Montmorillonite as support for peroxide in the melt grafting of maleic anhydride onto polypropylene

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ABSTRACT: Grafting of maleic anhydride onto polypropylene was performed in a Haake torque rheometer, in the presence of organically modified montmorillonite, MMT (used as support for the peroxide), according to a 2^3 factorial design, where the maleic anhydride concentration (C_{MA}), peroxide concentration (C_{per}) and reaction time (t_r) were varied. For comparison, the reaction in the absence of MMT was also conducted. Polypropylene degradation was assessed by parallel plate rheometry and size exclusion chromatography (SEC) and percentage of reacted maleic anhydride (%MA_g) was obtained by titration and FTIR spectroscopy. The results showed differences in both systems, conventional and in the presence of MMT. The structure of polypropylene grafted with maleic anhydride, PP-g-MA, indicates longer branches are formed in the presence of MMT compared to in its absence, demonstrated by FTIR analysis. As in conventional reaction systems, an increase in C_{per} caused an increase in %MA_g and a reduction in molar mass. The variable C_{MA} showed to be not significant in the grafting reaction in the presence of MMT, even at high DCP levels, at a 5% significance level. On the other hand, increase in C_{MA} resulted in significant increase in viscosity. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 44134.

INTRODUCTION

Incorporating graft copolymers as compatibilizers in incompatible systems has been a widely used strategy in recent decades.[1–7] Methods used for obtaining these compatibilizers include chemical modification of nonpolar polymers with vinyl monomers by reactive processing, such as the grafting of maleic anhydride (MA) onto polypropylene (PP).[8–12]

Polypropylene grafted with maleic anhydride (PP-g-MA) is one of the most widely used compatibilizers in PP composites and blends containing polar fillers or polymers. Produced mainly by reactive extrusion, PP-g-MA has low molar mass because of the use of organic peroxides as reaction initiators, as well as to thermo-mechanical degradation during the extrusion process.

The reaction mechanism of MA onto PP is not completely understood yet and still controversial, especially regarding the sites of MA grafting, number of MA units in the graft, as well as the formation of MA oligomers and/or homopolymers.[13,14] Some authors suggest MA reacts with the tertiary radicals from PP, which are generated via H abstraction by primary (RO•) radicals,[8] whereas others assume MA reacts at the chain ends after PP β scission.[15,16] Both assumptions are expected to occur

concurrently.[9,13,17,18] Russell[19] states that the parallel and concurrent homopolymerization reaction of MA, during reactive processing of MA onto PP, will not occur at temperatures above the ceiling temperature. De Roover et al.,[20] however, observed, by means of size exclusion chromatography, formation of MA oligomers during MA functionalization of PP.

Despite the aforementioned controversies, the consensus remains that during reactive processing of MA onto PP, PP undergoes severe degradation, especially when high grafting levels are required, because in order to achieve high grafting levels (close to or exceeding 1 wt %) higher peroxide concentrations must be used. Increasing peroxide concentrations increases the amount of tertiary radicals in PP, which in the absence of MA leads to chain scission.

These graft copolymers are used as compatibilizers, and their low molar mass may impair blend or composite properties, especially when the compatibilizer is added to the blends or (nano)composites at high concentrations, despite the increased phase dispersion provided by the compatibilizer.

To reduce PP chain scission during modification in the melt, some alternative reaction modification systems have been

proposed. These include the use of a co-monomer, such as styrene, capable of forming an alternating copolymer with MA and hence increasing the amount of MA grafted onto PP.[21,22] Another alternative is the use of nanoparticles containing peroxide to control its release, thus minimizing chain scission reactions caused by increased local concentration of MA on the surface of these particles.[23,24] According to Shi et al.[24] the nanoparticle system, termed nanoreactors by the authors, yields higher level of grafting and less reduction in molar mass compared to the conventional systems.

Muñoz e Bettini[25] investigated the controlled degradation of PP by reactive processing, in presence and absence of nanoparticles, and the results show that utilization of organically modified montmorillonite clay (MMT) nanoparticles, as dispersion agents for the peroxide, may reduce chain scission effects because of favorable positioning of the generated macroradicals.

In the present investigation, peroxide was incorporated either directly into the molten PP or firstly into montmorillonite, organically modified with quaternary ammonium salt, and then into the molten PP. The differences between the systems and their viability to increase selectivity of the grafting reactions with respect to chain scission reactions was assessed. A 2^3 factorial design with central points was used for the system in which the peroxide was dispersed in montmorillonite, and the factors assessed were peroxide concentration, MA concentration and reaction time.

The materials were characterized as to the total number of inserted acid groups, differentiation between long and short grafts and chain scission. The following techniques have been used: titration, infrared spectroscopy, parallel plate rheology and high temperature size exclusion chromatography (HT-SEC). The results were validated by response surface models using analysis of variance (ANOVA) with 5% significance level.

EXPERIMENTAL

Materials
The following materials have been used. PP homopolymer (MFR = 2.6 g/10 min), HP502H, donated by Braskem (Mauá, Brazil). Dicumyl peroxide (DCP) with trade name Luperox DC/SC was used as initiator, donated by Arkema (Rio Claro, Brazil). Cloisite 20A, an organically modified montmorillonite with quaternary ammonium salt (MMT), was purchased from Southern Clay Products (Gonzales, USA) and used as support for the peroxide. MA from Fluka (Sigma-Aldrich group) with purity higher than 99% was used as monomer modifier. To construct the calibration curve dodecen-1-succinic anhydride with 95% purity (Sigma-Aldrich) was used as received. Xylene and acetone were also used as received.

