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Maleic anhydride-grafted polypropylene: FTIR study of a model polymer grafted by ene-reaction

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Abstract

Ene-grafting of maleic anhydride on polypropylene previously enriched in double bonds by β-scission was promoted in order to obtain model grafted polypropylene. Ene-grafting was carried out in the presence of a radical-scavenger in order to limit at a minimum side-grafting and in presence of catalyst ($SnCl_2$) in order to maximise the ene-grafting. Nevertheless, it does not lead to high grafting content.

Ene-grafted PP confirms the single end-grafted succinic anhydride FTIR assignment at 1792 cm^{-1} (C=O symmetric stretching) while a disubstitution is also observed leading to a shift to a 1784 cm^{-1} absorption band. This latter band was more generally assigned to interacting anhydride (C=O) instead of an assignment to the particular polyanhydride species (as previously assigned by our team [De Roover B, Sclavons M, Carlier V, Devaux J, Legras R, Momtaz A. J Polym Sci, Part A: Polym Chem 1995;33:829. [14]]).
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1. Introduction

Grafting maleic anhydride onto polypropylene (PP-*g*-MA) is of considerable industrial interest to enhance its compatibility, adhesion and reactivity [1].

The mainly reported functionalisation process consists in grafting maleic anhydride (MA) onto molten polypropylene (PP), in the presence of an organic peroxide [2–5]. Extended and recent reviews presented by Jois et al. [6] or Moad [7] summarize the state-of-the-art.

The reaction is carried out by a radical mechanism: Peroxide initiator provides radicals amongst which some abstract a hydrogen from PP tertiary carbon to form PP macroradicals [2,8]. Beyond this step, the next ones are controversed. Therefore, location and nature of grafted anhydride species are proposed as follows:

- On one hand, MA is reported as reacting with the PP macroradicals and is then distributed along the chain as isolated succinic anhydride units [9,10].

- β-Scission may occur in a second step and then produces some itaconic anhydride units.
- On the other hand, the PP macroradicals are reported as first leading to chain scissions (β-scission) [11–13]. The secondary C-radical generated by β-scission may then form an adduct with MA [3,14,15]. The grafted MA is then located at the chain-ends as succinic anhydride units.

Other questions about formation or non-formation of poly(maleic anhydride) (PMA) appear unresolved: Some teams sustain that radical mechanism leads to some oligomerization of MA by radical transfer [14,16,17]; other ones support that temperature reaction is beyond the ceiling temperature of PMA [18] and that its formation is therefore impossible. Finally, some [9] reported the presence of such anhydride oligomerisation when grafting MA on PE but its absence when grafting MA on PP.

It is also important to mention that the varying processing conditions from team to team still increase the confusion.

According to FTIR spectra, our team supported grafted PMA species in relation with the two bands observed in the C=O stretching zone. There were respectively assigned to single grafted succinic anhydride (peak at 1792 cm^{-1}) and to grafted PMA (peak at 1784 cm^{-1}). These peaks were

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respectively assigned thanks to 2 model compounds [14]: *n*-Octadecylsuccinic anhydride and Beclene 200® ('commercial PMA').

In order to confirm those assignments, maleic anhydride grafting onto PP in absence of radical initiator in order to avoid as much as possible PMA side-grafting was sought in the present study. Because of its good enophile feature, MA can be grafted by ene-mechanism onto a PP containing unsaturated chain-ends [19–22]. This grafting route avoiding peroxide initiator was selected in order to provide a new polymeric model compound. This latter was studied in details after decomposition of its FTIR spectra. Possible mechanisms are again discussed.

2. Experimental

2.1. Materials

Toluene, methanol (Merck-Belgolabo, AR grade), maleic anhydride (Aldrich, 99% purity), bromothymol blue (Sigma) are used without further purification. TEMPO (free radical 2,2,6,6-tetramethyl-1-piperidinyloxy), catalyst ($SnCl_2 \cdot 2H_2O$) and tetra-butyl ammonium hydroxide (TBAOH) 0.1 N in toluene–methanol are purchased from Acros Organic.

