Grafting of Maleic Anhydride onto Polypropylene by Reactive Extrusion

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ABSTRACT: Maleic anhydride grafting onto polypropylene was conducted in a twin-screw extruder according to an experimental design in which the maleic anhydride and peroxide concentrations were varied. The modified polypropylene was characterized by FTIR spectroscopy, melt-flow index measurements, size-exclusion chromatography, differential scanning calorimetry, and nuclear magnetic resonance. The results showed that only the independent variable peroxide concentration influenced the amount of reacted maleic anhydride, whereas the two variables studied influenced the molecular weight of the grafted polypropylene. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 2706–2717, 2002

Key words: reactive extrusion; maleic anhydride; polypropylene

INTRODUCTION

Polymer research and development have gradually changed direction in the last few decades. There has been a significant reduction in the introduction of new polymers and the need to improve the performance of existing polymers has led to the development of commercially feasible techniques, such as chemical modification, blending, and reinforcement, among others, to modify them.

Among the techniques employed to modify polymers, controlled degradation of polypropylene and grafting of polyolefins with polar monomers have received special attention because of their potential applications.

Maleic anhydride grafting onto polypropylene (PP) has been carried out with the aim of achieving compatibility between polar and nonpolar polymers,[1–4] coupling between polypropylene and inorganic fillers,[5–9] and adhesion to metals.[10] These reactions are usually carried out in the presence of organic peroxides and can be conducted in the solid state,[11,12] in the melt,[12–24] or in solution.[22,25–28] Reaction in the melt, by reactive processing, has been the preferred method because of the low cost and easy operation involved. Continuous or discontinuous mixing equipment is used as chemical reactor in reactive processing.

Grafting reactions of maleic anhydride onto PP, in the presence of peroxides, have been carried out both in torque rheometers[12,15,22,23] and in both single-screw[15–19] and twin-screw extruders.[13,20,21] In the reactive extrusion process polymer modification reactions and processing are carried out simultaneously.[29]

Previous studies[14–18,20,21,23,24] of grafting reactions of maleic anhydride onto PP, in the melt, show that these reactions are accompanied by

undesirable side reactions (chain scissions in polypropylene).

In this study, maleic anhydride grafting reactions onto polypropylene were conducted in the presence of organic peroxides, using a twin-screw extruder, based on an experimental design in which two factors, maleic anhydride and peroxide concentrations, were varied. The amount of reacted maleic anhydride was determined by means of Fourier transformed infrared spectroscopy (FTIR), whereas the extent of PP degradation was verified by melt-flow index (MFI) measurements and by size-exclusion chromatography (SEC). Differential scanning calorimetry (DSC) analyses were also performed to verify the influence of the grafting level and of PP degradation on the thermal properties of the modified PP, as well as nuclear magnetic resonance (NMR) to get more insight into the grafting reaction.

EXPERIMENTAL

Materials

Polypropylene was supplied by Polibrasil S.A. Indústria e Comércio (Brazil), with 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. (Brazil) and the peroxide selected for our investigation was a 46.5% concentrate of 2,5-dimethyl-2,5-di(t-butyl-peroxy)hexane in $CaCO_3$, supplied by Elf Atochem Brasil Química (Luperox 101 XL; Brazil).

Reactive Extrusion

The reactive extrusion process was carried out in a Werner and Pfleiderer ZSK-25 corotational twin-screw extruder. The processing conditions were as follows: temperature profile: 180, 200, 200, 210, 210, 210, 200°C; screw rotation: 150 rpm; atmosphere: N_2 (g). All the formulations were first mixed in a Henshel mixer for approximately 1.5 min and then fed into the extruder hopper.

The parameters that were varied in this step were the maleic anhydride and peroxide concentrations. The experiments were conducted according to a factorial design at two levels (2^2), with a central point and two extra points. Table I presents the experimental design that was carried out.

Table I   Experimental Design

Test	C_{ma}[a] (phr)	C_{per}[b] (phr)
EX 01	1.5	0.05
EX 02	4.0	0.05
EX 03	1.5	0.1
EX 04	4.0	0.1
EX 05	2.75	0.075
EX 06	1.5	0.075
EX 07	4.0	0.075
EX 08	4.0	0.075
EX 09	4.0	0.075
EX 10	—	0.05
EX 11	—	0.075
EX 12	—	0.1

[a] C_{ma}, concentration of maleic anhydride.
[b] C_{per}, concentration of peroxide.

The formulations processed by reactive extrusion were purified by solubilization in xylene and precipitation in acetone (twice), dried in a vacuum oven, and analyzed by FTIR, SEC, DSC, and NMR. Nonpurified samples were subjected to MFI measurements.

