

Functionalization of Atactic Polypropylene by Succinyl-Fluorescein: A Two-Step Process of Chemical Modification in the Melt

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ABSTRACT: Chemical modification of an industrial waste (atactic polypropylene) using a two-step process to obtain a fluorescent-modified polyolefin is the subject of this article. For these purposes, a Box–Wilson statistical experimental design has been used. The product was obtained by a condensation reaction after a previous one *via* a radical reaction had taken place in the melt. Furthermore, the nature of this product reveals that only single succinic anhydride groups were previously grafted onto polymers coming from the previous radical reaction. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 689–696, 1998

Key words: two-step functionalization; atactic polypropylene; polymer waste; molten state; condensation; fluorescence

INTRODUCTION

Functionalization of polymers—especially polyolefins—has proven to be a very good way to improve the properties that limit their commercial value. Those functionalized polymers have been widely used as interfacial agents in composite materials and/or compatibilizers in polymer blends.^{1–8}

Industrial production processes of commercial polypropylenes (PPs) imply the generation of atactic PP (a-PP), as a byproduct, with almost no commercial value (~ 10% of the industrial PP produced all over the world). This aspect makes the waste very attractive for chemical modification to make it useful for industrial and/or scientific applications.

First, works in our group dealt with the modification of isotactic PP (iPP),^{9–11} and recently a-PP^{12–14} by maleic anhydride (MAH). From the

last studies—performed on a-PP—the hypothesis that MAH enters the polymer backbone as single succinic units was suggested.^{12,13} Many works in the literature conducted either on model compounds^{15–17} or polymers (PE^{18,19} and i-PP^{10,20}) also supported that idea. However, recent articles in the literature^{21–23} suggested grafting of poly-succinic anhydride.

The condensation reaction occurring between resorcinol and single succinic groups^{24–27} (previously bonded in the macromolecule) lead to the conclusion of the nonexistence of polysuccinic anhydride grafted into PPs chemically modified in the melt. From this, a new family of fluorescent additives,²⁸ that has proven to be efficient as an interfacial modifier in PP-based composites,²⁹ has emerged.

EXPERIMENTAL

Materials

a-PP, supplied as an industrial waste, was from Repsol Química; MAH was from Scharlau

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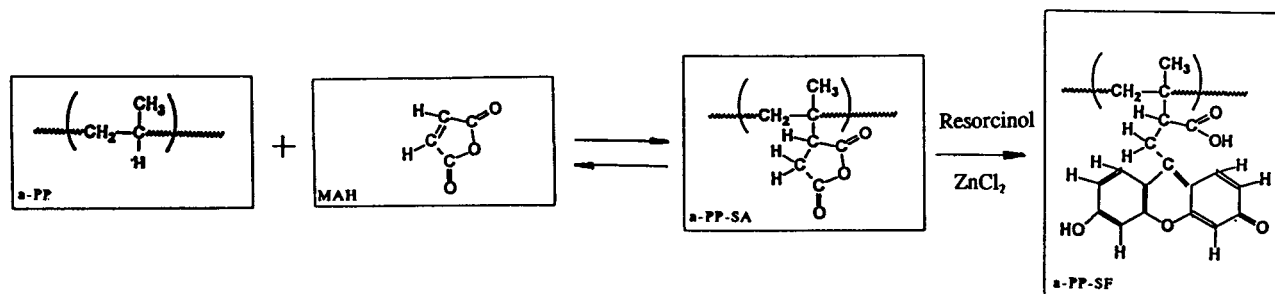


Figure 1 Reaction scheme of the two-step modification process.

(FEROSA); and the initiator dicumyl peroxide “Perkadox BC” was from Akzo. The second step of the reaction required the use of resorcinol (Fluka) as a condensation reactant and $ZnCl_2$ (Quimicen) as a catalyst.

Procedures

A set of experiments based on a Box–Wilson statistical design for two independent variables has been used in this work.

