Grafting of Maleic Anhydride onto Polypropylene by Reactive Processing. II. Effect of Rotor Speed and Reaction Time

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ABSTRACT: Grafting of maleic anhydride onto polypropylene was performed in a Haake torque rheometer, according to a central composite experimental design, in which four factors were varied: the maleic anhydride and peroxide concentrations, rotor speed, and reaction time. The current article investigates the effect of rotor speed and reaction time on the level of reacted maleic anhydride, obtained by infrared spectroscopy, and on the extent of degradation, by means of melt-flow index (MFI) measurements. The behavior of the variables studied depends on the levels of maleic anhydride and peroxide concentrations. The increase in rotor speed results in an increase in the percentage of reacted maleic anhydride and a reduction in MFI when the initial maleic anhydride concentration is high, and in a reduction in the percentage of reacted maleic anhydride and increase in MFI when the initial maleic anhydride concentration is low (for the central levels of peroxide concentration and reaction time). The effect of the variable reaction time depends on the remaining parameters. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 256–263, 1999

Key words: maleic anhydride; polypropylene; rotor speed; reaction time

INTRODUCTION

Polypropylene (PP) has been one of the fastest growing polymers in the last years, thanks to its intrinsic properties, low cost, and versatility, having expanded its applications to areas formerly restricted to other polymers, such as packaging and the automobile market.[1,2]

Utilization of polypropylene in the automobile industry is due to the growing trend towards using polypropylene composites and expanded polypropylene as substitutes for engineering plastics and polyurethane, respectively.

However, its apolar nature has limited its use in systems composed of polar polymers, inorganic fillers, and metals.[3–5] In this way, functionalization of polypropylene with polar monomers has been performed to use it as a third component in blends of PP and polar polymers and in composites of PP and inorganic fillers.

As functionalization involves grafting of small side chains of different monomer units onto the backbone chain of the homopolymer, conferring alterations on its chemical properties without drastic physical modifications, maleic anhydride has some advantage over other monomers, due to the difficulty in homopolymerizing brought about by the deficiency in electrons in the double bond.[6,7]

Functionalization of PP with maleic anhydride has been carried out both in the melt[3,5,7–16] and in

solution.[16–20] Due to low costs and operating facility such reactions are preferentially accomplished in the melt through reactive processing.

In reactive processing, continuous or batch mixing equipment are used as chemical reactors.

Grafting of maleic anhydride onto polypropylene through reactive processing involves reacting the molten polymer with maleic anhydride in the presence of organic peroxides.[10]

Finding the optimum conditions in the grafting process is very complicated in view of the great number of variables involved.

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 anhydride and the extent of degradation in the polypropylene were determined by means of Fourier transformed infrared spectroscopy (FTIR) and melt-flow index measurements, respectively. The current article will evaluate the effect of rotor speed and reaction time on the dependent variables presented above. The independent variables, namely maleic anhydride and peroxide concentrations, were analyzed in a previous article.[21]

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-butylperoxy) hexane in $CaCO_3$, 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 anhy-

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

dride 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 Davenport 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

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

at 200°C and 100 kgf/cm^2, 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 performed[22] 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:

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

where: A_{1790} = absorbance at 1790 cm^{-1}, characteristic of carbonyls from cyclic anhydrides with a five-member ring; and A_{1167} = absorbance at 1167 cm^{-1}, characteristic of CH$_3$ 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). Hence, 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.

Rotor Speed

The rotor speed is a variable that cannot be analyzed individually. Its influence on the responses depends on the level of the remaining independent variables.

Figure 2 illustrates the effect of the rotor speed and maleic anhydride concentration on the percentage of reacted maleic anhydride, %MAr, for the central levels of peroxide concentration and reaction time (Cper = 0.075 phr and t = 11.5 min).

Increasing the rotor speed the %MAr presents two distinct types of behavior for the different levels of initial maleic anhydride concentration: when the initial level of maleic anhydride is low, an increase in rotor speed reduces the %MAr slightly; when the initial level of maleic anhydride is high, an increase in rotor speed increases the %MAr.

