Grafting of *P*-Phenylen-bis-Maleamic Acid into Polypropylene in Melt

J. M. GARCÍA-MARTÍNEZ, A. G. COFRADES, S. ARESO, O. LAGUNA, E. P. COLLAR

Departamento de Física e Ingeniería de Polímeros, Instituto de Ciencia y Tecnología de Polímeros, C.S.I.C., C/Juan de la Cierva 3, 28006 Madrid, Spain

ABSTRACT: The determination of the influence of the reaction conditions on chemical modification yielding of polypropylene by a polar monomer (*p*-phenylen-bis maleamic acid) in melt by using a Box–Wilson experimental design is the main goal of this article. The following 4 independent variables were considered to be mainly affecting the process, initial concentration of reactants (polar monomer and peroxide), gear rate, and reaction time in a batch reactor. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 931–939, 1998

Key words: chemical modification; polypropylene; *p*-phenylen-bis-maleamic acid; experimental design; reactive processing

INTRODUCTION

Works on the topic of chemical modification of polyolefins, and particularly polypropylene, looking for a certain degree of polarity in the macromolecular substrate, have been broadly published. Interest in these kinds of products would be as compatibilizers in polymer composites[1–5] and polyblends.[6–10]

The polar monomer in most of those studies was maleic anhydride (MAH), and many attempts to explain the reaction mechanism have been made.[11–22] First, studies by authors of this article were conducted by using this same monomer,[23,24] and an interfacial phenomenon has been proposed recently as being mainly responsible for the reaction yielding.[25]

Because of the high complexity of the characterization of the reaction product on a macromolecular reactant, classical random planning works considering different kinds of peroxides and very high reaction times, among other variables acting on the system, gave opposite results when compared with one another. This seemed to indicate that some important aspect of the problem was not taken into account when the studies were undertaken. In these terms, the use of the Box–Wilson statistical experiment design method showed that results obtained have to be carefully evaluated when trying to establish the real evolution of the system and to find the interactions between variables acting on the process.[23–26]

In an attempt to check the proposed mechanism in which the main role of the grafting reaction are played by the polyolefin nature and the reaction time, the polar monomer to be grafted into the polymer, in this article, was *p*-phenylen-bis-maleamic acid (*p*-PBM).

On the other hand, and from an applied point of view, a new grafted polypropylene ready to be used as an interfacial modifier in a heterogeneous systems based on this polyolefin would be obtained.

EXPERIMENTAL

Materials

Polypropylene used in this work was a commercial-grade Isplen 050 (Repsol Química). Table I

Table I   Properties of ISPLEN 050 Polypropylene

| Molecular Weight | | HI | Melt Index | | | HDT | DSC (J/g); (°C) | | | | Density |
			Conditions								
M_w	M_n	(M_w/M_n)	T (°C)	P (Kg)	(g/10 m)	(°C)	ΔH_m	T_m	ΔH_c	T_c	(g/cm^{-3})
334,400	59,500	5.62	190	5.00	5, 80	58.5	56.4	164	−51.8	123	0.90

compiles Isplen 050 properties. Reactives used in the synthesis of p-PBM are listed in Table II.

A dycumile peroxide named Perkadox BC (AKZO) was used as initiator in the modification process. Thermal stabilizers used were Irganox 1010 and B225. For washing operations, xylene (PANREAC) and dimethyl-formamide (Scharlau/FEROSA) were used.

Procedures

The p-PBM acid was obtained by following the general way of bismaleimide obtention, but working below 10°C, avoiding the formation of bis-maleimide once the bismaleamic acid was obtained.[27−29]

The general reaction scheme for the obtention of p-PBM would be as follows:
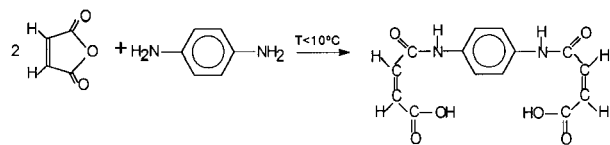
A yellow powder corresponding to the acid was obtained, and once recovered, was ready to be used as a modifier monomer.

Table II   Reactives Used at p-Phenylen-Bis-maleamic Acid Synthesis

Reactive	Supplier	Remarks
Maleic anhydride	Fluka	99% pure
n-Phenylen diamine	Merck	99% pure
Chloroform	Quimicen	99.8% extra pure
N-N-Dimethyl formamide	Scharlau (FEROSA)	99% pure
Nitrogen	Argón S.A.	inert gas

The modification of the polymer was conducted in a mixing chamber Rheomix 600 attached to a driver unit Rheocord 90 (Haake) working at 190°C as a set temperature. The other variables were set