The two-step chemical modification process took place in a mixing chamber Rheomix 600 as a reactor attached to a drive unit and microprocessor Rheocord 90 from Haake. Temperature was set up at $140^\circ C$ due to the inherent nature of the material. Gear rate was set up at 45 rpm (determined in previous works^{10–12}). The first step was a chemical reaction between a-PP and [MAH] in the presence of thermal stabilizers^{10–12} to minimize the parallel degradation reactions. A succinic anhydride-grafted modified polymer (a-PP-SA) was then obtained. In this first step, the time of reaction was fixed to 10 min and after that the second reaction step started once resorcinol was added to the reactor—in a resorcinol/initial [MAH] = 2/1 molar ratio—and the medium was homogenized. Then, the catalyst was put into the batch. This moment was considered as zero time for the condensation reaction that took place during the following 5 min. When the reaction ended (5 min), the reactor was opened and a colored polymer was recovered in an ice bath. The obtained polymer was washed in a solution of boiling xylene and then precipitated in methanol to remove nongrafted species. Then, the polymer was filtered and dried. The final polymer obtained [a-PP-succinyl-fluorescein (SF)] was dark brown to red-colored.^{12,13,24} Figure 1 shows a schematic reaction mechanism of the two-step chemical modification process.

Characterization

Grafting level was determined by an improved traditional hot titration method.^{10,11,30,31} A 1 g sample of polymer was put in 150 mL of refluxing xylene/*n*-butanol mixture for 60 min. The hot solution was then titrated without permitting it to cool, with 0.05N ethanolic KOH using Thymol blue as an indicator. Then, an excess of KOH solution was added and a deep-blue color was back-titrated to a yellow endpoint by addition of 0.05N isopropanolic HCl to the hot solution. Results were expressed as weight percent referred to as the MAH equivalent to make it easier to follow the reaction from the first step because the second step reaction was 100% quantitative.^{12,13}

Infrared spectra were recorded on a Nicolet 520 Fourier transform infrared spectroscope using the KBr pellet technique, and performing at 32 scan and 2 cm^{-1} . Ultraviolet spectra were recorded on a Shimadzu UV-265 FS spectrophotometer.

RESULTS AND DISCUSSION

Table I lists the grafting values (MAH equivalent) for the Box–Wilson experimental design, as well as the conversion values referred to the initial $[MAH]_0$ used to obtain a-PP-SA. Although the whole reaction time was 15 min, the first 10 min corresponded to the reaction between a-PP and MAH to give a-PP-SA, and the other 5 min to the condensation reaction between the grafted succinic groups and resorcinol to produce a-PP-SF.

This condensation reaction has been demonstrated to be 100% quantitative^{24–27} and was used in previous works^{12,13} to conclude the unsteady character of radical grafting reactions below 8 min of reaction time. That means that the process yielding is governed by the first-step

Table I Experimental Worksheet

Experiment No.	Sample	[POx] (%)	[MAH] ₀ (%)	[MAH] _{GRAFT} (%)	Conversion (%)
1	a-PP-SF-1	0.70	3.00	1.10	36.6
2	a-PP-SF-2	3.50	3.00	2.55	85.0
3	a-PP-SF-3	0.70	15.00	0.78	5.2
4	a-PP-SF-4	3.50	15.00	2.10	14.0
5	a-PP-SF-5	0.12	9.00	1.00	11.0
6	a-PP-SF-6	4.08	9.00	2.70	30.0
7	a-PP-SF-7	2.10	0.51	0.50	98.0
8	a-PP-SF-8	2.10	17.50	0.50	2.9
9	a-PP-SF-9	2.10	9.00	2.50	27.8
10	a-PP-SF-10	2.10	9.00	2.40	26.6
11	a-PP-SF-11	2.10	9.00	2.45	27.2
12	a-PP-SF-12	2.10	9.00	2.10	23.2
13	a-PP-SF-13	2.10	9.00	2.10	23.9