Polypropylene 'Finapro' and the organic peroxide (DHBP-Interox, Peroxid Chemie) were kindly provided by Fina Chemicals and Solvay SA, respectively.

2.2. Production of PP enriched in unsaturations

The PP is first enriched in double bonds by inducing β-scission during processing with a peroxide (DHBP) in a twin-screw corotative extruder. The extruder is a Werner and Pfleiderer ZSK30. A dry mixture of PP and DHBP is introduced into the extruder. The DHBP content is 5‰ (by weight). The temperature profile along the screw is 190, 200, 200, 210, 210 and 210 °C. The screw speed is held at 100 rpm and the extruded material is pelletized after water quenching at about 25 °C.

2.3. Ene-reaction

The ene-reaction is carried out in a Brabender Plasticorder equipped with an electrically heated W50EH mixing device of 50 ml volume. The polymer oxidation is highly reduced by a nitrogen flow of 5 l/min above the mixing chamber. The mixing speed is fixed at 100 rpm and the temperature at 230 °C.

MA grafting route similar to the one reported by Thompson et al. [19–22] was carried out as follows: When the unsaturation-rich PP (45 g) is melted, 0.04% (by weight) of $SnCl_2 \cdot 2H_2O$ is introduced, followed 2 min later, by a feeding of 0.04% (by weight) of TEMPO and 5% (by weight) of MA. Stannous chloride ($SnCl_2 \cdot 2H_2O$) which

is a weak Lewis acid catalyses the ene-reaction and improves grafted anhydride content onto the polymer for short reaction times. The catalyst is fed at first to promote its good dispersion within molten PP. The TEMPO is added (as radical scavenger) to hinder any unwanted radical reaction during the ene-reaction. Stability of this latter in the processing conditions (high temperature of molten PP) and its possible decomposition in the presence of Lewis acid were questioned during the study because such related side-products might be responsible of radicalar side-grafting of MA. Such a TEMPO effect on grafting was finally discarded as discussed further. The mixing time is of 60 min. Sampling is performed at different times just before the addition of MA and after its addition (after 2.5, 5, 10, 15, 30, 45 and 60 min).

In one trial, in view to increase the yield of the ene-reaction, catalyst, TEMPO and MA are again added stepwise every 12 min: Catalyst first and 2 min later, TEMPO and MA, in a similar amount as the first feeding (see above). Sampling for analysis is performed just before each catalyst addition (at 12, 24, 36, 48 and 60 min).

2.4. Analytical characterization of anhydride content

Before any characterization, grafted polyolefins are dissolved in 100 ml of toluene at reflux temperature in order to eliminate unreacted MA. The polymer is then precipitated in acetone and repeatedly washed with acetone. Finally, the recovered product is dried in a vacuum oven for 24 h at 110 °C in order to assure cyclisation of carboxylic acid into anhydride.

2.4.1. Acid–base titrations

One gram of grafted polyolefin is dissolved in 150 ml of toluene at boiling temperature according to the previously published method [23]. The TBAOH addition is started just after the coloured indicator (five drops of 1% (w/v) bromothymol blue in methanol). The titration is stopped at the visual endpoint when the colour change is stable. The MA content is calculated from the titrating agent volume and its concentration.

2.4.2. FTIR spectroscopy

The FTIR spectra were recorded on a Perkin–Elmer FTIR Spectrometer 1760-X from 4000 to 400 cm^{-1} with a 0.5 cm^{-1} resolution.

The PP samples were processed in 100 μm-thick films by compression moulding of 0.1–0.2 g between Teflon-covered aluminium sheets under 1 MPa pressure at 200 °C for 5 s.

The sublimation of unreacted maleic anhydride and the cyclisation of grafted MA are ascertained by FTIR controls, respectively, by the disappearance of the characteristic absorption band at 720 cm^{-1} associated with the CH out-of-plane deformation of MA, and by the disappearance of the

absorption band at 1715 cm^{-1}, assigned to the carboxylic acid.

The spectra are normalized with an internal standard peak at 1168 cm^{-1}, assigned to the –CH$_3$ wagging frequency.

