

Chemical Modification Process of an Atactic Polypropylene by *p*-Phenylene-bismaleamic Acid in the Melt

J. M. García-Martínez, A. G. Cofrades, S. Areso, E. P. Collar

Departamento de Física e Ingeniería de Polímeros, Instituto de Ciencia y Tecnología de Polímeros. Consejo Superior de Investigaciones Científicas (CSIC), Calle Juan de la Cierva 3, 28006 Madrid, Spain

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ABSTRACT: This study was concerned with the chemical modification process of an atactic polypropylene from polymerization reactor byproducts with *p*-phenylene-bismaleamic acid to obtain a new grafted polymer supposed to play an important role as an interfacial agent in heterogeneous systems based on polymers. The grafting process was undertaken with the aid of the Box–Wilson experimental worksheet, with two independent variables (or controlled factors), the level of polar monomer to be grafted in the polymer and the concentration of the initiator, and with the

agitation rate kept constant. Each item of the experimental design was performed at four different reaction times. This latter let us ascertain the transient nature of the process and the existence of a critical point in the concentration of both reactants conducting the system to the maximum grafting yield. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2202–2209, 2003

Key words: atactic; poly(propylene) (PP); functionalization of polymers; reactive processing; modeling

INTRODUCTION

The functionalization of polyolefins has been claimed as a very attractive methodology for obtaining new polymers from those commodities by the enhancement of some desired properties and an increase their commercial value. The grafting of polar monomers onto the polymer backbone changes the properties of the originally nonpolar macromolecular substrate. This aspect of the new grafted polymer is what makes it very useful as an interfacial modifier in polymer composites and/or polyblends.^{1–12}

However, although the grafting of polymers has been broadly used in commercial applications, the exact path involved in their obtention is still far from well established. The complex character of the process and the economical aspects related to grafting of polar monomers onto polyolefins explain the efforts devoted to this topic in the last 4 decades^{13–23} and nowadays, as several reviews such as those by Xu and Lin,²⁴ Jois and Harrison,²⁵ Naqui and Choudhary,²⁶ and more recently, by Moad²⁷ illustrate.

Earlier investigations have been devoted to the grafting of maleic anhydride (MAH) onto isotactic polypropylene (PP)^{28,29} and, more recently, onto the atactic homopolymer.^{30–33} Another family of modified

polymers emerged by the obtention of succinyl-fluorescein-grafted groups onto PP³⁴ by a two-step functionalization process in the melt. This implies that the succinic anhydride groups graft onto PP backbone as single units, as concluded by Russell and Kelusky.^{22,23} More recently, studies on the grafting of *p*-phenylene-bismaleamic acid (*p*-PBM) onto isotactic PP in the molten state were carried out by our group.^{35,36}

This study was concerned with the obtention of *p*-PBM-grafted atactic polypropylene (a-PP) as a way to obtain a new family of grafted polymers that would be able to be further employed as interfacial agents in heterogeneous materials based on polymers. The results, obtained from a Box–Wilson experimental design with two independent variables, and the polynomial fits obtained are discussed.

EXPERIMENTAL

Materials

As starting material, an a-PP (from polymerization reactor wastes) supplied by Repsol-YPF (Madrid, Spain) was used. The monomer to be grafted (*p*-PBM) was prepared and characterized in our laboratories; details are published elsewhere.^{35,36} As a reaction initiator for the radical grafting process, a dycumile peroxide (POx; Perkadox BC) from Akzo (Barcelona, Spain) was used. To prevent thermooxidative degradation in PP (mainly β -scission processes), a 50/50 mixture of Irganox 1010 and Irganox B225 from Ciba-Geigy (Barcelona, Spain) was used as a thermal stabilizer. The solvents used in the washing operation of

Correspondence to: E. P. Collar (ecollar@ictp.csic.es).

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TABLE I
Properties of a-PP Used in this Study

Molecular weight		HI (M_w/M_n)	T_g (°C)	Differential scanning calorimetry				Density (g/cm ³)
M_w	M_n			ΔH_m (J/g)	T_m (°C)	ΔH_c (J/g)	T_c (°C)	
54,000	2,700	20	-22.0	10.6	113	-20.1	75.9	0.85

^a M_w = weight-average molecular weight; M_n = number-average molecular weight; (HI = heterodispersity index) T_g = glass-transition temperature; (ΔH_m = melting enthalpy) T_m = melting temperature; (ΔH_c = crystallization enthalpy) T_c = crystallization temperature.

the modified polymers were xylene (Panreac) (Madrid, Spain) and dimethylformamide (Scharlau/ FEROSA, Madrid, Spain). Some properties of the a-PP used in this study are listed in Table I.