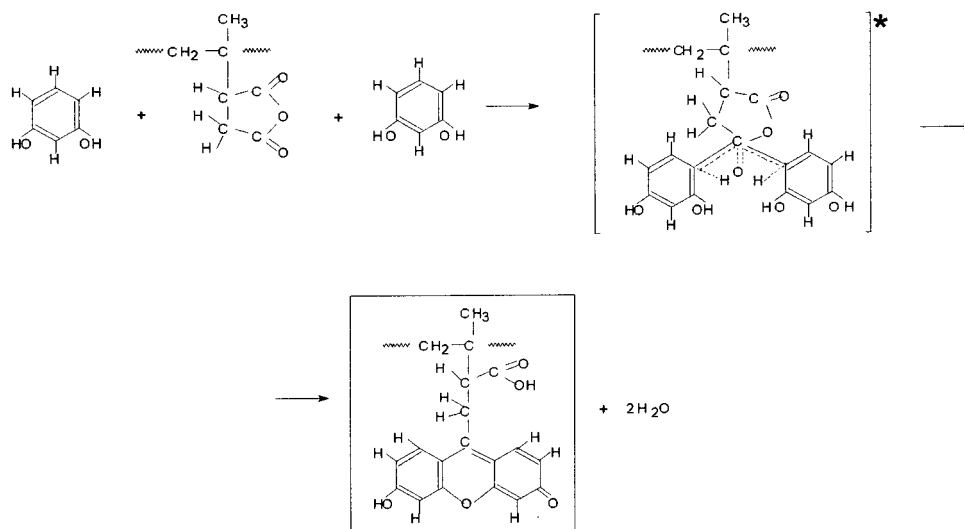
a-PP-SF results expressed as equivalent in succinic anhydride grafting.

grafting reaction and not by the second step condensation reaction. This fact is supported by additional results^{12,13} corresponding to the first reaction step (t minutes) and to the whole process ($t + 5$ minutes), listed in Table II, where an absolute coincidence can be concluded.

It is important to remember, as previously mentioned, that there are many works that have reported for many years on the existence of grafted polymaleic anhydride (Gaylord and col-

leagues³⁰⁻³⁶), and more recently in the last years (De Roover and colleagues²¹⁻²³). Findings reported herein clearly concluded the nonexistence of grafted oligomers in the polymer. This fact was supported by the condensation reaction mechanism between resorcinol and single succinic groups²⁴⁻²⁷ previously bonded in the macromolecule.

The reaction mechanism would be as follows:



From this scheme, the sharp exigences of reorganization, at an atomic level necessary to yield the succinyl-fluorescein structure, can be observed.

Then, if oligomeric structures were attached into polyolefin, only the end succinic anhydride groups would be able to pass to succinyl-fluorescein, thus

Table II Additional Results of Grafting in a-PP-SA and a-PP-SF Obtained in the Central Values of the Experimental Model Conditions at Different Reaction Times

Sample	Reaction Time (min) [t]	a-PP-SA Graft (%) [t]	a-PP-SF ^a Graft (%)
1	8.4	2.90	2.80
2	11.5	3.95	4.00
3	13.0	2.10	2.10
4	13.4	3.00	2.90
5	15.0	3.90	3.85

^a The second-step process was always 5 min for all of the samples.

avoiding such a reaction for the *n*-meric units because of the steric hindrance. Results displayed in Table II clearly demonstrate that all of the succinic groups are single units, because of the identity of the number of grafted succinil-fluorescein groups coming from those of the first reaction step.

In this sense, infrared spectra corresponding to three different samples of a-PP, as original and containing, respectively, 1% grafted succinic anhydride and 1% grafted succinil-fluorescein groups, have been plotted in Figure 2. Functionalized PPs (both a-PP-SA and a-PP-SF) show a characteristic band near 1790 cm⁻¹ corresponding to carboxylic groups. This band does not lead

to the conclusion of the existence or nonexistence of succinil-fluorescein-grafted groups. The evidence of the latter can be determined by the presence of a band at 1775 cm⁻¹ associated with γ -lactonic α,β -nonsaturated cycles, and another one near 1600 cm⁻¹ corresponding to carboxylic acid. Quantification of grafted groups by Fourier transform infrared spectroscopy is fully discussed elsewhere.^{13,37} Also, Figure 3 shows the preliminary absorption spectra corresponding to a-PP, with or without succinil-fluorescein-grafted groups, and where the existence of a peak at $\lambda = 450$ nm corresponding to a fluorescent group is clearly observed.²⁴⁻²⁸ This peak appears to be proportional to the amount of succinil-fluorescein grafted in the polyolefin backbone. A further study on this topic will be the subject of another article.