Table III   Box–Wilson Experimental Work Sheet Followed and Grafting Level Obtained in the Present Work

| | Controlled Factors | | | | |
Exp. Nr.	[POx] (%)	[p-PBM] (%)	Time (min)	Rate (r.p.m.)	Grafting (%)
1	1.0	3.50	8	50	1.52
2	1.0	10.00	8	50	4.71
3	3.0	3.50	8	50	1.21
4	3.0	10.00	8	50	3.04
5	1.0	3.50	20	50	1.49
6	1.0	10.00	20	50	1.50
7	3.0	3.50	20	50	1.49
8	3.0	10.00	20	50	2.73
9	1.0	3.50	8	100	0.76
10	1.0	10.00	8	100	3.04
11	3.0	3.50	8	100	0.76
12	3.0	10.00	8	100	1.50
13	1.0	3.50	20	100	1.49
14	1.0	10.00	20	100	2.28
15	3.0	3.50	20	100	0.91
16	3.0	10.00	20	100	2.28
17	2.0	0.25	14	75	0.15
18	2.0	13.25	14	75	2.99
19	0.0	6.75	14	75	0.91
20	4.0	6.75	14	75	1.67
21	2.0	6.75	2	75	2.88
22	2.0	6.75	26	75	2.28
23	2.0	6.75	14	25	2.28
24	2.0	6.75	14	125	2.28
25	2.0	6.75	14	75	2.28
26	2.0	6.75	14	75	2.28
27	2.0	6.75	14	75	2.73
28	2.0	6.75	14	75	2.58
29	2.0	6.75	14	75	2.73
30	2.0	6.75	14	75	2.58
31	2.0	6.75	14	75	2.28
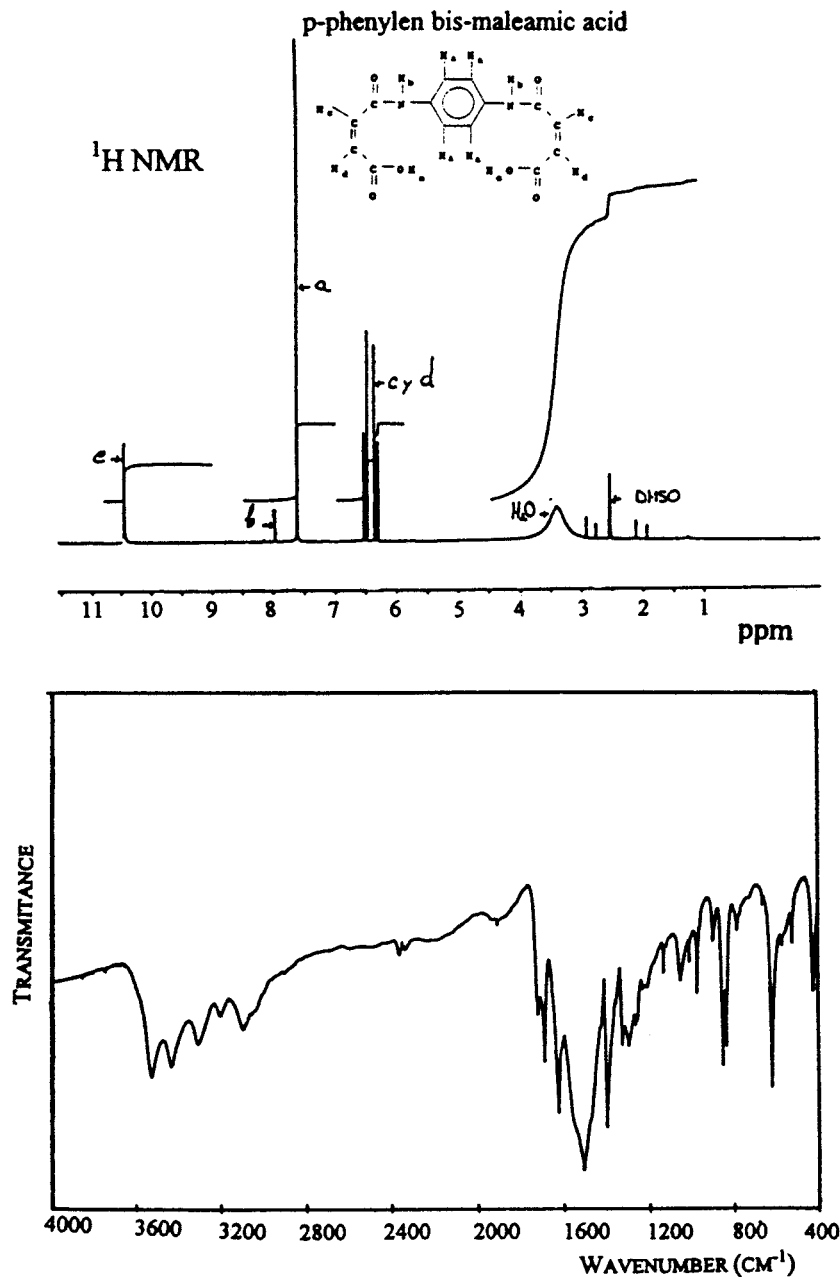
Figure 1 ¹H-NMR and FTIR spectra of *p*-phenylen-bis-maleamic acid (p-PBM).