Procedures

The chemical modification batch process in the melt was conducted in a Rheomix 600 mixing chamber attached to a Rheocord 90 driver unit (Haake, Barcelona, Spain). The processing temperature was set up at 140°C. The gear rate was 45 rpm for all the experiments. Reaction times were 3, 5, 7, and 10 min. As independent variables, we set up the concentration of *p*-phenylen-bismaleamic acid ([*p*-PBM]) and the concentration of dycumile peroxide ([POx]; named as controlled factors) by following the two independent variables from the Box–Wilson experimental worksheet (Table II). The experimental worksheet was performed for each of the reaction times considered. The processing operations were as follows: once the reactor was at the set temperature, the a-PP, 0.1% of the thermal stabilizers mixture, and the *p*-PBM were added. When the components were well mixed, the temperature was at set conditions, and torque values were stabilized (indicating a good homogenization of reactants),

peroxide (POx) was added. This moment was defined as the reaction start-up. Once the reaction time had elapsed (after 3, 5, 7, or 10 min), the reaction product was recovered into an ice bath. Afterward, the polymer was solved in boiling xylene (30 min) with the further addition of *N,N*-dimethylformamide to remove unreacted acid. The solution was then precipitated drop by drop onto cool methanol. The precipitated polymer (modified polymer) was then filtered off and dried, and a yellow product was obtained. Then, the polymer was ready to be characterized.

Characterization

The modified a-PPs we obtained (Fig. 1) were first qualitatively characterized by Fourier transform infrared (FTIR) spectroscopy. We recorded the IR spectra on a Spectrum One FTIR spectrometer (PerkinElmer, Madrid, Spain) with the KBr pellet technique with an average of 32 scans and at a resolution of 2 cm⁻¹. KBr pellets were prepared by the consideration of approximately 3 mg of polymer in approximately 170 mg of KBr in the usual way. Figure 2 shows the FTIR spectra of some modified polymers containing different levels of grafting. The spectral region between 1700 and 1600 cm⁻¹, corresponding to characteristic vibrations from

TABLE II
Grafting Values Obtained by the Chemical Modification of a-PP at Different Reaction Times for the Box-Wilson Experimental Worksheet Used in this Study

Experiment	Controlled factor		Reaction time (min)			
	[POx] (%)	[<i>p</i> -PBM] (%)	3	5	7	10
				[<i>p</i> -PBM] _{Grafted} (%)		
1	0.70	3.00	1.29	1.14	0.99	0.38
2	3.50	3.00	1.90	2.20	1.44	0.38
3	0.70	15.00	8.13	8.59	8.28	8.43
4	3.50	15.00	6.46	8.13	7.22	7.98
5	0.12	9.00	5.70	6.46	6.00	5.85
6	4.08	9.00	6.91	7.82	7.22	5.54
7	2.10	0.51	0.40	0.38	0.32	0.27
8	2.10	17.49	15.12	14.82	12.84	10.41
9	2.10	9.00	7.37	8.13	7.22	5.85
10	2.10	9.00	6.91	8.10	5.70	5.55
11	2.10	9.00	8.43	6.61	6.46	5.85
12	2.10	9.00	6.61	8.74	5.85	6.76
13	2.10	9.00	8.43	7.07	6.31	6.46

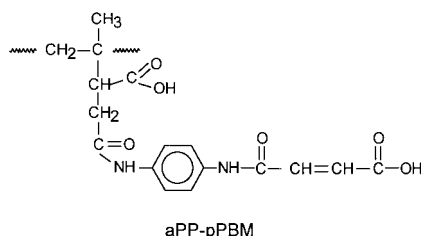


Figure 1 a-PP with *p*-PBM grafted groups (a-PP-pPBM).

carbonyl and amide groups, respectively, was observed clearly in the modified polymers and was more clear when the grafting degree was higher, not in the original PP. The spectra also let us observe two intense bands located in the 1400–1380 cm^{-1} region, corresponding to the stretching modes of NCO groups, which gained in intensity with the grafting level in the same way as the three different bands corresponding to the stretching vibrations of amide groups: one appeared at 1700 cm^{-1} (amide I); the second, a broad band, appeared at 1555 cm^{-1} (amide II); and the third appeared at 1303 cm^{-1} (amide III). Moreover, the presence of a band at 1624 cm^{-1} , which was assigned to $-\text{CH}=\text{CH}-\text{CO}-$ groups, was also clearly determined. From all of these results, the presence of grafted *p*-PBM groups onto a-PP could be clearly concluded.^{37,38}

The grafting level was obtained by a hot titration method,^{28,35,36,39,40} which determined the two acid groups present in the bismaleamic acid grafted on the PP backbone (Fig. 1). The titration process was as

follows: 1 g of polymer was put in 150 mL of a refluxing xylene–butyl alcohol–water mixture for 60 min. We titrated the hot solution without permitting it to cool with 0.05N ethanolic potasse with thymol blue as an indicator. Then, an excess of KOH was added, and a deep blue color was back-titrated to a yellow end point by the addition of 0.05N isopropanolic HCl to the hot solution. Results are expressed as weight percentages. In this way, the neglected values were obtained for the original polymer.

RESULTS AND DISCUSSION

We performed all of the experimental work by following a Box–Wilson experimental design to model the process.^{41–43} Table II compiles all the results for the experimental worksheet with two independent variables (controlled factors) and the grafting levels obtained at reaction times of 3, 5, 7, and 10 min. As mentioned before, the independent variables were the initial concentration of *p*-PBM ($[p\text{-PBM}]$) and the initial concentration of POx ($[POx]$) in the reaction media.