Polynomial Fits

Grafting level ([MAH] equivalent) and conversion values compiled in Table I were fitted according to the Box–Wilson quadratic model of surface response.³⁸⁻⁴⁰ The polynomial coefficients obtained are compiled in Table III. Here, it can be noted that the confidence factor of the regression ($\langle r^2 \rangle$) obtained is next to 1.0 (0.924 for grafting and 0.973 for conversion), an excellent quadratic model. That means the system can be studied from the predictions of these polynomials that

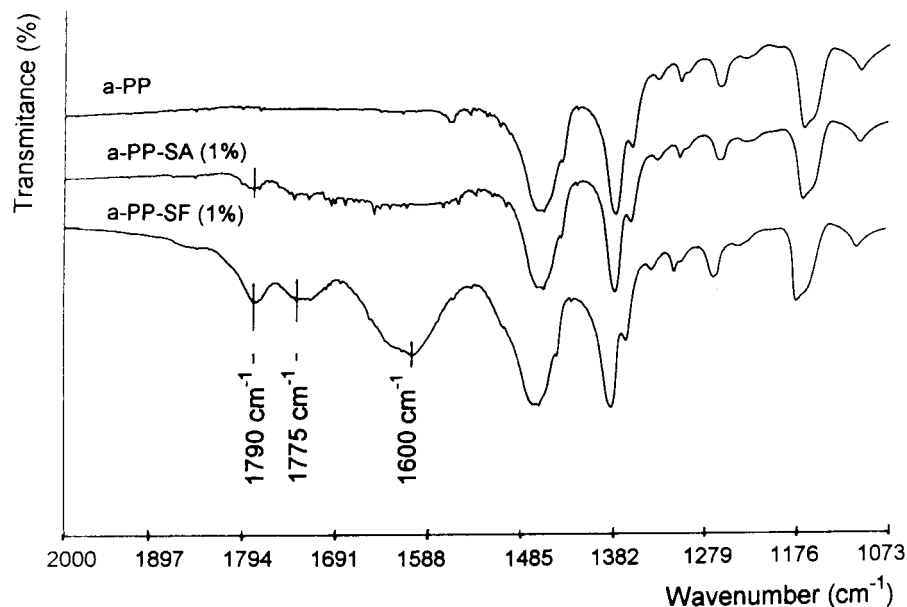


Figure 2 Infrared spectra of a-PP, a-PP-SA, and a-PP-SF.