Methods
Peroxide Incorporation into Montmorillonite (Montmorillonite Nanoreactors).
For the preparation of montmorillonite nanoreactors 4 g montmorillonite were added to 100 mL acetone and the system was kept in a closed ultrasound equipment for 1 h, to prevent 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
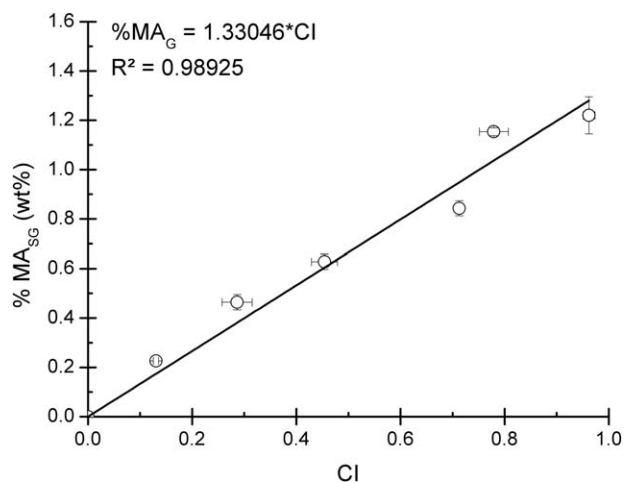

Figure 1. Calibration curve for short grafts (%MA$_{SG}$). Standard used: dodecenyl succinic anhydride.

stored in Teflon containers, dried in vacuum oven at 40 °C and subsequently conditioned in a desiccator.

X-ray Diffraction. X-ray diffraction analysis (XRD) was performed in a Philips X'Pert diffractometer (Almelo, The Netherlands) with a Cu Kα radiation source ($\lambda = 0.154$ nm) operated at 40 kV and 40 mA with a step size of 0.02° and count time 80s/°.

Reactive Processing. The grafting reactions of MA onto PP by reactive processing were conducted in a Haake torque rheometer with a Rheomix 600 mixing chamber and roller-blade rotors (Karlsruhe, Germany). The experimental design used was a two-level factorial design for three factors (2^3) with center points. The investigated variables (factors) and their levels were: peroxide concentration (C_{per}), 0.5 and 1.5 phr; MA concentration (C_{MA}), 2 and 5 phr and reaction time (t_R): 7 and 15 min. Table I shows the variations in factors in the experimental design. The tests were conducted at 180 °C and rotor speed of 50 rpm under an atmosphere of nitrogen. In all formulations shown the peroxide was incorporated into the montmorillonite at a 1:1 ratio (montmorillonite:peroxide). The same variables and levels have been investigated in a previous study, however in the absence of MA.[25]

To remove unreacted MA, the samples obtained during reactive processing were purified by liquid phase extraction. Samples containing 8 g of material were solubilized in 1 L xylene under reflux for 1 h at 120 °C, approximately. The material was cooled to approximately 80 °C and 1 L pure acetone was added. The addition of acetone leads to precipitation of PP and PP-g-MA and maintains MA and the possibly formed MA oligomers in solution. The precipitated material was filtered under vacuum and washed with small portions of acetone to remove the MA not grafted onto PP. Subsequently, the material was dried in a vacuum oven at temperature of 75 °C for 24 hours for removal of retained solvent.

Assessment of Grafting Level. *Titration of succinic groups.* Samples of approximately 0.5 g purified PP-g-MA were solubilized in 150 mL xylene for 1 h under reflux. After
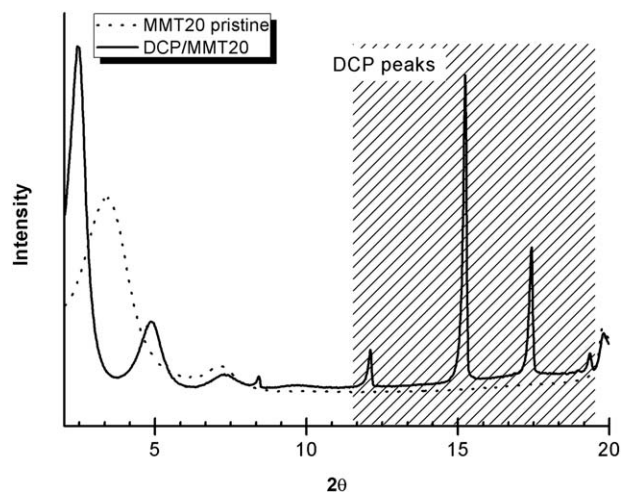
Figure 2. XRD spectrum of organically modified montmorillonite, Cloisite 20A, neat (dotted line), and after recrystallization in the presence of dicumyl peroxide, DCP (solid line).

