FTIR Quantitative Characterization of Chemically Modified Polypropylenes Containing Succinic Grafted Groups

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ABSTRACT: The FTIR quantitative evaluation of grafting succinic anhydride onto polypropylenes is presented. It was done by correlating relative absorbance values obtained from IR spectra with grafting levels of the sample as determined by an improved traditional hot titration method. The results obtained seem to be valid for either atactic or isotactic modified polypropylenes and suggest a careful review about how this technique is usually used in the quantification of polar groups grafted onto polyolefins. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2837–2847, 1999

Key words: polypropylene; FTIR; succinic anhydride grafted polypropylene

INTRODUCTION

Polypropylene (PP) is one of the most widely used synthetic polymers today and in the near future. Many studies have been conducted, from the industrial point of view and the most basic aspects, on the chemical characterization of this polymer. The latter is strongly supported by the recent appearance of scientific and technical books on this topic^{1,2} that compile a large number of references related to the different fields such as synthesis (Ziegler-Natta catalyst, metallocene catalyst, etc.); polymer characterization (thermal behavior, determination of stereosequences, spectroscopy of polar groups and/or impurities present, molecular weight distribution, crystallinity); and processing methodologies, especially reactive processing.³⁻⁸

Interfacial modifiers reach their highest relevance when we are trying to obtain "tailor-made" heterogeneous materials based on polymers. In this sense the chemical modification of PPs for further use as interfacial modifiers for those materials is a very important topic on which a lot of literature has emerged. Nevertheless, the ratio between empirical and basic scientific works can be said to be very high, probably because there are only a few accurate quantitative studies that can be undertaken on the most basic aspects of the chemical modification processes over macromolecular substrates.

In previous publications^{9,10} the solution and molten state processes to carry out the reaction between isotactic PP (i-PP) and maleic anhydride in the presence of dicumil peroxide were compared.

Atactic PP (a-PP) was then considered as the macromolecular substrate and higher modification degrees were obtained,^{11,12} so the stereospecificity of the polymer was demonstrated to have great influence on the reaction yielding. It was also described that a condensation reaction between the already grafted succinic groups and resorcinol produced a new grade of chemically modified polymer containing succinil-fluoresceine

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No.	Name	Reaction Conditions			
		[Peroxide] [% (w/w)]	[MAH] [% (w/w)]	Time (min)	Graft (%)
1	i-PP-SA (0.5%)	3.0	4.5	3.0	0.5
2	a-PP-SA (1%)	0.1	9.0	10.0	1.0
3	a-PP-SA (1.5%)	0.7	3.0	4.0	1.5
4	a-PP-SA (2%)	2.1	17.5	6.0	2.0
5	a-PP-SA (3%)	0.7	15.0	4.0	3.0
6	a-PP-SA (4%)	4.1	9.0	6.0	4.0
7	i-PP-SA (5%) ^a	_	_	—	5.0

Table I Experimental Conditions for Preparation of Samples

^a Commercial grade.

groups.^{12–14} This quantitative condensation reaction proved the accuracy of the previous determination of the grafted groups in the polymer and then made possible the correlation of grafted values and their absorbances obtained by FTIR.

EXPERIMENTAL

Materials

The PPs used for modification were i-PP (ISPLEN 050) and a-PP (from industrial wastes) supplied by Repsol Química. They were previously described.⁹⁻¹⁴

Maleic anhydride (Scharlau/Ferosa) and dicumil peroxide (Perkadox BC, Akzo) were used as the reactant and initiator, respectively. The thermal stabilizers (antioxidants) used were Irganox 1010 and Irganox B225, both from Ciba–Geigy.

A modified PP containing a 5% (w/w) grafting level (from Himont) was used as a control for highly grafted a-PPs and i-PPs.