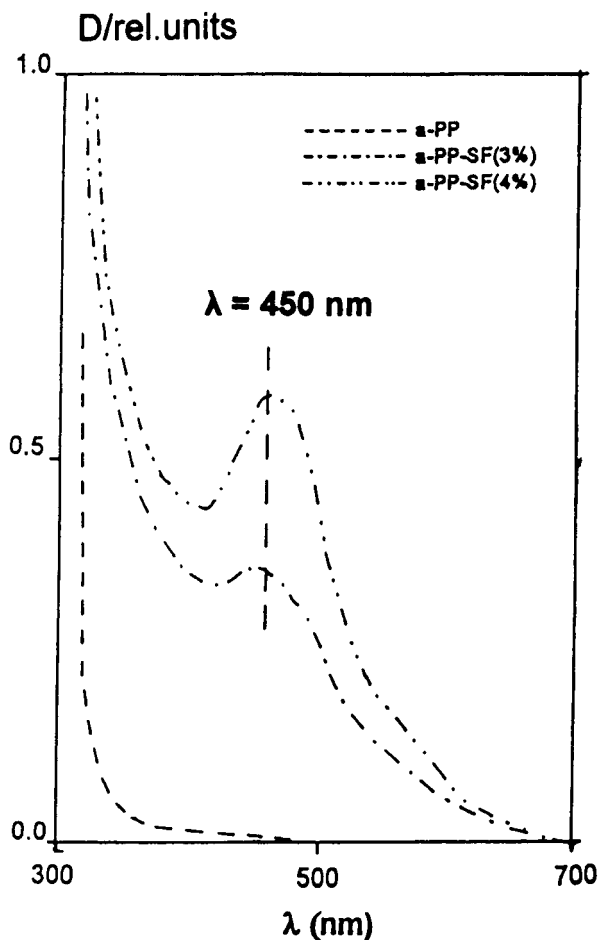


Figure 3 UV-vis absorption spectra of a-PP with and without succinyl-fluorescein-grafted groups.

model the process in the experimental range scanned. From the latter, the statistical significance of the model is concluded. This statement is supported by parameters of analysis of variance compiled in Table IV.

It is important to note that the term of pure error (lack of fit in both models) presents values of 9.0% and 2.3%, respectively. This parameter is related to any factor having influence in the response and is not considered as an independent variable by the model. The higher value of the former would be in accordance with data obtained in a previous work,¹² wherein it was found that pure error increased while reaction time did. It also confirms our ideas about the fact that, when studying the process only at long reaction times, it is impossible to appreciate the real evolution of the a-PP/MAH system in an accurate way.^{12,13}

Isoline Maps

The isoline maps plotted in Figure 4 concludes in the same way as previous works^{12,13} about the reaction between MAH and a-PP, and the unfavorable long time role that reaction plays in reaction yielding. Once again, it is important to remember that, in the process performed for this work, the first step time of reaction was 10 min. So, with the level of grafting after 3, 6, and 9 min,^{12,13} a decrease in the graft level was expected to occur at 10 min. The net amount of grafts (in number of groups) would be the same after the second step because of the quantity of the condensation reaction.

Map A in Figure 4 shows a typical evolution on the rising ridge when peroxide concentration [POx] increases, with the optimum concentration of [MAH]₀ nearly 9.0%. This map indicates the favorable effect that [POx] plays in the governing reaction step and then in the whole process. Map B exhibits evolution of conversion as a function of initial [MAH]₀ and [POx] in the reaction media. Here, it can be observed that, in terms of conversion, low values of [MAH]₀ are favorable, and high

Table III Coefficients of the Response Surface Polynomials

	<i>t</i> (min)	<i>r</i> ²	Linear Terms			Interaction Terms	Quadratic Terms	
			<i>a</i> ₀	<i>a</i> ₁	<i>a</i> ₂	<i>a</i> ₃	<i>a</i> ₄	<i>a</i> ₅
Grafting level	5 ^a	0.924	-0.6405	0.7553	0.3899	-0.003869	-0.06154	-0.02210
Conversion	5 ^a	0.973	53.80	23.82	-8.594	-1.177	-1.368	0.3404

$$\text{Polynomial equation: } a_0 + a_1x_1 + a_2x_2 + a_3x_1x_2 + a_4x_1^2 + a_5x_2^2$$

$$x_1 = [\text{POx}]$$

$$x_2 = [\text{MAH}]_0$$

^a Referred to the second step of reaction (condensation reaction between grafted succinic anhydride and resorcinol).

Table IV Statistical Parameters of the Analysis of Variance

Process		r^2	Mean Sum of Squares	Pure Error	Confidence Factor (%)	Deviation Due to Pure Error (%)
Molten state (succinil-fluorescein)	Graft	0.924	0.170	0.133	99.6	9.0
	Conversion	0.973	81.564	4.157	99.9	2.3

values of [POx] would contribute to maximize the conversion. From these two plots, it can be deduced that it is one thing to reach a maximum level of grafting, and it is another thing to optimize the process in terms of the amount of initial

reactant concentrations (economical optimization). This would indicate that, in future applications, it must be taken into account what the researcher (or industry) is looking for: to maximize the grafting level reached or to optimize the reactant concentration. Strategies would be sharply different.

