Grafting of Maleic Anhydride onto Polypropylene by Reactive Processing. I. Effect of Maleic Anhydride and Peroxide Concentrations on the Reaction

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ABSTRACT: Grafting reactions were performed in a Haake torque rheometer, according to a central composite experimental design, where the maleic anhydride and peroxide concentrations, rotor speed, and reaction time were varied. The 27 formulations were analyzed by Fourier transformed infrared spectroscopy and melt-flow index measurements (MFI). An increase in peroxide concentration caused an increase in the percentage of reacted maleic anhydride and in MFI. The effect of initial maleic anhydride concentration presented different types of behavior, depending on the peroxide level. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 247–255, 1999

INTRODUCTION

In recent years, the demand for polypropylene, PP, has increased, owing to the diversification of its applications. However, its potential applications like matrix for reinforced materials, blends, and metal coating, have been harmed by its apolar nature, which make it incompatible with metals, inorganic fillers, and polar polymers.^{1–3}

With the aim to obtain satisfactory performance in incompatible blends and in polypropylene composites containing inorganic fillers, PP modified with maleic anhydride (PP-g-MA) has been introduced into these systems as a third component.⁴⁻⁶ Among the possible routes of obtaining PP-g-MA reactive processing is worth mentioning, due to obtaining facility and low cost.

Grafting reaction of maleic anhydride onto polypropylene by reactive processing involves reacting the polymer melt with maleic anhydride, in

the presence of organic peroxides. Investigations regarding such reactions have been carried out in equipment like torque rheometers, $^{1,3,7-9}$ single screw extruders, $^{10-12}$ and in twin screw extruders.^{7,13,14} The organic peroxides are thermally unstable and undergo homolytic scission at the oxygen-oxygen bonds to form primary radicals at the processing conditions used. The radicals withdraw hydrogen atoms from the polypropylene chains, forming macroradicals on the polymer backbone, onto which, theoretically, the maleic anhydride is added, initiating the grafting process. However, such reactions are accompanied by chain scission, which alters the rheologic characteristics of PP.¹⁰ Finding the optimum conditions of the grafting process is a very complicated investigation, in virtue of the great number of variables involved, among which are: type and concentration of peroxide, maleic anhydride concentration, reaction time, reaction temperature, rotor speed, addition sequence of the reagents, and presence or not of stabilizers.

In our work, the grafting reactions were carried out in a torque rheometer through a central composite experimental design, in which four factors were varied. The amount of reacted maleic

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anhydride and the extent of degradation in the polypropylene were determined by means of Fourier transformed infrared spectroscopy (FTIR) and melt-flow index, respectively. The current article will evaluate the effect of the concentrations of maleic anhydride and peroxide on the dependent variables presented above, and in a second article the effect of rotor speed and reaction time on the dependent variables will be presented.

EXPERIMENTAL

Materials

Polypropylene was supplied by Polibrasil S.A. Indústria e Comércio, with a melt-flow index (MFI) of 2.0 g/10 min (JE-6100). The maleic anhydride used in this work was supplied by Carbocloro Oxypar Indústrias Químicas S.A., and the peroxide selected for our investigation was a 46.5% concentrate of 2,5-dimethyl-2,5-di(t-butyl-peroxy) hexane in CaCO₃, supplied by Elf Atochem Brasil Química Ltda (Luperox 101 XL).

Reactive Processing

The grafting reactions of maleic anhydride onto polypropylene by reactive processing were carried out in a Haake torque rheometer System 90, equipped with a Rheomix 600 mixing compartment. To verify the effect of the process variables on the grafting efficiency and on the degradation of polypropylene and to construct response surface plots capable of describing the behavior of these in the experimental region, the experiments were realized according to a Central Composite Experimental Design, in which the maleic anhydride concentration (Cma), peroxide concentration (Cper), rotor speed (Rot), and reaction time (t) were varied.

The reactions were carried out at 180°C, under nitrogen atmosphere. All components of the reaction were simultaneously introduced in the mixing compartment of the rheometer.

