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Gamma radiation induced maleation of polypropylene using supercritical CO_2: preliminary results

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Abstract

The charging of maleic anhydride (MA) and dicumyl peroxide (DCP) into polypropylene matrices has been carried out by CO_2 in supercritical conditions. The grafting of MA into polymer chains was done through gamma irradiation in CO_2 atmosphere (0.1 MPa, 25°C). The grafting was successful and the amount of grafted anhydride was dependent on the amount of MA and DCP charged into the polypropylene matrix. The presence of grafted succinic anhydride was shown by FT-IR spectroscopy and its amount was determined through a calibration curve derived from standard samples. The effect of swelling due to supercritical CO_2, maleic anhydride grafting and gamma irradiation on the molecular structure and molecular weight of the modified polypropylene has been investigated through dynamic-mechanical tests in the melt state and through calorimetric analysis.

Keywords: Supercritical CO_2; Polypropylene; Grafting

1. Introduction

Grafting of maleic anhydride (MA) into polypropylene matrices is a well established technique used to improve the polymer adhesion to materials, e.g. glass and metals, or its compatibility in blends with polar polymers, such as polyamides [1–3]. This process is usually performed via a radical mechanism using thermally decomposed peroxides [4]. The reaction is usually carried out either in a homogeneous or heterogeneous solution or in a polymer melt by reactive extrusion [5–7]. Solution processes suffer from the problem of removing the organic solvents used from the final product. The melt process can be accompanied by the molecular degradation of the polymer. Furthermore MA is not soluble in molten polypropylene, thus requiring efficient mixing and limiting the degree of maleation to a lesser mole percent.

It is well known that one of the most stimulating applications of ionising radiation technology is the grafting of functional groups into polymer backbones [8,9]. Usually, this is carried out by irradiating the polymer in the solid state; the functionalising monomer can be grafted through a simultaneous irradiation or in a second step after the irradiation of the polymer. The main problem arising from this processing is that the reaction is controlled by the diffusion of the monomer into the bulk of the polymer and a non-homogeneous grafting can occur. Moreover this methodology hinders the grafting of functionalising species in the solid state.

These drawbacks can be overcome by the use of supercritical CO_2 ($scCO_2$).The use of dense or $scCO_2$ as a carrier for delivering small molecules into or extracting small molecules from solid matrices is a well experimented technique [10,11]. At the properly chosen density values $scCO_2$ dissolves non-polar or not exceedingly polar compounds [12] and modifies the morphology of the polymer, both plasticising and swelling the matrix. In this way the diffusion resistances are overcome and the solute is molecularly dissolved in the amorphous domains of the bulk polymer. The release of pressure allows the precipitation of the finely dispersed solute into the polymer structure.

Partitioning of solutes between the supercritical and the polymer phases both by in situ spectroscopy [13] and by gravimetry [11] has been studied.

Polymer domains obtained by delivering and polymerisation of monomers into a swollen pre-existing polymer matrix is also reported [14,15].

Recently thermal initiating grafting of MA onto poly(4-methyl-1-pentene) has been reported [16].

In this work preliminary results about the use of $scCO_2$ in order to deliver MA and dicumyl peroxide (DCP) into the polypropylene bulk and the use of gamma radiation to graft, in mild conditions, the solubilised MA are presented.

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Table 1
Experimental conditions of charging and grafting ($T = 80°C$ $d = 0.65$ g cm^{-3})

Charging conditions		Charged amounts		Grafted amounts	
MA[a] (wt%)	DCP[b] (wt%)	I_{MA}/I_{CH3}	I_{DCP}/I_{CH3}	Dose (kGy)	Grafted MA[c] (wt%)
0.5	6.3	0.04	0.04	85	0.12
1	7.3	0.06	0.09	18	–
1	7.3	0.08	0.09	85	0.33
3	10	0.05	0.09	85	0.29
3	10	0.08	0.03	85	0.27
3	0	0.065	0	85	0.17

[a] With respect to CO_2.
[b] With respect to MA.
[c] With respect to polymer.