The previously described data are confirmed when studying the evolution of the system in Figure 5, where graft and conversion *versus* [POx] or [MAH]₀, keeping constant the other independent variable in the experimental design central value, have been plotted. From these, it can be observed that the higher the [POx] level, the higher are graft and conversion; but, when represented *versus* [MAH]₀, a clearly perceptible maximum in the surrounding of [MAH]₀ = 9.0% can be observed, with conversion nearly 30%. The maximum conversion found in the experimental range scanned is when grafting level is ~ 1.5%. When represented conversion *versus* [MAH]₀, a decrease in values close to 10% can be observed, looking to stabilize the conversion values in this value. Data indicate the main role played by [POx] in the reaction mechanism,¹² not only if compared with classical kinetics, but also for the need of a radical-like initiator to start the process.

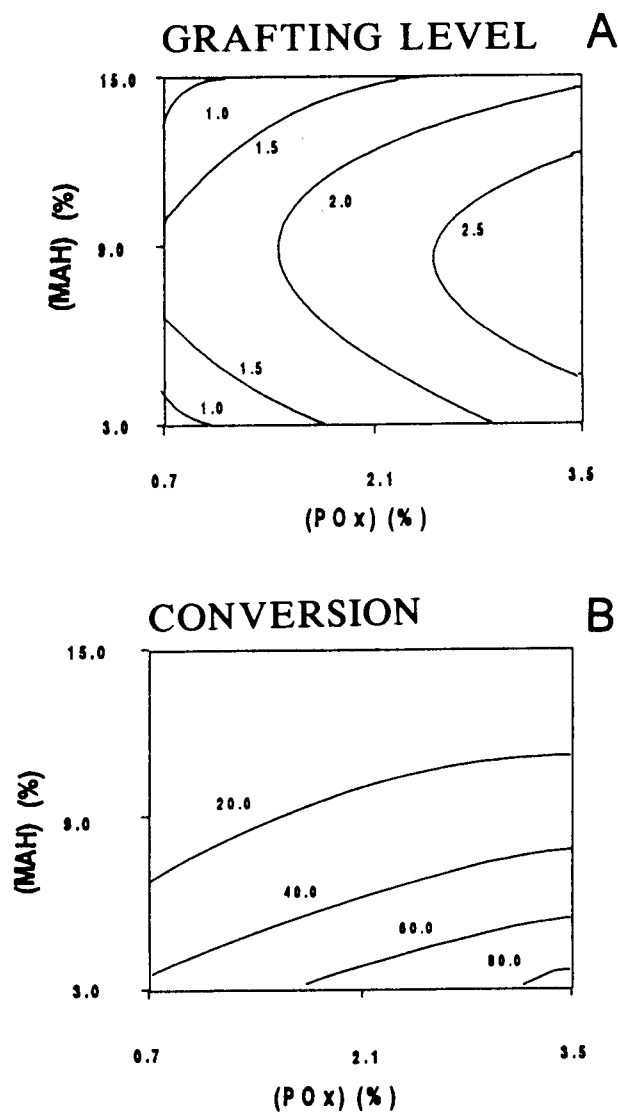


Figure 4 Isoline map showing concentration and grafting levels.

CONCLUSIONS

The feasibility to obtain a fluorescent product by a two-step process in the molten state is clearly concluded. Preliminary characterization studies of modified polymers support this conclusion. Also, as an important conclusion of this work, the absolute absence of any kind of succinic oligomeric species grafted into a-PP obtained in the molten state must be noted. This modified polymer (a-PP-SF)—among other applications—would be used as an interfacial agent in heterogeneous materials based on PP.

