ of polypropylene as a function of the concentration of peroxyl radicals added.

Figure 9. Termination mechanism by recombination of peroxyl radicals for DHBP, in the controlled degradation of polypropylene in the melt. (a) Thermal decomposition of DHBP. (b) Termination by recombination between polypropylene macroradical and monofunctional DHBP peroxyl radical (c) chain extension of polypropylene macroradicals induced by the reaction with bifunctional DHBP peroxyl radical.

dispersant for DHBP showed to increase its ability to reduce molecular weight, which might be related to the improved peroxide dispersion in the medium. In the case of solution, coalescence of the drops might occur. Furthermore, DHBP produces two times more radicals per mol than DCP as shown in Figure 7. Therefore, the higher efficiency of DHBP is likely related to both factors: dispersion and number of radicals.

When the number of added radicals per unit mass is considered, different results are obtained, as shown in Figure 8. DCP shows to be more effective in reducing molecular weight compared to DHBP.

The lower molar efficiency of DHBP in polypropylene controlled degradation might be related to the occurrence of parallel reactions involving recombination of radicals. Although DHBP may present improved dispersion in the melt it generates a bifunctional radical, which may act as chain extender and hence reduce the efficiency of the peroxide in reducing the molecular weight of polypropylene, as can be seen in Figure 9.

Kamath and Pallys[15] in an investigation regarding the efficiency of several peroxides on the grafting of maleic anhy-

dride onto polyolefins concluded that DHBP presents improved equilibrium between chain scission and modification extent in relation to DCP. Bettini and Agnelli,[5] who studied grafting of MA onto PP in the presence of DHBP/CaCO₃, observed that at long processing times MFR of the material slightly decreases, when the initial maleic anhydride concentration is low. They related this phenomenon to a possible recombination of the macroradicals remaining in the reaction medium. On the basis of these observations we speculate that the use of multifunctional radical releasing peroxides may, during processing, reduce the drop in molecular weight by means of chain extension reactions originated by radical recombination.