Table I. Experimental Design

Run	C_{MA} (phr)	C_{per} (phr)	t_r (min)
1	2.0	0.5	7
2	5.0	0.5	7
3	2.0	1.5	7
4	5.0	1.5	7
5	2.0	0.5	15
6	5.0	0.5	15
7	2.0	1.5	15
8	5.0	1.5	15
9	3.5	1.0	11
10	3.5	1.0	11
11	3.5	1.0	11

refluxing, the samples were cooled to 80 °C and then titrated with 0.05M KOH solution in ethanol, using phenolphthalein as an indicator. An excess of approximately 0.2 mL KOH was used and a back titration was performed with 0.05M HCl in isopropanol. The final percentage of chemical modification was calculated by the following equation:

$$\%MA_R = \frac{0.2450(V_{KOH}C_{KOH} - V_{HCl}C_{HCl})}{m_{sample}} \quad (1)$$

The final acidity value refers to the total amount of reacted MA by weight.

FTIR spectroscopy. Hot-pressed PP-g-MA films, with thickness between 50 and 100 μm, were dried in a vacuum oven for 24 h at 130 °C to convert acid groups into their anhydrides. The dried films were then analyzed in a Nicolet 6700 FTIR spectrometer (Madison, USA), using 128 scans and resolution of 2 cm^{-1}.

The carbonyl index was calculated as the ratio of the absorbances in the regions indicated as follows:

$$CI = \frac{A_{1792}}{A_{1168}}$$

where A_{1792} is the absorbance at 1792 cm^{-1}, characteristic of cyclic anhydrides with five-membered rings, associated with grafted succinic anhydride; and A_{1168} is the absorbance at 1168 cm^{-1}, characteristic of CH$_3$ groups, proportional to the amount of PP.

Quantification of succinic groups by this technique is associated with short grafts. From the CI values the percentage of short grafts, %MA$_{SG}$, can be assessed using the calibration curve shown in Figure 1. The calibration curve was obtained from blends prepared in the torque rheometer, with known amounts of PP and dodecenyl succinic anhydride.

The difference between %MA$_R$ and %MA$_{SG}$ was denominated %MA$_{LG}$, percentage of long grafts:

$$\%MA_{LG} = \%MA_R - \%MA_{SG}$$

where %MA$_R$ refers to the total amount of reacted MA, determined by titration of the acid groups.

Assessment of Degradation Level. *Parallel plate rheometry.* Parallel plate rheometry was used to assess the reduction in molar mass in order to study the effect of investigated variables on the degradation of PP. Viscosity at zero shear (η_0) was obtained in steady state by means of an AGR2 rheometer (New Castle, USA). 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.

High temperature size exclusion chromatography (HT-SEC). SEC analyses were performed in a GPCV 2000 Waters liquid chromatograph (MA, USA), equipped with a set of four

Table II. Multiple Linear Regression Coefficients for the Different Response Surfaces Obtained by ANOVA

Response	R^2	Linear parameters				Quadratic parameters	
		a_0	a_1	a_2	a_3	a_4	a_5
%MA$_R$	0.9074	0.2230	0.00466	—	0.56742	—	−0.02902
%MA$_{SG}$	0.9440	0.09986	−0.00096	0.17207	−0.00548	—	−0.00922
%MA$_{LG}$	0.8608	0.14065	0.39535	—	—	—	−0.0198
η_0	0.8432	−1941.60	180.53	467.43	—	—	—

The representative equation of the surfaces is shown at the end of the table.
$Resp = a_0 + a_1 t_R + a_2 C_{MA} + a_3 C_{DCP} + a_4 t_R C_{MA} + a_5 t_R C_{DCP}$

Waters HT columns as well as Viscotek refraction index (RI) and viscometer (VD) detectors.

For calibration monodisperse polystyrene standards were used with molar mass between 500 and 7,000,000 Daltons. Samples obtained during the reactive processing were dissolved in tri-chlorobenzene (TCB) at a temperature of 140 °C and injected into the chromatograph at a flow of 1 mL/min of the main and auxiliary pumps.

RESULTS AND DISCUSSION

### Recrystallization of Montmorillonite Clay

MMT was recrystallized in the presence of DCP and subsequently subjected to XRD to assess peroxide inclusion in MMT lamellae. When peroxide is intercalated into MMT lamellae the diffraction angle referent to the basal spacing decreases.[23–25] Figure 2 shows the X-ray diffraction spectrum for organically modified MMT, Cloisite 20A, as received and after recrystallization in the presence of DCP. It is observed that when peroxide is introduced into MMT, the diffraction peak shifts to lower 2θ values, which indicates increase in basal spacing of MMT, after recrystallization in the presence of DCP, suggesting that at least in part, peroxide intercalated the MMT silicate lamellae. Hence, the methodology used for inserting peroxide into the clay has shown to be adequate. In addition the XRD spectrum of the recrystallized sample (Figure 2) exhibits peaks related to the crystalline structure of DCP (shaded area in the figure), indicating that some of the peroxide recrystallized on the clay surface, as observed in previous work[25]

Analysis of Variables C_{MA}, C_{per}, and t_R on the Chemical Modification of PP

The recrystallized clay was used for the reactive processing of PP with MA. The ratio of peroxide and the clay was kept constant in all formulations at 1:1 weight ratio. The modification process of PP with MA in the presence of montmorillonite (MMT) was assessed by a 2^3 experimental design with center point, according to Table I. The experimental design was subjected to analysis of variance (ANOVA) with a 5% significance level and four response variables were analyzed: zero shear viscosity; percentage of reacted MA (%MA$_R$), obtained by titration; percentage of short grafts (%MA$_{SG}$), measured by FTIR analysis and calibration curve; and percentage of long grafts (%MA$_{LG}$), measured as the difference between %MA$_R$ and %MA$_{SG}$. The regression coefficients obtained from ANOVA, for all variables, are shown in Table II.