### 2.4.3. Curve fitting of the carbonyl frequency range of the anhydride

Spectral decompositions were performed by fitting to the experimental data a model consisting of a sum of peaks of mixed Gaussian/Lorentzian shape. Parameters were the location of the peaks, their half width at half-maximum, their amplitude, and their Lorentzian percentage, together with a set of parameters to describe the background. A Marquardt–Levenberg algorithm was used to minimize the chi-square (χ^2).

In the carbonyl frequency range of the anhydride (1820–1750 cm^{-1}) the background was approximated by a straight line and the bands were approximated by Lorentzian functions. The iterative soft so defines the location of the peaks, their amplitude, and the half width at half-maximum of each band in order to restore the IR spectrum when adding all the Lorentzian's. The position and the half width at half-maximum of each peak were controlled constant in order to ensure reliability (appropriateness) of the method but not the uniqueness of the curve-fitting solution, which is impossible to ascertain [24,25].

3. Results and discussion

In order to graft significant amount of maleic anhydride onto PP by ene-reaction, the PP must contain a large number of unsaturated bonds. For this purpose, PP was processed with peroxide in a twin-screw extruder to induce β-scission. Chains are first cleaved as presented in Scheme 1. By this way, unsaturated bonds are almost exclusively located at the ends of chains [11–13]. Appearances of bands at 888 cm^{-1} (assigned to vinylidene) and at 1648 cm^{-1} (assigned to double bonds stretching) are observed by FTIR after chain-scission as reported, respectively, in Fig. 1(I) and (II).

The number of unsaturated bonds, which have appeared can be maximized with the half number of chain ends (N) arising from the β-scission [14]. This number expressed in μequiv/g is: $N = 10^6 \times 1/2 \left(2/M_n - 2/M_n^0 \right)$ where M_n and M_n^0 are, respectively, the number average molecular weight (g/mol) of the PP after and before β-scission, measured by SEC (10^6 is a scaling factor converting mol/g into μequiv/g.).
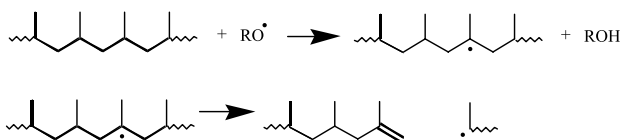
Scheme 1. Mechanism of β-scission and production of unsaturated bonds.

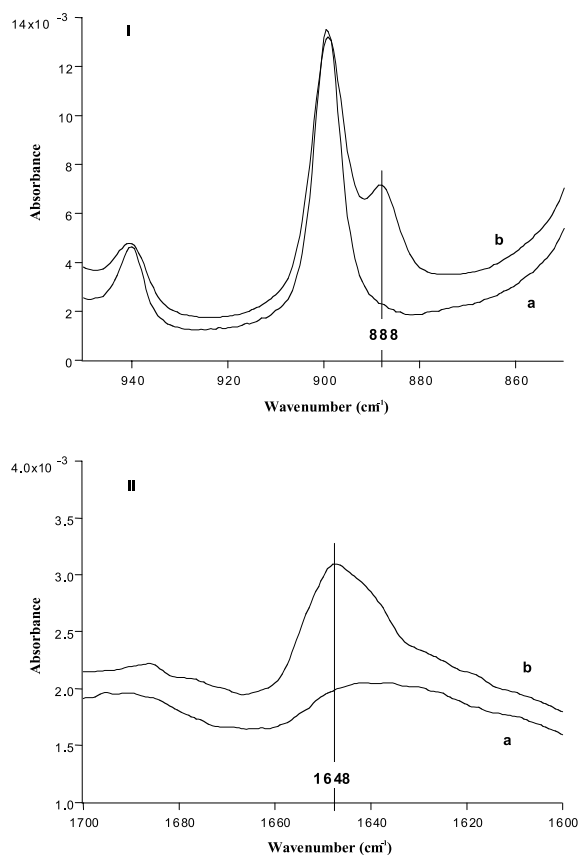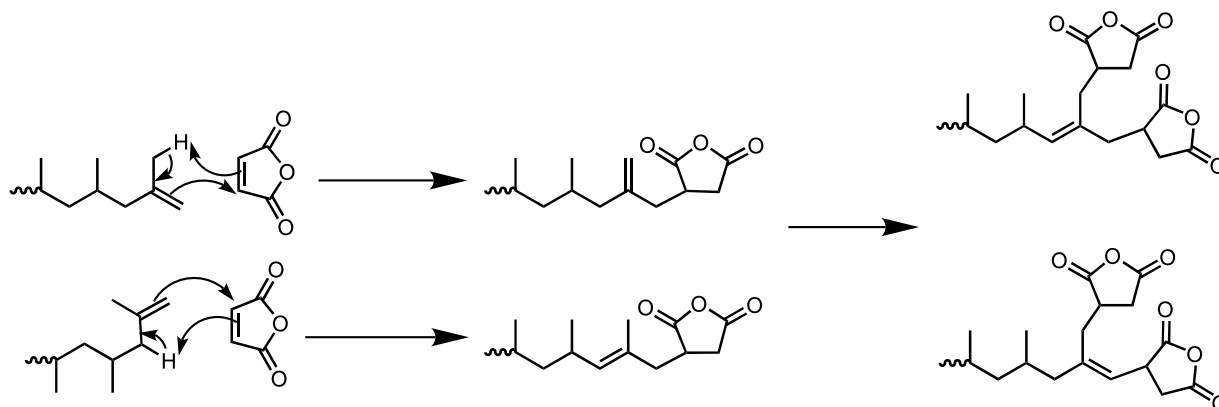Fig. 1. FTIR spectra of PP (a) and PP after β-scission (b) in the zone of 850–950 cm^{-1} (I) and 1600–1700 cm^{-1} (II). The β-scission was induced by melt-reaction with 5‰ (w/w) of DHBP.

