

The Anhydride Content of Some Commercial PP-*g*-MA: FTIR and Titration

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SYNOPSIS

A set of anhydride-grafted polypropylenes was collected from various companies. They were studied in light of our recent results on polypropylene melt grafted with maleic anhydride.¹ This work confirmed that an important decrease of the anhydride content is recorded on heating or washing, due to the elimination of free, ungrafted products, respectively, by sublimation of maleic anhydride and by polymaleic anhydride solubilization. The deconvolution of the infrared spectra of washed anhydride-grafted polypropylenes (PP-*g*-MA) revealed two types of grafted anhydride: succinic anhydride form and polymaleic anhydride form. All in all, four forms of anhydride functions were detected: two grafted and two free, each being either on monomeric or polymeric forms. Nevertheless, one PP-*g*-MA (Hercoprime) can be distinguished by its very high grafting level. This polymer is therefore discussed in more detail. Finally, all the present results are discussed with regard to the principal applications of the PP-*g*-MA as a blend compatibilizer or as an adhesion promoter. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The anhydride grafted polypropylenes (PP-*g*-MA) are greatly studied.²⁻⁶ This large interest originates in the wide use of reactive polyolefins: sometimes they are used as blend compatibilizers, sometimes as composite matrices, coating resins, or adhesives.

Recently, a series of PP-*g*-MA melt-synthesized from maleic anhydride and peroxide was systematically studied in our Laboratory.^{1,7} These studies gave rise to some useful conclusions. A β -scission of the chain was proposed as the first reaction step. Consecutively, succinic anhydride or polymaleic anhydride grafting occurs on the radical chain end. Figure 1 summarizes the general reaction scheme. Moreover, ungrafted anhydrides moieties were detected. They were assigned to exceeding unreacted maleic anhydride and to polymaleic anhydride originating from a maleic anhydride homopolymerization.

The present paper aims at broadening the characterization expertise obtained during the previous systematic study to a set of commercial PP-*g*-MA collected from different companies. The study deals with the determination of the global anhydride content for each PP-*g*-MA and with a relative proportion of each anhydride form (grafted or ungrafted, succinic or polymaleic). Those results will be finally discussed in a practical scope.

EXPERIMENTAL

Materials

Maleic anhydride-grafted polypropylenes (PP-*g*-MAs) under study were MODIC F300H, MODIC P300M, and MODIC P300F, supplied by Mitsubishi Petrochemical Co Ltd. (Brussel); ADMER QF500E, POLYBOND 3002, OREVAC PP-CH, EXXELOR 1015, and HERCOPRIME G, supplied respectively by Mitsui Petrochemical Industries Ltd (Brussel), British Petroleum Company plc (Amsterdam), ATOchem (Paris), Exxon Chemical (Brussel), and Himont Inc (Brussel).

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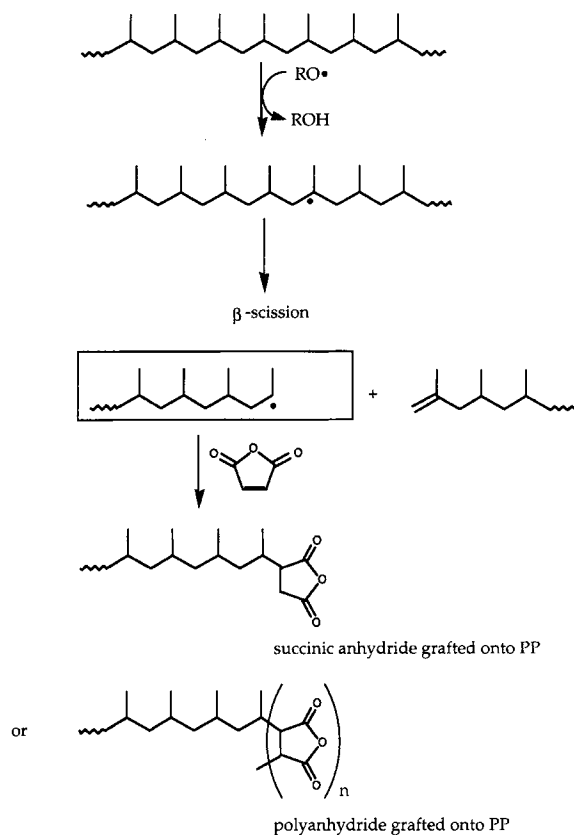


Figure 1 Main reactional path for the grafting of PP⁽¹⁾.

The toluene was reagent grade and was used without further purification. Methanol and acetone were distilled before use.

Sample Preparation

Raw PP-g-MA

Pellets of commercial resins were analyzed as received, without further treatment.

