Role of Reaction Time in Batch Process Modification of Atactic Polypropylene by Maleic Anhydride in Melt

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ABSTRACT: Following our studies on chemical modification proceses of polypropylenes by maleic anhydride, some new experimental works are shown here that check the possibilities of processing atactic polypropylene in the melt by a batch process. A modified polymer that is supposed to be useful as an interfacial agent if used in heterogeneous systems based on polypropylene is also clearly obtained. The favorable effect of the nonstereoregularity of the polymer can be noted. This polymer has a higher level of modification than the stereoregular polymer (isotactic polypropylene), despite the lower processing temperature used that causes a decrease in the initiator activity. Otherwise, this article deals with the role played by the reaction time during the process. A mechanism of chemisorption and some considerations about the fractal nature of the reaction kinetics are proposed to explain the results obtained. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 1333–1347, 1997

Key words: functionalization; atactic polypropylene; industrial waste; molten state; radical process; reaction time; chemisorption

INTRODUCTION

Polypropylene (PP) is a very interesting polymer, not only for its enormous industrial possibilities as a commodity or as an engineering thermoplastic, but also from an academic point of view for its behavior due to its stereoregularity.[1,2] This is the reason that there are a lot of works dealing with aspects related to this polymer, as recently compiled by LaMantia.[3]

Nowadays it is well known that the industrial production of isotactic PP (iPP) along with the production of atactic PP (aPP) (nonuseful as a structural material) is around 10% of overall production. So aPP can be considered as an industrial waste.

Chemical modification of polymers is a good chance to improve and/or modify some properties that would limit the commercial use or potential applications of the polymers. In this sense it is possible to obtain modified polymers to be used as interfacial agents in heterogeneous systems based on polymers (polymer blends and composites). Much has been written dealing with the different aspects and particularities of this problem: the chemical reaction, the process, the role played by the modified polymer in the heterogeneous system properties, and so on.[4–7]

The nature of the PP chemical modification process has been studied in our group for a few years. Our first studies were conducted on isotactic homopolymer (iPP).[8,9] We and many other authors concluded that there was a maximum grafting level, that is, the existence of a "ceiling," whatever was the initial concentration of maleic anhydride (MAH) and/or peroxide (POx) in the reaction media. The use of a statistical design method for experimental runs showed that results needed to be carefully evaluated in order to find the true evolution of the process.

Such a maximum or ceiling could only be

reached when reactions were conducted in conventional systems, either in solution or a molten state. Otherwise this value seemed to be quite far from what could be expected according to the stereochemistry imposed by the backbone structure of the PP polymer chains.

On the other hand, the existence of a secondary and undesirable reaction, the degradation process associated with the addition of POx to the reaction media, plays an important role in the maintenance of the modified polymer properties in an acceptable range of values. Once again the Box–Wilson response surface was very useful to discriminate between grafting and degradation processes as being mainly responsible for the grafted levels at any given time of reaction.

Both modification and degradation process aspects were considered. This article shows the results of chemical modification of aPP (industrial waste) in the molten state using a batch process.

EXPERIMENTAL

The chemical modification process was conducted on an industrial polymer waste (aPP) supplied by Repsol Química. This waste was first purified by dissolving in boiling xylene and then precipitation into methanol. MAH (Scharlau/FEROSA) and dicumyl peroxide (Perkadox BC, Akzo) were used as reactant and initiator, respectively.

The modification reaction was carried out in the molten state by using a Rheomix 600 attached to a Rheocord 90 (Haake) driver unit.

Reaction times of 4, 6, and 9 min were considered. The other independent variables were the initial concentrations of [MAH] and [POx]. Their concentration values were chosen according to a Box–Wilson experimental design.

Thermal stabilizers were also incorporated into the reaction media to minimize the degradation process occurring simultaneously in the modification reaction in the PP. Irganox 1010 and Irganox B225 (Ciba–Geigy) thermal stabilizers were used.

The experimental procedure was as follows. When the reactor was at the setup conditions (temperature and gear rate), the polymer, stabilizers, and MAH were all introduced into the reactor. After passing a homogenization time (two or three min), POx was added to the reactor. This moment was considered to be the start of the reaction.

When the reaction was finished (after 4, 6, or

Table I   Experimental Ranges of Experimental Variables

Independent Variable	Name	Experimental Range (%)	
		Min.	Max.
Dicumyl peroxide	POx	0.12	4.08
Maleic anhydride	MAH	0.51	17.49

9 min), the reactor was opened and the reaction product was recovered and cooled in an ice bath.

Unreacted MAH was then eliminated by washing the reaction product in boiling xylene and later precipitation into methanol. In this way the washed polymer grafting level was ready to be quantified, so a titration method was used.

The grafting content was determined by heating a 1-g sample of the polymer for 60 min in 150 mL refluxing water and xylene/n-butanol mixture. The hot solution was then titrated, without cooling, with 0.005N ethanolic KOH using thymol blue as the indicator. Then a 1-mL excess of KOH solution was added and a deep blue color was backtitrated to a yellow end point by addition of 0.005N isopropanolic HCl to the hot solution. Results were expressed as acid number (mg KOH/g polymer) and weight percentage in the polymer, the way they are shown in this article.

Unmodified polymer was also titrated giving, as expected, neglected values, as did water and n-butanol. Then, the existence of pendant succinic groups could be clearly concluded.

RESULTS AND DISCUSSION

It is very important to consider the preliminary results obtained by us in the study of the chemical modification of molten iPP using a batch reactor.[8,9] In those works the time of reaction played a key role in the grafting level obtained. This is then the main reason for choosing two independent variables for the experimental design, [MAH] and [POx] concentrations. The role of time was determined by considering different times of reaction. The experimental ranges for the two independent variables in the design are compiled at Table I.

Times of 4, 6, and 9 min were chosen to carry out the reactions in order to evaluate the effect of time on the grafting level obtained.
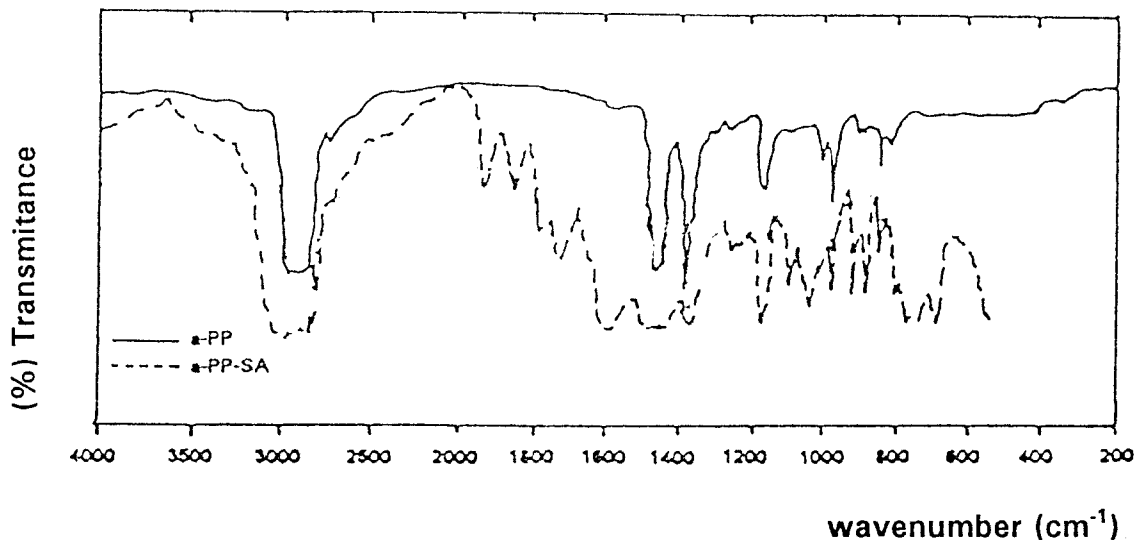
The order in which the reactants are added to