Table I presents the experimental design performed. The tests were carried out at random.

After processing, the samples were hot pressed at 180°C into thin sheets to facilitate cutting into small pellets.

Melt-Flow Index

The samples were analyzed through melt-flow index measurements (230°C and 2.16 kg) in a Dav-

Table I Experimental Design

Test	Cma (phr)	Cper (phr)	Rot (rpm)	t (min)
1	1.5	0.05	30	8
2	6.5	0.05	30	8
3	1.5	0.1	30	8
4	6.5	0.1	30	8
5	1.5	0.05	80	8
6	6.5	0.05	80	8
7	1.5	0.1	80	8
8	6.5	0.1	80	8
9	1.5	0.05	30	15
10	6.5	0.05	30	15
11	1.5	0.1	30	15
12	6.5	0.1	30	15
13	1.5	0.05	80	15
14	6.5	0.05	80	15
15	1.5	0.1	80	15
16	6.5	0.1	80	15
17	4.0	0.075	55	11.5
18	4.0	0.075	55	11.5
19	4.0	0.075	55	11.5
20	7.5	0.075	55	11.5
21	0.5	0.075	55	11.5
22	4.0	0.11	55	11.5
23	4.0	0.04	55	11.5
24	4.0	0.075	90	11.5
25	4.0	0.075	20	11.5
26	4.0	0.075	55	16.5
27	4.0	0.075	55	6.5

enport plastometer, according to ASTM D-1238, to verify the extent of degradation in the polypropylene. Analyses were performed in duplicate.

FTIR Spectroscopy

To quantify the reacted maleic anhydride, the samples were pressed into films in a Luxor press at 200°C and 100 kgf/cm² and submitted to heat treatment at 130°C for 24 h, to convert the acid groups to anhydrides. The samples were not purified, as the tests performed¹⁵ to verify the need for purification showed that the unreacted maleic anhydride was eliminated during the reaction, owing to the fact that the reaction system remained open for nitrogen entrance and exit.

Transmitting FTIR analyses were performed in triplicate, in a Nicolet Magna IR750 spectrophotometer, at the following analysis conditions: resolution of 2 cm⁻¹ and 128 scans per spectrum. From the FTIR spectra the Carbonyl Index (CI) was calculated:

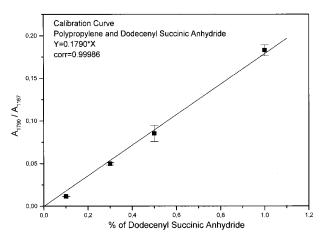


Figure 1 Calibration curve for the determination of the percentage of reacted maleic anhydride.

$$CI = \frac{A_{1790}}{A_{1167}}$$

where: A_{1790} is the absorbance at 1790 cm⁻¹, characteristic of carbonyls from cyclic anhydrides with a five-member ring; and A_{1167} is the absorbance at 1167 cm⁻¹, characteristic of CH₃ groups, proportional to the amount of PP.

As CI is a relative measurement, a calibration curve should be constructed. The blends were prepared in the torque rheometer, with known amounts of polypropylene and dodecenyl succinic anhydride. The calibration curve is presented in Figure 1.

RESULTS AND DISCUSSION

The results of the spectroscopy analyses and melt-flow index measurements are presented in Table II.

Multiple regression analyses realized through statistical software allowed fitting of the results of the percentage of reacted maleic anhydride, %MAr, obtained by FTIR analyses, and of MFI to second- and third-order models, respectively. The coefficients of the fitted polynomial equations are presented in Table III.

The fitted equations show that it is difficult to analyze the effect of each independent variable by simple observation of the equation that correlates them to the dependent variable (%MAr or MFI). So, analysis of the behavior of the responses with the independent variables requires the construction of surface response plots. To facilitate understanding of such behavior the effect of each independent variable will be discussed separately.

Peroxide Concentration

The peroxide concentration is the independent variable that has the greatest effect on the amount of reacted maleic anhydride.