Figure 3 shows the response surface for the weight percentage of reacted MA on PP (%MA$_R$) as a function of the variables MA concentration (C_{MA}), DCP concentration (C_{per}) and reaction time (t_R). Figure 3(a) shows that the increase in peroxide concentration leads to higher %MA$_R$. This increase can be explained by the increased amount of alkoxyl radicals added to the medium, i.e., the higher the amount of radical added to the system, the greater the number of formed PP macroradicals, which increases the probability of reaction between PP and MA. However, it should be mentioned that, not only the grafting reaction will be more likely to happen, but also other unwanted radical initiated side reactions, such as chain scissions.
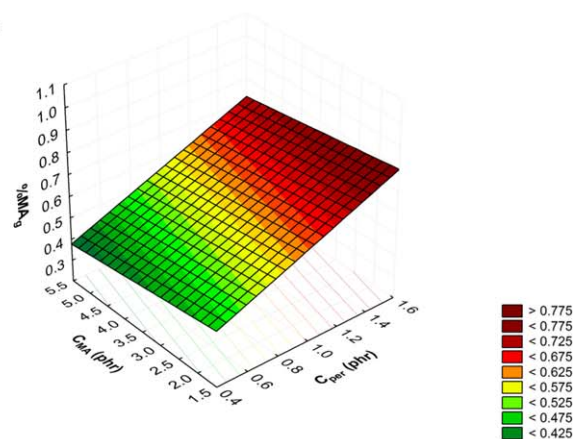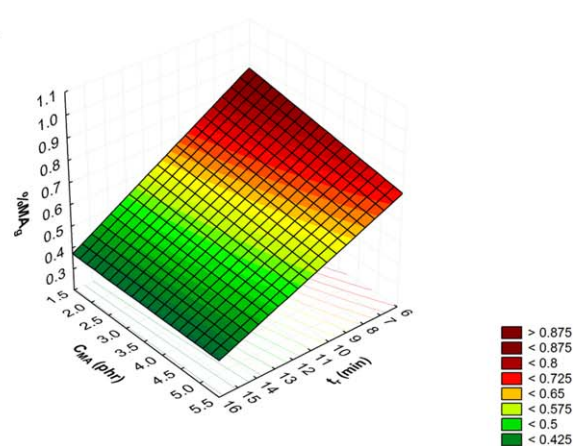
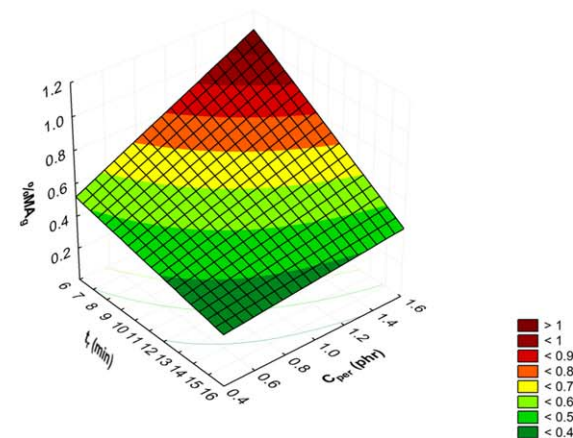**Figure 3.** Response surfaces of %MA$_R$ as a function of the investigated variables: maleic anhydride concentration (C_{MA}), peroxide concentration (C_{DCP}), and reaction time (t_R). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The variable C_{MA} showed to be not significant in the system, even at high DCP levels, at a 5% significance level. Despite the fact that the increase in C_{MA} did not result in increase in %MA$_R$ investigating this variable allowed detection of a significant difference between the present system and the conventional reaction system conducted in the absence of MMT. In the conventional system, without MMT, a MA phase of about 4 phr is formed,
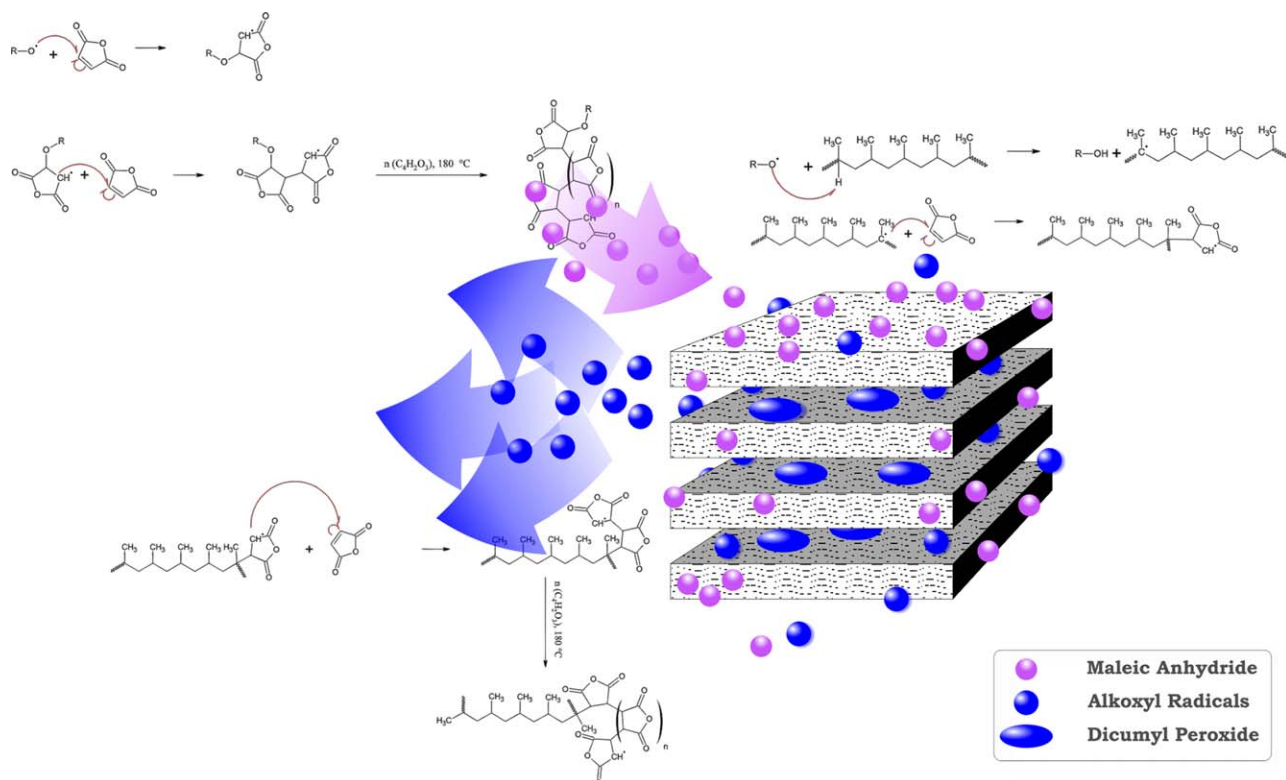
Figure 4. Scheme of grafting of onto polypropylene in presence of montmorillonite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