Figure 1 IR spectra of the atactic polymer, before and after modification.

the reactor is also very important. In fact, the results obtained in this kind of work can only be reproduced when POx is the last product added after the MAH and molten PP are well mixed.

One additional and very important consideration must be made: aPP can not be processed at the same temperature as iPP (190°C in our previous experiments). This is due to the intrinsic nature of that homopolymer.

Figure 1 shows the IR spectra of the aPP used in this work before and after being modified. The need of working at lower temperature produces variations in the POx activity, as can be noted in Figure 2.

Figure 2 shows the results of the reaction at 140 and 120°C. The reason for chosing 140°C as the process temperature was because it was the highest one that the aPP could be processed in the batch while still being handleable.

Otherwise, this processing temperature would be very interesting in the way it could let us compare these results with those obtained when the reaction took place in solution using hot xylene as the solvent (boiling temperature 140°C). These results will be discussed in future articles.

The grafting levels obtained at 140 and 120°C can be observed in Figure 2. As expected, the results were higher at 140 than at 120°C. This agrees with the fact that at 120°C the activity of the dicumyl POx decreases almost 40% compared with that at 140°C (32, 37, and 37% at 4, 6, and 9 min, respectively).[10,11] This is the main reason why the experimental designs were run at 140°C. Tables II and III show the experimental work-

sheet as well as the grafting levels, conversions, and reaction times.

Our experimental ranges are a magnification of those used in previous works dealing with iPP.[8] They were chosen to demonstrate that it is not true that the more MAH initial concentration is added to the reaction media, the more grafting is obtained.

Table IV is a compilation of the coefficients of the fittings from values in Tables II and III. It must be noted that the coefficients corresponding to the POx terms seem to have the highest significance.

Analysis of variance of the experimental design and fits are compiled at Table V. This analysis formed our conclusions about the kind of model to be used. In this sense it is important to note, from a statistical point of view, that the error parameter can be considered to have two components: a random component (fully inherent to experimental runs) and another component due to some factor not included in the experimental scheme but definitely acting on the dependent variable.

The last column in Table V shows that this second error factor increases as the time of reaction does. This fact confirms the role played by the time of reaction all along the process. In other words, random experimental runs where the reaction time was distant from these values could not inform us about the nature and yielding of the grafting process.

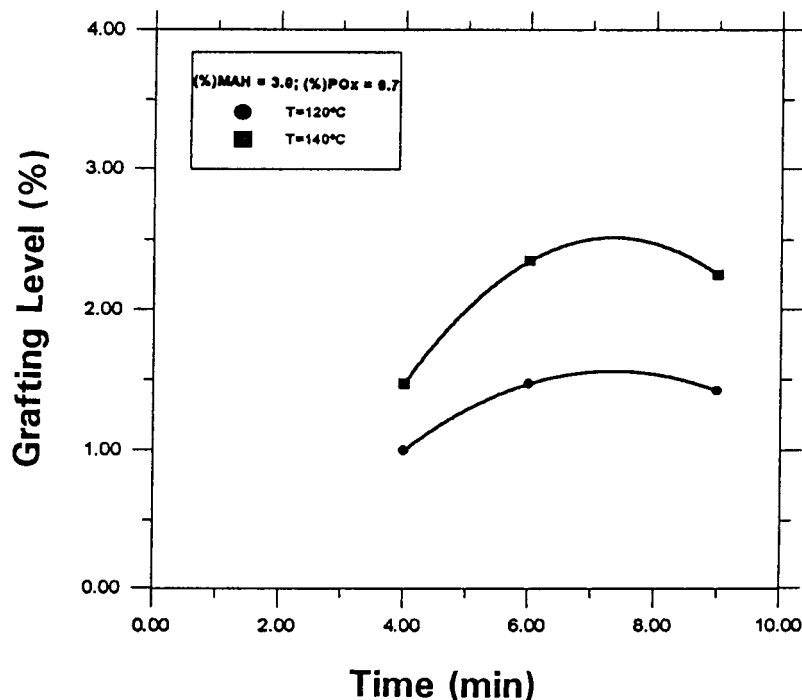As an example, Table VI shows a set of references[12-23] about a large number of works related

Figure 2 Evolution of the grafting level with temperature.

to the chemical modification of polyolefins by MAH using a POx as the initiator. Those processes were carried out in a batch reactor but at longer reaction times. So, the highest levels of grafting would have been obtained at the first stages of those processes.

The isolines map for the obtained grafting polynomials of the response surface at 3, 6, and 9 min can be observed in Figure 3. This figure clearly shows the existence of a critical point in the concentration of the reactants.

It is very important to note that the highest grafting levels were obtained for the 6-min batch design. On the other hand, at 9 min the values began to be lower than the previous ones.

The evidence of an optimum time of reaction placed between 5 and 6 min was found again.[9] From the industrial point of view, this is of great

Table II   Grafting and Conversion Levels Along Reaction Times

Exp. No.	4 min		6 min		9 min	
	Grafting Level (%)	Conversion (%)	Grafting Level (%)	Conversion (%)	Grafting Level (%)	Conversion (%)
1	1.47	49.00	2.36	78.00	2.25	75.00
2	2.06	68.70	2.45	81.70	1.86	62.00
3	2.94	19.60	2.90	19.30	2.75	18.30
4	3.89	25.93	3.97	26.47	3.01	20.10
5	1.76	19.60	2.20	24.50	2.00	22.20
6	3.10	35.00	4.10	45.20	3.40	37.60
7	0.34	67.25	0.44	86.50	0.39	78.40
8	1.70	9.00	2.00	11.80	1.75	11.10
9	3.20	37.00	4.00	44.44	3.00	33.30
10	3.10	36.00	4.10	45.50	3.10	34.40
11	3.25	36.11	4.20	46.70	3.60	40.00
12	3.30	36.50	4.20	46.70	3.40	37.80
13	3.25	36.90	4.20	44.44	3.40	37.80

Table III   Experimental Worksheet

	Independent Variables	
Experiment	POx (%)	MAH (%)
1	0.70	3.0
2	3.50	3.0
3	0.70	15.0
4	3.50	15.0
5	0.12	9.0
6	4.08	9.0
7	2.10	0.51
8	2.10	17.49
9	2.10	9.0
10	2.10	9.0
11	2.10	9.0
12	2.10	9.0
13	2.10	9.0

importance because those times of reaction are quite similar to those for an extruder. This opened the possibility of obtaining a succinic anhydride modified polymer (aPP-SA) by a continuous process with at least similar grafting levels.