This effect can be seen in the response surface plot, shown in Figure 2, where the peroxide and maleic anhydride concentrations are varied and the rotor speed and reaction time are fixed for the central point of the design (55 rpm and 11.5 min).

This figure shows that the percent reacted maleic anhydride increases with peroxide concentration. This behavior is observed for all levels of rotor speed and reaction time studied.

In the investigation developed, peroxide is used as initiator of the reaction of maleic anhydride with polypropylene. The peroxide decomposes thermally, giving origin to two primary radicals that withdraw hydrogen atoms from the polypropylene chains, forming polymer macroradicals (reactions 1 and 2 of the mechanism proposed). Maleic anhydride reacts with the macroradicals (reaction 4), which, in its absence, undergo β scission (reaction 3).

In this way, the higher the peroxide concentration in the reactional bulk, the larger will be the amount of primary radicals formed and, consequently, the higher the concentration of macroradicals available for the reaction with maleic anhydride. Therefore, the higher will be the level of grafting.

The effect of maleic anhydride and peroxide concentrations on the behavior of the melt-flow index, for the central level of the experimental design, are presented in Figure 3.

The increase in peroxide concentration in the reactional bulk is seen to cause an elevation in the melt-flow index. This behavior is observed for all levels of rotor speed and reaction time. However, the rate of this increase depends on other variables. The general behavior is explained by the elevation in the concentration of the macroradicals when the peroxide concentration is increased. As the β scission is a very quick reaction, in case no maleic anhydride is present when the macroradical is formed, this will undergo chain scission. The shorter the polypropylene chain, the higher its melt-flow index.

		A ₁₇₉₀ /A ₁₁₇₀	%MAr	MFI			A_{1790}/A_{1170}	%MAr	MFI
H-01	а	0.05658	0.316	37.7	H-15	а	0.10125	0.566	137.3
	b	0.05956	0.333	36.2		b	0.10027	0.560	105.6
	с	0.05843	0.326	_		с	0.10664	0.596	_
H-02	а	0.05129	0.287	14.7	H-16	а	0.11739	0.656	70.9
	b	0.04988	0.279	15.5		b	0.11417	0.638	80.1
	с	0.04944	0.276	_		с	0.11690	0.653	
H-03	а	0.11234	0.628	89.2	H-17	а	0.07518	0.420	37.8
	b	0.11375	0.635	118.8		b	0.07236	0.404	42.3
	с	0.11274	0.630	_		с	0.07775	0.434	
H-04	а	0.11608	0.648	62.9	H-18	а	0.07698	0.430	36.3
	b	0.11646	0.651	67.9		b	0.07688	0.429	38.9
	с	0.11323	0.633	_		с	0.07100	0.397	
H-05	а	0.05491	0.307	44.1	H-19	а	0.07085	0.396	35.7
	b	0.05763	0.322	41.6		b	0.07120	0.398	34.4
	с	0.05616	0.314	_		с	0.07444	0.416	
H-06	a	0.06173	0.345	23.2	H-20	а	0.07791	0.435	24.9
	b	0.06288	0.351	21.7		b	0.08002	0.447	23.6
	c	0.06202	0.346			с	0.07685	0.429	_
H-07	a	0.10589	0.592	240.8	H-21	а	0.05013	0.280	49.5
	b	0.10740	0.600	213.6		b	0.04959	0.277	54.4
	c	0.10390	0.580			с	0.05007	0.280	_
H-08	a	0.10148	0.567	48.9	H-22	а	0.11677	0.652	96.4
	b	0.10845	0.606	49.4		b	0.11388	0.636	89.1
	c	0.10473	0.585			с	0.11980	0.669	_
H-09	a	0.05541	0.310	38.6	H-23	а	0.04700	0.263	18.4
	b	0.06136	0.343	37.2		b	0.04751	0.265	20.9
	c	0.05626	0.314			с	0.04573	0.255	
H-10	a	0.05043	0.282	14.9	H-24	а	0.08242	0.460	57.3
	b	0.04981	0.278	14.1		b	0.07799	0.436	54.4
	c	0.05266	0.294			с	0.08247	0.461	
H-11	a	0.10012	0.559	86.4	H-25	а	0.08014	0.448	42.4
	b	0.09342	0.522	82.5		b	0.08240	0.460	46.8
	c	0.10811	0.604			с	0.07671	0.429	_
H-12	a	0.10522	0.588	55.5	H-26	а	0.08517	0.476	51.0
11-12	b	0.10322 0.10442	0.583	61.3		b	0.08244	0.461	46.8
	c	0.09916	0.555			с	0.07970	0.445	
H-13	a	0.05022	0.354 0.281	42.2	H-27	a	0.08064	0.451	76.4
11-10	a b	0.03022 0.04574	0.251 0.256	42.2		b	0.08458	0.473	74.9
	b c	0.04574	0.230 0.280	41.0		č	0.07538	0.421	
H-14	c a	0.06813	0.280 0.381	30.2		-			
11-1.4	a b	0.06993	0.381 0.391	30.2 30.9					
	b c	0.06993	$0.391 \\ 0.385$	50.9					
	С	0.00900	0.000						