Utilization of montmorillonite clay (MMT20) as support for the peroxides has also been studied. According to Kamath and Pallys[15] the use of clays facilitates dispersion of the peroxides in the medium, increasing their efficiency. However, as can be seen in Figure 10, when clay was used as dispersant for DHBP a lower value of MFR_r was observed, indicating that reduction in molecular weight was less pronounced in relation to other systems.
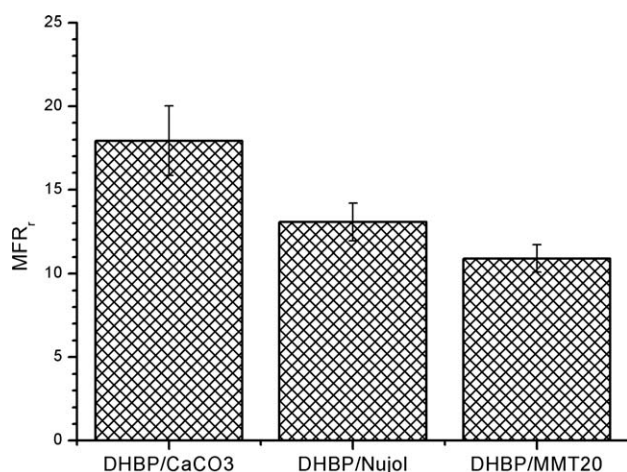
Figure 10. MFR_r of polypropylene processed with 0.10 phr of DHBP dispersed in different media.
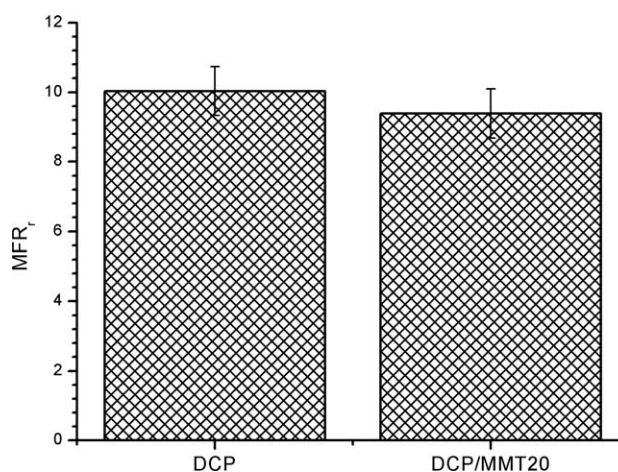
Figure 11. MFR_r of polypropylene processed with 0.10 phr of pure DCP dispersed in organically modified montmorillonite (MMT20).
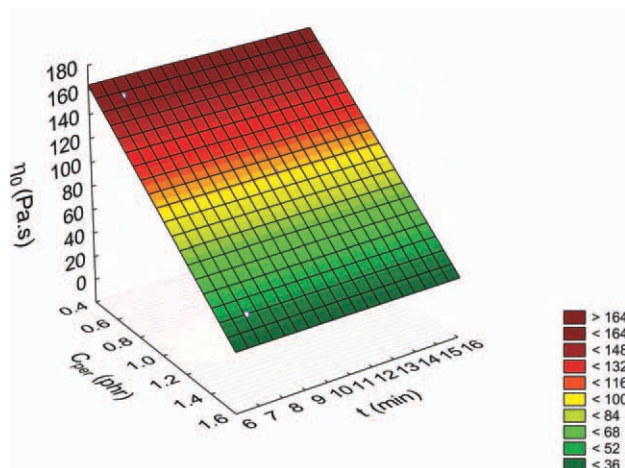
Figure 12. Response surface plot of the kinetic study on the degradation reaction of polypropylene processed with DCP incorporated into organically modified montmorillonite clay. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The same phenomenon has been observed in the controlled degradation systems using DCP, as shown in Figure 11. All averages were compared by means of the t test with a 95% confidence interval. Hence, utilization of montmorillonite as dispersant diminishes the ability to reduce molecular weight of both DHBP and DCP.