The increase in rotor speed improves mixing and at the same time favors the formation of more macroradicals in polypropylene due to the high shear. Hence, when there is a high concentration of maleic anhydride and mixing is improved, the maleic anhydride molecules are distributed more efficiently in the reaction bulk, resulting in a higher level of reaction. If the higher rotor speed also favors formation of macroradicals and if anhydride is present, the %MAr will increase.

The effect of mixing is only significant if there is enough maleic anhydride available to be dispersed in the polymer bulk. This is not the case for low maleic anhydride levels. If the increase in rotor speed causes the generation of new macro-

Table II   Spectroscopy and Melt-Flow Index Results of the Samples of the Proposed Experimental Design

		A_{1790}/A_{1170}	%MAr	MFI			A_{1790}/A_{1170}	%MAr	MFI
H-01	a	0.05658	0.316	37.7	**H-15**	a	0.10125	0.566	137.3
	b	0.05956	0.333	36.2		b	0.10027	0.560	105.6
	c	0.05843	0.326	—		c	0.10664	0.596	—
H-02	a	0.05129	0.287	14.7	**H-16**	a	0.11739	0.656	70.9
	b	0.04988	0.279	15.5		b	0.11417	0.638	80.1
	c	0.04944	0.276	—		c	0.11690	0.653	—
H-03	a	0.11234	0.628	89.2	**H-17**	a	0.07518	0.420	37.8
	b	0.11375	0.635	118.8		b	0.07236	0.404	42.3
	c	0.11274	0.630	—		c	0.07775	0.434	—
H-04	a	0.11608	0.648	62.9	**H-18**	a	0.07698	0.430	36.3
	b	0.11646	0.651	67.9		b	0.07688	0.429	38.9
	c	0.11323	0.633	—		c	0.07100	0.397	—
H-05	a	0.05491	0.307	44.1	**H-19**	a	0.07085	0.396	35.7
	b	0.05763	0.322	41.6		b	0.07120	0.398	34.4
	c	0.05616	0.314	—		c	0.07444	0.416	—
H-06	a	0.06173	0.345	23.2	**H-20**	a	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	—		c	0.07685	0.429	—
H-07	a	0.10589	0.592	240.8	**H-21**	a	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	—		c	0.05007	0.280	—
H-08	a	0.10148	0.567	48.9	**H-22**	a	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	—		c	0.11980	0.669	—
H-09	a	0.05541	0.310	38.6	**H-23**	a	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	—		c	0.04573	0.255	—
H-10	a	0.05043	0.282	14.9	**H-24**	a	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	—		c	0.08247	0.461	—
H-11	a	0.10012	0.559	86.4	**H-25**	a	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	—		c	0.07671	0.429	—
H-12	a	0.10522	0.588	55.5	**H-26**	a	0.08517	0.476	51.0
	b	0.10442	0.583	61.3		b	0.08244	0.461	46.8
	c	0.09916	0.554	—		c	0.07970	0.445	—
H-13	a	0.05022	0.281	42.2	**H-27**	a	0.08064	0.451	76.4
	b	0.04574	0.256	41.8		b	0.08458	0.473	74.9
	c	0.05006	0.280	—		c	0.07538	0.421	—
H-14	a	0.06813	0.381	30.2					
	b	0.06993	0.391	30.9					
	c	0.06900	0.385	—					

radicals and there is no anhydride for the reaction, the %MAr will not increase.

Another important fact observed during the experiments is that a certain amount of maleic anhydride sublimates during loading and processing, as the adaptation of the mixing compartment for nitrogen inlet and outlet turned the system into an open one. With the increase in rotor speed the temperature of the melt increases (this fact was verified by the torque rheometer temperature curves), which might lead to an even higher decrease in the effective Cma and, hence, decreasing %MAr. This fact is more critical for lower Cma levels.