Procedures

Chemical modification reactions were carried out in the molten state by using an internal mixer Rheomix 600 attached to a driver unit Rheocord 90 from Haake. The gear rate set value was 45 rpm. Materials were added in the following way: first PP, maleic anhydride, and the thermal stabilizer dry blend were introduced into the reactor. When the materials were melted and well mixed, peroxide was added. Addition of the peroxide was considered as the start time for the modification reaction. Reaction temperatures were 190°C for i-PP and 140°C for a-PP. Table I is a compilation of the reaction conditions for every sample. The modified polymers were first dissolved in boiling xylene to remove nongrafted species and stabilizer traces and then precipitated into methanol to recover the functionalized polymer. The next stage was to filter the precipitated polymer, followed by drying.

The graft content was first determined by heating 1 g of sample for 60 min in 150 mL of a refluxing water/xylene/n-buthanol (6.6/60/33.3) mixture. The hot solution was then titrated without cooling with 0.05N ethanolic KOH, using Bromothymol 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 the addition of 0.05N isopropanolic HCl to the hot solution.^{9–16} The results are expressed as a weight percentage of the grafted groups onto PP. Unmodified PPs were also titrated and insignificant values were obtained. Thus, the existence of pendant succinic groups in the PP could be clearly concluded.

The IR spectra were recorded on a Nicolet 520 FTIR using the KBr pellet technique with an averaging of 32 scans at a resolution of 2 cm^{-1} . KBr pellets were prepared by varying the concentration of the polymer in a range from 1 to 4 mg of polymer in 170 mg of KBr.

In order to examine the heterogeneity of the macromolecular system, 1.5 g of modified a-PP sample was fractionated in boiling *n*-heptane for 3 h by using a Soxhlet apparatus. While the original atactic polymer was totally dissolved by this treatment, three fractions were obtained from the grafted samples as follows: a solid fraction re-

mained insoluble in the Soxhlet cartridge; the second fraction was recovered by precipitation of polymer from the *n*-heptane solution into methanol; and finally, the nonprecipitated fraction was recovered by evaporation of the solvent. The three fractions obtained were dried and weighted and then hot titrated to determine their grafting levels.

RESULTS AND DISCUSSION

Quantification by IR Spectroscopy: Fundamentals

IR spectroscopy has been widely used as an analytical and characterization tool in the polymer field. It is well known that there is a great complexity in the spectra obtained from polymers due to the existence of overlapped bands, changes in their shapes, and displacements all along the frequency axis. These facts may be a serious problem when trying to quantify accurately.

Part of the above-mentioned problems are a consequence of the different treatments applied, thermal and processing histories of the samples, and/or chemical reactions taking place on the polymer when modified. All these aspects may make this technique (FTIR) inappropriate when used in quantitative determinations.

Upon processing, the semicrystalline nature of the polymer (e.g., i-PP) could have changes in the crystalline content. Then an overlapping phenomena is expected to occur between the vibration modes of groups present in the amorphous regions and those belonging to crystalline regions; besides, bands corresponding to crystalline regions are expected to be narrower and more intense than those corresponding to amorphous regions. Thus, it would be very important to choose adequate reference bands in order to avoid skewness in handled data, which would lead to wrong results.

Although there are occasions when it is possible to find linear correlations between peak intensity and film thickness or sample concentration, in other cases (like FTIR) the peak of interest is overlapped, so curve deconvolution techniques to separate overlapped peaks could be used. After having well-defined FTIR spectra, some basic considerations about the Lambert–Beer rule must be done before quantifying polar groups attached to PP if accuracy is desired. According to the Lambert–Beer rule, absorbance is defined as follows:

$$A = -\log I/I_0 = -\log T = \log 1/T = a \cdot b \cdot c \quad (1)$$

where the ratio between the intensity of transmitted (I) and incident radiation (I_0) is called transmitance (T), c is the concentration of the sample, b is the path length the radiation travels through the sample, and a is the "absorptivity" and is wavelength dependent. One may find cases where the concentration is linearly correlated with the measured absorbance. However, numerous studies can be found in which the correlation between sample concentration and absorbance is not linear. 17-19 This is plotted in Figure 1 where the linear evolution [Fig. 1(a)] follows the Lambert-Beer rule but has a residual absorbance that must be considered in further studies on quantification. Figure 1(b) indicates a nonlinear correlation between absorbance and concentration beyond a given range of concentrations (c_1 and c_2). Finally, Figure 1(c) indicates a combination between the behavior shown in Figure 1(a,b).