Polynomial fits and analysis of variance (ANOVA)

Each set of the experimental grafting values obtained at each one of the reaction times (Table II) was fitted according to a quadratic model after the surface response method.⁴² Then, four different polynomials describing the evolution of the chemical modification process in the whole experimental space scanned were

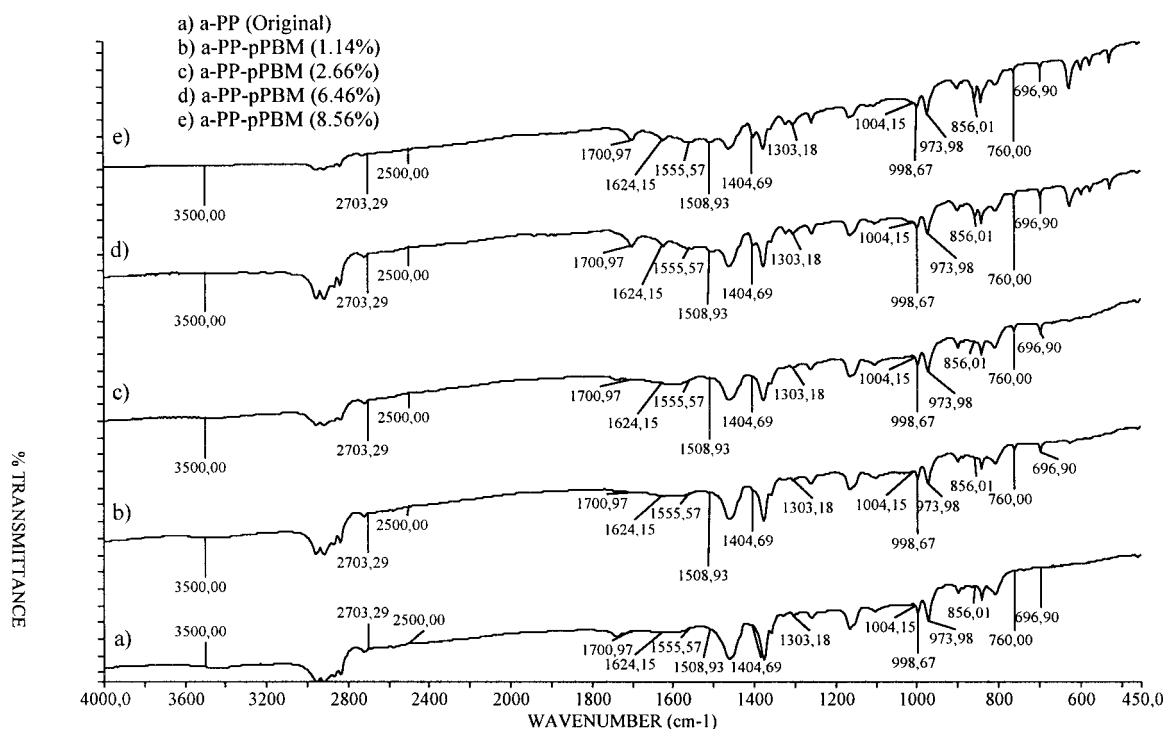


Figure 2 FTIR spectra of unmodified and modified isotactic PPs containing *p*-PBM grafted groups.

TABLE III
Coefficients of the Response Surface Polynomials

Reaction time (min)	$\langle r^2 \rangle$	Linear term			Interaction term	Quadratic term	
		a_0	a_1	a_2	a_3	a_4	a_5
3	0.8364	-3.932	3.365	1.079	-0.06577	-0.6451	-0.015
5	0.8804	-3.381	2.509	1.129	-0.04643	-0.4468	-0.018
7	0.8988	-2.257	1.313	0.9337	-0.0456	-0.1922	-0.011
10	0.9652	-2.293	1.124	0.9954	-0.01357	-0.2573	-0.019

^a Polynomial equation: $a_0 + a_1x_1 + a_2x_2 + a_3x_1x_2 + a_4x_1^2 + a_5x_2^2$, where $x_1 = [\text{POx}]$ and $x_2 = [p\text{-PBM}]$.

obtained. The terms of these four polynomials are compiled in Table III.

The statistical parameters for the ANOVA of the models are compiled in Table IV. As shown, the coefficient of determination $\langle r^2 \rangle$ values for the different models were excellent in all cases for a quadratic model (much higher than 0.75⁴¹⁻⁴³). Furthermore, the little values for pure error observed appeared to support

the accuracy of the results. Likewise, the very high value for the confidence factor (close to 100% in all cases) indicated that all of the factors considered by the model played very important roles in the overall behavior of the system. So, from the latter, we could assume that the process followed a quadratic evolution that agreed with the interfacial phenomena and the chemisorption mechanism supposed to govern the process that was already suggested for the chemical modification process of isotactic PP by *p*-PBM³⁶ or MAH^{28,29,31} or a-PP by MAH.³⁰⁻³³ According to the results, we could assume that the system could be fully discussed from the model forecasts.