It is important to observe from Table II that the variations in %MAr caused by rotor speed are

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

	R^2	Linear Parameters					Quadratic Parameters			
		a_0	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8
%MAr	95.4	0.695182	0.008955	−0.56	−0.00644	−0.05817	—	2.736×10^{-4}	0.001189	—
MFI	95.7	171.002	65.947	551.576	−1.335	−50.84	−282.25	−0.0549	−3.897	40.41

Quadratic Parameters						Cubic Parameters				
a_9	a_{10}	a_{11}	a_{12}	a_{13}	a_{14}	a_{15}	a_{16}	a_{17}	a_{18}	a_{19}
—	1.28×10^{-4}	−0.00374	41.6	3.52×10^{-5}	0.002016	—	—	—	—	—
−238.043	−0.149	−10.027	14022.4	0.009	5.342	−6.911	39.191	0.037	0.836	−0.127

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

very small when compared to the variations caused by the peroxide and maleic anhydride concentrations.

As to the MFI, the effect of rotor speed should be analyzed together with the remaining variables. The effect of maleic anhydride concentration and rotor speed on MFI, for the central levels of peroxide concentration and reaction time (Cper $= 0.075$ phr and $t = 11.5$ min), is presented in Figure 3.

The increase in rotor speed, which is supposed to create new macroradicals, at low initial levels of maleic anhydride, accelerates the degradation process. At high initial levels of maleic anhydride, an improved mixing results in a better distribution of the anhydride molecules in the reaction mass, which will react with the macroradicals formed, reducing the occurrence of chain scission by the competitive process chain scission/maleic anhydride grafting.

Regarding the interaction between the independent variables rotor speed and peroxide concentration, the dependent variable %MAr is little affected by the variation in rotor speed at the several peroxide addition levels. For the MFI, the effect of this interaction will also depend on the initial maleic anhydride concentration in the mixture. Figures 4 and 5 are shown for visualization of this discussion.

At low peroxide levels, the increase in rotor speed does not cause significant modifications in the MFI (practically constant), for high (Fig. 5) as well as low initial maleic anhydride concentrations (Fig. 4).

Figure 2   Effect of rotor speed and maleic anhydride concentration on the percentage of reacted maleic anhydride, for a peroxide concentration of 0.075 phr and reaction time of 11.5 min.

Figure 3   Effect of rotor speed and maleic anhydride concentration on MFI, for a peroxide concentration of 0.075 phr and reaction time of 11.5 min.

maleic anhydride concentration: 1.5 phr and reaction time: 8 min

Figure 4 Effect of rotor speed and peroxide concentration on MFI, for a maleic anhydride concentration of 1.5 phr and reaction time of 8 min.

At high levels of peroxide, the increase in rotor speed causes an increase in MFI when the maleic anhydride is at an inferior level (Fig. 4) and causes either a reduction or slight increase when the maleic anhydride concentration is high (Fig. 5).

In the case of high levels of peroxide a large amount of macroradicals will be formed. In this way, the increase in rotor speed, when the level of anhydride is high, results in a better dispersion of this in the polymer mass, reducing the occurrence of chain scission. When the concentration of anhydride is low, besides the fact that an increase in rotor speed will not cause significant mixing effects as there is little anhydride present, this increase contributes to an increasing sublimation of the maleic anhydride, reducing the effective concentration in the reaction mixture.

maleic anhydride concentration: 4.0 phr and rotor speed: 55 rpm

Figure 6 Effect of reaction time and peroxide concentration on the percentage of reacted maleic anhydride, for a maleic anhydride concentration of 4.0 phr and rotor speed of 55 rpm.

Reaction Time

The effect of the independent variable reaction time on the behavior of %MAr and of MFI varies according to the levels of the remaining variables studied.

The central levels of Cma and rotor speed (4.0 phr and 55 rpm) show the following behavior (Figs. 6 and 7): the increase in reaction time alters very little the level of grafting, %MAr, for all levels of peroxide concentration.

The MFI, however, is reduced to the central level of reaction time, 11.5 min, after which it remains constant.