FTIR Spectra of Modified PPs Containing Succinic Anhydride Pendant Groups

Different FTIR spectra corresponding to various i-PP and a-PP qualitative characterizations are presented in Figure 2.

The most common way to obtain IR spectra (in the case of PP) is from thin films prepared by a melting and compression process under controlled conditions. However, the atactic homopolymer films did not have enough mechanical strength to be handled. Therefore, KBr pellets were made to obtain the FTIR spectra. The thermal histories of all the polymers were similar because the samples of modified polymers came from similar purification operations. The presence of a carbonyl band in the neighborhood of 1790 cm⁻¹ in the polymers containing succinic grafted groups indicates the presence of these groups.

At this point we must remark that the method usually followed by many authors (not having samples with well-known grafting levels) is to obtain calibration curves from samples with a previously determined amount of the polar coreactant physically dispersed into the polymer matrix²⁰⁻²⁸ or even from solution of the

polar monomer in different solvents, such as octene²⁹ or carbon tetrachloride.^{30,31} This does not seem to be a reasonable method of accurate quantification if the previously mentioned considerations about the changes produced in the spectral band intensities, shape, and size of peaks caused by chemical reactions (grafting and β scissions produced during the process of chemical modification, orientation and crystal-linity changes, etc.) and processing methodologies are taken into account.⁹ It is because of this reason that a sufficient number of samples of



Figure 1 Deviations from the Lambert–Beer rule: (a) residual absorbance; (b) nonlinearity in a given range of concentrations; (c) nonlinearity plus residual absorbance.



Figure 2 FTIR spectra of modified and unmodified polypropylenes (atactic and isotactic).

modified polymers were prepared containing well-determined amounts of grafting obtained under well-set experimental conditions, and the accurate quantitative determination of grafts by FTIR was undertaken. These spectra were obtained from samples containing grafting levels of succinic anhydride moeties in a range from 0.5 to 5% by weight.

In fact, it is very important to note that, in addition to the desired grafting reactions, a degradation process is occurring at the same time. The β -scission processes, although minimized by the addition of stabilizers, are affecting the vicinity of the IR active species, especially the so-called chain ends. In the same way, the conformational state of such groups would be affected by the graft content.

According to the general reaction scheme traditionally proposed for this kind of process, the structure may be written as follows:

0. I
$$\longrightarrow$$
 2R[•] \longrightarrow 2R[•] 2 .
1. R[•] + Ar $-$ CH₃ \longrightarrow RH + Ar $-$ CH₂
 \longrightarrow 3.
2. R[•] + $\left(CH_2 - CH \right)_n \longrightarrow$
RH + $\left(CH_2 - \dot{C} \right)_n$
RH + $\left(CH_2 - \dot{C} \right)_n \longrightarrow$
RH + $\left(CH_2 - \dot{C} \right)_n \longrightarrow$
4.

5. $\operatorname{Ar}-\operatorname{CH}_{2}-\operatorname{SA}^{\bullet} + \operatorname{Ar}-\operatorname{CH}_{3} \longrightarrow$ $\operatorname{Ar}-\operatorname{CH}_{2}-\operatorname{SA} + \operatorname{Ar}-\operatorname{CH}_{2}^{\bullet}$ 6. $\operatorname{Ar}-\operatorname{CH}_{2}-\operatorname{SA}^{\bullet} + \left(\operatorname{CH}_{2}-\operatorname{CH}_{-}\right) \longrightarrow$ $\operatorname{Ar}-\operatorname{CH}_{2}-\operatorname{SA}^{\bullet} + \left(\operatorname{CH}_{2}-\operatorname{CH}_{-}\right) \longrightarrow$ $\operatorname{Ar}-\operatorname{CH}_{2}-\operatorname{SA} + \left(\operatorname{CH}_{2}-\operatorname{CH}_{-}\right) \longrightarrow$ $\operatorname{CH}_{3}/_{n} \longrightarrow$ 4. 7. $\operatorname{Ar}-\operatorname{CH}_{2}-\operatorname{SA}^{\bullet} \longrightarrow$ $\operatorname{SA} + \operatorname{Ar}-\operatorname{CH}_{2}^{\bullet}$

→ 3.