FTIR Spectroscopy

After the samples were purified by solubilization in xylene and precipitation in acetone to eliminate residual maleic anhydride, they 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, for conversion of the acid groups into anhydrides. The need to purify and thermally treat the samples was verified through preliminary studies.[30]

Quantification of the reacted maleic anhydride was done by means of FTIR transmission spectroscopy. The samples were analyzed using a Nicolet Magna IR750 spectrophotometer (Nicolet Instruments, Madison, WI), 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 as

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

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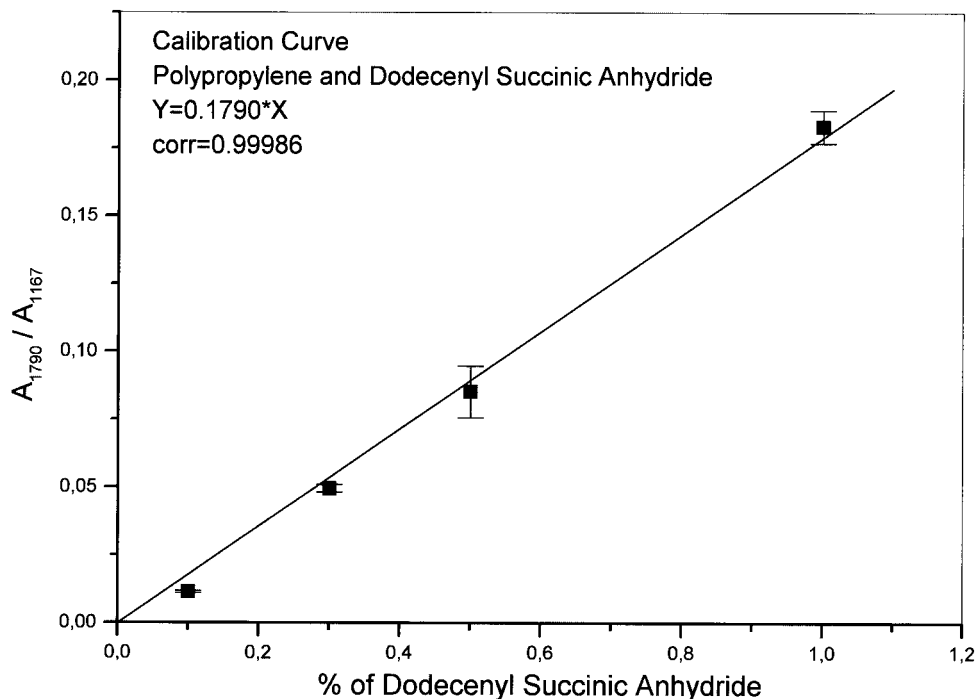
Figure 1   Calibration curve for the determination of the percentage of reacted maleic anhydride.

1167 cm^{-1}, characteristic of the CH_3 groups, proportional to the amount of polypropylene.

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

Melt-Flow Index (MFI)

The samples were analyzed through MFI measurements in a Davenport plastometer, according to ASTM D-1238, to verify the extent of degradation in the polypropylene.

Because of the high MFI of most of the samples processed by reactive extrusion, the analyses were carried out twice under the following conditions: 230°C and 2.16 kg, 190°C and 2.16 kg, and 190°C and 0.325 kg.

Size-Exclusion Chromatography (SEC)

The analyses performed to determine the molecular weight of the samples subjected to the reactive extrusion process were carried out using a Waters 150-C size-exclusion chromatographer

(Waters Associates, Milford, MA) at high temperature. The type of column used was PS-DVB and the solvent was trichlorobenzene.

Differential Scanning Calorimetry (DSC)

The thermal analyses were carried out with a DuPont differential scanning calorimeter, model DSC 2910 (DuPont, Wilmington, DE). Samples with weights ranging from 6 to 10 mg, in powder form, were subjected to a linear heating rate of 10°C/min up to 200°C.

To verify the effect of the molecular weight and the grafting level on the thermal properties of the samples, the thermal history previous to the analysis was eliminated and the samples were subjected to controlled cooling and reheated. Cooling was carried out at a rate of 10°C/min down to 30°C. The second heating run was conducted under the same conditions as the first run.

The melt enthalpy, obtained from the DSC thermogram, was used to calculate the degree of crystallinity, by means of the following equation:

$$\text{Degree of cystallinity} = \frac{\Delta H_m}{\Delta H_{100\%}} \times 100\%$$

where ΔH_m is the melt enthalpy of the sample and $\Delta H_{100\%}$ is the melt enthalpy of the hypothetically 100% crystalline polypropylene (165 J/g).

This analysis was performed on the extruded and purified samples.

Nuclear Magnetic Resonance (NMR)

Analyses of ^{13}C-NMR were carried out using an Oxford Instruments 2 T magnet spectrometer. The samples subjected to this analysis were EX 04 and EX 12, both purified. The analyses were carried out in the solid state, according the CP/MAS (crossed polarization with magic-angle spin) technique, under the following conditions: 1 ms contact time for crossed polarization, 3 kHz spin frequency of the sample at the magic angle, 40,000 acquisitions, and 1.5 s experiment acquisition time.

RESULTS AND DISCUSSION

FTIR Spectroscopy and MFI Measurements

Table II shows the results obtained from the analyses of FTIR and MFI measurements.