The isolines map in Figure 4 shows the evolution of the conversion all along the process. There the highest values for conversions are obtained at the lowest initial concentrations of MAH. The conversion isolines have a constant tendency at a given initial concentration of MAH by varying the initial POx concentration.

However, at 4 min conversion isolines have a constant tendency to the central value of the POx range. It is very important to notice that the gradient between isolines is about 30% lower at a 4-min reaction time than the others at 6 and 9 min.

This seems to indicate the PP/MAH system varies more quickly at the first stages of the process.

Evolution of the system when one of the independent variables is kept as a constant and equal to the central value of the experimental design is showed in Figure 5.

Keeping constant the initial concentration of MAH and varying the POx concentration, an increase in the grafting level up to 3.4% when POx concentration increases can be observed (at the 4-min plot). This is quite similar to what occurs for the 9-min plot. Here the limit reached is 3.2% when the POx concentration is nearly 3.0%.

The plot for 6 min shows the maximum level of grafting was obtained (nearly 4%).

In the same way, when keeping [POx] constant, the existence of a critical point (maximum) when studying the conversion evolution (Fig. 6) can be clearly concluded. This agrees with the latter. We also realize the increasing evolution of the conversion when POx peroxide does (refer to the 6-min experiments). The existence of an asymptotic conversion value at this reaction time and a sudden fall in the evolution when POx values become higher and higher is also remarkable. Then, this asymptotic value for the conversion concerns the highest value for the POx, keeping [MAH] as a constant.

All the above mentioned facts suggest to us the very important role played by time in the evolution of the process.

To check this role and knowing the statistic significance of the results obtained, a set of additional experiments were carried out. They correspond to samples taken from the reactor at different times, keeping constant the initial concentra-

Table IV   Coefficients of Response Surface Polynomials

Dependent Variable	t (min)	r^2	Linear Terms			Interaction Terms	Quadratic Terms	
			a_0	a_1	a_2	a_3	a_4	a_5
Grafting level	4	0.854	−0.5916	0.5933	0.5282	0.01071	−0.09120	0.002455
	6	0.917	−0.3641	0.7100	0.6569	0.02887	−0.14890	−0.034910
	9	0.853	0.3219	0.3219	0.5185	0.01935	−0.07876	−0.026930
Conversion	4	0.959	49.58	13.3700	−3.802	−0.3979	−1.31500	0.078760
	6	0.969	83.68	9.1180	−6.858	0.1033	−1.53900	0.114800
	9	0.951	88.16	0.5937	−7.736	0.4405	−0.86030	0.152500

Polynomial equation:

$a_0 + a_1x_1 + a_2x_2 + a_3x_1x_2 + a_4x_1^2 + a_5x_2^2$
$x_1 = $ [POx]
$x_2 = $ [MAH]

Table V   Statistics Parameters of ANOVA Analysis for Fittings in Table IV

Process	t (min)	r^2	Sum of Squares Mean	Pure Error	Confidence Factor (%)	Deviation Due to Pure Error (%)
Melt	4	0.854	0.583	0.006	98.6	0.9
	6	0.917	0.454	0.010	99.5	1.3
	9	0.854	0.415	0.060	98.6	6.4
	4	0.956	48.781	0.203	99.8	0.7
	6	0.965	75.475	1.277	99.8	1.1
	9	0.951	76.985	7.538	99.8	4.2

tions of MAH and POx, and equal to those of the central point (9 and 2.1%, respectively).

Table VII compiles experimental values for succinic groups grafted into aPP and their variation along with time. These results are plotted in Figure 7. As expected from the experimental design predictions, a minimax evolution is found.

To check that this was not an experimental artifact, we used the condensation reaction reported in the literature.[24–27] That reaction takes place between succinic anhydride groups and resorcinol in the presence of zinc chloride. As can be seen, when those reactants were introduced into the reactor at any given time, the radical grafting process stopped quickly, being only dependent on the zero time for the condensation reaction.

The red-brown color typical of succinil–fluoresceine pendant groups attached onto the PP persisted after washing the modified polymer. In fact, Figure 8 shows that when resorcinol is added to the system, a drastic change in the reaction mechanism is produced that keeps the level of grafting almost constant 10 min before the addition of the resorcinol to the reaction media. This operation

stabilized the grafting level in the system and the minimax evolution did not take place.

Coming back again to Figure 7, a few remarks about the concept of solubility must be made. When speaking in dynamic terms about low molecular weight reactives, qualitative approach may be used on the basis of the equivalence between the spatial sizes of the molecules traveling along the reaction media. But when one of the reactants has a macromolecular character, this assumption does not seem to be correct, especially because of the heterogeneity of the macromolecular size of a given polymer. That is, it is very difficult to believe that the MAH molecules were equally feasible for each one of the PP macromolecules. In other words, referring to the problem in terms of a physically heterogeneous system, as a consequence of this the consideration of a dynamic interface is possible. This is not quite unusual because there are many well-known processes where a surface or an interface controls and defines the yielding of those processes.

In fact, when defining adsorption as the necessary saturation of nonequilibrated forces on the

Table VI   Reaction Time in Radical Modifications Processes for Polyolefins Reported in Literature

Funcionalization Process	Reaction Medium	Reaction Time (min)	References
LDPE/MAH/POx	Solution	120–7200	Porejko et al.[12]
LDPE/MAH/POx	Solid	120–3600	Gabara and Porejko[13]
iPP/MAH/POx	Melt	20	Ide et al.[14]
LDPE/MAH/POx	Solution	10	Gaylord and Mehta[15]
iPP/MAH/POx	Melt	10	Gaylord and Mishra[16]
EPR/MAH/POx	Solution	10	Gaylord et al.[17]
LDPE/MAH/POx	Solution	15	Gaylord and Mehta[18]
HDPE/MAH/POx	Solution	10	Gaylord et al.[19]
SEBS/MAH/POx	Solution	10–185	Wu et al.[20]
iPP/MAH/POx	Melt/solid	$t \gg$ optimum[a]	Khunova and Zamersky[21]
iPP/MAH/POx	Solid	>120	Koul et al.[22]
iPP/MAH/POx	Solid	1440	Priola et al.[23]