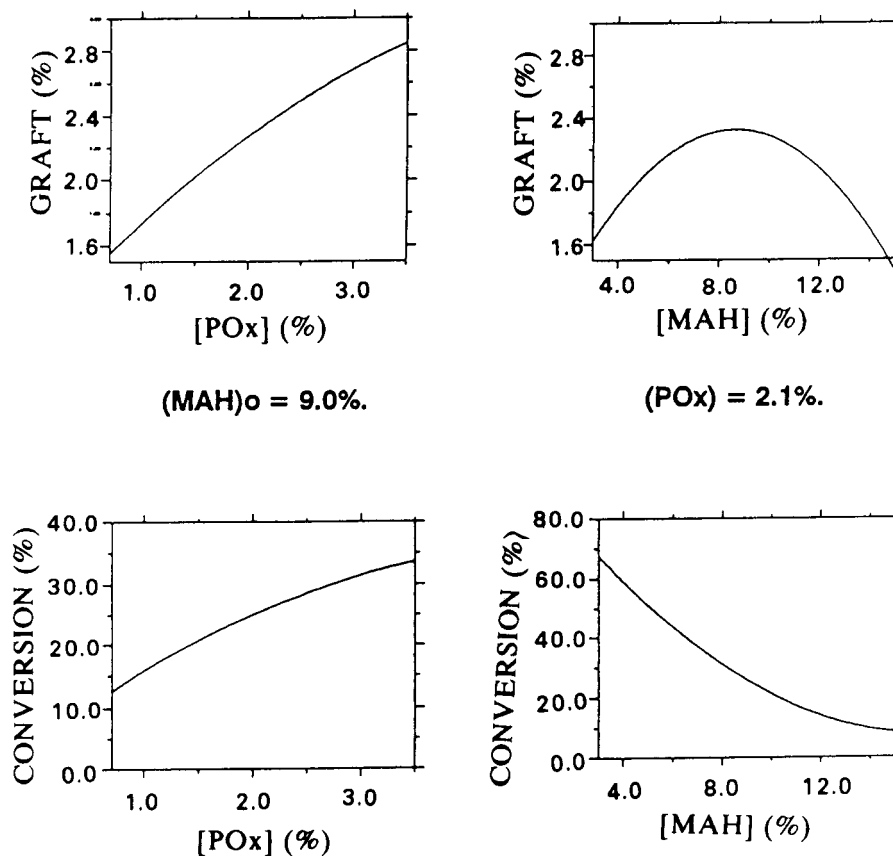


Figure 5 Conversion and grafting level at a given peroxide (2.1%) or anhydride maleic concentration (9.0%).