up by following the 4 independent variables from the Box-Wilson experimental work sheet (Table III). The operation mode was as follows. First, polypropylene, *p*-PBM, and thermal stabilizers (0.1%) were introduced into the reactor. Then (after 2–3 min) when molten, the temperature again reached set conditions, and torque values were stabilized (indicating a good homogeneization of all reactants), then peroxide was introduced, starting the reaction time. Once the reaction time elapsed, the chamber was opened, and the reaction product was recovered into an ice bath.

Once washed in boiling xylene (30 min) and with further addition of *N,N*-dimethylformamide in order to remove unreacted acid, the solution was precipitated onto methanol; and after filtered and dried, the grafted polymer was ready to be characterized.

Modifier Monomer and Grafted Polymer Characterization

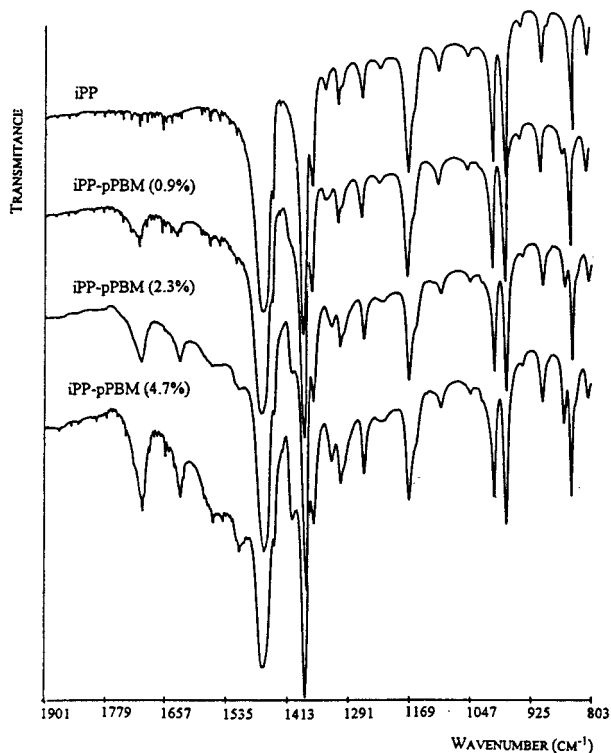The *p*-phenylen-bismaleamic acid (*p*-PBM) was first characterized by using an EA 1108-Elemen-

Figure 2 FTIR spectra of iPP and grafted p-PBM samples [iPP–pPBM $(X\%)$] containing different amounts of grafting ($X\% = 0.9$, 2.3, and 4.7).

tal Analyzer (Carlo Erba Instruments), and the results obtained (49.9% C, 4.7% H, 36.86% O) agreed with the expected values. Further characterization was performed by ^{1}H nuclear magnetic resonance (NMR) (Bruker AM-200) and by Fourier transform infrared (FTIR) spectroscopies (Nicolet 520). Figure 1 shows both spectra where characteristics signals have been pointed at.

FTIR qualitative characterization of the modified polymer was performed on a Nicolet 520 spectrophotometer working at 32 scans and $2\,\mathrm{cm}^{-1}$. As an example, Figure 2 shows the spectra of grafted polymers at different modification levels.

The grafting level on modified polypropylene was determined by a hot titration method. Then, 1 g of modified sample was put for 60 minutes in 150 mL of refluxing xylene–n-butyl alcohol–water mixture. The carboxilic acid groups in the solution were neutralized by addition of an excess of $0.05N$ ethanolic potasse, using thymol blue as an indicator. An excess of potasse meant a deep blue color in the solution that was back-titrated to a yellow end point by the addition of $0.05N$ isopropanolic HCl to the hot solution. Expressions used to determine the modification level were as follows:

$$\text{Acid Nr} \cdot (\text{mg}_{\text{KOH}}/\text{gpolym})$$

$$= \frac{\text{mL}_{\text{KOH}} \cdot N_{\text{KOH}} \cdot 56.1}{\text{g}(\text{polym})} \quad (1)$$

$$\text{Grafting}\,(\%) = \frac{\text{Acid Nr} \cdot 304}{2 \cdot 561} \quad (2)$$

where the term mL_{KOH} is the net amount of KOH used by the titration ($V_{\text{KOH}} - V_{\text{HCl}}$).