Heated PP-g-MA

Pellets were dried in a vacuum oven at 120°C for at least 100 h.

Washed PP-g-MA

One gram of pellets was dissolved in 100 ml of toluene at reflux temperature. The polymer was then precipitated in acetone and repeatedly washed with acetone and methanol. Finally, the recovered product was dried in a vacuum oven for 100 h at 120°C.

Evaluation of the Concentration of Grafted Species by Titration

The anhydride contents in raw, heated, and washed PP-g-MA were determined by titrating the acid groups. After dissolution of 1 g of polymer in 100 ml of toluene at reflux temperature, 200 μ l of water were added to help the anhydride ring opening. The reflux temperature was maintained for 1 h. The resulting carboxylic groups were determined by alkali titration. The hot solution was titrated immediately before cooling, with 0.025N potassium hydroxide in methanolic/benzoyl alcohol 1/9 (vol/vol) after adding of five drops of 1% phenolphthalein in methanol as indicator. When the coloration remained for 1 min, titration was stopped.

The polymer was completely soluble at the reflux temperature and did not precipitate during titration.

A blank test (without any sample) was carried out by the same method.

Size Exclusion Chromatography (SEC)

Molecular weight measurements of washed PP-g-MA were carried out on a high-temperature size exclusion chromatograph (Waters 150C) equipped with three Shodex columns (two Shodex AT-80M/S and one Shodex Styragel 300Å).

A differential refractometer detector coupled with a Vax Chromatography Data Station of Digital was used to record and analyze the signal.

1,2,4-trichlorobenzene stabilized with 2% Irganox 1010 was the permeation solvent and the sample preparation diluent.

The samples ranged in concentration from 6 to 8 mg/ml. Their dissolution was achieved by shaking at 160°C during 1 h.

The injection volume was 120 μ l. The system was maintained at 135°C throughout the analysis.

The system was calibrated with polystyrene standards using a universal calibration method and the equation $\log \eta = 1.21 \times 10^{-5} M_n^{0.71}$ for PS.⁸ The intrinsic viscosity (η) of PP in 1,2,4-trichlorobenzene was obtained using the following equation: $\log \eta = 1.76 \times 10^{-5} M_n^{0.73}$. This relation was developed for PP homopolymer.⁹ The molecular weight values obtained by this method are of course not absolute, but they provide a good basis for a comparison between the polymers studied. Nevertheless, the hydrodynamic volume change due to the grafting and a possible change in elution time after retention on column must be kept in mind.

Table I Maleic Anhydride Content Measured Out by Titration onto Raw, Heated, and Washed PP-*g*-MA for Various Commercial Products

Commercial Polymers	AM Content ($\mu\text{eq/g}$) Raw PP- <i>g</i> -MA	AM Content ($\mu\text{eq/g}$) Heated PP- <i>g</i> -MA	AM Content ($\mu\text{eq/g}$) Washed PP- <i>g</i> -MA
Modic f300h	18	18	10
Modic p300m	18	11	9
Modic p300f	19	12	8
Polybond 3002	30	16	11
Orevac pp-chv	11	9	7
Admer Qf 500e	8	8	4
Exxelor 1015	96	44	33
Hercoprime G	561	441	303

Infrared Spectroscopy

The infrared (IR) spectra were recorded on a Perkin-Elmer 580B spectrometer from 4000 to 400 cm^{-1} . The PP-*g*-MA samples were processed in 100- μm -thick film by a cold pressing. The absorption bands between 1850 cm^{-1} and 1650 cm^{-1} , and between 1106 cm^{-1} and 1097 cm^{-1} were mathematically analyzed by an "iterative curves fitting" method Igor[®] and provided by Wavemetrics, Inc. Each absorption band was approximated by a Lorentzian function.¹⁰ The iterative soft defines the position, the amplitude, and the bandwidth of each band in order to restore the IR spectrum by adding all the Lorentzians. The so-deconvoluted Lorentzians are considered as the actual absorption bands. A calibration work was elsewhere performed.¹ The absorption parameters previously defined are used here. They are defined respectively for the *n*-octadecyl succinic anhydride and for polymaleic anhydride as follows:

$$[\text{anhydride}_{\text{succinic}}] =$$

$$21.5 \left(\frac{\text{abs } 1792 \text{ cm}^{-1}}{\text{abs } 1100 \text{ cm}^{-1}} \right) + 24.5 \left(\frac{\text{abs } 1715 \text{ cm}^{-1}}{\text{abs } 1100 \text{ cm}^{-1}} \right)$$