M_n and M_n^0 are, respectively, measured at 9100 and 32,000 g mol. The number of generated unsaturated bonds (N) is of about 79 μequiv/g.

In order to trap any radical side-reaction when ene-grafting MA, a radical scavenger (TEMPO) is used to hinder all radical species in the molten PP [19–22]. This particular radical scavenger was selected because it does not absorb in the C=O region and does not give artefacts with the anhydride stretching band. Moreover, a nitrogen flow is forced during the reaction to prevent oxidation. To promote ene-reaction, a catalyst (SnCl$_2$·2H$_2$O) is also used. Lewis acids are reported to be efficient catalysts for ene-reaction [19–22].

The general mechanism of the ene-reaction is presented in Scheme 2. This reaction is a concerted mechanism in which MA abstracts a hydrogen from the PP chain and in which the double bond is displaced to the next C–C bond. A new carbon–carbon bond is formed between PP and MA. Because of the double bond shift, a second MA can be again grafted onto the polymer chain. Indeed, the occurrence of such a ene-disubstitution was already reported by Tessier and Marechal [26]. They first detected it by FTIR on a model compound (2,4,4-trimethyl-1-pentene). Then, they clearly identified by GPC, ^{1}H and ^{13}C NMR such a

Scheme 2. Mechanism of ene-reaction.

disubstitution by the formation of α,α'-disuccinico-grafted molecule.

FTIR spectra on Fig. 2(I) show in the zone of 1700–1850 cm^{-1}, the appearance of a low absorption band near

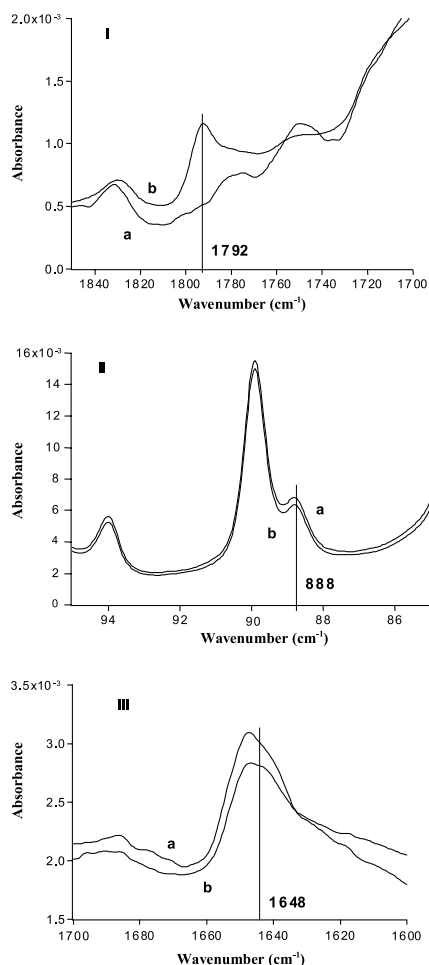Fig. 2. FTIR spectra of PP after β-scission (a) and PP grafted by ene-mechanism (b) in the zone of 1700–1850 cm^{-1} (I), 850–950 cm^{-1} (II) and 1600–1700 cm^{-1} (III). The grafting was carried out after 10 min of mixing in the presence of 0.04% (w/w) of SnCl$_2\cdot$2H$_2$O; 0.04% (w/w) of TEMPO and 5% (w/w) of MA.