which reduces the contact area between the reactants, leading to reductions in %MA_R.[9,11] In the present study no change has been observed in %MA_R with increasing C_{MA}, probably because of side reactions, which consume radical initiators, such as the homopolymerization of MA. Because of the adsorption of MA on the surface of MMT, which is rich in alkoxyl radicals during processing, the probability that MA homopolymerizes increases. Figure 4 presents a proposed reaction scheme. From a thermodynamic point of view, this reaction is possible. According to thermodynamic data obtained by Kellou,[26] who investigated the free radical polymerization of MA in solution, it is estimated that only 0.15 mol/L of MA will not react at 180 °C. The hypothesis that MA homopolymerizes has been refuted in recent decades based on its ceiling temperature (T_c).[19] Therefore, the significance of ceiling temperature should be fully understood for precise assessment of its effect on the undesirable parallel reaction of MA homopolymerization.

According to Odian,[27] for most chain-reaction polymerizations there is a temperature at which this reaction is reversible. An increase in temperature initially causes increase in polymerization rate up to a certain temperature at which the depolymerization rate becomes significant. This depolymerization rate keeps increasing with temperature up to the ceiling temperature, T_c, at which the polymerization and depolymerization rates become equal, i.e., the gross polymer production rate becomes zero. This is, thus, an equilibrium condition, and hence T_c may vary, depending on the monomer concentration in the system. Hence, higher temperatures in the system require higher

monomer concentrations for the polymer production to take place, before equilibrium is established. There is a temperature above which no polymer will be formed, even when pure monomer is present. Furthermore, T_c is a parameter that allows us to estimate the amount of residual monomer in the homopolymerization process. Evidence of MA oligomer formation and subsequent reaction on the PP chain will be discussed in FTIR analysis.

Figure 3(b,c) show that the %MA_R decreases as reaction time increases and that the higher the peroxide concentration, the greater this reduction, showing the statistical interaction between the variables (at low peroxide concentrations, the effect "time" is small). Another possible way to assess this interaction is to accompany the increase in %MA_R at extreme times (shortest and longest times). At longer times, the effect of peroxide concentration on %MA_R is less, since the peroxide adsorbed on the clay has likely completely reacted, and only radicals from the confined peroxide (absorbed into MMT) remain, which diffuse slowly into the molten polymer mass, maintaining always low local concentration. As %MA_R is higher at shorter times, regardless of C_{per}, there are indications that the insertion reactions of succinic groups on PP are reversed, brought about by peroxide confined in MMT.