Table IV Coefficients and Fit Parameters of Response Surface Polynomials[a]

	Coefficient	Term	Standard Error	t Value	Confidence Factor (%)
Independent term	0.2536	1 (constant)	1.957	0.1296	20.6
Linear terms	2.684	[POx]	0.6216	4.319	99.9
	0.2975	[p-PBM]	0.1926	1.545	85.8
	−0.1763	time	0.1068	1.651	88.5
	−0.01184	rate	0.0274	0.4316	34.6
Interaction terms	−0.02292	[POx] $\times$ [p-PBM]	0.0359	0.6385	45.6
	−0.04992	[POx] $\times$ time	0.0194	2.567	98.5
	−0.002480	[POx] $\times$ rate	0.0047	0.5313	39.8
	0.01356	[p-PBM] $\times$ time	0.0060	2.267	97.0
	−0.000898	[p-PBM] $\times$ rate	0.0014	0.6256	44.9
	0.001847	time $\times$ rate	0.0008	2.374	97.6
Quadratic terms	−0.2321	[POx]^2	0.0873	2.659	98.8
	−0.02908	[p-PBM]^2	0.0083	3.519	99.8
	0.000844	time^2	0.0024	0.3482	30.4
	−0.000071	rate^2	0.0001	0.5111	38.7

[a] Polynomial Equation: $y = a_0 + a_1 x_1 + a_2 x_2 + a_3 x_3 + a_4 x_4 + a_5 x_1 x_2 + a_6 x_1 x_3 + a_7 x_1 x_4 + a_8 x_2 x_3 + a_9 x_2 x_4 + a_{10} x_3 x_4 + a_{11} x_1^2 + a_{12} x_2^2 + a_{13} x_3^2 + a_{14} x_4^2$, where $x_1 = [\text{POx}]\,(\%)$, $x_2 = [p\text{-PBM}]\,(\%)$, $x_3 = \text{time}\,(\text{min})$, $x_4 = \text{rate}\,(\text{rpm})$.

Table V   Analysis of Variance (ANOVA) for the Box–Wilson Experimental Design Run

Source	Freedom Degree	Sum Square	Square Mean	F-Ratio
Total				
(corrected)	30	25.2781		
Regression	14	21.7925	1.55661	
Residual	16	3.4856	0.21785	7.145
Lack of fit	10	3.2913	0.32913	
Pure error	6	0.1943	0.03238	10.164

RESULTS AND DISCUSSION

Modification levels obtained in the chemical modification process are compiled in Table III. As mentioned before, infrared spectra (IR) corresponding to some of the modified polymers have been plotted in Figure 2. The presence of two bands in the neighborhood of 1700 and 1600 cm^{-1}, corresponding to carbonyl and amide groups, respectively, can be clearly observed, and then the presence of grafted bismaleamic acid was concluded.

Grafting Level, Polynomial Fits, and Analysis of Variance

Grafting levels from Table III were fitted to a quadratic model following the surface response method.[30]

Table IV compiles the polynomial coefficients and the statistical parameters obtained from those fits. The $\langle r^2 \rangle$ value was 0.8621, which is very good for a quadratic model. Regarding the level of statistical significance of the polynomial terms, it can be seen that linear term in peroxide [POx], interaction terms of time with either [POx], [*p*-PBM]; or gear rate, and the quadratic term of (POx) are showing to be statistically significant above 95% (*t* value higher than 2).[30–32] Also, the [*p*-PBM] term is significant above this confidence factor. Analysis of variance (ANOVA), results have been listed in Table V. The F-ratio, obtained as a ratio between square mean of the lack of fit and residuals, is informing, that with a confidence factor of 99.9%, the polynomial terms are nonzero. The same parameter obtained as the ratio between the lack of a fit square mean and the correspondent to the pure error from the replications of the model explains that there is only a 1.4% lack of fit due to other factors having influence and not considered by the model. In other words, the predictions obtained from the response surface satisfy the evolution of the grafting level of *p*-PBM onto iPP in the experimental space scanned. Then the system can be studied from the isoline map generated by the polynomial equation.

Evolution of the System: Isoline Maps

In Figure 3, the isoline grafting level map when varying [POx] and [*p*-PBM], keeping a constant (in their central values) time of reaction (14 minutes) and gear rate (75 rpm), can be observed. A typical evolution on rising is that the ridge becomes narrower when a [POx] and [*p*-PBM] increase can be clearly seen. Furthermore, the ridge has at least two different slopes, as can be deduced from the distances between isolines. One of them, the highest, would be placed at the lowest concentration region -[*p*-PBM] and [POx]- up to their mean values. Isolines here are closer to each other than in the other regions of the map.

The parabolic shape showed by the isolines means the existence of a maximum for any set of reaction conditions in terms of concentration; afterwards, significant decreases on reaction yielding would be obtained.