Because the half-lifetime of the peroxide used at the reaction temperature of 180°C is 68 s, and

maleic anhydride concentration: 6.5 phr and reaction time: 8 min

Figure 5 Effect of rotor speed and peroxide concentration on MFI, for a maleic anhydride concentration of 6.5 phr and reaction time of 8 min.

maleic anhydride concentration: 4.0 phr and rotor speed: 55 rpm

Figure 7 Effect of reaction time and peroxide concentration on MFI, for a maleic anhydride concentration of 4.0 phr and rotor speed of 55 rpm.

Figure 8 Effect of reaction time and maleic anhydride concentration on the percentage of reacted maleic anhydride, for a peroxide concentration of 0.1 phr and rotor speed of 80 rpm.

according to Kamath and Palys[23] complete decomposition requires six half-lives, our process would require 6.8 min. Hence, after this period, no primary radicals would be produced, and as a consequence, no macroradicals from the initiation process. If there are no significant increases in the level of grafting with time and if MFI continues dropping, this might indicate recombination of the macroradicals formed. This effect would be more significant than the possible formation of macroradicals with reaction time, due to thermal or shearing effects.

It is worth noting that on analyzing MFI, from Table II, for the sample pairs that differ only by reaction time and are at the lower level of peroxide concentration, the variations in melt-flow index with reaction time are slightly significant compared to the same variations when the peroxide level is high. As examples of these variations, for low peroxide levels, we have: H01/H09 (36,9/ 37,9 g/10 min), H02/H10 (15,1/14,5 g/10 min), H05/H13 (42,8/42,0 g/10 min) and H06/H14 (22,4/ 30,6 g/10 min).

For high levels of peroxide concentration and rotor speed (0.1 phr and 80 rpm) the following behavior was observed (Figs. 8 and 9): The increase in reaction time, for high levels of maleic anhydride, leads to an increase in %MAr. At low levels of maleic anhydride the increase in reaction time does not cause significant variations in %MAr. As to the MFI, at high levels of maleic anhydride the increase in reaction time increases the MFI and at low levels of maleic anhydride the MFI decreases.

A possible explanation for the behavior of the reaction time with %MAr would be the following: because the levels of peroxide concentration and rotor speed are high, a large amount of macro-radicals will be formed by the action of primary radicals, from the shearing and thermal effect. If there is still maleic anhydride in the reaction mixture, this will lead to an increase in %MAr. In the case of a low level of maleic anhydride, if this is already depleted, there will be no significant alterations.

When the level of Cma is high, the grafting reaction probably occurs before chain scission,[21] which results in an MFI value lower than that obtained for low Cma. However, the behavior of MFI with reaction time shows that this increases for high levels of Cma. The explanation for this case is that probably the reaction of the maleic anhydride present occurs with the secondary macroradicals (after decomposition of the peroxide) and the recombination of these will, therefore, decrease, due to the fact that the secondary succinic macroradical is less reactive than the secondary polymeric radical. The termination reactions of the succinic macroradicals likely occur by chain transfer, which would explain the increase in MFI with reaction time. Because for low Cma levels there is no increase in %MAr, there is also no reduction in secondary macroradicals formed and, therefore, the possible recombinations are not reduced with reaction time.

CONCLUSION

The experimental design showed to be adequate in conducting the grafting reactions of maleic an-

Figure 9 Effect of reaction time and maleic anhydride concentration on MFI, for a peroxide concentration of 0.1 phr and rotor speed of 80 rpm.

hydride onto polypropylene, as it allowed analysis of the results for the several levels of variables proposed.

The effect of rotor speed and reaction time on the reacted maleic anhydride content and on the MFI depends on the levels of maleic anhydride and peroxide concentration, which could not be analyzed separately.

Analysis of the effect of rotor speed on the %MAr and the MFI results from the fact that the increase in rotor speed leads to better mixing of maleic anhydride in the reaction mass, an increase in the production of macroradicals and sublimation of the maleic anhydride, due to the increase in reaction temperature.

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