Because the half life of both peroxides is well below the processing time, it is assumed that even when addition of the peroxyl radicals occurs by diffusion, all peroxide has been decomposed and added to the medium prior to the end of the processing. The clay used contains a modifier which facilitates dispersion in the polymer matrix, guaranteeing improved dispersion of the peroxide contained in the clay. Hence, the drop in efficiency of the peroxides can be separated from diffusion effects of as well as from the effects of phase coalescence which impede degradation in the bulk of the melt. An explanation for the reduction in efficiency might be a possible reaction between the peroxyl radicals and the clay modifier. However, the quaternary ammonium salts used as clay modifier are electrophiles stable in acid medium even above 150°C and exhibit little tendency to react with nucleophiles, even strong ones.[20] Hence, a possible explanation for the reduction in efficiency of the peroxides in the presence of the clay is the significant increase in the recombination reactions of the radicals.
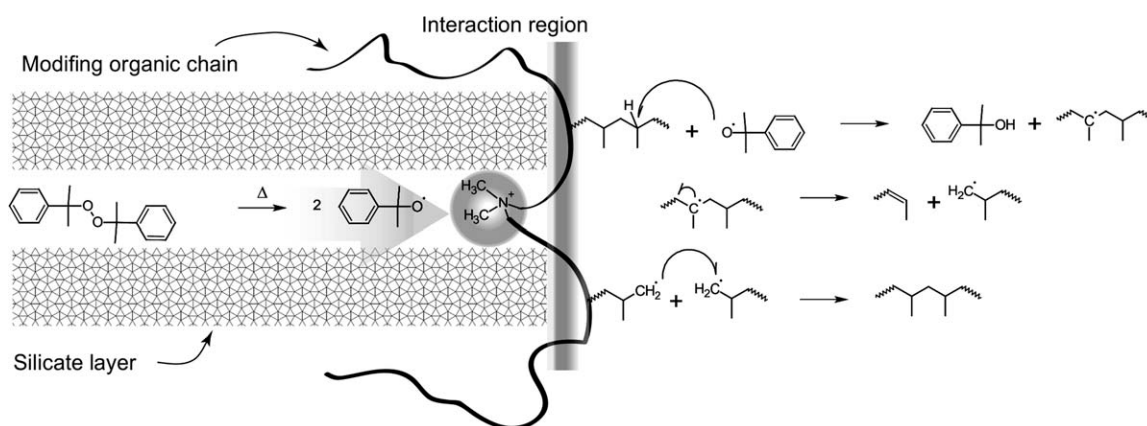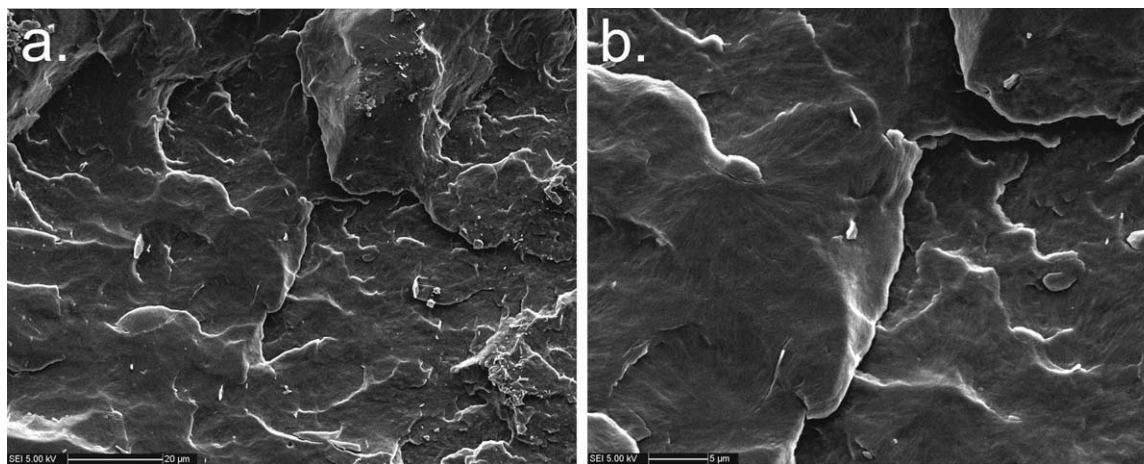

Figure 13. Catalytic mechanism proposed for the recombination reactions of the polypropylene macroradicals for the DCP/MMT20 system.
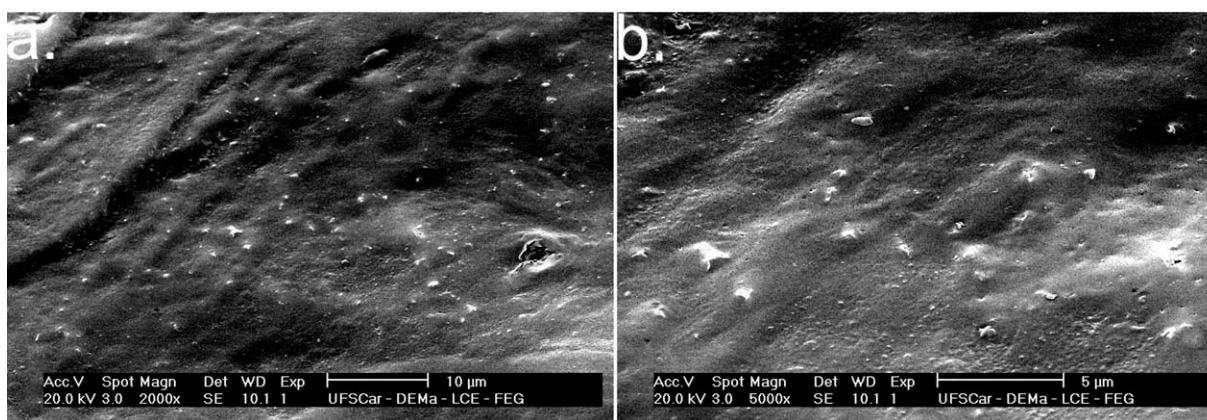
Figure 14. Scanning electronic microscopy images of controlled degraded polypropylene using 0.1 phr of DHBP into calcium carbonate.