The evolution of the grafting isolines when varying (A) [POx], (B) [*p*-PBM], and (C) gear rate as the first independent variable (*x*-axis), and with the reaction time being the second one, are plotted in Figure 4. When map A is observed, where the reaction time versus [POx] has been represented for a constant level of *p*-PBM and gear rate (6.75% and 75 rpm, respectively), a noncentered minimax evolution for grafting level isolines is found. This causes the isoline values to rise when the POx level does and is more when the POx value is higher, with the
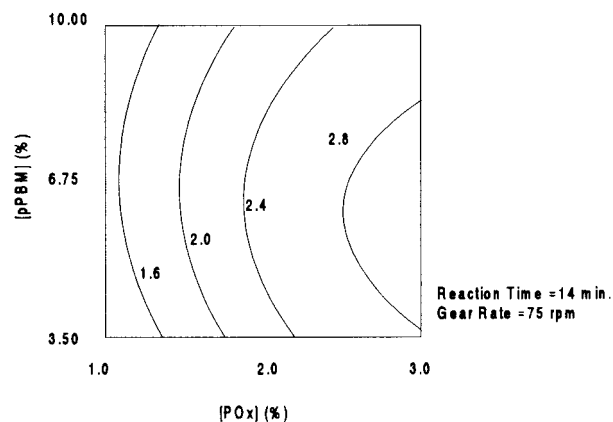

Figure 3 Grafting level of p-PBM isolines plotted as a function of initial [p-PBM] versus [POx] concentrations.
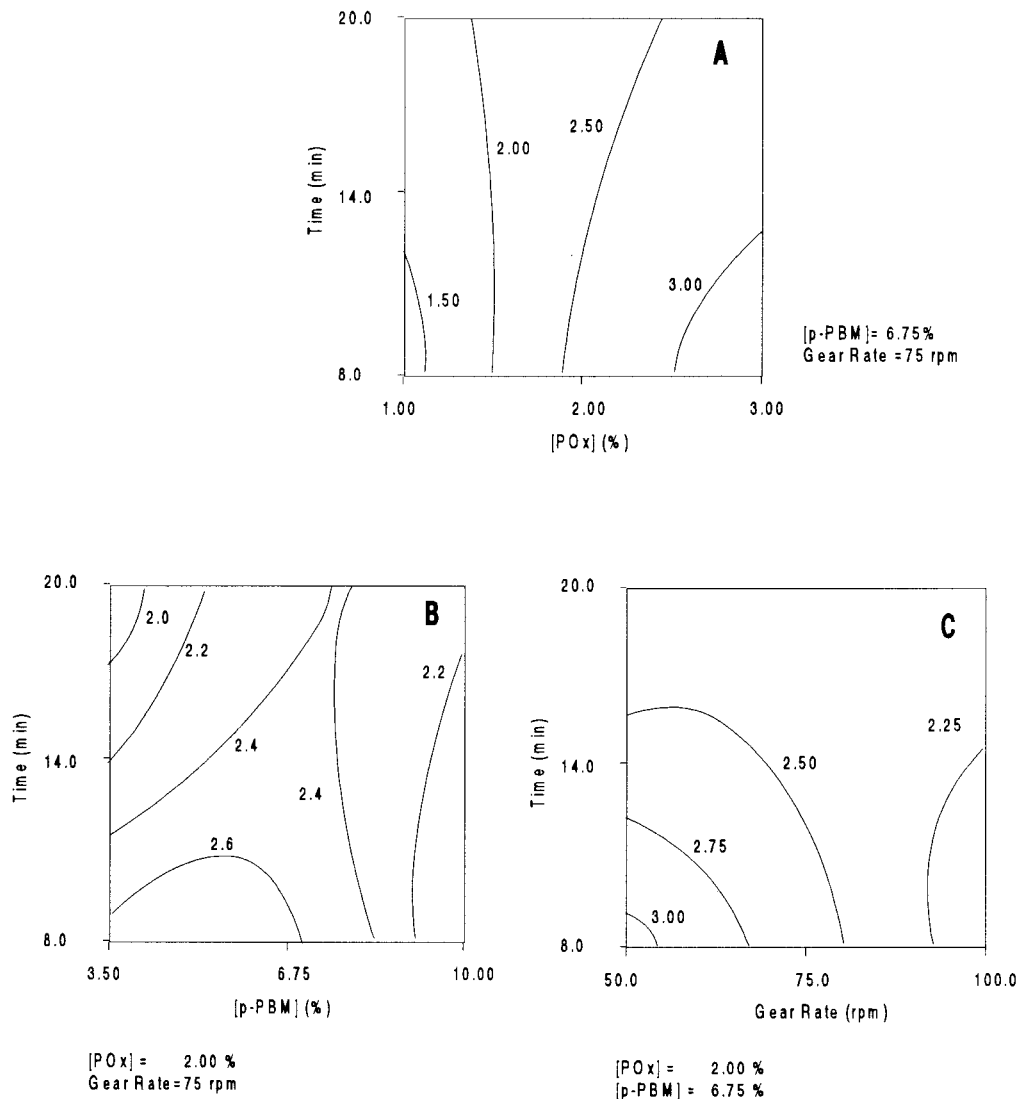
Figure 4   Grafting level of p-PBM isolines plotted as a function of reaction time versus (A) initial concentration of peroxide, (B) p-phenylen-bis-maleamic acid, and (C) gear rate.