TABLE IV
Statistical Parameters of the ANOVA

Reaction time (min)	$\langle r^2 \rangle$	Sum of square mean	Pure error	Confidence
				factor (%)
3	0.8364	8.395	0.698	98.2
5	0.8804	5.8421	0.7522	99.0
7	0.8988	4.0543	0.3495	99.3
10	0.9652	1.0747	0.2495	99.8

Evolution of the system: isoline maps

Figure 3 shows the isoline maps corresponding to the grafting levels obtained as a function of the initial

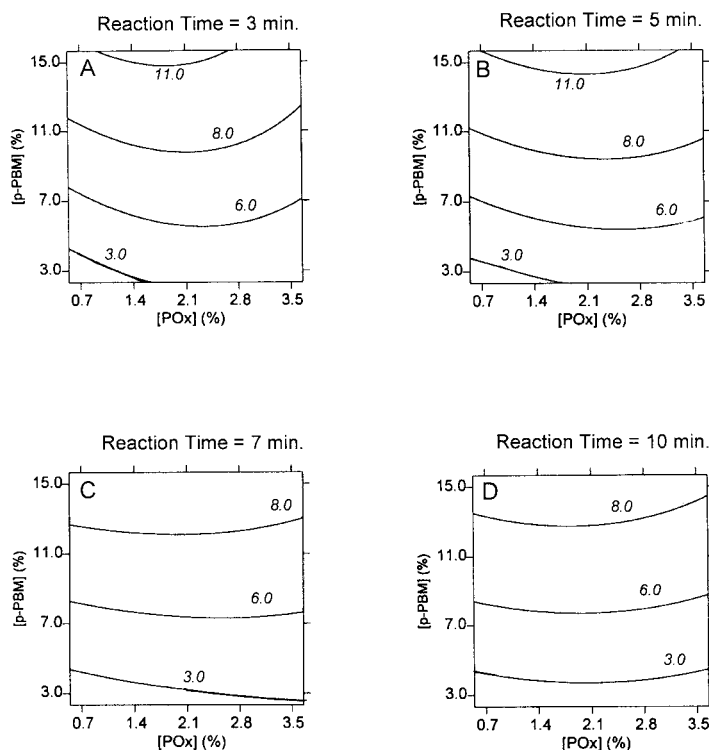


Figure 3 Isoline maps showing the grafting level at the indicated reaction times (3, 5, 7, and 10 min).

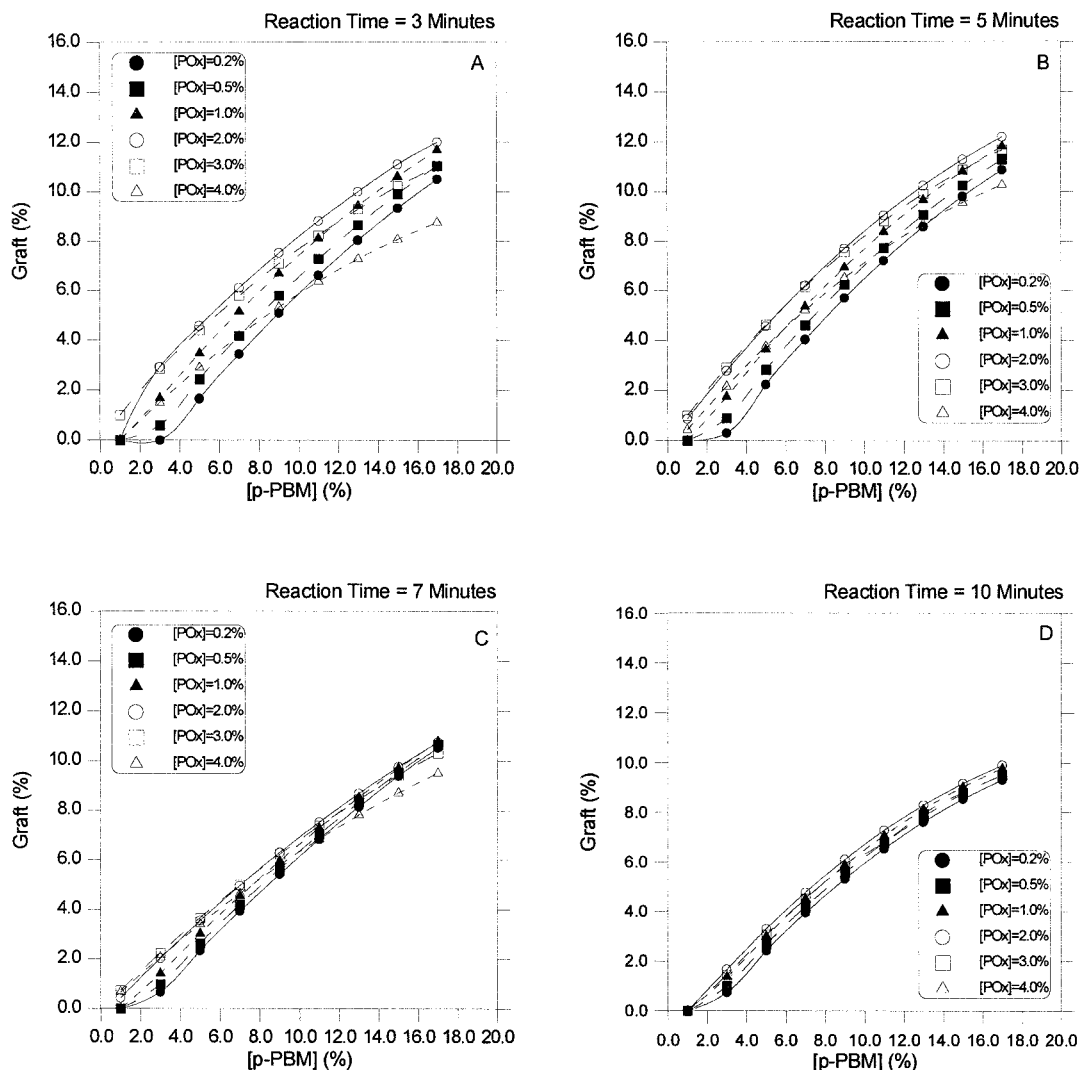


Figure 4 Evolution of the grafting level versus $[p\text{-PBM}]$ at different amounts of initiator and at the indicated reaction times (3, 5, 7, and 10 min).