[a] Critierion followed to finish the reaction was a sharp fall in the torque values (i.e., when the PP was absolutely degraded).
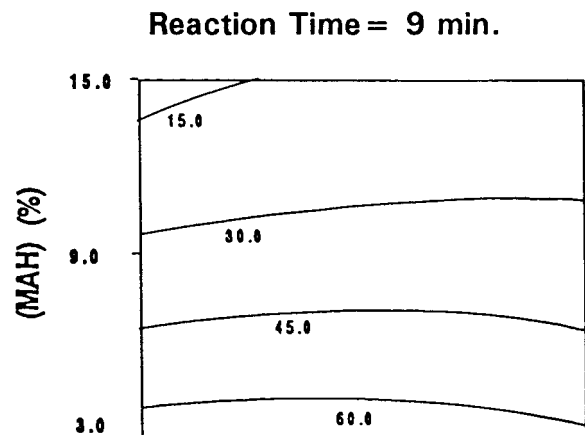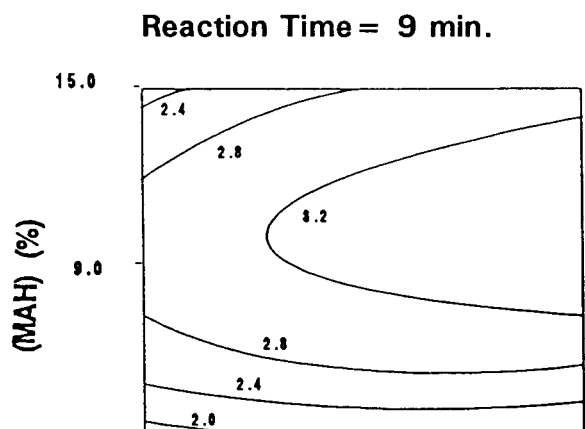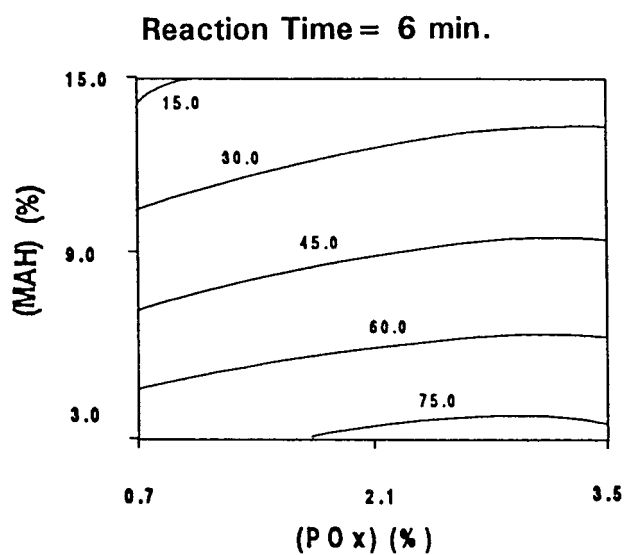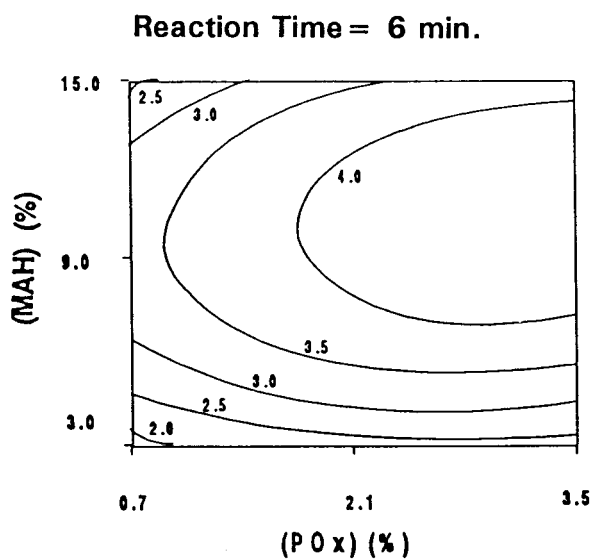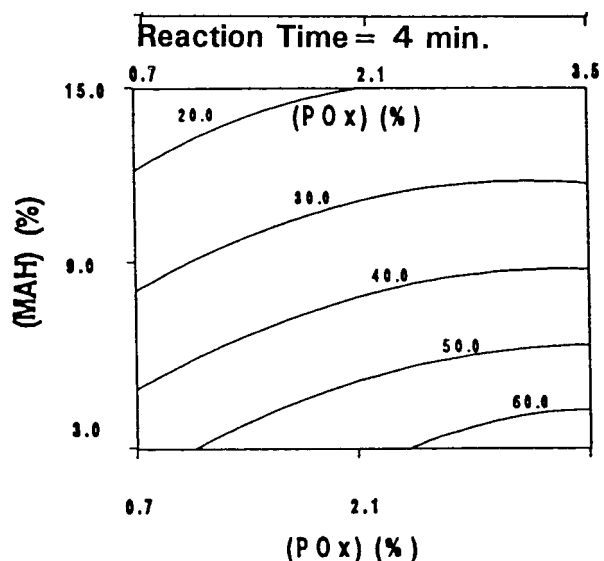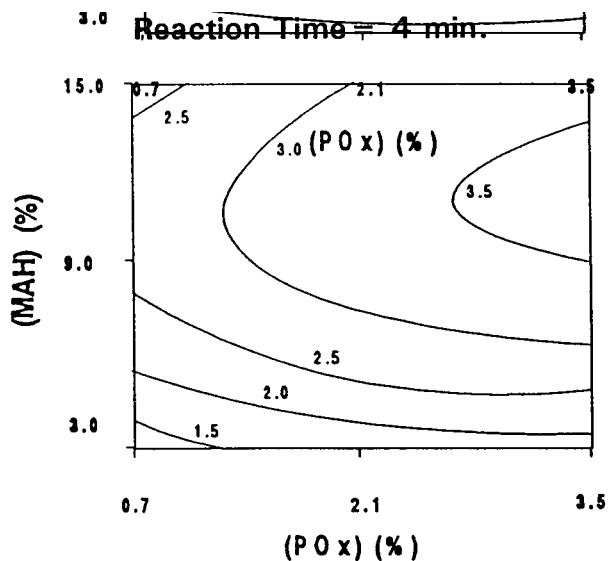
Figure 3 Isolines map showing the grafting level at different times of reaction.

Figure 4 Isolines map showing the conversion level at different times of reaction.

Reaction Time = 4 min.

Reaction Time = 6 min.