nonpositive effect played for reaction time being noticeable, and is worse when the [POx] is the higher. This effect is similar to that found in previous works when the grafted group was succinic anhydride.[23-26]

In the same sense, when the reaction time versus [p-PBM] (plot B) is represented, the values of [POx] keeping constant (2%) and gear rate (75 r.p.m.), the grafting level isolines show a descendent ridge evolution as the maximum, where the highest grafting levels are located noncentered at the experimental region scanned, which means that the region of low reaction time and [p-PBM] values are below 6.75%.

These results coincide fully with previous work in our group.[23-26] In other words, it can be assumed that an excess of polar monomer plays an unfavorable effect in the graft yielding. When plotted, as seen in Fig. 4; map (C), the reaction time versus the gear rate ([POx], 2%; [p-PBM], 6.75%; constant) it can be clearly seen that the highest stirring rates mean an unfavorable effect for the obtainment of high grafting levels.

So, high gear rates are not useful, not only for economy, in terms of saving process energy, but for lower reaction yielding too. The fact is that, again, the zone of lower reaction time, which leads to a better yielding in the process, appears to be relevant and suggests the undertaking of a study
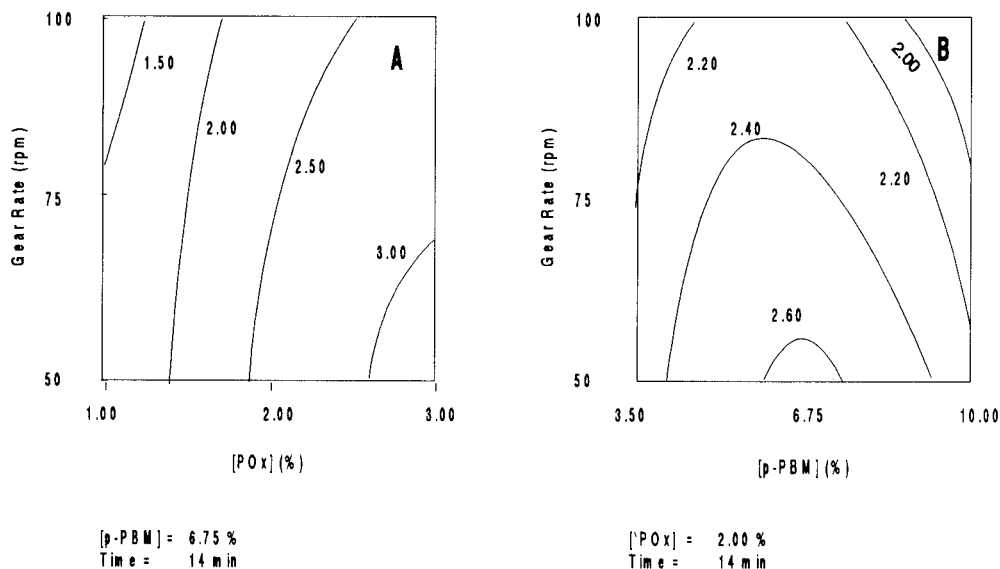
Figure 5 Grafting level of p-PBM isolines plotted as a function of gear rate versus (A) peroxide and (B) *p*-phenylen-bis-maleamic acid.

of the evolution of the system at a lower reaction time. Future work will deal with this aspect of the problem.

This unfavorable effect played for a high gear rate is confirmed on plots in Figure 5, which show isoline maps representing gear rate versus (A) [POx] and (B) [*p*-PBM], respectively, at the indicated constant values of other two independent variables. In Fig. 5(A), an almost negligible effect that the increases in gear rate values play in the final reaction yielding when [POx] is low can be observed. However, as soon as the central value is surpassed, the distance between isolines increases asymmetrically, and the incipient curvature on the 1.5 and 2.0 isolines becomes significant at 2.5 and 3.0 isolines. This means a decrease in the favorable effect caused by a higher POx degree when the gear rate increases, and it does it more rapidly when the gear rate is higher.

This agrees with the negative value of coefficient in the polynomial fit (Table IV). Besides, these plots exhibit a clearly noticeable evolution far from the optimum conditions, as mentioned before in Figure 3, because the high value of reaction time considered (14 min). In future works, a study considering the lower reaction time will be performed in order to determine optimized processing conditions.