1792 cm^{-1} assigned to symmetric C=O stretching of anhydride functions grafted on PP. It is to be noticed that no absorption band is observed for PP sample processed only in presence of radical scavenger and catalyst under the same experimental conditions. The intensities of the bands at 888 cm^{-1} (zone 850–950 cm^{-1} in Fig. 2(II)) and at 1648 cm^{-1} (zone 1600–1700 cm^{-1} in Fig. 2(III)) do not decrease very much, witnessing of a very low yield in anhydride grafting.

On Fig. 3, one can observe how the reaction time affects the absorption of the C=O stretching bands of anhydride. There is a maximum in grafted species content after about 10 min. Increasing periods of reaction do not increase anymore the grafted content.

The maximum grafted anhydride concentration was measured by acid–base titration at about 1.5 µequiv/g.

The concentration of added MA does not strongly affect the grafted content as reported in Fig. 4 for trial with successive MA feedings. The grafting content is maximum after 2 additions (10% MA) and quantified by titration at
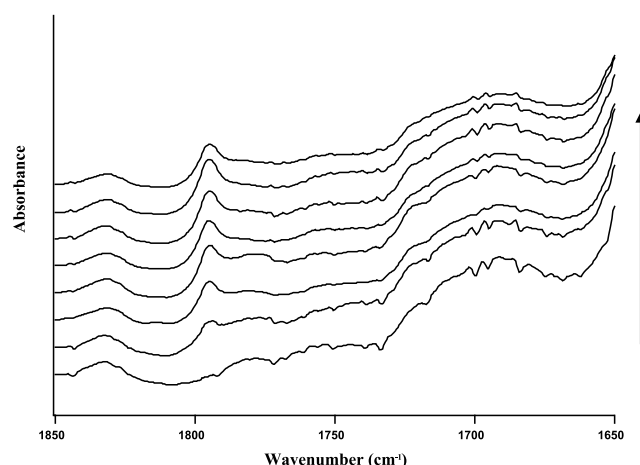

Fig. 3. Effect of the reaction time on the FTIR spectra in the MA area when grafting MA, in presence of catalyst, TEMPO at 220 °C. Samplings are performed at different times just before the AM addition and 2.5, 5, 10, 15, 30, 45 and 60 min after its addition.

Fig. 4. Evolution of the FTIR spectra after several adding of $SnCl_2 \cdot 2H_2O$, TEMPO, MA. Each addition at the same concentration as the first one (0.04% (w/w) of $SnCl_2 \cdot 2H_2O$; 0.04% (w/w) of TEMPO and 5% (w/w) of MA) was performed after 12 min: Catalyst first and 2 min later, TEMPO and MA. Sampling was performed just before each catalyst addition (12, 24, 36, 48 and 60 min after first MA feeding).

3 μequiv/g. Subsequent additions do not increase anymore the grafted content. The grafting yield is low and can be calculated as limited as 4% of the number of generated unsaturated bonds. Ene-grafting is very difficult to promote as already reported [14]. Fig. 3 and Fig. 4 results indicate that radical reactions are not favoured during the grafting and this is observed even if higher and higher contents of anhydride, TEMPO and catalyst are introduced. This observation definitively discards any side-grafting effect related to TEMPO instability or TEMPO possible decomposition.