 $Ar-CH_3$

where

would be the solvent molecule (when performed in solution) and $% \left({{\left[{{{\mathbf{n}}_{{\mathbf{n}}}} \right]}_{{\mathbf{n}}}}} \right)$

$$\left(\begin{array}{c} \operatorname{CH}_2 - \operatorname{CH} \\ & | \\ & \operatorname{CH}_3 \\ \\ & \end{array} \right)_n$$

would be the repetitive unit on the macromolecule backbone.

On the other hand, and according to our findings,¹² we must consider the following species that are generated as the time of reaction goes by:





The degradation reaction structure can be written as follows:



where the conditions of the lowest oxygen concentration would be the case of applicability in our experimental runs, because of the presence of the thermal stabilizers.

It must be noted that reactions 1, 3, 5, 6, and 7 would be concerning with the classical transference to the solvent effect.³² In the molten state process (the way our samples were obtained) this would mean the substitution of the solvent molecule in steps 1, 3, 5, 6, and 7 by another chain of the PP. Consequently, 1 is similar to 2; 3 is identical to 4; and the 5, 6, and 7 set would be the same as 8, 9, and 10, respectively.

This means the reaction product would be changing with the reactant concentrations and experimental conditions used to modify the polymer, affecting then any quantitative determination carried out by nonabsolute methods.

The transient nature of the process, according to the above-mentioned reaction set, can be drawn by the following process scheme (Scheme 1) proposed and fully discussed in a previous study.¹¹ In other words, it must be considered that the sample is a heterogeneous system conducted, from the macroscopic point of view, to an averaged grafting level that would present substantial changes on a molecular scale as a function of the experimental conditions from which the modified polymer was obtained.

In the same way, the physical sense of the former oblige to carefully choose the reference band useful for each sample minimizes the effects of changes in the IR spectral response, for instance, to avoid effects caused by a little degradation occurring for short reaction times or tacticity variations caused by high grafting levels.

The magnification of FTIR spectra corresponding to i-PP and a-PP recorded from 1540 to 760 cm^{-1} can be observed in Figure 3, and differences



 (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.

Scheme 1 A process scheme showing the transient nature of the process.



Figure 3 Comparison of FTIR spectra of atactic and isotactic polypropylenes in the range from 1540 to 760 cm^{-1} .

between both spectra are clearly perceptible. Burfield and Loi³³ recomended the use of the band at 973 or 1167 cm^{-1} as a reference band. If both bands in the i-PP are compared, the first one is observed as more intense and narrower. This band has been always assumed to be related to head to tail sequences on the polymer backbone and to the presence of little isotactic sequences.³⁴ Furthermore, Quym et al.³⁵ demonstrated that there is a linear correlation between the amount of crystalline phase present in the polymer and how narrow and intense this band is (973 cm^{-1}) and Kissin et al.^{36,37} showed that only in the case of highly crystalline polymers (fully isotactic) is the band at 1167 cm^{-1} recommended as the internal reference. Thus, the band at 973 cm^{-1} was chosen as the internal reference for either the isotactic or atactic modified polymer. A decrease in the level of tacticity is expected when isotactic polymer is modified because of the constraint the grafted groups (on the backbone) place on the crystallization phenomena. Besides, the band at 973 cm^{-1} does not undergo substantial changes when the polymers are modified. However, the band at 1167 cm^{-1} (traditionally assumed to be affected by the tacticity balance in the polymer) changes its shape when the polymer is modified. The latter can be clearly noticed in reproductions in Figure 4.