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REFERENCES

- J. Taranco, O. Laguna, and E. P. Collar, *J. Polym. Eng.*, **11**, 315 (1992).
- J. Taranco, O. Laguna, and E. P. Collar, *J. Polym. Eng.*, **11**, 325 (1992).
- J. Taranco, O. Laguna, and E. P. Collar, *J. Polym. Eng.*, **11**, 345 (1992).
- J. Taranco, J. M. García-Martínez, O. Laguna, and E. P. Collar, *J. Polym. Eng.*, **13**, 287 (1994).
- F. P. LaMantia, *Adv. Polym. Technol.*, **12**, 47 (1993).
- B. Majumdar, H. Keskkula, and D. R. Paul, *J. Appl. Polym. Sci.*, **54**, 339 (1994).
- A. Datta, H. H. Chen, and D. G. Baird, *Polymer*, **34**, 759 (1993).
- G. Xu and S. Lin, *J. Macromol. Sci., Rev. Macromol. Chem. Phys.*, **C34**, 555 (1994).
- E. P. Collar, O. Laguna, E. Fontán, and J. M. Ter-cero, *Polypropylene: The Way Ahead*, Actas del Congreso, Madrid, 1989.
- J. M. García-Martínez, J. Taranco, O. Laguna, and E. P. Collar, *Int. Polym. Proc.*, **9**, 246 (1994).
- J. M. García-Martínez, J. Taranco, O. Laguna, and E. P. Collar, *Int. Polym. Proc.*, **9**, 304 (1994).
- J. M. García-Martínez, O. Laguna, and E. P. Collar, *J. Appl. Polym. Sci.*, **65**, 1333 (1997).
- J. M. García-Martínez, *Ph.D. Dissertation*, Univ. Complutense, Madrid, 1995.
- J. M. García-Martínez, O. Laguna, and E. P. Collar, *J. Appl. Polym. Sci.*, **68**, 483 (1998).
- K. E. Russell and E. C. Kellusky, *J. Polym. Sci., Polym. Chem.*, **26**, 2273 (1988).
- K. E. Russell, *J. Polym. Sci., Polym. Chem.*, **33**, 555 (1995).
- A. Sipos, J. McCarthy, and K. E. Russell, *J. Polym. Sci., Polym. Chem.*, **27**, 3353 (1989).
- D. Brown and U. Eisenlohr, *Angew. Makromol. Chem.*, **55**, 43 (1976).
- N. C. Liu, W. E. Baker, and K. E. Russell, *J. Appl. Polym. Sci.*, **41**, 2285 (1990).
- R. Rengarajan, V. R. Parameshwaran, S. Lee, and M. Vicic, *Polymer*, **31**, 1703 (1990).
- B. de Roover, M. Slavovs, V. Carlier, J. Devaux, R. Legras, and A. Montaz, *J. Polym. Sci., Polym. Chem.*, **33**, 829 (1995).

22. B. de Roover, J. Devaux, and R. Legras, *J. Polym. Sci., Polym. Chem.*, **34**, 1195 (1996).
23. M. Sclavons, V. Carlier, B. de Roover, P. Franquinet, J. Devaux, and R. Legras, *J. Appl. Polym. Sci.*, **62**, 1205 (1996).
24. M. J. Pineda, *Ph.D. Dissertation*, Univ. Complutense, Madrid, 1993.
25. N. Spassouska and I. Panayotov, *Comp. Rend. Acad. Bulg. Sci.*, **23**, 1369 (1970).
26. N. Spassouska and I. Panayotov, *Comp. Rend. Acad. Bulg. Sci.*, **18**, 445 (1965).
27. Y. Graff, *Bull. Soc. Chem.*, **6**, 1106 (1961).
28. N. N. Barashkov and O. A. Gunder, *Fluorescent Polymers*, Prentice Hall-Ellis Horwood, London, 1994.
29. J. M. García-Martínez, O. Laguna, and E. P. Collar, *J. Polym. Eng.*, **17**, 269 (1997).
30. N. G. Gaylord, R. Mehta, V. Kumar, and M. Tazi, *J. Appl. Polym. Sci.*, **38**, 359 (1989).
31. N. G. Gaylord and M. Mishra, *J. Polym. Sci., Polym. Letters*, **21**, 23 (1983).
32. N. G. Gaylord, *J. Macromol. Sci., Rev. Macromol. Chem.*, **C13**, 235 (1975).
33. N. G. Gaylord and R. Mehta, *J. Polym. Sci., Polym. Chem.*, **26**, 1189 (1988).
34. N. G. Gaylord, M. Mehta, and R. Mehta, *J. Appl. Polym. Sci.*, **33**, 2549 (1987).
35. N. G. Gaylord and M. Mehta, *J. Polym. Sci., Polym. Letters*, **20**, 481 (1982).
36. N. G. Gaylord, *Appl. Polym. Symp.*, **26**, 197 (1975).
37. J. M. García-Martínez, S. Areso, O. Laguna, and E. P. Collar, *J. Appl. Polym. Sci.*, submitted.
38. G. E. P. Box, W. G. Hunter, and J. S. Hunter, *Statistics for Experimenters*, Wiley, New York, 1978.
39. S. M. Ross, *Introduction to Probability and Statistics for Engineers and Scientist*, J. Wiley, Singapore, 1987.
40. S. M. Ross, *Introduction to Probability Models*, Academic Press, San Diego, 1993.