amounts of *p*-PBM and POx used in the process and for the four different reaction times considered. In all cases, increasing levels of *p*-PBM resulted in higher grafting degrees. The role played by reaction time could also be ascertained by the observation that the highest isoline values in the maps were obtained for the lowest reaction times [Fig. 3(A,B)]. Then, the existence of a critical point for the radical initiator could be clearly appreciated in the nearest 2.1% of [POx], being the more noticeable at shorter reaction times, because of the higher slopes exhibited by the curves.

Influence of reactant concentration and reaction time

Grafting levels obtained from the polynomials shown in Table III are plotted in Figures 4 and 5. These were obtained by variation of the $[p\text{-PBM}]$ or the [POx] and plotted as a function of the [POx] and the $[p\text{-PBM}]$, respectively, present in the reaction media. So, one

plot was obtained for each of the four reaction times (3, 5, 7, and 10 min).

Figure 4(A) displays the grafting level versus $[p\text{-PBM}]$ obtained at 3 min of reaction time. An almost linear increase of grafts with *p*-PBM was observed. Nevertheless, the role played by [POx] was positive until values were close to 2%, but a higher [POx] meant sharp decreases in grafting, which was especially noticeable in the case of 4% POx. As the reaction time increased [Fig. 4(B,D)], the trend of the range of variability of the grafting values was to decrease, at a time that the maximum achievable grafting values also did. This would indicate the negative effect of a high reaction time over the maximum grafting yielding in this kind of processes.^{30–33,35,36} Besides, the critical value of [POx] appeared to be close to 2%.

This fact can be more clearly appreciated in plots of Figure 5, where grafting versus [POx] was plotted for the different amounts of $[p\text{-PBM}]$ and for each fixed