$$[\text{anhydride}_{\text{polyanh.}}] =$$

$$51.3 \left(\frac{\text{abs } 1784 \text{ cm}^{-1}}{\text{abs } 1100 \text{ cm}^{-1}} \right) + 52.5 \left(\frac{\text{abs } 1715 \text{ cm}^{-1}}{\text{abs } 1100 \text{ cm}^{-1}} \right)$$

where [anhydride] is the anhydride concentration expressed in μeq ; abs 1792 cm^{-1} is the absorbance of succinic anhydride symmetric C=O stretch; abs 1784 cm^{-1} is the absorbance of polymaleic anhydride symmetric C=O stretch; abs 1715 cm^{-1} is the absorbance of the carboxylic acid C=O stretch; and abs 1100 cm^{-1} is the polypropylene reference absorbance. The value of absorbance is taken as the maximum value of the Lorentzian curves obtained by curve fitting.

RESULTS AND DISCUSSION

In the previous study dealing with the grafting mechanism of anhydride groups onto PP in the melt, it has been shown that the grafted polymer generally contains residual amounts of free (ungrafted) maleic anhydride as well as free ungrafted polymaleic anhydride sequences. It has been shown that the free maleic anhydride can be removed by vacuum-drying while the free polymaleic anhydride is removed by washing.

In order to distinguish the fractions of free maleic anhydride from free polymaleic anhydride and grafted anhydride functions, the measurements were performed on raw PP-*g*-MA, heated PP-*g*-MA in a vacuum oven, and on washed PP-*g*-MA.

The titration results are presented in Table I. In spite of the wide use of the titration in organic solution by the authors,^{1,2,4,11-12} here we must direct attention to the low reproducibility of the results.

Table II Number-Average Molecular Weights (M_n), Weight-Average Molecular Weights (M_w), Peak Molecular Weight (M_p) and Polydispersity (H) of Commercial PPMA, Measured by High-Temperature SEC Analyses with a PP Calibration

Washed Commercial PP- <i>g</i> -MA	M_n	M_w	M_p	H
Modic f300h	80,900	216,800	103,300	2.68
Modic p300m	58,100	176,600	94,800	3.04
Modic p300f	78,200	268,200	134,500	3.43
Polybond 3002	33,500	163,700	757,600	4.89
Orevac pp-chv	36,600	188,400	107,300	5.15
Admer Qf 500e	63,700	252,200	94,800	3.69
Exxelor 1015	47,600	104,800	87,000	2.2
Hercoprime G	22,700	54,400	48,700	2.4

Table III Comparison Between the Maximum Radical-Generated Sites (Calculated from M_n Data following a β -scission Scheme) and the Titrated Anhydride Content

Commercial PP- <i>g</i> -MA	M_n	Total Anhydride Content ($\mu\text{eq/g}$) by Titration	Maximum Radical-Generated Sites
Modic f300h	80,900	10	12
Modic p300m	58,100	9	17
Modic p300f	78,200	8	12
Polybond 3002	33,500	11	29
Orevac pp-chv	36,600	7	27
Admer Qf 500e	63,700	4	15
Exxelor 1015	47,600	33	21
Hercoprime G	22,700	303	44

An average value is presented here because up to $\pm 40\%$ of variations between measurements occurs in some cases when reproducibility is tested. The technique seems particularly difficult to perform when the anhydride content increases. A more systematic study of the titration in organic solutions is ongoing in view of a better understanding of the problems encountered and of attempting a better reproducibility.

In Table I, the tendency of maleic anhydride amounts to decrease after drying can be explained by the free maleic anhydride sublimation during heating. Upon washing, the solubilization of free maleic anhydride and of low-molecular-weight compounds (free polymaleic anhydride or/and low-molecular-weight grafted PP) must occur.

The third column of Table I gives the concentration of anhydride grafted on the polymer. This generally amounts to about half of the titrated quantities recorded for the raw material. It should be emphasized here that Hercoprime G PP-*g*-MA differs by its very large amount of grafted anhydride functions. This polymer will be discussed later. If the grafting of succinic or polymaleic anhydride occurs after β -scission onto radical chain ends as previously assumed,¹ the grafting sites can be maximized by the number of radical chain ends (N) arising from the scission. This number is

$$N = 10^6 \times \left(\frac{1}{M_n} - \frac{1}{M_n^0} \right) \quad (1)$$

where M_n is the number average molecular weight of the PP after grafting (mole/g); M_n^0 is the number average molecular weight of the PP before grafting (mole/g); N is the concentration of radical chain ends created during grafting ($\mu\text{eq/g}$); and 10^6 is a scaling factor converting mol/g into $\mu\text{eq/g}$.