The multiple-regression analyses were done using computational programs, and the results of percentage of the reacted maleic anhydride (% MA$_r$), obtained by FTIR spectroscopy, and of MFI, were fitted to first- and second-order models, respectively. The regression analysis for the MFI variable was performed with the values measured at 190°C and 2.16 kg. Table III shows the coefficients of the fitted polynomial equations.

To analyze the behavior of the responses with the independent variables, it is necessary to construct surface-response plots based on the proposed equations.

Figures 2 and 3 show the behavior of the percentage of MA$_r$ and of the MFI with the variation of maleic anhydride and peroxide concentrations (independent variables). For a better understanding of the above, the effect of the independent variables on the percentage of the MA$_r$ and on the MFI are shown separately.

Peroxide Concentration

An analysis of the equation fitted to the percentage of MA$_r$ and Figure 2 show that this variable is affected only by the peroxide concentration added to the reactional mass. Increasing the peroxide concentration leads to an increase of the percentage of MA$_r$ and of the MFI.

In this work peroxide was used as the initiator for the reaction of maleic anhydride with the PP. Peroxide decomposes on heating, creating two primary radicals (reaction 1 of the proposed reaction mechanism, presented below), which abstract hydrogens from the PP chain, forming the polymer macroradicals (reaction 2). The maleic anhydride present reacts with the macroradicals (reaction 4) that, in the absence of the former, suffer a β-scission (reaction 3).

Hence, the higher the peroxide concentration, the larger the quantity of primary radicals formed and, consequently, the higher the concentration of macroradicals available for the reaction with the maleic anhydride. Thus, as a result there will be a higher level of grafting.

Figure 3 shows that the increased concentration of peroxide in the reactional mass causes an elevation of the MFI. This behavior is explained by the increased concentration of macroradicals when the peroxide concentration is increased. As the β-scission is a fast reaction, if maleic anhydride is not present when the macroradical is formed the latter will undergo chain scission. The shorter the PP chain is, the higher its MFI will be.

For the variation levels studied, the only way to increase the percentage of MA$_r$ would be to increase the initial concentration of peroxide.

Maleic Anhydride Concentration

The increase in the initial concentration of maleic anhydride in the reactional mass did not lead to any variation in the percentage of MA$_r$. In the case of the MFI, it can be seen that an increase in the maleic anhydride concentration leads to a reduction of this variable, which holds for all the peroxide concentration levels. However, the reduction rate of the MFI is larger for high concentrations of peroxide.

Given that the increased initial maleic anhydride concentration does not cause a significant increase in the percentage of MA$_r$, the reduction of MFI with this variable can be explained by the fact that the increased concentration of maleic anhydride increases the probability of the latter being present when macroradicals are being formed, thus decreasing the occurrence of β-scission. With the increase in the initial maleic anhydride concentration, the reaction of maleic anhydride with the macroradicals likely occurs before

Table II   Results of A_{1790}/A_{1167} and Percentage of Grafted Maleic Anhydride of Samples Subjected to Reactive Extrusion

		Variable				Melt Flow Index (g/10 min)		
Test	Sample	C_{ma} (phr)	C_{per} (phr)	A_{1790}/A_{1170}	% MA_r	190°C; 2.16 kg	190°C; 0.325 kg	230°C; 2.16 kg
EX 01	a	1.5	0.05	0.05938	0.332	33.60	2.80	110.63
	b			0.05958	0.333	33.63	2.88	88.48
	c			0.06470	0.361	—	—	—
EX 02	a	4.0	0.05	0.06369	0.356	25.35	2.16	60.28
	b			0.06289	0.351	25.25	2.28	55.83
	c			0.05847	0.327	—	—	—
EX 03	a	1.5	0.1	0.09664	0.540	83.84	7.31	—
	b			0.10557	0.590	84.36	6.95	—
	c			0.10394	0.581	—	—	—
EX 04	a	4.0	0.1	0.09232	0.516	63.50	5.51	—
	b			0.10996	0.614	63.45	5.30	—
	c			0.09642	0.539	—	—	—
EX 05	a	2.75	0.075	0.07669	0.428	45.25	4.27	—
	b			0.07895	0.441	47.76	4.31	—
	c			0.07517	0.420	—	—	—
EX 06	a	1.5	0.075	0.08647	0.483	57.83	5.16	—
	b			0.08782	0.491	58.24	5.03	—
	c			0.08729	0.488	—	—	—
EX 07	a	4.0	0.075	0.08186	0.457	52.13	4.41	—
	b			0.08435	0.471	51.33	4.17	—
	c			0.07417	0.414	—	—	—
EX 08	a	4.0	0.075	0.08469	0.473	47.81	4.18	—
	b			0.08600	0.480	48.32	4.09	—
	c			0.08370	0.468	—	—	—
EX 09	a	4.0	0.075	0.07539	0.421	42.16	3.40	—
	b			0.07048	0.394	39.22	3.34	—
	c			0.07708	0.431	—	—	—
EX 10	a	—	0.05	—	—	11.55	0.89	26.47
	b			—	—	11.53	0.89	26.70
	c			—	—	—	—	—
EX 11	a	—	0.075	—	—	20.59	1.46	45.26
	b			—	—	20.77	1.46	44.39
	c			—	—	—	—	—
EX 12	a	—	0.1	—	—	31.36	2.12	72.23
	b			—	—	31.64	2.40	65.94
	c			—	—	—	—	—
JE-6100	a	—	—	—	—	0.92	0.07	2.03
	b			—	—	0.90	0.06	2.04
	c			—	—	—	—	—