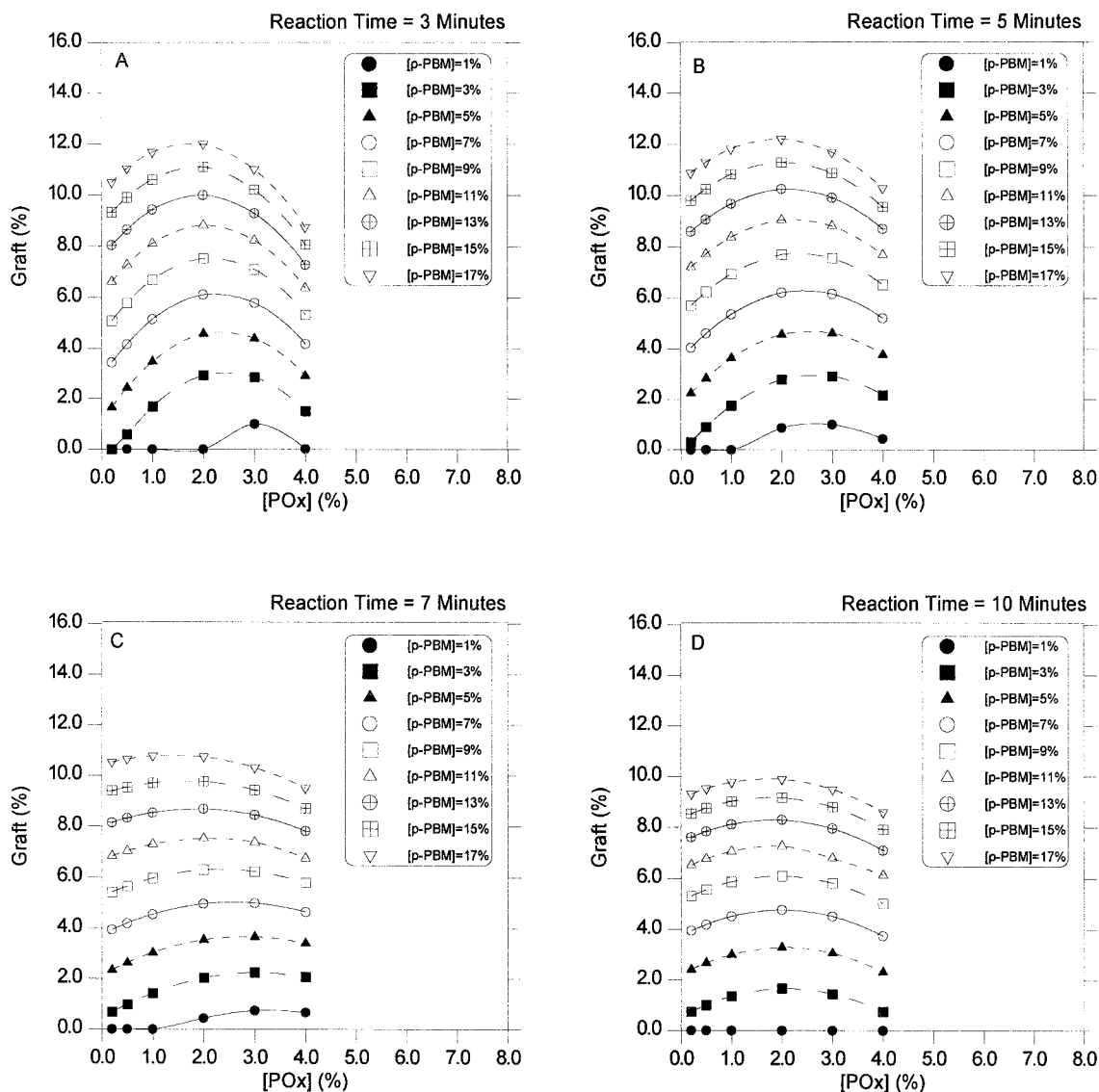


Figure 5 Evolution of the grafting level versus [POx] at different amounts of [p-PBM] and at the indicated reaction times (3, 5, 7, and 10 min).

reaction time. The quadratic evolution of grafting values and the critical point for [POx] located in the surroundings of 2% can be appreciated. The grafting values showed more sensitivity to variations of [p-PBM] when this was low than when this was higher. This was related to the existence of a certain optimum of interfacial area feasible for *p*-PBM as a reactant and agrees with the chemisorption mechanism proposed elsewhere for a similar processes.^{30–36}

Figure 6 shows grafting versus [p-PBM] as a function of reaction time when [POx] was kept constant in the central value of the Box–Wilson experimental design. In this plot, an almost linear response was illustrated, and the highest grafting levels were reached at the two lowest reaction times (3 and 5 min), which were observed before a decay in grafts with reaction time. This agrees with the dynamic process described

by a consecutive reaction scheme as proposed in other works.^{33,34}

Figure 7 plots grafting versus [POx] as a function of reaction time with [p-PBM] kept constant in the central value of the experimental design for this variable. The two shortest reaction times showed the highest slopes for their curves, with the critical point placed into the 2–2.5% interval for POx.

Values for grafting versus reaction time as a function of either [POx] [Fig. 8(A)] or [p-PBM] [Fig. 8(B)] were plotted. Besides the minimum–maximum evolution observed, the unfavorable effect that an excess of [POx] played in the reaction yielding could be ascertained from plots in Figure 8(A). In this sense, values of this variable higher than 3% produced grafting degrees in the same range as 0.2–0.5% of POx and lower than those when the peroxide level was as little

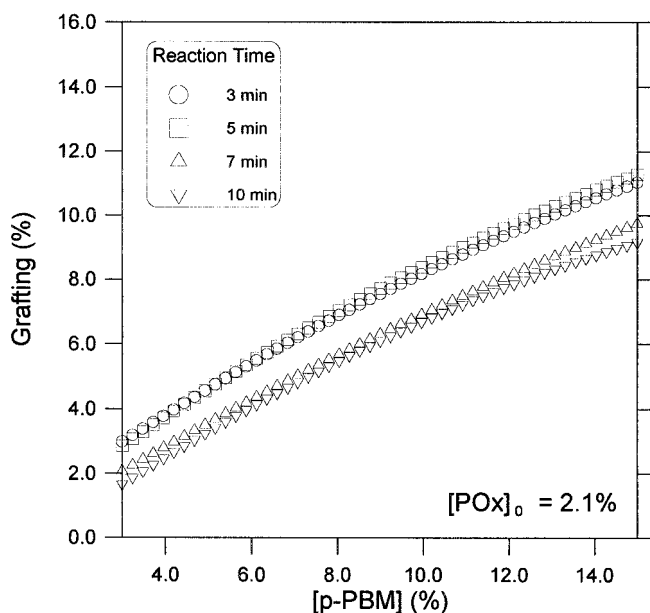


Figure 6 Evolution of the grafting level versus $[p\text{-PBM}]$ when $[\text{POx}]_0 = 2.1\%$, at reaction times of 3, 5, 7, and 10 min.

as 1%. Nevertheless, and as was concluded before, the maximum efficiency of [POx] appeared to be centered around 2%, as was already found for other PP/reactive systems.^{30–36} Also, as shown in Figure 8(B), the quadratic evolution of grafting (typical of transient processes) with time as a function of $[p\text{-PBM}]$ was observed. Besides, a decreasing trend in the separation between the curves corresponding to values of $[p\text{-PBM}]$ between 1 and 17% was found, with these closer each other when $[p\text{-PBM}]$ increased.