The number average molecular weights of the commercial PP-*g*-MA were measured by SEC. The results are reported in Table II. The number-average

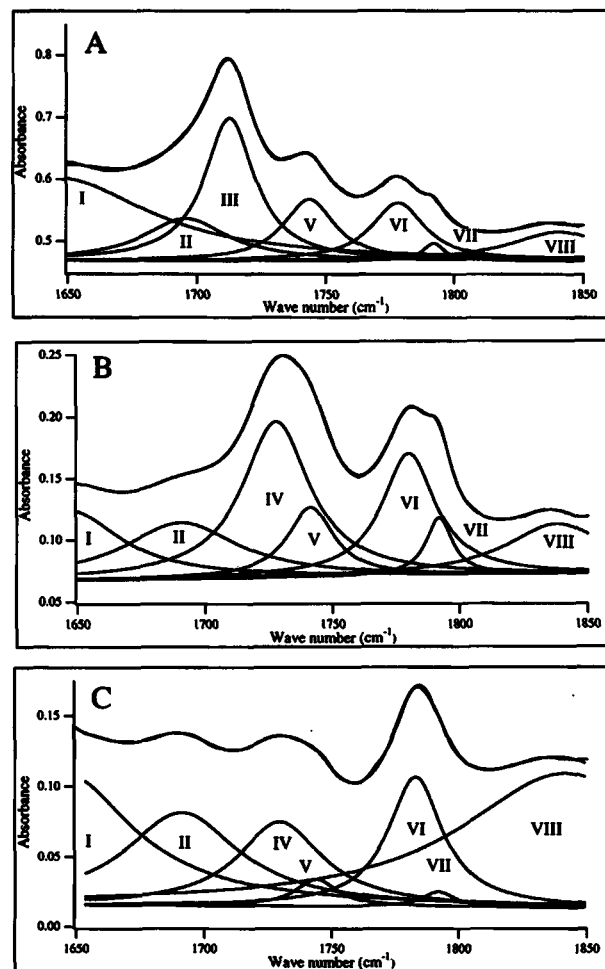


Figure 2 FTIR spectrum and its deconvolution for a raw Polybond 5002 sample (a), after heating (b), and after washing (c).

Table IV Anhydride Contents of Commercial PP-*g*-MA are Measured Out by FTIR and Titration

Commercial PP- <i>g</i> -MA	By FTIR			By Titration
	Succinic Anhydride Content ($\mu\text{equiv/g}$)	Polymaleic Anhydride Content ($\mu\text{equiv/g}$)	Total Anhydride Content ($\mu\text{equiv/g}$)	Total Anhydride Content ($\mu\text{equiv/g}$)
Modic f300h	3	9	12	10
Modic p300m	2	7	9	9
Modic p300f	~1	7	8	8
Polybond 3002	~1	10	11	11
Orevac pp-chv	2	6	8	7
Admer Qf 500e	<1	<1	~1	4
Exxelor 1015	1	28	29	33
Hercoprime G	57	280	337	303

By deconvolution of the FTIR spectra, the succinic anhydride and polymaleic contents can be split.

molecular weights of these commercial PP before grafting were not known. Nevertheless, even taking M_n^0 as infinity, the maximum number of grafting sites generated by β -scission [as calculated from eq. (1)] sometimes largely exceeds this limiting value (Table III). The occurrence of polymaleic grafting may explain this result and allows us to keep a β -scission reaction pathway hypothesis.

Actually, the polymaleic anhydride has always been observed by deconvolution of the IR spectra in the anhydride region: two characteristic bands, 1791 cm^{-1} and 1784 cm^{-1} , are then observed. A study on model compounds assigned those bands respectively to succinic anhydride and polymaleic anhydride.¹

Taking the polybond 5002 sample as an example, Figure 2 presents the deconvoluted IR spectra of the raw material [Fig. 2(a)] after heating in a vacuum oven [Fig. 2(b)], and after washing [Fig. 2(c)]. After heating, even if diacids close them in anhydrides (disappearance of the 1715 cm^{-1} band), the absor-

bance of the peak assigned to anhydride decreases: the free anhydride sublimates. After washing, both characteristic peaks decrease; free anhydride as well as free polymaleic anhydride and/or low-molecular-weight grafted PP can be eliminated. The bands around 1730 cm^{-1} and 1745 cm^{-1} are assigned to processing additive of the PP. All the other bands are contributions of the PP absorbance.

Table IV summarizes the deconvolution results for all samples after application of the absorption parameters. The succinic anhydride and polymaleic anhydride grafted on washed commercial PP-*g*-MA samples are given, respectively, in columns 2 and 3. Those anhydride contents are in the range of the total amount of anhydride previously titrated (column 5). It was of prime interest to emphasize here that an important part of the grafted anhydride functions arises from a polymaleic anhydride form.