PP Containing Succinic Anhydride Pendant Groups: Absorbance Versus Concentration

According to the spectra displayed in Figure 2, by expanding the $1900-1680 \text{ cm}^{-1}$ region, it is pos-

sible to obtain the plots represented in Figure 5. For homopolymers, insignificant intense bands are detected in this region and only a slight absorption area with respect to the baseline can be observed. On the contrary and as expected, graft polymers show a lot of intense absorption bands in the same area associated with the characteristic carbonyl group vibration frequencies.

In fact, carbonyl groups on anhydrides involved in five member rings present characteristic assymmetric and symmetric stretch vibrations in the 1875–1855 and 1795–1775 cm⁻¹ regions, respectively. The more intense band is usually the one associated with the symmetric stretch of the carbonyl group at 1790 cm⁻¹ for the maleic anhydride case. By this reason this band was chosen for the quantitative purposes of this study.

The intensity peak method was adopted because of the aspect ratio of that band. As the baseline criterium, the dotted line in the graft sample spectra in Figure 5 was adopted,¹⁷ because of the complexity of the spectra for quantitative purposes, due to the coupling between the absorption peaks detected in this spectrum region and related to changes on the molecular interaction levels imposed by variations on sample concentration.

Samples of well-characterized modified PPs containing different polymer concentrations were



Figure 4 Shape variations in the IR band at 1167 cm^{-1} for atactic and isotactic polypropylenes (before and after modification).



Figure 5 Comparison of FTIR spectra for grafted and unmodified polypropylenes in the range from 1900 to 1680 cm^{-1} .

recorded in an FTIR spectrophotometer. As mentioned previously, reaction conditions under which these samples were obtained have been compiled in Table I.

Absorbance ratios (A_{1790}/A_{973}) for each of the samples were calculated from the spectra and are compiled in Table II. These values are represented versus the concentration of the modified polymer in the KBr pellet (Fig. 6). The exponential evolution between the detected response due to the grafting level present in the polymer and the amount of sample present in the KBr pastille can be clearly observed in Figure 6. Such evolution corresponds to Figure 1(b). Note that this effect is more and more important when less and less of the averaged grafting level is present in the polymer, as usually occurs in modified polymers coming from i-PP. Hence, the fact that such evolution is found either in samples coming from isotactic or atactic polymers is also remarked.

With the data represented in Figure 6 and considering the well-determined grafting levels of each sample by the titration method, a correlation between the absorbance ratio A_{1790}/A_{973} and the

grafting level for each of the KBr pellet concentrations was obtained (Fig. 7).

For the highest grafting levels [i.e., above 4% (w/w) of grafted species], the variation between the absorbance ratios with sample concentration is very small. Nevertheless, in the lowest grafting levels is where the heterogeneity of the polyolefin would be mainly affecting the evaluation and thus incorrect results would be obtained. An immediate consequence of these results would be the segregation of grafted groups in the sample or a heterogeneous distribution of those grafts. In order to check the latter, an exhaustive extraction was carried out. This was possible because a-PP dissolves in boiling n-heptane.

A 3-g sample of unmodified a-PP was introduced into a Soxhlet apparatus containing boiling *n*-heptane for 3 h. After a 20-min boiling, the a-PP sample was completely dissolved in the boiling n-heptane. When the test was finished, no traces of a-PP remained in the Soxhlet cartridge. However, when a modified sample containing a 3% grafting was treated in the same way for 3 h, three different fractions were obtained. The first of them corresponds to the nonsoluble fraction remaining in the Soxhlet cartridge. This fraction results were very small but contained a high graft percentage. A second fraction was obtained by precipitation of the polymer from the hot solution into methanol. This amount represents 33.25% (w/w) of the whole sample (Table III) and it contained a very low grafting level (0.25%). The third fraction, which remained soluble in the precipitant/solvent mixture, was recovered by evaporating the liquid phase. These latter results were the major part of the soluble fraction [62.89% (w/w)] and contained a level of grafting (2.72%) close to the average the original sample had.