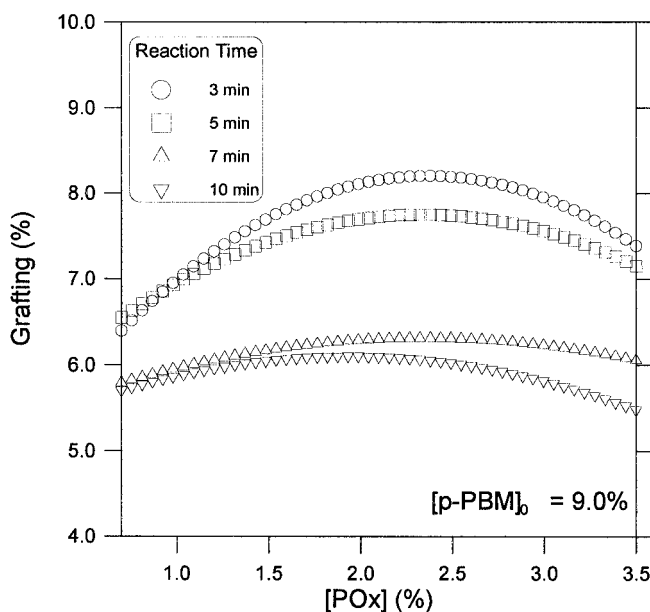


Figure 7 Evolution of the grafting level versus $[\text{POx}]$ when $[p\text{-PBM}]_0 = 9.0\%$, at reaction times of 3, 5, 7, and 10 min.

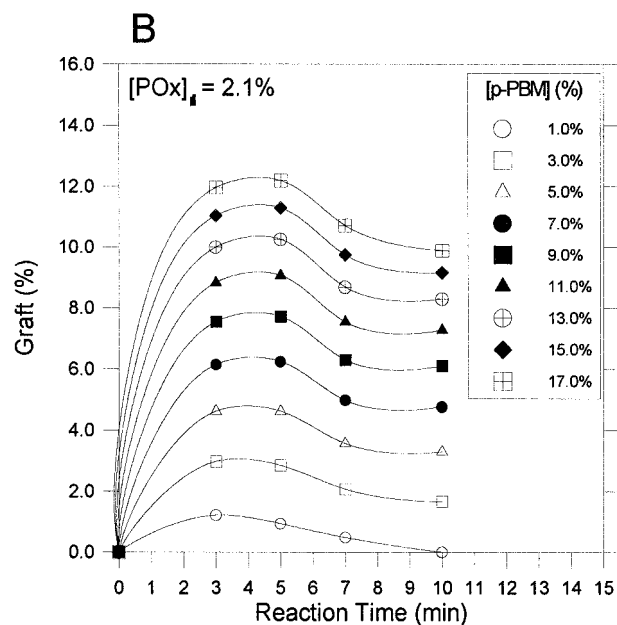
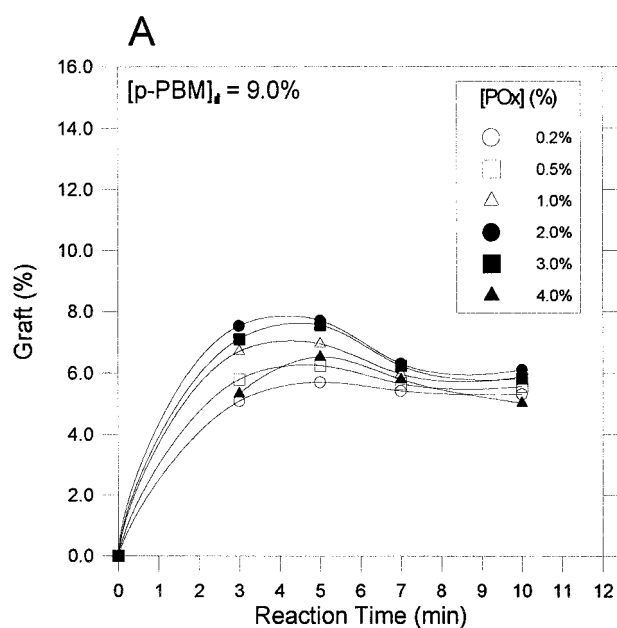


Figure 8 Evolution of the grafting level all along the reaction time (A) for $[p\text{-PBM}] = 9.0\%$ and at different amounts of $[\text{POx}]$ and (B) for $[\text{POx}] = 2.1\%$ and at different amounts of $[p\text{-PBM}]$.

This kind of evolution agrees with the chemisorption phenomena assumed to govern other similar processes, such as the chemical modification of PPs by MAH,^{30–32} and shows the typical pattern of unsteady processes resulting from consecutive reactions.^{31,33,34} Otherwise, the obtention of this family of modified polymers is directed toward their use as interfacial agents in heterogeneous systems based on polymers, and works on this topic will be published later.

CONCLUSIONS

The obtention of a modified polymer suitable for use as interfacial agent to enhance interactions in heterogeneous systems based on polymers, mainly polymer composites and polyblends, was discussed in this article. The quadratic evolution of the reaction yielding with reaction time agreed with the dynamic and then with the complex character of the chemical modification process of a-PP by a polar monomer such as *p*-PBM. In this situation, the Box–Wilson experimental design methodology was a very powerful tool for attempting to model this kind of system and also was very useful for obtaining and discussing the experimental results; otherwise, it would be very difficult to understand because of the inherent transient nature of the chemical modification process of a macromolecular substrate by a low-molecular-weight polar monomer, wherein the polymer governs the overall reaction yielding.