However, for the Hercoprime G sample the polymaleic anhydride formation cannot conciliate the number of radical sites generated by β -scission and

Table V Summary of Results from Tables III and IV Useful for Questioning on the β -scission Scheme

Commercial PP- <i>g</i> -MA	Succinic Anhydride Content ($\mu\text{equiv/g}$)	Polymaleic Anhydride Content ($\mu\text{equiv/g}$)	M_n (by SEC)	Maximum Radical-Generated Sites
Modic f300h	3	9	80900	12
Modic p300m	2	7	58100	17
Modic p300f	1	7	78200	12
Polybond 3002	1	10	33500	29
Orevac pp-chv	2	6	36600	27
Admer Qf 500e	<1	1	63700	15
Exxelor 1015	1	28	47600	21
Hercoprime G	57	280	22700	44

the number of grafted anhydride as shown in Table V. In fact, the grafted succinic anhydride content already exceeds the number of generated radical sites. It is clear that grafting via β -scission is not the only way acceptable in the case of Hercoprime G: a grafting within the chain must occur. Nevertheless, this counter-example does not refute the β -scission scheme developed for PP grafted in the melt¹ because this polymer is known¹³ as a PP grafted in the solid phase.

For all the other polymers, from the calculated data of Table V, the β -scission scheme holds, taking into account the maximizing of the starting molecular weight hypothesis and also the possibility of recombination of some radicals.

CONCLUSION

The present work on commercial PP-*g*-MA samples correlates well with previous studies carried out in our laboratory.

Only one polymer, Hercoprime G, falls out of the retained reactional scheme, but its grafting does not proceed in the melt, which therefore does not refute our previous results.

Nevertheless, even if a chain-end grafting after β -scission is not acceptable in this particular polymer, the most important results for PP-*g*-MA users remain true for all commercial polymers studied here: four forms of anhydride are always detected.

- Free maleic anhydride and polymaleic anhydride were extracted.
- Two forms of grafted anhydride (succinic anhydride and polymaleic anhydride) were revealed by IR spectra deconvolutions.

This observation leads us to conclude that only a fraction of the anhydride content in commercial PP contributes to the adhesion or to the compatibilizer formation. Indeed, the presence in PP-*g*-MA of fast-diffusing free anhydride species can lead to the capping of the reactive functionalities by these

ungrafted molecules. Consequently, a weak effect of the grafting on adhesion or compatibilization might arise.

A long vacuum heating of the PP-*g*-MA can decrease the free anhydride content but only a washing suppresses the free polymaleic anhydride.

Finally, the presence of grafted polymaleic anhydride can lead to the capping of several reactive functions of the substrate by only one chain of PP. Again, this effect can decrease the number of chains participating in adhesion or compatibilization. In that case, only the choice of another PP-*g*-MA grade containing less polyanhydride form can be envisaged.

REFERENCES

1. B. De Roover, M. Sclavons, V. Carlier, J. Devaux, R. Legras, and A. Momtaz, *J. Polym. Sci., Part A, Polym. Chem. Ed.*, **33**, 829 (1995).
2. Y. Minoura, M. Ueda, S. Mizunuma, and M. Oba, *J. Appl. Polym. Sci.*, **13**, 1625 (1969).
3. N. G. Gaylord and M. K. Mishra, *J. Polym. Sci., Polym. Lett. Ed.*, **21**, 21 (1983).
4. A. H. Hogt, *Proc. Second Int. Cong. on Compatibilizers and Reactive Polymer Alloying*, Compalloy, New Orleans, LA, 1990.
5. P. A. Callais and R. T. Kazmierczak, *ibid.*
6. B. De Roover, J. Devaux, M. Sclavons, V. Carlier, and R. Legras, *Proc. of Colloque National du GFP*, Lyon, France, 1992.
7. B. De Roover, R. Legras, and J. Devaux, *J. Polym. Sci., Part A, Polym. Chem. Ed.*, to appear.
8. W. Scheinert, *Angew. Makromol. Chem.*, **63**, 117 (1977).
9. Chalmers, IUPAC, October 20, 1976.
10. V. F. Maddams, *Appl. Spectrosc.*, **34**, 245 (1980).
11. J. M. G. Martinez, J. Taranco, O. Laguna, and E. P. Collar, *Intern. Polym. Proc.*, **IX**, 251 (1994).
12. B. J. Kim and J. L. White, *Intern. Polym. Proc.*, **X**, 213 (1995).
13. Hercules-Powder Co., Patent BE 0681931 (1966).

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