Map (B) in Figure 5 confirms the above-mentioned results, as well as the fact that the optimum gear rate is placed near 50 rpm. As mentioned before, higher values of the gear rate would play a negative effect in the reaction yielding. The latter would indicate the convenience to set the gear rate and not be considered as an independent variable in future studies. As a summary of foregoing results, plots in Figure 6 illustrate the above-mentioned by showing the favorable effect on the grafting level played for dycumile peroxide (A); the initially favorable effect, until reaching a maximum, and then the unfavorable effect played for the level of *p*-phenylen-bis-maleamic acid (B); the clearly counterproductive role played for high times of reaction (C); and high gear rates (D). Each plot in Figure 6 has been built up by varying one of the independent variables and by considering the other 3 independent variables as a constant in their central values of the experimental design.

Future work will deal with the behavior of this system at lower times of reaction by a Box-Wilson design with 2 independent variables performed at different times of reaction in order to maximize the grafting level onto modified polyolefins.

CONCLUSION

The possibility of obtaining a new modified polypropylene containing *p*-PBM grafted groups is clearly concluded from the results discussed here.

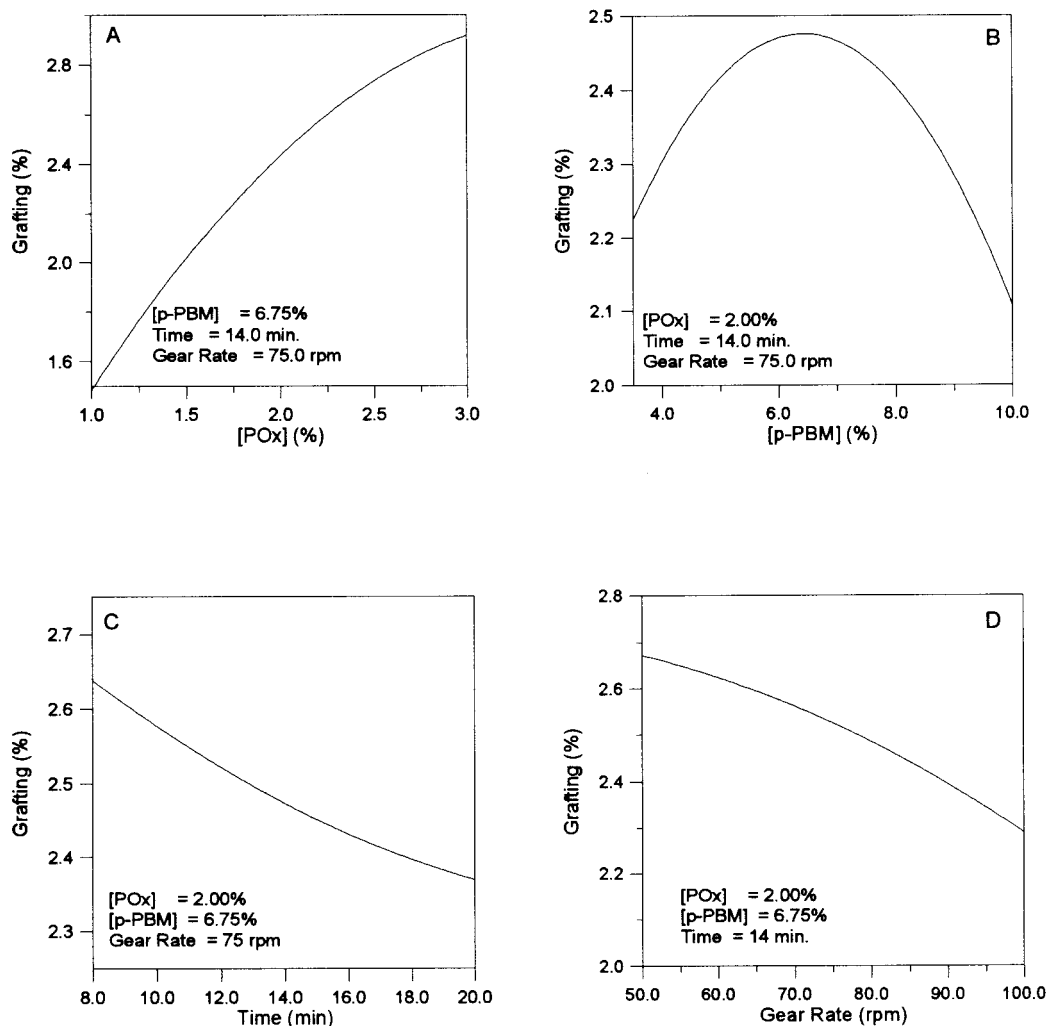The Box-Wilson experimental method has dem-

Figure 6 Evolution of the grafting level with each one of the independent variables having influence on the process remained constant at each plot, the other 3 indicated.

onstrated to be a very useful tool in order to explain the influence of the process conditions in the chemical modification reaction yielding. From this study, the negative effects of high gear rates can be concluded. This is in good agreement with the existence of an optimum in the degree of surface modification in the polymer, yielding the maximum grafting level. The fact that reaction time plays a very important role in the modification yielding is also confirmed because low values for this variable appear to conduct at higher levels of functionalization. This fact would be an advantage from the point of view of a further obtainment of these additives by a continuous process of reactive extrusion.