Reaction Time = 9 min.
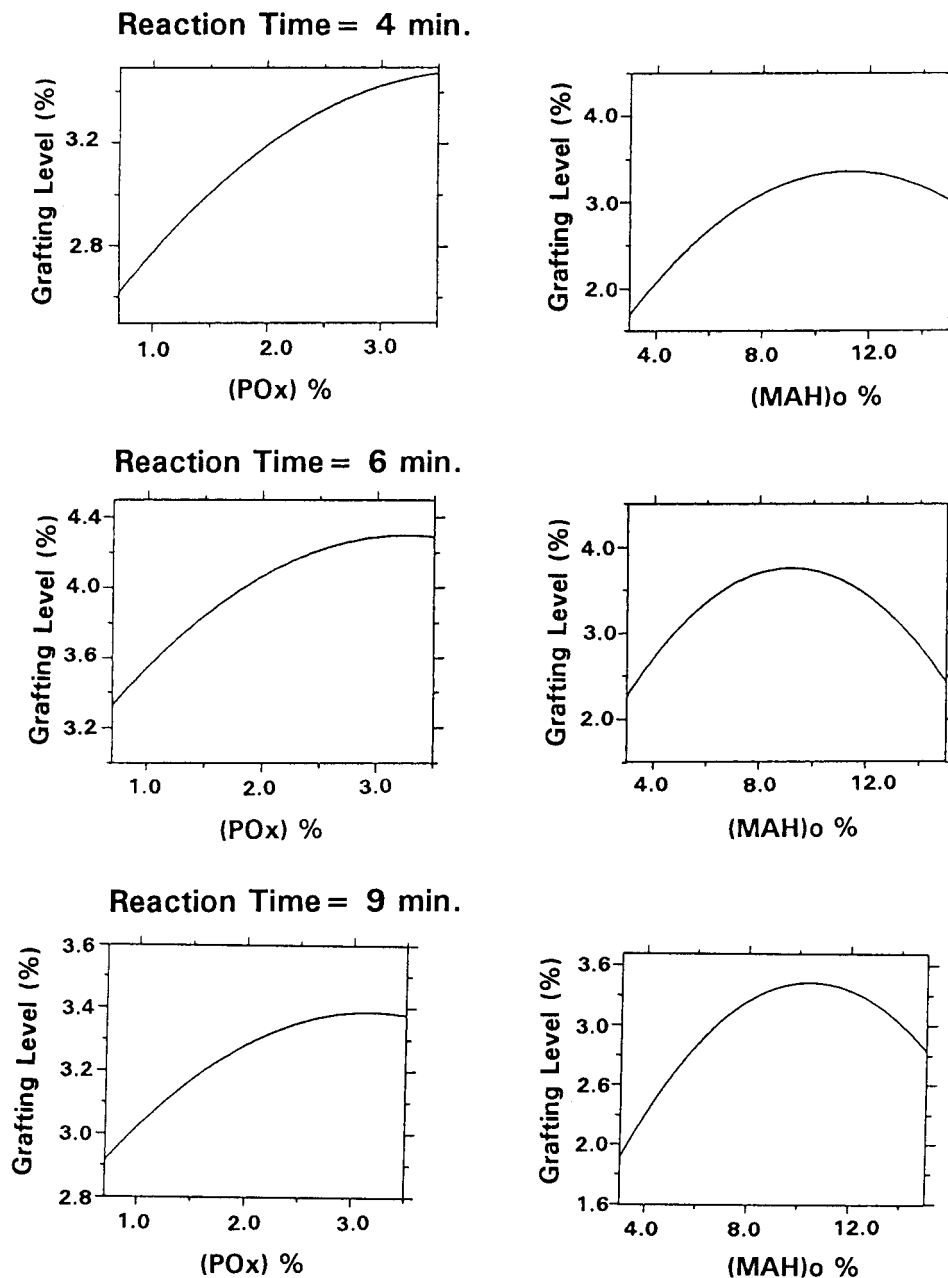
Figure 5 Grafting levels at a given initial concentration of peroxide (2.1%) or maleic anhydride (9%).

surface atoms defining the interface, it appears to be a way to focus the problem of low yielding found in radical reactions taking place in macromolecular systems.

According to the literature on adsorption,[23,28–35] when forces are of a secondary character (van der Waals and so on), this is said to be a physisorption phenomena. On the other hand, when forces are equilibrated by primary bonds, the phenomena is called chemisorption.

Nevertheless, a fundamental of sorption processes is that that kind of phenomena are governed by dynamic equilibria. Then the reaction scheme for the PP/MAH system can be assumed (Fig. 9). The latter let us make and interpret the system (Fig. 7) on the basis that we can consider MAH as the adsorbate coming from an adsorbable region, both interacting during the reaction time. This phenomena is called a chemisorption process where tertiary carbons are supposed to be on the
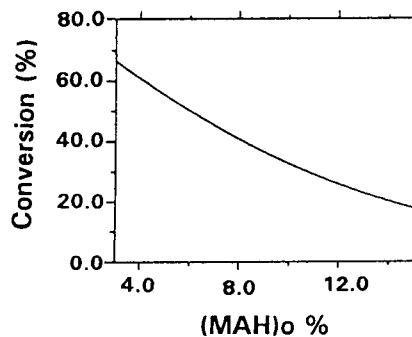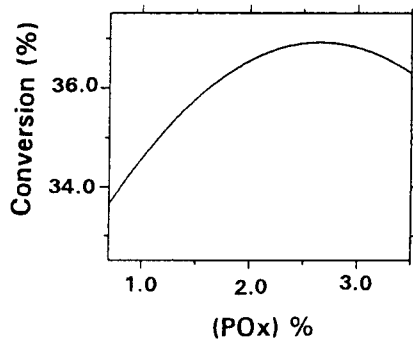
Reaction Time = 4 min.
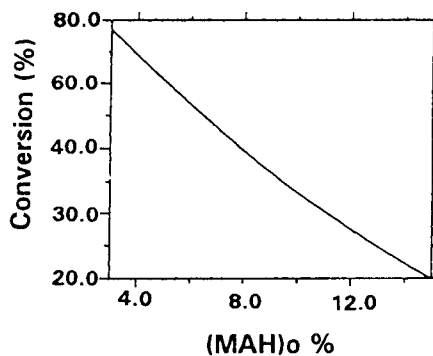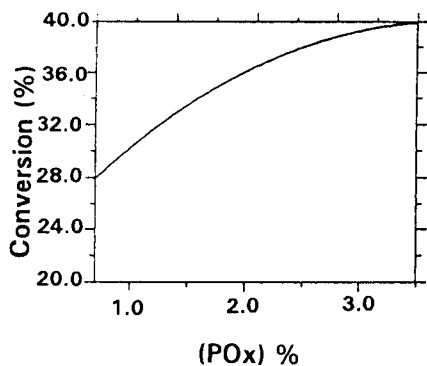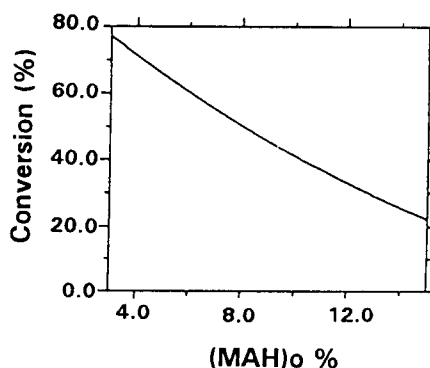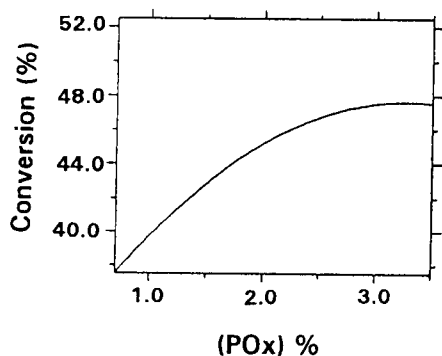
Reaction Time = 6 min.