Table IISpectroscopy and Melt-Flow Index Results of the Samples of the ProposedExperimental Design

When the peroxide concentration is increased to a level of low maleic anhydride concentration (0.5 phr), the increase in melt-flow index is more pronounced than for high levels of maleic anhydride (7.5 phr). This behavior becomes very evident when one compares the extremes of the graph in Figure 3. All levels of rotor speed and reaction time studied presented such behavior. This may be explained by the fact that when the maleic anhydride is present in greater quantity in the reactional mass, the probability that it is present at each reactive center initiated is higher, and therefore, the higher will be the probability of reaction between the maleic anhydride and the polypropylene macroradical before the β scission, reducing, in this way, the degradation of the polymer.

			Quadratic Parameters								
	R^2	<i>a</i> ₀	<i>a</i> ₁	a_2	a_3	a_4	a_5	a_6		a_7	<i>a</i> ₈
%MAr MFI	95.4 95.7		0.008955 65.947	$-0.56\ 551.576$	$-0.00644 \\ -1.335$	$-0.05817 \\ -50.84$	-282.25	2.736 imes -0.0549		$0.001189 \\ -3.897$	
			Quadratic Pa	arameters				Cubi	c Paran	neters	
a_9		<i>a</i> ₁₀	<i>a</i> ₁₁	a_{12}	a_{13}	a_{14}	a_{15}	<i>a</i> ₁₆	a_{17}	a_{18}	a ₁₉
-238.0		$1.28 imes 10^{-4} \ -0.149$	$-0.00374 \\ -10.027$	41.6 14022.4	$3.52 imes10^-\ 0.009$	5 0.002016 5.342	-6.911	 39.191	 0.037	 0.836	-0.127

Table III Coefficients of the Fitted Equations for the Construction of the Surface Response Plots

Polynomial equation: $a_0 + a_1 \operatorname{Cma} + a_2 \operatorname{Cper} + a_3 \operatorname{Rot} + a_4 t + a_5 \operatorname{Cma} \operatorname{Cper} + a_6 \operatorname{Cma} \operatorname{Rot} + a_7 \operatorname{Cma} t + a_8 \operatorname{Cper} \operatorname{Rot} + a_9 \operatorname{Cper} t + a_{10} \operatorname{Rot} t + a_{11} \operatorname{Cma}^2 + a_{12} \operatorname{Cper}^2 + a_{13} \operatorname{Rot}^2 + a_{14} t^2 + a_{15} \operatorname{Cma} \operatorname{Cper} \operatorname{Rot} + a_{16} \operatorname{Cma} \operatorname{Cper} t + a_{17} \operatorname{Cma} \operatorname{Rot} t + a_{18} \operatorname{Cma}^3 + a_{19} t^3$.