References

1. Wu, S. *Polymer Interface and Adhesion*; Marcel Dekker: New York, 1982.
2. Karger-Kocsis, J. *Polypropylene: Structure, Blends and Composites*; Chapman & Hall: London, 1995.
3. Taranco, J.; Laguna, O.; Collar, E. P. *J Polym Eng* 1992, 11, 315.
4. García-Martínez, J. M.; Laguna, O.; Collar, E. P. *J Polym Eng* 1997, 17, 269.
5. García-Martínez, J. M.; Laguna, O.; Collar, E. P. *J Polym Mater* 1998, 15, 127.
6. García-Martínez, J. M.; Laguna, O.; Areso, S.; Collar, E. P. *J Polym Sci Part B: Polym Phys* 2000, 38, 1564.
7. García-Martínez, J. M.; Laguna, O.; Areso, S.; Collar, E. P. *J Appl Polym Sci* 2001, 81, 625.
8. La Mantia, F. P. *Adv Polym Technol* 1993, 12, 47.
9. Majumdar, B.; Keskula, H.; Paul, D. R. *J Appl Polym Sci* 1994, 54, 339.
10. Datta, A.; Chen, H. H.; Baird, D. G. *Polymer* 1993, 34, 759.
11. García-Martínez, J. M.; Areso, S.; Collar, E. P. *J Macromol Sci Phys* 2001, 40, 387.
12. Collar, E. P.; Marco, C.; Areso, S.; García-Martínez, J. M. *J Macromol Sci Phys* 2001, 40, 369.
13. Natta, G.; Severini, F.; Pegoraro, M.; Tavazzany, C. *Makromol Chem* 1968, 119, 201.
14. Porejko, S.; Gabara, W.; Blazajewitz, T.; Lecka, M. *J Polym Sci Part A-1: Polym Chem* 1967, 5, 1547.
15. Gabara, W.; Porejko, S. *J Polym Sci Part A-1: Polym Chem* 1967, 5, 1563.
16. Minoura, Y.; Ueda, M.; Mizunuma, S.; Oba, M. *J Appl Polym Sci* 1969, 13, 1625.
17. Gaylord, N. G.; Maiti, S. *J Polym Sci Polym Lett Ed* 1969, 124, 269.
18. Gaylord, N. G.; Metha, M.; Kumar, V.; Tazy, M. *J Appl Polym Sci* 1989, 38, 359.
19. de Roover, B.; Sclavons, M.; Cartier, V.; Devaux, J.; Legras, R.; Montaz, A. *J Polym Sci Part A: Polym Chem* 1995, 33, 829.
20. de Roover, B.; Devaux, J.; Legras, R. *J Polym Sci Part A: Polym Chem* 1996, 34, 1195.
21. Sclavons, M.; Cartier, V.; de Roover, B.; Franquinet, P.; Devaux, J.; Legras, R. *J Appl Polym Sci* 1996, 62, 1205.
22. Russell, K. E. *J Polym Sci Part A: Polym Chem* 1995, 33, 555.
23. Russell, K. E.; Kelusky, E. C. *J Polym Sci Part A: Polym Chem* 1988, 26, 2273.
24. Xu, G.; Lin, S. *J Macromol Sci Rev Macromol Chem Phys* 1994, 34, 555.
25. Jois, Y. H. R.; Harrison, J. B. *J Macromol Sci Rev Macromol Chem Phys* 1996, 36, 433.
26. Naqui, M. K.; Choudhary, M. S. *J Macromol Sci Rev Macromol Chem Phys* 1996, 36, 601.
27. Moad, G. *Prog Polym Sci* 1999, 22, 81.
28. García-Martínez, J. M.; Taranco, J.; Laguna, O.; Collar, E. P. *Int Polym Proc* 1994, 9, 246.
29. García-Martínez, J. M.; Taranco, J.; Laguna, O.; Collar, E. P. *Int Polym Proc* 1994, 9, 304.
30. García-Martínez, J. M.; Laguna, O.; Collar, E. P. *J Appl Polym Sci* 1997, 65, 1333.
31. García-Martínez, J. M.; Laguna, O.; Collar, E. P. *J Appl Polym Sci* 1998, 68, 483.
32. García-Martínez, J. M.; Areso, S.; Laguna, O.; Collar, E. P. *Macromolecules*, submitted.
33. García-Martínez, J. M.; Areso, S.; Laguna, O.; Collar, E. P. *Macromolecules*, submitted.
34. García-Martínez, J. M.; Areso, S.; Laguna, O.; Collar, E. P. *J Appl Polym Sci* 1998, 70, 689.
35. García-Martínez, J. M.; Cofrades, A. G.; Laguna, O.; Areso, S.; Collar, E. P. *J Appl Polym Sci* 1998, 69, 931.
36. García-Martínez, J. M.; Cofrades, A. G.; Laguna, O.; Areso, S.; Collar, E. P. *Eur Polym J* 2000, 36, 2253.
37. Bellamy, L. J. *The Infra-Red Spectra of Complex Molecules*; Methuen: London, 1966.
38. Conley, R. T. *Infrared Spectroscopy*; Allyn & Bacon: Boston, 1972.
39. Gaylord, N. G.; Mehta, R.; Kumar, V.; Tazy, M. *J Appl Polym Sci* 1989, 38, 359.
40. ASTM Standard D 1045; American Society for Testing and Materials: West Conshohocken, PA, 1996.
41. Fisher, R. A. *The Design of Experiments*; Hafner: New York, 1960.
42. Box, G. E. P.; Hunter, W. G.; Hunter, J. S. *Statistics for Experimenters*; Wiley: New York, 1978.
43. Ross, S. M. *Introduction to Probability Models*; Academic: San Diego, 1993.