Reaction Time = 9 min.

Figure 6 Conversion levels at a given initial concentration of peroxide (2.1%) and maleic anhydride (9%).

PP surface. This surface is continuously changing with the gear imposed for the reactor where reaction takes place.

The radicals created on those tertiary carbons are due to the presence of a initiator like POx. These radicals are supposed to be unable to produce important degradation reactions at the first stages of the reaction but not later. Then grafting is mainly produced. This fact would explain the alternate cycles observed when the phenomena are studied. This can be assumed to be the response of the system through chemisorption and chemidesorption steps where the propagation and/or termination steps (from a radical process) successively govern the overall modification process occurring in the system referring to the physical microscale sizes of the molecules involved in the reaction.

Table VII   Grafting Levels onto aPP-SA as Function of Time of Residence in Reactor

Experiment No.	Time (s)	Grafting Level (%)
1	145	3.30
2	155	3.90
3	180	4.10
4	210	3.90
5	255	2.70
6	285	3.30
7	295	3.70
8	310	4.15
9	390	4.00
10	480	2.10
11	490	2.60
12	505	2.90
13	600	4.15
14	690	3.95
15	780	2.10
16	790	2.70
17	805	3.00
18	900	4.00

Throughout this work we can see that the higher the time of reaction, the lower the fluctuation effect.

In the simplest and most basic studies on fractal kinetics[35–38] the rate constant turns into a time dependent coefficient $[k(t)]$. Then the kinetic constant $k(t)$ would vary not only with temperature but also with the time of reaction (Table VIII).

According to the simplest theory for the chemidesorption process we have

$$r_d = k_d(t) \cdot \theta \qquad (1)$$

where r_d is the chemidesorption rate, $k_d(t)$ is the chemidesorption constant that is time dependent, and θ is the coating. (This is related to the probability of a reactant interacting with an already occupied active center.)

The general way in which the time dependence of the kinetic constant may be expressed can be written as

$$k_d(t) = k_o \cdot t^{-h} \qquad (2)$$

where h is defined as the heterogeneity parameter with values from 0 to 1. This parameter can be expressed as follows:

$$h = 1 - D_s/2 \qquad (3)$$

In this expression D_s is the spectral dimension, usually lower than 2. The spectral dimension can be used for the description of the molecular motion, that is, the probability of going back to a given spectral dimension after a given time.[37]

If eq. (2) is substituted into eq. (1), the expression for the chemidesorption rate can be expressed as
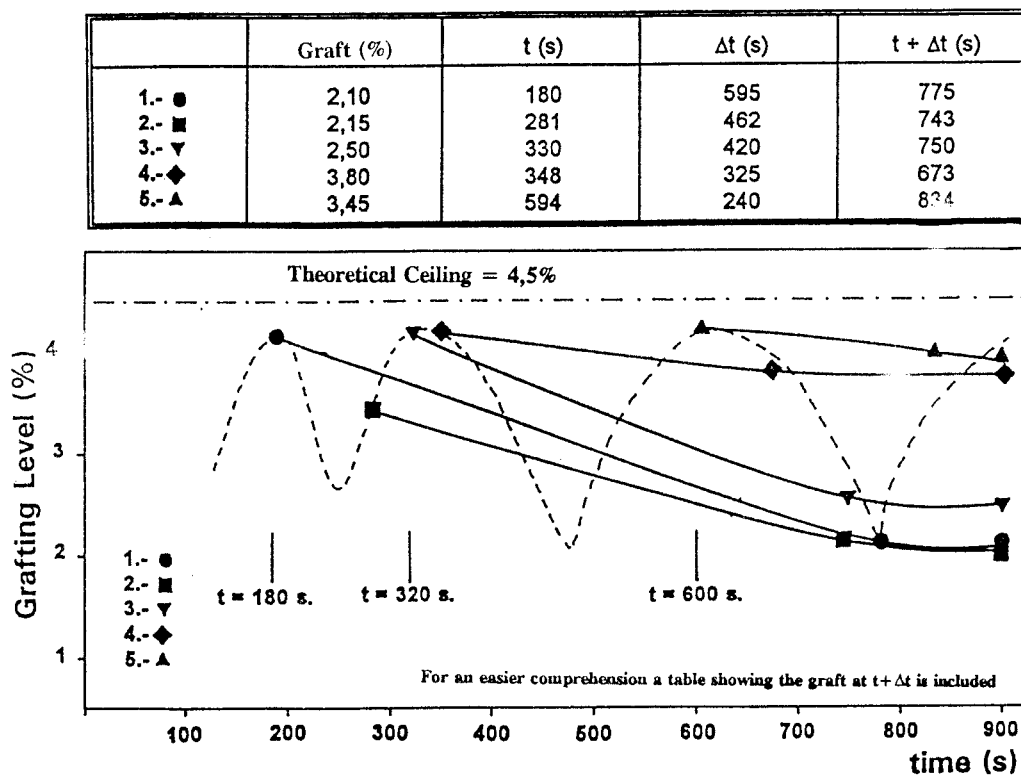
$$r_d = k_o \cdot t^{-h} \cdot \theta \qquad (4)$$