the chain scission. This does not imply the occurrence of a higher level of grafting but, rather, the probability that the event occurs before chain scission. At a lower concentration of initial maleic anhydride, there will be a lower probability of MA molecules being present together with the macroradicals at the moment of their formation, increasing the probability of chain scission and reaction of maleic anhydride with the macroradicals after this event.

The presence of maleic anhydride, at the lowest concentration level, elevates the MFI. This fact is observed when one compares the formulations with a lower level of maleic anhydride (1.5 phr)

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

|		Polynomial equation: $a_0 + a_1 C_{ma} + a_2 C_{per} + a_3 C_{ma} C_{per} + a_4 C_{ma}^2 + a_5 C_{per}^2$					
		Linear Parameters			Quadratic Parameters		
	R^2	a_0	a_1	a_2	a_3	a_4	a_5
% MA_r	87.0	0.121852	—	4.4	—	—	—
MFI	96.9	1.352276	-17.815121	1157.42	-98.48	3.656107	—

with those containing none (Table II). However, an increase of its concentration (4.0 phr) reduces the value of this variable.

At low peroxide and anhydride levels, the reaction of maleic anhydride with PP should occur mainly after the chain scission (reaction 5) as a result of the low probability of maleic anhydride molecules being present during the formation of macroradicals. Moreover, termination reactions should occur principally by chain transfer (reaction 6), through the abstraction of H from the PP tertiary carbons, thus intensifying the degradation process.

The predominance of chain-transfer reactions over those of combination (reactions 7–9) can be attributed to two factors: the low population of macroradicals, given the low level of peroxide; and the lower reactivity of the secondary succinic radicals in relation to the terminal secondary macroradicals. According to Triacca et al.[31] the presence of terminal secondary macroradicals contributes toward termination by combination (reaction 9). Because the radical of the secondary succinic carbon, P-M·, is less reactive than the secondary macroradical, $^2P_t\cdot$, their presence reduces the possibility of their recombining, leading to accelerated degradation by chain transfer.

This does not mean that combination reactions (reactions 7 and 8) will not occur, but that they are less probable than chain-transfer reactions (reaction 6). Terminations by combination of polymeric macroradicals (reaction 9) and by dispro-
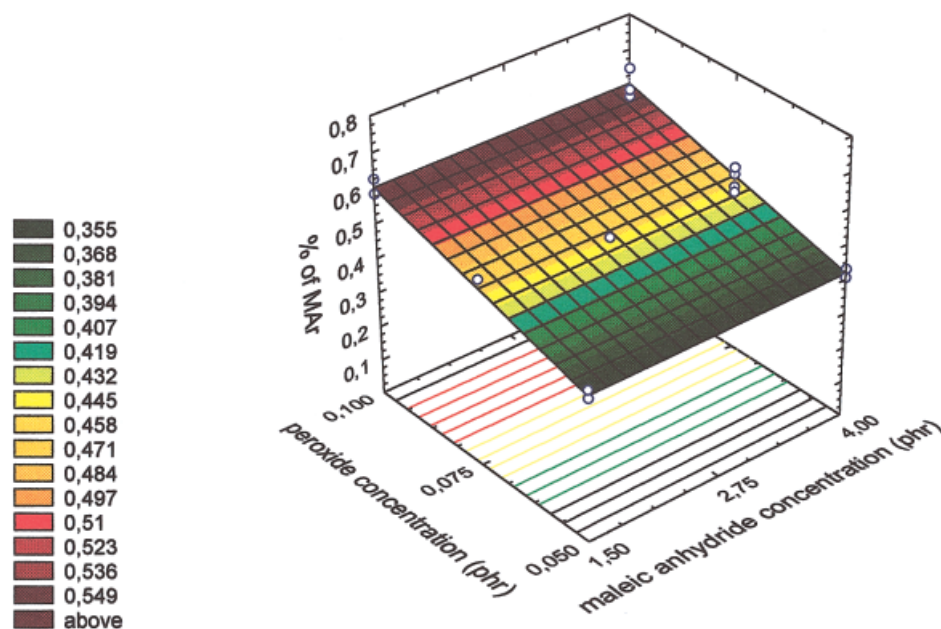
Figure 2 Effect of maleic anhydride and peroxide concentrations on the percentage of reacted maleic anhydride. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
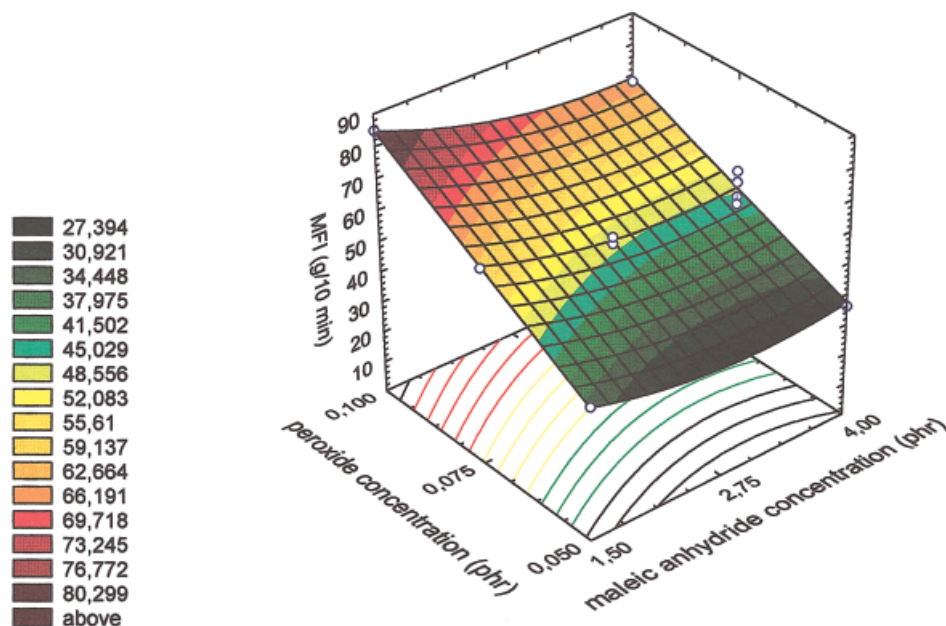
Figure 3 Effect of maleic anhydride and peroxide concentrations on the melt flow index (MFI). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