The decomposition of the FTIR absorption bands in the carbonyl frequency range of 1820–1700 cm^{-1} for this PP grafted by ene-reaction allows us to discuss in more details the grafted species. A peak at 1792 cm^{-1} with a half-width at half maximum of 4.7 ± 0.4 cm^{-1} is seen on Fig. 5. It was
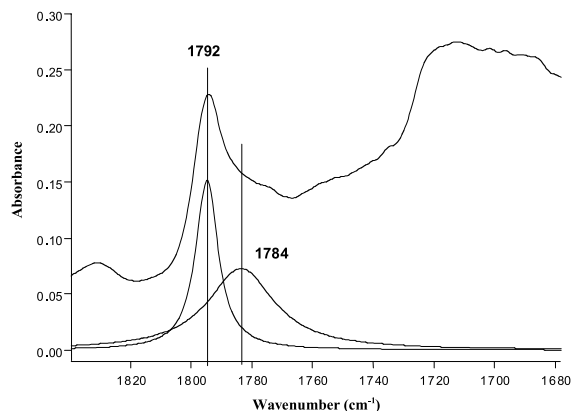

Fig. 5. FTIR spectra decomposition in the zone of the C=O stretching (1700–1850 cm^{-1}) of a PP grafted by ene-reaction. The grafting was carried out for 10 min of mixing in the presence of 0.04% (w/w) of $SnCl_2 \cdot 2H_2O$; 0.04% (w/w) of TEMPO and 5% (w/w) of MA.

previously assigned by De Roover et al. [14] to single succinic grafted units. Whilst, the second band observed at 1784 cm^{-1} with a half width at half-maximum of 12.7 ± 2.1 cm^{-1} was assigned to poly(maleic anhydride) (PMA) ($n=4$–5) [14]. In the present ene-grafting conditions, avoiding radicalar initiator and showing no increase of grafting with reaction time and with additional MA feedings, one can assume an absence of radical formation and therefore such an oligomerisation of PMA could be discarded. We then prefer to assign more generally this 1784 cm^{-1} band as a result of ene-disubstitution to the existence of close grafted anhydrides giving rise to interaction and band displacement. Such anhydrides close to each other also exist in PMA.

Therefore, it does not seem anymore relevant to assign the 1784 cm^{-1} to a peculiar anhydride species but rather to interacting anhydride species for instance two anhydrides close to each others.

This interaction effect could also be supported by the following observation already reported by De Roover et al. [14]: When *n*-octadecylsuccinic anhydride is mixed in PP in low concentration, a band located at 1792 cm^{-1} is only observed, however, when *n*-octadecylsuccinic is mixed to PP in higher concentration 1792 and 1784 cm^{-1} are both observed, probably by MA clustering.

If the molar coefficients of extinction proposed by De Roover et al. [14] are used on the decomposed ene-grafted polymer reported in Fig. 5, the non-interacting grafted anhydride species absorbing at the 1792 cm^{-1} are quantified at 0.3 μequiv/g while the interacting ones absorbing at 1784 cm^{-1} are quantified at 1.4 μequiv/g. This FTIR result and the titration quantification (total amount) are in good agreement, respectively, 1.7 and 1.5 μequiv/g.

4. Conclusions

By ene-grafting of MA onto PP terminal unsaturated bonds, both 1792 and 1784 cm^{-1} absorption bands were observed. The former band can be assigned unambiguously to a grafted succinic anhydride on the chain-end. The latter could be explained by an anhydride disubstitution reported in the ene-reaction mechanism. The interaction between close grafted succinic anhydrides resulting from the disubstitution shifts the 1792 cm^{-1} absorption to 1784 cm^{-1}. Such a shift was already assigned to interacting anhydrides, even in absence of grafting for increasing amount of *n*-octadecylsuccinic anhydride in PP.

This study leads us to revisit our previous univoqual 1784 cm^{-1} assignment to PMA and to propose a more general assignment of this band to a shift related to anhydride–anhydride interactions due to close anhydrides: Closely grafted, clustered or homopolymerised as in PMA.

Acknowledgements

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