Zero shear viscosity measurements were performed to monitor the level of polymer chain degradation during reactive processing (Figure 5). Analysis of this figure shows that C_{per} does not affect the variation in viscosity, at 5% significance level.
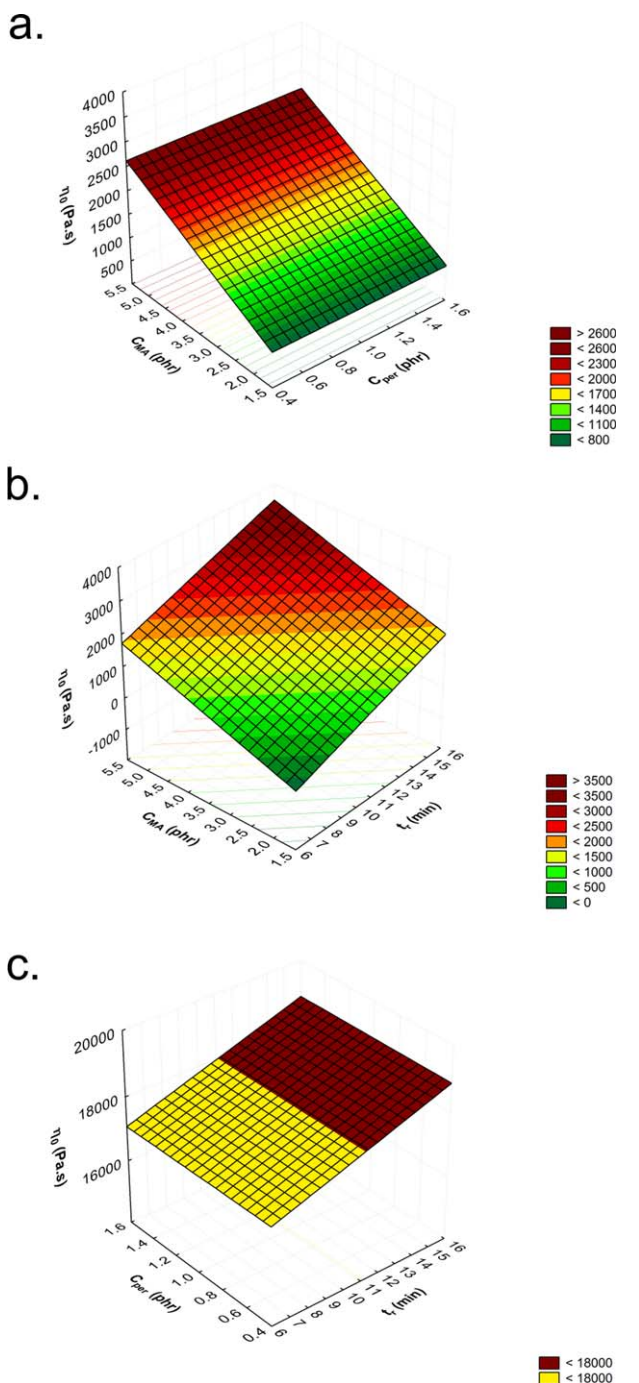
Figure 5. Response surfaces obtained by ANOVA for zero shear viscosity (η_0) as a function of the different variables: (a) C_{MA} and C_{DCP}; (b) C_{MA} and t_r; (c) t_r and C_{DCP} [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

However, molar mass assessment by SEC (Table III) shows that C_{per} affects final molar mass of the product, and the higher the level of peroxide used, the greater the reduction in molar mass. As statistical analysis is based on the variation in response, it is likely that the variation in viscosity for a given C_{per} is lower than the variation considered statistically significant. The decrease in η_0 occurs because of the fact that the higher amount of initiator increases the probability of chain scission reactions.

On the other hand, increase in C_{MA} results in significant increase in viscosity. As C_{MA} increases, the probability that radical attacks to the structure occur increases. Termination of the succinic radicals likely occurs by chain transfer, through abstraction of the tertiary hydrogens of PP, or by recombination of its macroradicals.

Since the reaction surface is populated by different types of radicals, including PP macroradicals, recombination reactions of the several radicals will be favored. When macroradicals recombine with each other, chain growth and apparent reduction in chain scission will be observed. In addition, high MA concentrations and possible formation of poly(maleic anhydride) contribute to reduction in chain scission because of the probable recombination reactions between PP macroradicals and poly(maleic anhydride), or their oligomers, which also consume part of peroxide during formation.

Secondary reactions start gaining significance during reaction time. The current system contained partially confined peroxide in MMT,[28] and release of this peroxide occurs by diffusion[23–25] However, diffusive mechanisms tend to be slow, and there may still be some residual peroxide left, even after 7 min of reaction. Confinement of the peroxide inside MMT increases its half-life, as it favors recombination of the formed peroxyl radicals, since the diffusion process is slower than the peroxide decomposition process. Previous studies have shown that inclusion of peroxide in MMT clay slows radical reactions as a whole, and complete containment of peroxide may lead to problems in further processing when it is released.[28]

This portion of contained peroxide affects the final product obtained, because the reactive clay surface is likely populated by products from reactions, occurring in less than 7 min, with the peroxide adsorbed on the clay. Thus, when confined peroxide is released in the form of alkoxyl radicals, it tends to react with the products adhered onto the MMT surface. As a result, there is a reduction in %MA$_R$ and an increase in molar mass with increasing t_R, as shown in Figure 5.

The molar mass distribution curves, presented at Figure 6, show that molar mass distribution becomes narrower after reactive processing. This narrowing, which is also observed in the polydispersity data presented in Table III, indicates that chain scission and possibly the grafting reactions occur at the chains with higher molar mass. Analysis of the data with respect to the influence of reaction time, showed that when processing time was increased from 7 to 15 min for a sample processed with 0.5 phr DCP and 2.00 phr MA, Mn, and Mw increased in approximately 9.6% and 13%, respectively. This phenomenon thus suggests that there is a tendency of the chains to recombine, leading to the formation of chains of larger size than those found at lower processing times. Along with the increase in chain size a decrease in %MA$_g$ was observed, which, again, suggests a mechanism of succinic group removal.