portioning (reactions 10–12) are also probable reactions.

The increased concentration of anhydride, at the low peroxide level, caused a slight decrease of MFI because of the increased availability of these molecules at the formed macroradicals.

Degradation is far more accentuated at high peroxide and low maleic anhydride levels as a result of the higher formation of primary radicals and, as a consequence, of polymeric macroradicals. Degradation is higher than that in the absence of maleic anhydride because termination reactions occur preferentially by chain transfer. At high peroxide levels, a larger amount of maleic anhydride reacts with the PP, increasing the concentration of secondary succinic radicals, which, because of their lower reactivity, reduce the possibility of combinations with the other macroradicals.

Chain scissions decrease when the maleic anhydride concentration increases because of the increased availability of maleic anhydride molecules during the formation of macroradicals, thus reducing the MFI. However, the value of this variable continues to be higher than that measured for the material processed without maleic anhydride. Two factors can explain this fact: the first is that, possibly, the relation between the peroxide

and maleic anhydride concentrations is not high enough to practically avoid the reaction after the chain scission; and the second is that, because of the amount of reacted maleic anhydride, there is a larger number of reactions of the latter with the PP's terminal secondary carbons, thus reducing the possibility of recombinations occurring.

It is interesting to note, in Figure 3, that the increase of the maleic anhydride concentration to a level above 3.375 phr did not lead to significant variations in the MFI. In the preceding paragraph, in discussing the relation between anhydride and peroxide concentrations, the proposition was to effectively increase this relation. The formation of two phases in the reactional mixture is probably initiated at a level of maleic anhydride above 3.375 phr. Therefore, a simple increase in the initial maleic anhydride concentration would not affect the MFI; it would be necessary to modify the processing conditions to avoid the formation of two phases at higher initial C_{ma} (concentration of maleic anhydride) levels.

Size-Exclusion Chromatography

In addition to the MFI measurements, SEC analyses were also carried out to determine the molecular weight of PP. Table IV shows the values of

Table IV   Values of Molecular Weight Measured by SEC, Based on Analyses of Purified Samples Processed by Reactive Extrusion

Sample	M_w	M_n	M_w/M_n	M_z	M_v
EX 01	145,318	61,885	2.35	301,351	132,441
EX 02	147,717	51,238	2.88	303,526	134,026
EX 03	121,650	55,317	2.2	232,556	111,848
EX 04	124,045	47,872	2.59	238,977	113,192
JE-6100	329,848	50,452	6.54	1,516,380	269,667
EX 10	158,586	48,360	3.28	410,391	140,357
EX 11	129,936	49,147	2.64	271,506	117,618
EX 12	124,369	49,120	2.53	272,413	112,378

molecular weight obtained by SEC. The samples subjected to the grafting reaction (EX 01–EX 04) were purified before the SEC analysis.

The samples processed with PP and peroxide, without maleic anhydride, show $\overline{M}_w$ values that are in agreement with the MFI values (EX 10–EX 12), that is, the increase in the peroxide concentration reduces molecular weight; in other words, it increases the MFI.