The grafting level obtained from the two soluble fractions let us appreciate that although the fraction recovered by precipitation had a very low grafting average if compared to the 3% present in the whole sample, the portion recovered by evaporation had an averaged value close to that of the whole sample. By a mass balance between the three fractions recovered, an averaged grafted value of 2.75% was obtained (close to the 3% obtained before fractionation). Nevertheless, these values can be considered as being in good agreement if the loss produced during the separation processes are taken into account. Obviously there is a variability in the composition of the three fractions obtained from a determined sample of

	$[C] imes 10^2$			
	(mg polymer/mg KBr)	A_{1790}	A_{973}	A_{1790}/A_{973}
i-PP-SA (0.5%)	0.432	2.0781	0.9398	2.2111
	1.260	1.6504	0.5712	2.8891
	2.376	1.5338	0.4389	3.4948
	3.593	1.4790	0.3791	3.9016
a-PP-SA (1%)	0.360	2.1203	1.3389	1.5836
	1.240	1.7283	0.8610	2.0072
	2.410	1.6545	0.7843	2.1095
	2.900	1.5592	0.6845	2.2778
	3.480	1.5876	0.7084	2.2409
a-PP-SA (1.5%)	0.361	2.3848	1.5578	1.5309
	1.239	1.9547	0.9936	1.9672
	2.480	1.9248	0.9190	2.0944
	2.990	1.9967	1.0027	1.9917
	3.380	1.8457	0.8625	2.1395
a-PP-SA (2%)	0.360	2.0986	1.5757	1.3319
	1.270	2.0690	1.3750	1.5047
	2.610	1.8767	1.1171	1.6800
	3.450	1.8761	1.9590	1.9550
a-PP-SA (3%)	0.418	1.6699	1.3326	1.2531
	1.307	1.6390	1.0987	1.5025
	2.700	1.5949	1.0491	1.5202
	2.940	1.5356	0.9833	1.5616
	3.570	1.3637	0.8119	1.6795
a-PP-SA (4%)	0.350	1.6074	1.3733	1.1704
	1.170	1.3384	1.0907	1.2271
	2.350	1.1853	0.9023	1.3137
	3.740	1.3071	0.9251	1.4129
	4.700	1.6663	1.1095	1.5018
i-PP-SA (5%)	0.414	2.0073	1.7063	1.1764
	1.262	1.5112	1.1660	1.2961
	2.476	1.3249	0.9762	1.3615
	3.441	1.3904	0.9948	1.3977

grafted polymer, and the necessary relationship between such variability and the conditions and nature of the chemical modification process from the modified polyolefin was obtained. New investigations and experimental plans on this topic are now in progress.

CONCLUSION

Two main remarks can be clearly made: the intrinsic heterogeneous character the process of chemical modification of PP, and macromolecules in general, has and the peculiarities that such a heterogeneous character causes in the quantification procedures to obtain the necessary values for a further evaluation of reaction yielding.

Thus, nonlinearity can be assumed between the concentration of samples of modified PPs (isotactic and atactic) and the absorbance ratio between the succinic anhydride characteristic band at 1790 cm⁻¹ and that of the internal reference at 973 cm⁻¹ when quantified by FTIR spectroscopy.

Handling a variety of samples containing a well-known average concentration of grafted polar groups made the correlation of both parameters possible by using a log-log representation. Such a correlation let us accurately quantify the number of groups grafted into PP.



Figure 6 Absorbance ratio (A_{1790}/A_{973}) versus concentration for the modified polypropylenes.

The above-mentioned heterogeneous character of the chemical modification yielding suggests a further structural characterization of those modified polymers. Thermal behavior and fraction segregation in the grafted polymer will be the object of our next articles.



Figure 7 Absorbance ratio (A_{1790}/A_{973}) versus grafting level for the modified polypropylenes.

Table III Segregation Produced in Sample
Containing 3% Averaged Grafting When
Extracted in Soxhlet Apparatus
Using Boiling <i>n</i> -Heptane

	Weight/Weight	Graft	
Fraction	(%)	(%)	
Nonsoluble	4.84	19.90	
Precipitated	33.27	0.25	
Dry recovered	62.89	2.72	

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