The structural changes of the molecules were analyzed by FTIR. FTIR analysis allows us not only to identify modification in polymer functional groups, but also their quantification, with suitable calibration. Since the titration method is not able to quantify possible reactions between succinic groups and MMT

Table III. SEC data of grafted samples. Maleic anhydride concentration of 2.00 phr. In the first column, notation x/y refers to x phr DCP and reaction time of y min

Sample (C_{per}/t_r)	η_0 (Pa.s)	M_n (g/mol)	M_w (g/mol)	M_w/M_n (−)	%MA$_{SG}$ (wt %)	%MA$_{LG}$ (wt %)
0.5/07	680	66266	163351	2.5	0.1390	0.3074
0.5/15	1587	72656	184577	2.5	0.1095	0.3098
1.5/07	263	51246	121569	2.4	0.2408	0.5823
1.5/15	1244	57702	179433	3.1	0.2227	0.5484
Control	19047	70938	293362	4.1	–	–

organic modifier, all FTIR spectra were analyzed for bands related to amide groups. No band was found in the amide group characteristic regions, and amidification reaction was discarded.

To understand the reactions, Figure 7 shows FTIR spectra of grafted samples in the absence and presence of MMT. As can be seen, the presence of MMT changes the absorption spectrum of the carbonyls attached to PP. It should be mentioned that since the grafted samples were purified by solubilization in xylene and precipitation in acetone, the carbonyls from the spectrum refer to the MA reacted onto PP, i.e., succinic anhydride, and not the unreacted MA. As can be seen, absorption of the carbonyl in the spectrum without MMT appears at 1792 cm^{-1} whereas in the presence of MMT, this peak is shifted to 1775 cm^{-1}. Both samples present absorption in the same region, but the intensities change for PP-g-MA, when MMT is present or absent in the reaction system, indicating a change in the structure of the products.

In fact, there was a significant increase in band intensity at 1775 cm^{-1}, when the reactions were conducted in the presence of MMT. This band is close to 1772 cm^{-1}, which was associated with poly(maleic anhydride). Assuming total acidity of the system, quantified as %MA$_R$ (by titration), is caused by the contributions of the grafts with peaks at 1792 and 1775 cm^{-1} (by FTIR and dodecenylsuccinic anhydride calibration curve, Figure 1), the acidity related to the band at 1775 cm^{-1} can be obtained by the difference between %MA$_R$ and %MA$_{SG}$, relative to the absorption at 1792 cm^{-1}. The materials analyzed had been previously purified and the analyses showed to be repeatable, so
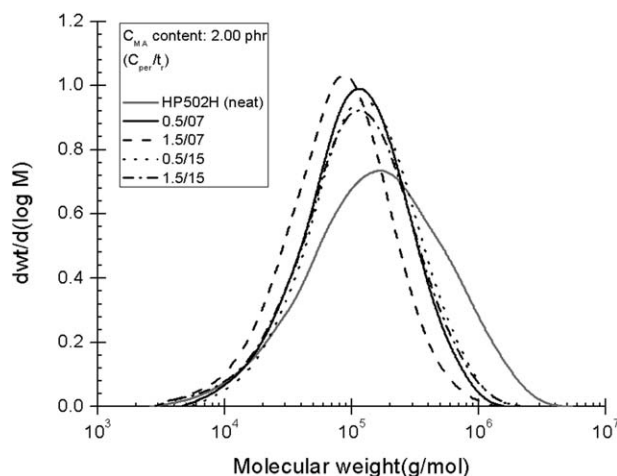
the peak at 1775 cm^{-1} may be associated with vibration of succinic groups that were long enough for their vibrational mode practically not to be affected by the presence of the PP chains.

Thus the absorption at 1792 cm^{-1} will be associated with short branches (% MA$_{SG}$) and the absorption at 1775 cm^{-1} will be associated with longer branches (% MA$_{LG}$), likely related to grafted oligomers.

The %MA$_{SG}$ values were estimated using the calibration curve shown in Figure 1. This calibration curve was obtained by physical mixture of PP and dodecenyl succinic anhydride and therefore contains only one bonded anhydride unit.

From the results of absorbance ratio between 1792 and 1168 cm^{-1} of the grafted samples obtained by reactive processing, CI was calculated, which was associated with a known amount of succinic groups to %MA$_{SG}$, as shown by the calibration curve (Figure 1). The %MA$_{LG}$ was calculated as the difference between %MA$_R$ (obtained by titration) and %MA$_{SG}$. Analysis of the regression coefficients of Table II and %MA of long and short branches, presented in Table IV, shows that the increase in C_{MA} reduces the percentage of short branch grafted MA (% MA$_{SG}$) characterized in the 1792 cm^{-1} region of the FTIR spectrum. In systems without MMT, the reduction in % MA$_{SG}$ with increasing C_{MA} has been related to the formation of a MA phase, which reduces the contact area between the

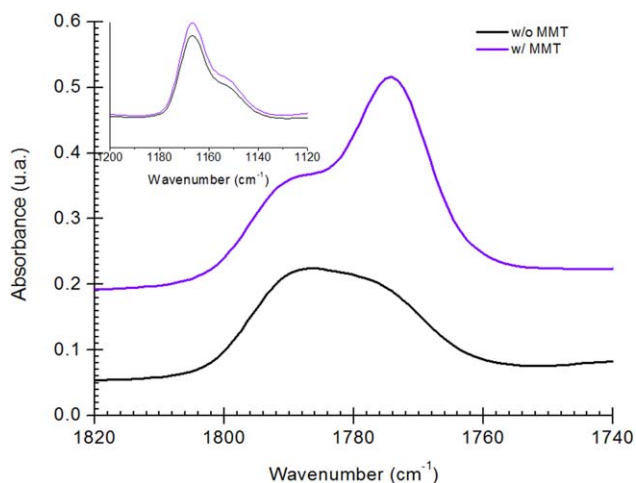**Figure 6.** Molar mass distribution curves of the grafted samples.