The presence of maleic anhydride at its lowest level reduces the $\overline{M}_w$ of the modified PP samples. However, the increase in the initial concentration of maleic anhydride in the reactional mass increases the sample's molecular weight, for both peroxide levels. All the $\overline{M}_w$ values obtained by the SEC technique are in agreement with the MFI measurements.

Another important fact, which can be verified by analyzing the results shown in Table IV, is that the samples with high initial maleic anhydride levels present values of $\overline{M}_w$ close to those of the samples processed only with PP and peroxide, for the same levels of peroxide. These results reaffirm the greater probability that reactions between maleic anhydride and macroradicals occur before chain scissions.

Another important observation concerning SEC molecular weight measurements is that the molecular weight distribution M_w/M_n decreases in the case of the grafted samples, following the same behavior as that of the rheology-controlled polypropylenes.

Effect of Molecular Weight and Percentage of MA$_r$ on the Thermal Properties of Grafted Samples

The samples processed by reactive extrusion were subjected to DSC analyses to verify the effect of molecular weight and the percentage of MA$_r$ on the thermal properties.

Table V presents the values of melt temperature (T_m), melt enthalpy (ΔH_m), percentage of crystallinity, crystallization temperature (T_c), and crystallization enthalpy (ΔH_c) of the samples studied. The values of the properties presented herein refer to the second heating to which the samples were subjected to eliminate process variables.

Empirical modeling by multiple regression presented a very low correlation coefficient, which led to the decision not to use it to describe the response behavior because this would lead to analysis errors.

From the Tukey comparison test of the experimental averages, for a 5% significance level, it can be seen that there are no significant differences among the percentages of crystallinity of the grafted samples. On the other hand, there are significant differences between the grafted samples and the pure PP (JE-6100).

The Tukey test carried out on the JE-6100 samples and the PPs treated solely with peroxide (EX 10 and EX 12) showed that there are significant differences between the JE-6100 and the other samples. There are no differences between samples EX 10 and EX 12.

Based on the previous analysis we can conclude that the reduction of molecular weight deriving from the degradation of the PP and the grafting of maleic anhydride in PP increase the percentage of crystallinity of the grafted samples. This behavior can be attributed to the fact that the decrease in molecular weight reduces the entanglements of PP molecules, increasing their degree of order and, thus, enhancing overall crystallinity.

Table V   Thermal Properties of the Samples Subjected to the Reactive Extrusion Process, Measured by DSC

| Test | Noncoded Variables | | T_m | ΔH_m | Percentage Crystallinity | T_c | ΔH_c |
	C_{ma}	C_{per}					
EX 01	1.5	0.05	158.62	103.2	62.45	114.76	96.64
			158.41	102.3	62.00	114.78	96.97
EX 02	4.0	0.05	160.40	102.5	62.12	115.02	95.32
			161.10	100.4	60.85	114.63	93.90
EX 03	1.5	0.1	159.73	103.6	62.79	117.03	96.90
			159.46	105.4	63.88	116.49	97.27
EX 04	4.0	0.1	158.31	104.4	63.27	114.25	99.42
			158.68	105.4	63.88	114.02	95.37
EX 05	2.75	0.075	158.96	103.2	62.55	113.28	96.63
			159.27	102.1	61.88	112.64	97.66
EX 06	1.5	0.075	159.05	103.1	62.49	113.68	98.11
			159.56	99.15	60.09	113.72	93.52
EX 07	4.0	0.075	158.59	104.8	63.52	113.43	98.07
			158.85	104.9	63.58	113.50	97.98
EX 08	4.0	0.075	160.17	100.3	60.79	114.56	95.23
			159.93	102.6	62.18	114.58	95.53
EX 09	4.0	0.05	159.40	101.9	61.76	112.36	96.15
			159.68	102.3	62.00	113.11	94.11
EX 10	—	0.05	160.50	100.5	60.91	114.17	96.65
			161.43	99.20	60.12	114.25	98.38
EX 11	—	0.075	160.53	96.25	58.33	113.47	94.30
			162.2	98.23	59.53	111.92	97.97
EX 12	—	0.1	158.97	98.10	59.45	110.02	90.40
			159.20	93.86	56.88	110.18	89.09
JE-6100	—	—	165.05	76.93	45.08	104.78	75.30
			165.67	74.39	46.62	104.33	72.69

Another possible explanation for the enhanced crystallinity of the samples subjected to the reactive extrusion process is the nucleating effect of the CaCO$_3$, given that this was used to disperse the peroxide.

The presence of maleic anhydride molecules grafted onto PP increases the polarity of the medium, intensifying the interaction forces between the grafted polypropylene molecules and increasing the polymer's crystallinity percentage.

When one analyzes the effect of molecular weight on samples JE-6100 and EX 10, which were not subjected to the grafting reaction, one can see that the reduction of molecular weight caused an increase in the percentage of crystallinity. However, when the initial concentration of peroxide in the reactional mass was increased and the polymer, as a consequence, suffered higher degradation (i.e., a reduction of molecular

weight), there was a reduction in the PP's percentage of crystallinity. This effect can be observed in the samples treated solely with peroxide (EX 10–EX 12). Therefore, up to a certain level, the reduction of molecular weight led to increased crystallinity, which can be attributed to the reduction of the entanglements and the nucleating effect of CaCO$_3$. However, at a higher level of degradation, the reduction of molecular weight caused a reduction of order, resulting in a drop in the percentage of crystallinity.