Concentration of Maleic Anhydride

The effect of the initial maleic anhydride concentration on the percent of reacted maleic anhydride and on the degradation of polypropylene is an issue that has most divided authors who have been investigating this reaction. The previous analyses are satisfactory to explain the behavior of the variables in restricted areas of the experimental design; however, when performing experiments in broader regions of the design, these are not adequate to explain such behavior. Because the proposed design involved a very broad range, it was possible to propose a reaction mechanism (which is presented at the end of the article) and explain several types of behavior in different experimental regions.

The increase in initial maleic anhydride concentration leads to the elevation in the percent of reacted maleic anhydride, %MAr, passing through a maximum value, with posterior decline (Fig. 2). This maximum depends on the levels of rotor speed and reaction time.

The increase in initial maleic anhydride concentration increases the probability that maleic anhydride gets into contact with the macroradicals, and therefore, of reaction between these, elevating the %MAr.

The maximum value of %MAr may be attributed to the formation of two distinct phases when the concentration of anhydride is increased—the

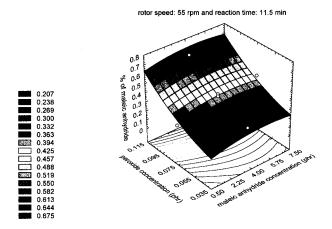


Figure 2 Effect of maleic anhydride and peroxide concentrations on the percentage of reacted maleic anhydride, for a rotor speed of 55 rpm and reaction time of 11.5 min.

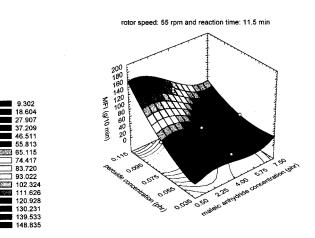


Figure 3 Effect of maleic anhydride and peroxide concentrations on the melt-flow index, for a rotor speed of 55 rpm and reaction time of 11.5 min.

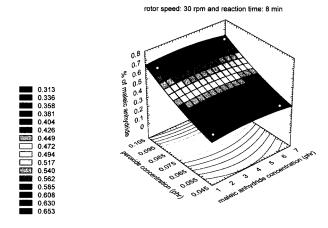


Figure 4 Effect of maleic anhydride and peroxide concentrations on the percentage of reacted maleic anhydride, for a rotor speed of 30 rpm and reaction time of 8 min.

maleic anhydride and the polypropylene phase. This value shifts to higher initial maleic anhydride concentrations when the rotor speed and the reaction time are increased. Through Figures 4 and 5, which show the effect of maleic anhydride and peroxide concentrations on the %MAr, for 30 rpm and 8 min and 80 rpm and 15 min, the shift of this maximum can be seen for higher Cma values when the rotor speed and the reaction time are increased.

When the rotor speed is increased, the mixing in the reaction medium is improved. In this way, the maleic anhydride is distributed more effi-

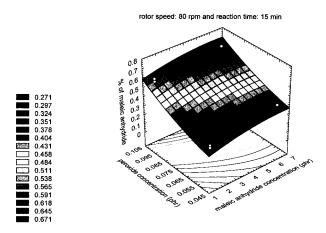


Figure 5 Effect of maleic anhydride and peroxide concentrations on the percentage of reacted maleic anhydride, for a rotor speed of 80 rpm and reaction time of 15 min.

Figure 6 Effect of maleic anhydride and peroxide concentrations on the melt flow index, for a rotor speed of 80 rpm and reaction time of 15 min.

ciently and the formation of two phases is only observed for higher maleic anhydride concentrations. This leads to an effectively higher initial maleic anhydride concentration, increasing the %MAr. This maximum was also observed by other authors.^{7,17}

As to the interaction between the reaction time and the initial maleic anhydride concentration, it is observed that longer reaction times shift the maximum value of %MAr to higher Cma. With a longer reaction time, the residual maleic anhydride in the bulk may react with polymer radicals, originating from thermal and frictional degradation of the process, leading to a higher %MAr, therefore, shifting the value of the maximum for higher %Cma.