which in log–log relationship will be

$$\ln(r_d/\theta) = \ln k_o - h \cdot \ln t \qquad (5)$$
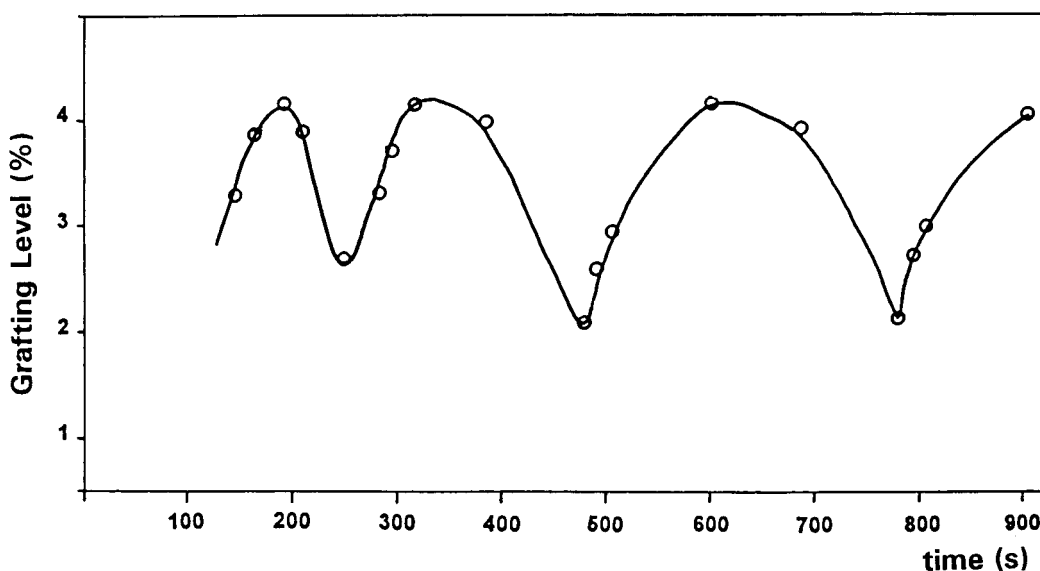
Figure 7   Evolution of the grafting level with the time of reaction in the process for obtaining aPP-SA.

	Graft (%)	t (s)	Δt (s)	t + Δt (s)
1.- ●	2,10	180	595	775
2.- ■	2,15	281	462	743
3.- ▼	2,50	330	420	750
4.- ◆	3,80	348	325	673
5.- ▲	3,45	594	240	8?4

Figure 8 Grafting level evolution when resorcinol is added. The dotted line shows the evolution for its homologous aPP-SA.

So, in a chemidesorption process occurring in a heterogeneous system underlined by a physical surface, we can calculate the k_o and h values, which when substituted into eq. (2) give us the changes in the kinetic constant during the reaction time.

Table IX compiles the values associated with each of the chemidesorption processes occurring in the system. These values can be seen in Figure 7. When these three set points are plotted they result in straight lines with the same value for the intercept, $\ln k_o$, and almost the same for the slope referred to as the heterogeneity parameter (h). The calculated value for h (approximately 0.3) is in good agreement with fractal theory.

Thus, the expression for the desorption rate constant can be written as follows:

$$k_d = 1.5 \cdot 10^{-3} \cdot t^{-0.3} \qquad (6)$$

From the latter we can conclude that a sharp decay in the rate constant is produced when the time of reaction increases. So, it can also be said that the cyclical mode the process presents is due to the relative importance of propagation and/or termination steps for a viable radical process. This mode is possible to detect because of the lower efficiency of the POx activity due to the fact that the temperature necessary to process the atactic polymer is lower than that necessary to process iPP.[8,9]

These conclusions allowed us to make some connections with our preliminary studies.[8,9] Those previous works dealt with the chemical modifications of a commercial grade of iPP using MAH and conducted both in solution and in the molten state. The above mentioned results let us make a few remarks about the influence of the stereospecific nature of the modified polymer. The present studies conducted on aPP suggested a few considerations that are compiled in Figure 10. This plot was derived using data from polynomial fits obtained in previous works on chemical modification in solution and in the melt.[8] These values are the filled dots in Figure 10. Clear significantly higher graftings values are obtained in the molten state if compared with those in solution (at the same initial concentration values) when either aPP or iPP is used. In both cases, as in Figure 7, we find a minimax evolution.

If we use the polynomial fit obtained in the present work to make predictions of different

Figure 9   Reaction mechanism proposed for the chemical modification of PP by maleic anhydride using peroxide.
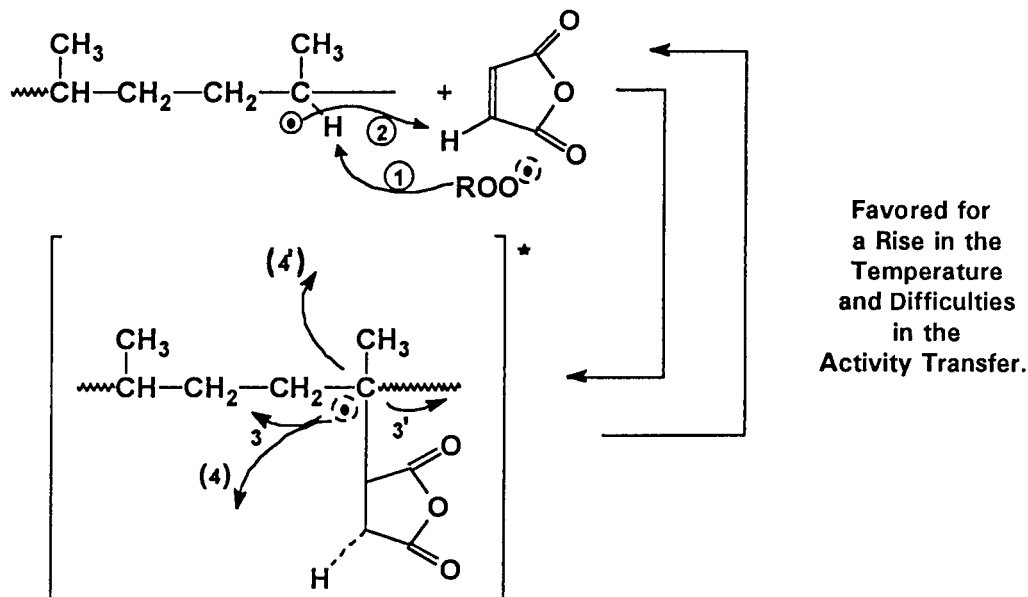
(3, 3'): Possibility of transference for any side of the backbone of the polymer chain, from other one nearly enough. The new radical will be able to give a new chemisorption complex going to a grafting specimen if it is able to transfer its activity immediately, and so on. This always taking into account the stereospecificity and steric impediments that could avoid the coating process, that is, the stable occupation of the reactive positions by the maleic anhydride.

- (4): Activity transfer to the "solvent" polypropylene due to a minimum presence in this area (chemisorption area) of MAH molecules. The macromolecule will lose its activity for a disproportion phenomena conducting to insaturations and chain ends.

- (4'): Activity transfer to units of maleic anhydride in the adsorbable phase, and then not able for yielding on the chemisorption phenomena.

Table VIII   Variations of Desorption Constant with Time of Reaction

t (s)	$k(t)$
1	0.0015
5	9.25×10^{-4}
30	5.41×10^{-4}
60	4.40×10^{-4}
180	3.20×10^{-4}
300	2.70×10^{-4}
420	2.40×10^{-4}
600	2.20×10^{-4}
900	1.90×10^{-4}

times of reaction using aPP, we can see they follow the same type of evolution. We also do that with iPP with the same reaction conditions and other different times (filled squares in Fig. 10).