In the case of PP grafted with maleic anhydride, even for high levels of degradation, the percentage of crystallinity remained high. This behavior can be ascribed to the compensation of degradation by the increase of polarity.

The melt temperature and the Tukey test show that there is a significant reduction in T_m for the grafted samples. This reduction can be explained

by the structural changes caused by the reaction of maleic anhydride with the PP and by the PP degradation that occurred with grafting. Despite the fact that grafting caused the percentage of polypropylene crystallinity to rise, the presence of side groups in the PP, such as maleic anhydride, and of possible branching resulting from recombination reactions between radicals, led to a reduction in the amount of perfect crystals and, thus, reduced the T_m.

Analysis by NMR

The ^{13}C-NMR technique was used in an effort to obtain more information about how maleic anhydride is connected to PP. Sample EX 04 was selected for NMR analysis because, of the several formulations, this one presented the highest level of grafting, whereas formulation EX 12 was analyzed as a reference of a material totally devoid of grafting but that, nonetheless, showed a high level of degradation. Figure 4 presents the ^{13}C-NMR spectra of the two above-mentioned formulations.

According to Rengarajan et al.,[11] who analyzed PP grafted with maleic anhydride in the solid state, maleic anhydride carbonyl shows a signal in the ^{13}C-NMR spectrum in the region between 172 and 174 ppm.

Analysis of Figure 4 shows a signal in sample EX 04 that, at first, could be considered a peak in the region of 175 ppm, which is characteristic of anhydride carbonyls. This "signal," however, is very small and of the same order of magnitude as noise. Thus, one cannot state that the signal observed at 175 ppm results from grafted anhydride carbonyl.

The reason that it is difficult to obtain signals lies in the level of grafting achieved. Given that the percentage of reacted maleic anhydride for sample EX 04 was 0.56%, the PP signal is approximately 177 times larger than the maleic anhydride signal, which is why it is so difficult to detect the latter.

Sample EX 12, which presents no grafting, shows no signals in the 175 ppm region. However, the noise observed is of the same order of magnitude as the "signal" observed in sample EX 04, confirming that definitive statements should not be made regarding the sign detected in sample EX 04.

Elucidations of the grafting mechanism by the NMR technique have been seldom used for melt reactions because of the low levels of grafting normally achieved. Heinen et al.[32] used the ^{13}C-NMR technique to analyze grafted maleic anhydride; however, the reactions were conducted with maleic anhydride enriched with ^{13}C.

Proposed Reaction Mechanism

Decomposition of the Initiator

$$ROOR \rightarrow RO\cdot + \cdot OR \qquad (1)$$
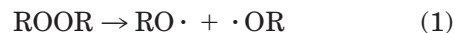
Abstraction of Hydrogen

$$(^3P\cdot) \qquad (2)$$

β-Scission

$$(3P\cdot) \qquad\qquad (3P\cdot) \qquad (3)$$

Grafting of Maleic Anhydride

$$(P\text{-}M\cdot) \qquad (4)$$

$$(P\text{-}M\cdot) \qquad (5)$$
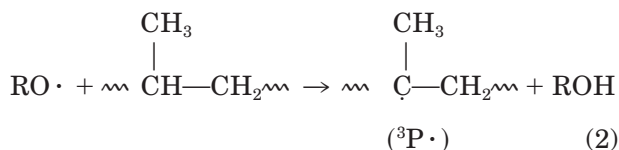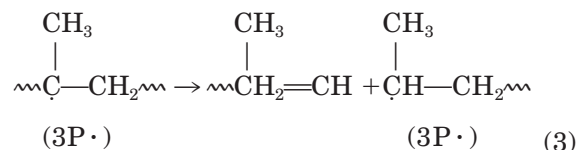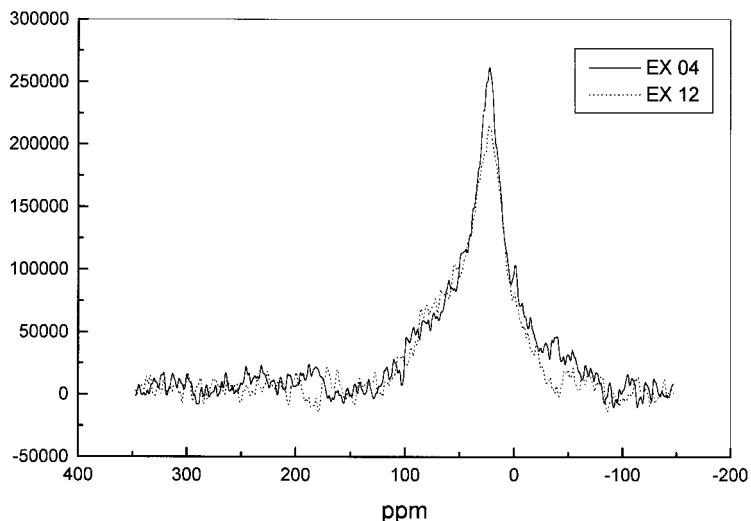
Figure 4 ^{13}C-NMR spectra of the EX 04 and EX 12 samples.