The effect of the maleic anhydride concentration on the melt-flow index has been subject to controversy.

For the experimental design region studied, the melt-flow index presents distinct behavior, depending on the peroxide concentration employed. Figures 3 and 6 present such behavior.

For low levels of peroxide, the increase in maleic anhydride concentration leads to a slight increase in melt-flow index, passing through a practically constant region, with a tendency to decrease and with a slight increase afterwards. Depending on the rotor speed and reaction time levels, this increase may be significant or not.

For high peroxide levels, the increase in maleic anhydride concentration leads to a reduction in melt-flow index.

Both sets of behavior are observed for all rotor speed and reaction time levels studied.

		Variables				
	Cma	Cper	Rot	t	Average MFI	Average MFI ^a
1	1.5	0.05	30	8	36.9	15.8
2	6.5	0.05	30	8	15.1	15.8
3	1.5	0.1	30	8	104.0	43.6
4	6.5	0.1	30	8	65.4	43.6
5	1.5	0.05	80	8	42.8	22.9
6	6.5	0.05	80	8	22.4	22.9
7	1.5	0.1	80	8	227.2	44.9
8	6.5	0.1	80	8	49.2	44.9
9	1.5	0.05	30	15	37.9	15.4
10	6.5	0.05	30	15	14.5	15.4
11	1.5	0.1	30	15	84.4	41.6
12	6.5	0.1	30	15	58.4	41.6
13	1.5	0.05	80	15	42.0	30.1
14	6.5	0.05	80	15	30.6	30.1
15	1.5	0.1	80	15	121.4	74.6
16	6.5	0.1	80	15	75.5	74.6

Table IVMFI Results of the Experimental Design Samples and of Thosewithout Maleic Anhydride (Blank)

^a Values of MFI of the samples containing peroxide and polypropylene, without the addition of maleic anhydride, for all levels of peroxide concentration, rotor speed, and reaction time studied.

For a better understanding and analysis of the effect of the maleic anhydride concentration on the melt-flow index, Table IV presents the values of the melt-flow index for all levels of peroxide concentration, rotor speed, and reaction time studied, with and without addition of maleic anhydride.

When one compares the melt-flow index of the sample with PP and peroxide, without maleic anhydride (represented by MFI^a in Table IV) and with the inferior level of anhydride (1.5 phr), its addition is seen to cause an increase in the melt-flow index. This behavior was observed by Gaylord and Mishra,⁹ Hogt,¹³ and Ho et al.⁸

However, a further increase in the maleic anhydride concentration (6.5 phr) results in a drop in MFI to values very close to those of the samples processed without maleic anhydride.

When there are low levels of peroxide and maleic anhydride, a small amount of maleic anhydride present reduces the probability of these being present when the macroradicals are formed. As the β scission is a quick reaction, the tendency is that the maleic anhydride reacts with the polymeric macroradical after chain scission (reaction 5). As the concentrations of succinic and polymeric macroradicals are low, the probability of termination by combination (reactions 7 to 9) of the radicals is low, being, therefore, more probable that the terminations of the succinic radicals occur through chain transfer (reaction 6), with the abstraction of tertiary hydrogen atoms from the polymer chain, further accelerating the degradation process.

When the polypropylene undergoes chain scission, secondary macroradicals are formed at the end of the chain ($^{2}Pt\bullet$). According to Triacca et al.,¹⁸ who studied the controlled degradation of polypropylene, the presence of these final secondary macroradicals contributes to the termination by combination (reaction 9). Due to the fact that the succinic secondary carbon radical (PM•) is less reactive than the secondary macroradical ($^{2}Pt\bullet$), their presence reduces the possibilities of recombination, leading to the acceleration of degradation due to termination by chain transfer (reaction 6). As a consequence, degradation is higher in the presence of low maleic anhydride levels than in its absence.

This does not mean that the combination reactions (reactions 7 and 8) will not occur, but these are less probable than the chain transfer reactions (reaction 6).