Figure 7. FTIR spectra for samples grafted in the presence of MMT and sample without MMT (reference). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. Measurements of Chemical Modification, Fraction of Long Grafts and Zero Shear Rate Viscosity for the Samples of the Experimental Design

Run	Replica	%MA$_R$	%MA$_{SG}$	%MA$_{LG}$	x_{LG}	η_0 (Pa.s)
1	a	0.4111	0.1358	0.2754	0.670	680
	b	0.4784	0.1420	0.3365	0.703	
	c	0.4494	0.1392	0.3102	0.690	
2	a	0.4067	0.1078	0.2989	0.735	1736
	b	0.4695	0.1193	0.3502	0.746	
	c	0.3818	0.1015	0.2803	0.734	
3	a	0.8576	0.2394	0.6183	0.721	263
	b	0.8298	0.2389	0.5909	0.712	
	c	0.7817	0.2441	0.5376	0.688	
4	a	0.7404	0.2231	0.5173	0.699	1011
	b	0.8074	0.2386	0.5688	0.704	
	c	0.7657	0.2065	0.5592	0.730	
5	a	0.3496	0.0886	0.2610	0.747	1587
	b	0.3729	0.0904	0.2825	0.758	
	c	0.3236		0.3236		
6	a	0.3112	0.0679	0.2433	0.782	3115
	b	0.3644	0.0766	0.2878	0.790	
	c	0.3671	0.0634	0.3037	0.827	
7	a	0.4431	0.1074	0.3356	0.758	1244
	b	0.4080	0.1038	0.3042	0.746	
	c		0.1085			
8	a	0.5035	0.1174	0.3860	0.767	3521
	b	0.5222	0.1153	0.4069	0.779	
	c	0.5490	0.1113	0.4376	0.797	
9	a	0.5152	0.1554	0.3597	0.698	2198
	b	0.5555	0.1573	0.3981	0.717	
	c	0.5840	0.1482	0.4358	0.746	
10	a	0.6020	0.1622	0.4397	0.731	1239
	b	0.6134	0.1552	0.4582	0.747	
	c	0.5646	0.1708	0.3938	0.698	
11	a	0.4537	0.1336	0.3201	0.706	1887
	b	0.4747	0.1394	0.3352	0.706	
	c	0.4547	0.1275	0.3272	0.720	

reagents.[9,11] In this system, however, no evidence was found of the formation of a second phase, because the general behavior of chemical modification (% MA$_R$) is not to change with C_{MA}.

In addition, the increase in DCP levels (C_{DCP}) increases %MA$_{SG}$ because of the increase in the number of initiator radicals. The effects of %MA$_{SG}$ increments with increasing C_{DCP} are more pronounced at short times, i.e. at high reaction times the probable side-reactions that occur decrease the effect of peroxide on the system, leading to similar levels of %MA$_{SG}$, regardless of the initial amount of peroxide used. It should be noted that levels of %MA$_{SG}$ and %MA$_R$ differ significantly, i.e. this route allows the chemical modification of PP with MA, but does not yield PP-g-MA$_{SG}$ (with short grafting) as the major product.

With respect to %MA$_{LG}$, C_{MA} shows no effect on %MA$_{LG}$ (Table VI). However, with increasing C_{DCP} %MA$_{LG}$ increases because of the increase in the number of initiator radicals, which leads to increased occurrence of all radical reactions. The effect of interaction between C_{MA} and C_{DCP} on the response of the %MA$_{LG}$ system showed to be statistically significant and indicates reduction in % MA$_{LG}$ with the increase in reagents. An increase in C_{MA} and C_{DCP} tends to increase all probabilities of MA reaction onto PP, but also increases the possibility of the occurrence of MA homopolymerization, which competes with graft growth. Analysis of %MA$_R$, %MA$_{SG}$, and %MA$_{LG}$ indicates a trend of succinic graft growth which leads to the conversion of PP-g-MA$_{SG}$ to PP-g-MA$_{LG}$.

CONCLUSIONS

The use of MMT as support for peroxide showed to alter the structure of MA grafted PP. However, unlike originally proposed

by Shi,[23,24] the system does not improve selectivity of the PP-*g*-MA formation reaction, but leads to the formation of long branch products. Likewise, the higher molar mass of the product showed to be primarily a result of the radical recombination mechanism, having no relationship with the improvement in selectivity of the grafting reactions with respect to chain scissions. Among the investigated variables, peroxide concentration was found to be the most influential in the reaction system in the presence of MMT, leading to higher levels of reacted MA. MA concentration did not affect the % of reacted MA, which was attributed to possible oligomerization side reactions on MMT surface, with subsequent insertion onto PP chains.

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