Chain Transfer

$$\text{P-M}\cdot + \text{\scriptsize www} \overset{\overset{\displaystyle CH_3}{|}}{CH}—CH_2\text{\scriptsize www} \rightarrow \text{PM} + \text{\scriptsize www} \overset{\overset{\displaystyle CH_3}{|}}{\underset{.}{C}}—CH_2\text{\scriptsize www}$$
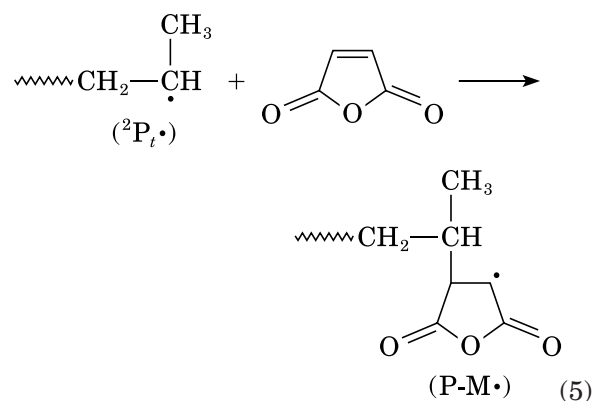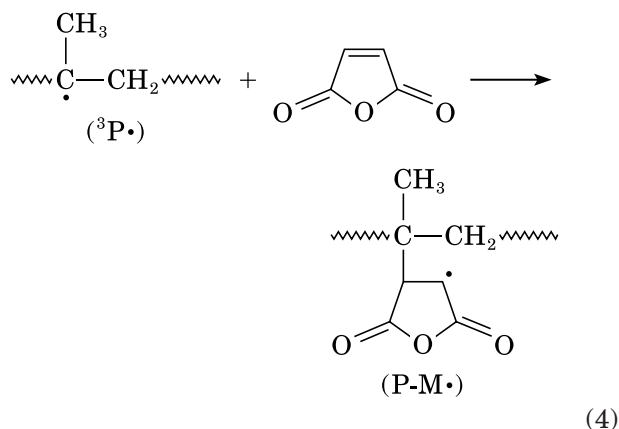
$$(^3P\cdot) \quad (6)$$

Termination by Combination

$$\text{P-M}\cdot + {}^3P_c\cdot \rightarrow$$

$$\text{P-M-P (ramification or reticulation)} \quad (7)$$

$$\text{P-M}\cdot + {}^2P_t\cdot \rightarrow \text{P-M-P (ramification)} \quad (8)$$

$${}^3P_c\cdot + {}^2P_t\cdot \rightarrow \text{P—P (ramification)} \quad (9)$$
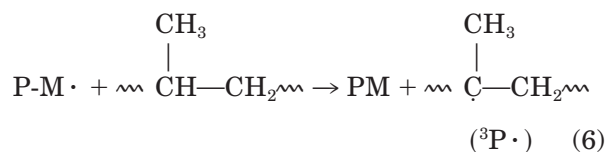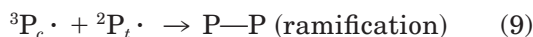
Termination by Disproportioning

$$2\ \text{P-M}\cdot \rightarrow 2\ \text{P-M} \quad (10)$$

$$\text{P-M}\cdot + {}^2P_t\cdot \rightarrow 2\ \text{P-M} + \text{P} \quad (11)$$

$$\text{P-M}\cdot + {}^3P\cdot \rightarrow 2\ \text{P-M} + \text{P} \quad (12)$$

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

CONCLUSIONS

The results obtained showed that, for the reactive extrusion process studied, the independent variable concentration of peroxide influenced both the amount of reacted maleic anhydride and the molecular weight of grafted polypropylene, whereas the variable concentration of maleic anhydride influenced only the molecular weight. The increased concentration of peroxide caused an elevation of the percentage of MA_r and a reduction of molecular weight. The presence of maleic anhydride, at low concentrations, caused the reduction of molecular weight. However, an increase of this concentration to its high level increased the molecular weight.

The PP samples grafted with maleic anhydride presented narrower molecular weight distributions than the distribution of nonmodified PP, following the same behavior as that shown by rheology-controlled PP.

The PPs grafted with maleic anhydride presented higher crystallinity percentages and lower melt temperatures than did the nonmodified PP. The rise in the percentage of crystallinity was attributed to the reduction in molecular weight and to increased polarity of the grafted samples. The reduction of melt temperature was ascribed to the reduced perfection of the crystals, deriving from the anhydride groups, and the presence of possible branching.

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