Figure 15. Scanning electronic microscopy images of controlled degraded polypropylene using 1.0 phr of DCP into montmorillonite.

Assessment of Reaction Time and Peroxide Concentration in the Controlled Degradation of Polypropylene

Analysis of the effect of time on the controlled degradation of polypropylene, in the presence of DCP inserted into organically modified montmorillonite (DCP/MMT20), shows that for this system the effect of time on the viscosity (η_0) of the degraded polymer is not significant. This investigation was carried out using a 2^2 experimental design with center point. The response surface plot is shown in Figure 12. A linear dependency of viscosity on amount added peroxide and no dependency on time are seen. The decrease in viscosity with the increase in peroxide amount might be related to the increase in the primary peroxyl radicals formed. When the amount of peroxyl radicals increases, more hydrogens are abstracted from the polypropylene backbone, increasing chain scission and hence lowering melt viscosity.

The nondependency on time is an indication that chain scission rate and radical recombination rate are the same and therefore viscosity remains constant over time and, consequently, likely molecular weight as well.

It is likely that both chain scission and chain extension reactions occur at the surface of the clay where the organic chains of the clay modifier are present. Because of the probable diffusion of the peroxyl radicals from the interior of the clay to its surface, the outer region of the clay likely presents a large amount of peroxyl radicals that may react with polypropylene, generating the macroradicals, which on stabilizing by disproportionation promotes chain scission. Because the clay surface is rich in macroradicals the probability of recombination increases. Thus, utilization of montmorillonite clay organically modified with quaternary ammonium salt may catalyze radical recombination reactions and the chain extension rate rapidly equals the chain scission rate. The proposed mechanism is depicted in Figure 13.

Analysis of the Distribution of Clay or Calcium Carbonate in Degraded Polypropylene

Particle size distribution of calcium carbonate and montmorillonite clay was examined with the aid of SEM. Figure 14 shows SEM images of degraded samples using peroxide in calcium car-

bonate. Several bright spots can be seen distributed throughout the matrix, which are related to the calcium carbonate clusters. Image analysis confirms statements by Kamath and Paladins[15] that the use of carbonates may assist in dispersing the peroxide throughout the matrix.

Figure 15 displays the distribution of montmorillonite clay in the matrix. The irregular fractured surface is indicative of proper distribution of the clay. According to Lee et al.[21] and Gupta et al.[22] fractures occur near the clay tactoids. Analysis of Figure 15(a) reveals that the spherulites, as well as the fractures, develop around the tactoids. The presence of these tactoids was expected, since montmorillonite has no affinity with the matrix and thus does not disperse in the matrix, as shown by TEM micrographs in Figure 4.

CONCLUSIONS

When selecting peroxides to chemically modify polymers one should take into account not only the ease in handling, but also the secondary reactions that may affect the end properties of the material. The use of peroxides that release multifunctional radicals may reduce the effect of chain degradation, due to their chain extension reactions. Utilization of organically modified montmorillonite clay nanoparticles, as dispersion agents for the peroxide, may also reduce chain scission effects due to favorable positioning of the generated macroradicals. The assumption that the organically modified montmorillonite clay catalyzes radical recombination reactions is supported by the fact that the viscosity at zero shear, which is an indirect measurement of molecular weight, does not vary with processing time.

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