Although differences between processing temperatures will be discussed in our next article, it is very important to observe that despite the expected lower efficiency of an initiator like POx, the grafting values obtained at 140 and 190°C are quite similar.

The polynomial fits used for obtaining the response of the experimental design central value present the typical minimax evolution taking place in chemisorption phenomena. The experimental variations (unfilled dots) are included in

Table IX   Data Fittings for Each Desorption Stage Plotted in Figure 1 Using Fractal Kinetic Model

| Cycle No.	Initial Time (s)	Final Time (s)	MAH$_{DESORB}$ (%)	Intercept ln K_0	Slope $-h$
I	180	255	2.90	−6.41	0.38
II	312	480	2.40	−6.51	0.32
III	600	780	2.45	−6.48	0.33

Figure 10 in order to make the comparison easier. This situation seems to suggest a dynamical nature of the grafting phenomena similar to findings in the literature.[39–42]

Our next study deals with the effect that the stereochemical origin and the number of tertiary carbons present on the polyolefin have on the yield in the grafting process.

Finally (Fig. 3) we see it is possible to obtain a modified polymer of about 4% grafting. The importance of this is the fact that the obtained grafts are very similar to those used commercially as interfacial agents and are based on iPP. The latter have demonstrated to be very interesting for the better properties they improve when incorporated to polymer blends and composites based on PP.[4,5]

Although not the object of this work, Figure 11 shows as an example of the variations that elastic moduli have when interfacial agents are added (to a composite material, reinforced with a 30% w/w talc or mica, based on PP): either a commercial product (iPP-SA) having a 5% of grafting, or one of ours having nearly such a grafting level (aPP-SA). It must be noted that our product is even better than the commercial one. It is well known that this is a very important aspect of a molded specimen. In this sense our product will have a spectacularly improved surface aspect, as can be concluded from the data in Figure 12. Our next works will be dealing widely with this aspect of the problem.

Furthermore, the real option of being able to
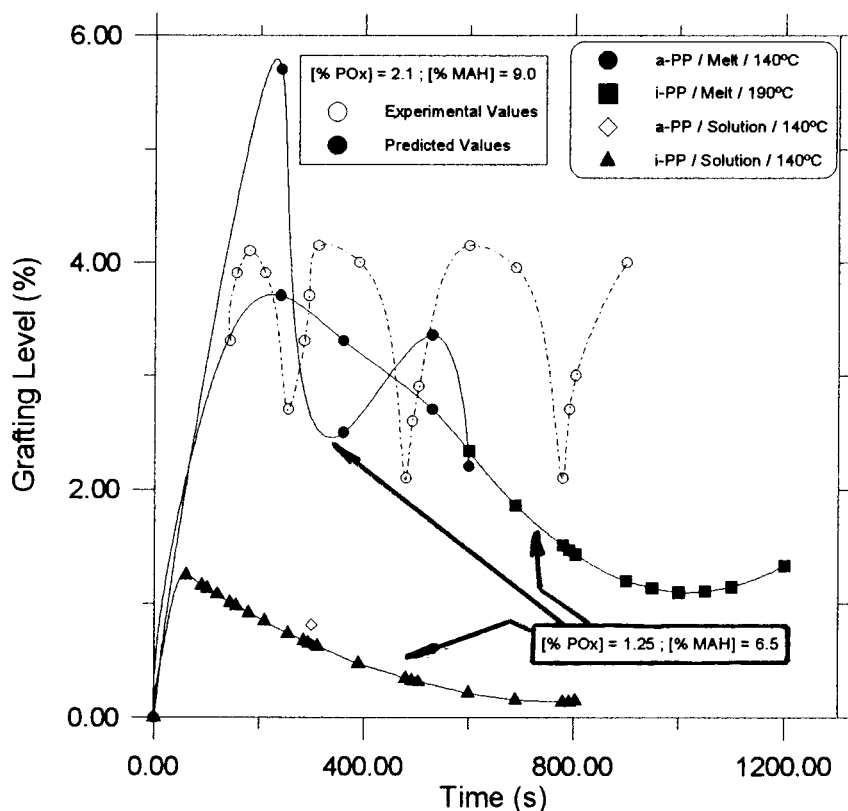
Figure 10   Grafting levels for aPP and iPP, both in solution and in the molten state (from the fittings).

obtain modified polymers with different levels of grafting varying from 1% to the theoretical ceiling near 5% gives us the possibility of exploring the changes in the interfacial activities of those agents as a function of the grafting levels, and not only at a 5% grafting percentage as the commercial type has.

CONCLUSION

The possibility of obtaining a chemically modified PP from an atactic polymer (a nonuseful industrial waste) was shown. This product can be widely used as an interfacial agent and/or compatibilizer in polymer composites and polyblends.

From the point of view of the most fundamental aspects associated with the chemical processes conducted on polymers, very important differences in the graft levels were found when aPP was used. In fact, when compared to iPP, a great difference was found in spite of the lower activity of POx at 140°C (aPP) than at 190°C (iPP).

The very important role played by a short reaction time (<10 min) was proven for aPP and iPP. The tacticity may explain some of the differences found in the grafting levels obtained.

The consideration of the existence of a heterogeneous reaction media due to the very different molecular sizes and the motion capability of the species involved seems to explain the findings of this investigation. An interfacial phenomena was proposed to be responsible for the overall grafting level of succinic anhydride into the PP (either aPP or iPP) with no dependence on the tacticity of the phenomena. An immediate consequence of this situation would be the microsegregation of the
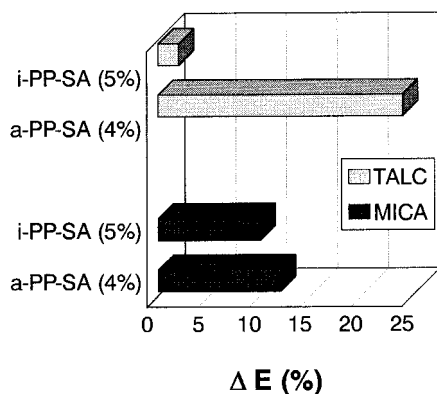
Figure 11 Elastic moduli variations in composite materials when interfacial agents are added.
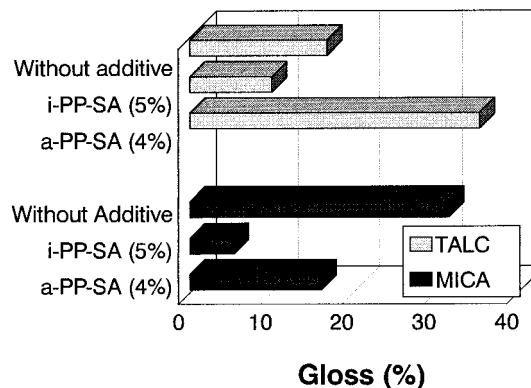
Figure 12 Gloss measurements (60°) in composite materials with or without interfacial agents.

grafted groups into the modified PP. Future studies will deal with these aspects.

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