When the concentration of maleic anhydride is increased, the melt-flow index decreases. As the population of maleic anhydride increases, the probability of these being present when a macroradical is formed increases, reducing in this way, the β scissions. Therefore, analysis of the results indicate that when the maleic anhydride concentration is high, the maleic anhydride tends to react before the chain scission (reaction 4).

When the concentration of peroxide is high and the concentration of maleic anhydride is low, the degradation is much more pronounced due to the higher number of macroradicals formed. The interpretation is similar to that for low peroxide and anhydride concentrations; however, with a more pronounced degradation process.

Increasing the concentration of maleic anhydride, for high levels of peroxide, the melt-flow index approaches that measured for PP and peroxide. However, in the presence of anhydride, the MFI is still a little higher. As explained before, the reaction of anhydride with PP likely occurs, predominantly, before chain scission; however, the ratio between the concentrations of maleic anhydride and peroxide decreases; a certain amount of anhydride might be reacting after chain scission. Another important factor is that, with the increase in %MAr, the population of final secondary carbons that might recombine decreases, increasing termination by chain transfer.

Termination by combination of polymeric macroradicals (reaction 9) and by disproportioning (reactions 10 to 12) are still likely to occur.

Reaction Mechanism Proposed

Decomposition of the Initiator

$$ROOR \to RO\bullet + \bullet OR \tag{1}$$

Abstraction of Hydrogen

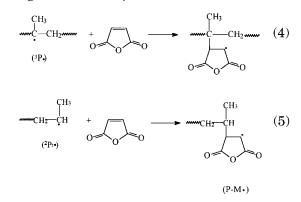
(2)

β Scission

$$\begin{array}{cccc} CH_{3} & CH_{3} & CH_{3} \\ | & | & | \\ m & C - CH_{2}m \rightarrow m & CH_{2} = CH + & CH - CH_{2}m \\ \bullet & & \bullet \\ & (^{3}P \bullet) & (^{2}P_{t} \bullet) \end{array}$$

$$(3)$$

Grafting of Maleic Anhydride



Chain Transfer

Termination by Combination

$$P-M\bullet + {}^{3}P_{c}\bullet \to P-M-P$$
(ramification or reticulation) (7)

$$P-M \bullet + {}^{2}P_{t} \bullet \rightarrow P-M-P \text{ (ramification)}$$
 (8)

$${}^{3}P_{c} \bullet + {}^{2}P_{t} \bullet \rightarrow P-P \text{ (ramification)}$$
 (9)

Termination by Disproportioning

$$2P-M \bullet \to 2P-M \tag{10}$$

$$P-M\bullet + {}^{2}P_{t}\bullet \rightarrow 2P-M + P$$
(11)

$$P-M\bullet + {}^{3}P\bullet \to 2P-M + P$$
(12)

where ${}^{2}P_{t}\bullet$ is the radical at the final secondary carbon; ${}^{3}P\bullet$ is the tertiary carbon radical; P is the polypropylene chain; M is the maleic anhydride; and P-M• is the succinic radical, after grafting.

CONCLUSION

Among the factors in the experimental design realized in the torque rheometer, the maleic anhydride and peroxide concentrations were those that affected most the level of grafting and the extent of degradation in PP. The increase in peroxide concentration resulted in the elevation in the percent reacted MA and in the MFI. The elevation in the initial maleic anhydride concentration in the reaction mixture led to an increase in percent reacted MA, passing through a maximum value, with posterior decline. This maximum depends on the levels of rotor speed and reaction time. The effect of initial Cma on the degradation extent in PP led to different types of behaviors, depending on the peroxide level. The presence of maleic anhydride in the reaction mixture increased the MFI. However, the increase in Cma reduced the MFI. At low Cma, the reactions of maleic anhydride with PP likely occur mainly after chain scission, whereas at higher Cma, the reactions likely occur mainly at the tertiary carbon of PP, reducing the degradation process.

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