REFERENCES

1. J. Taranco, J. M. García-Martínez, O. Laguna, and E. P. Collar, *J. Polym. Eng.,* **13,** 287 (1994).
2. J. Taranco, O. Laguna, and E. P. Collar, *J. Polym. Eng.,* **11,** 359 (1992).
3. J. Taranco, O. Laguna, and E. P. Collar, *J. Polym. Eng.,* **11,** 325 (1992).
4. J. Taranco, O. Laguna, and E. P. Collar, *J. Polym. Eng.,* **11,** 335 (1992).
5. E. P. Collar, J. M. García-Martínez, O. Laguna, J. Taranco, *J. Polym. Mat.,* **13,** 111 (1996).
6. F. Ide and A. Hasegawa, *J. Appl. Polym. Sci.,* **18,** 963 (1972).
7. M. Xhantos, *Polym. Eng. Sci.,* **28,** 1392 (1988).
8. S. Hosoda, K. Kojima, Y. Kanda, and M. Aoyagi, *Polym. Network Blends,* **1,** 51 (1991).
9. T. Nishio, Y. Suzuki, K. Kojima, and M. Kakugo, *Kobunshi Ronbunshu,* **47,** 331 (1990).

10. S. Cimmino, C. Mancarella, E. Martuscelli, R. Palumbo, and G. Ragosta, *Polym. Eng. Sci.,* **24,** 48 (1984).

11. S. Porejko, W. Gabara, T. Blazejewitz, and M. Lecka, *J. Polym. Sci.,* **A1,** 1547 (1967).

12. W. Gabara and S. Porejko, *J. Polym. Sci.,* **A1,** 1553 (1967).

13. F. Ide, K. Kamade, and A. Hasegawa, *Kobunshi Kagaku,* **25,** 107 (1968).

14. N. G. Gaylord and M. Mehta, *J. Polym. Sci.,* **20,** 481 (1992).

15. N. G. Gaylord and M. K. Mishra, *J. Polym. Sci., Polym. Lett. Ed.,* **21,** 23 (1983).

16. N. G. Gaylord, M. Mehta, and R. Metha, *J. Appl. Polym. Sci.,* **23,** 2549 (1987).

17. N. G. Gaylord and R. Mehta, *J. Appl. Polym. Sci.,* **26,** 1189 (1988).

18. N. G. Gaylord, R. Mehta, V. Kumar, and M. Tazy, *J. Appl. Polym. Sci.,* **38,** 389 (1989).

19. C. J. Wu, C. U. Chen, G. Woo, and J. F. Kuo, *J. Polym. Sci., Polym. Chem.,* **31,** 3045 (1993).

20. V. Khunova and Z. Zamersky, *Polym. Plast. Technol. Eng.,* **32,** 289 (1993).

21. V. Koul, S. K. Guha, and V. Choudharq, *Polym. Int.,* **30,** 411 (1993).

22. A. Priola, R. Bongiovanni, and G. Gozzelino, *Eur. Polym. J.,* **9,** 1047 (1994).

23. J. M. García-Martínez, J. Taranco, O. Laguna, and E. P. Collar, *Int. Polym. Proc.,* **9,** 246 (1994).

24. J. M. García-Martínez, J. Taranco, O. Laguna, and E. P. Collar, *Int. Polym. Proc.,* **9,** 304 (1994).

25. J. M. García-Martínez, O. Laguna, and E. P. Collar, *J. Appl. Polym. Sci.,* **65,** 1333 (1997).

26. J. M. García-Martínez, O. Laguna, and E. P. Collar, *J. Appl. Polym. Sci.,* to appear (1998).

27. C. Elgorriaga, E. Fernández-Alvárez, and O. Nieto, *An. Quím.,* **75,** 317 (1979).

28. D. Tsiurvas and C. M. Paleos, *J. Appl. Polym. Sci.,* **38,** 257 (1989).

29. M. S. Jacovic, J. Djonlagic, W. J. Macknight, and R. W. Lenz, *Polym. Eng. Sci.,* **25,** 751 (1985).

30. S. M. Ross, *Introduction to Probability Models,* Academic Press, San Diego, 1993.

31. G. E. P. Box, W. G. Hunter, and J. S. Hunter, *Statistics for Experimenters,* John Wiley, New York, 1978.

32. S. M. Ross, *Introduction to Probability and Statistics for Engineers and Scientist,* John Wiley, Singapore, 1987.