2. Experimental

The polymer used is an isotactic polypropylene (iPP) Stamylan P13E10 ($M_W = 500\,000$, density = 0.903 g cm^{-3}) supplied by DSM. Polymer sheets were prepared from pellets by compression moulding in a laboratory press; the samples were kept at 180°C under a pressure of 12.5 MPa for 10 min, then they were quickly cooled down to room temperature by running cold water through the press plates. From these sheets, samples of uniform thickness of 70 microns were chosen.

CO_2 from Sol, 99.997% pure, and MA, 99%, supplied by Janssen were used as received. The initiator DCP, 98%, with a half-life of 1 h at 132°C and 10 h at 112°C, was used as received from Aldrich.

Swelling through $scCO_2$ was carried out in a PARR reactor with a volume of 86 cm^3 at 80°C. The system was carefully washed with CO_2 and then charged with the right amount of CO_2 to reach the density of 0.65 g cm^{-3}. Then the system was kept at 80°C for 6 h. After that the system was quickly cooled down to room temperature and vented.

Charging of MA and DCP into iPP matrices was carried out in the same PARR reactor and both the charge and the discharge of the reactor with CO_2 followed the same procedure previously described, but in two separated tests; the first one in presence of MA, and the second one with further addition of DCP. The charging conditions are reported in Table 1. After the second run in presence of DCP, the system was finally vented, iPP samples were carefully washed with distilled water, dried, and analysed through FT-IR spectroscopy. The charged amounts were estimated through the absorption peaks of 1851 cm^{-1} (MA) and 761 cm^{-1} (DCP), using the methyl peak at 1167 cm^{-1} as internal reference and the values are reported in Table 1. The irradiation was performed using IGS-3, a ^{60}Co irradiator.

Both pure-iPP and iPP samples, subjected to the charging procedure previously described, were irradiated in CO_2 atmosphere (0.1 MPa, 25°C) at 72 Gy min^{-1} in the dose range 18–85 kGy. After irradiation the samples were stored under vacuum for 24 h at 120°C in order to remove the ungrafted MA, to reconvert hydrolysed grafted succinc acid to succinic anhydride and to eliminate the free radicals still present in the iPP matrix. Irradiation tests of iPP in presence of MA and DCP alone were also done.

FT-IR analysis was carried out through a Perkin Elmer Spectrum 2000 Explorer. The amount of grafted succinic anhydride was determined using a calibration curve, derived from standard samples supplied by DSM, based on the absorption peak intensity of succinic anhydride at 1785 cm^{-1}, assuming as internal reference the peak of methyl group at 1167 cm^{-1} [17].

In order to confirm the presence of grafted MA, the irradiated samples were dissolved in boiling xylene and precipitated in cold methanol. The solid phase was analysed through FT-IR spectroscopy. Supercritical CO_2 extraction tests of some irradiated samples were also done.

Dynamic-mechanical tests in the melt state were carried out through a RDA2 Rheometrics analyser used in the dynamic mode with the plate and plate geometry (R = 12.5 mm). The frequency sweep tests were carried out at 180°C and 20% strain in the angular frequency range 10^{-1}–5×10^2 rad s^{-1}.

Calorimetric analysis was done through a Perkin Elmer DSC7 calorimeter. Samples of about 10 mg were heated from 30 to 200°C, cooled down to 30°C and finally subjected to a second heating run up to 200°C. Both heating and cooling rates were 10°C min^{-1}.

3. Results and discussion

The effect of swelling on the molecular structure of iPP was analysed through dynamic-mechanical tests in the melt state. Flow curves, not reported, do not show significant differences between virgin and treated materials, thus indicating that the swelling process does not induce molecular weight modifications of the polymer.

The qualitative results of MA grafting through gamma-irradiation are shown in Fig. 1 where FT-IR spectra for test 1 of Table 1 are reported. With reference to the virgin iPP sample the spectrum relative to sample only swelled in $scCO_2$ in presence of MA and DCP evidences the presence of additional peaks, at 1850, 1790, 1780 cm^{-1}, typical of MA, and at 761 cm^{-1}, typical of DCP. After irradiation and

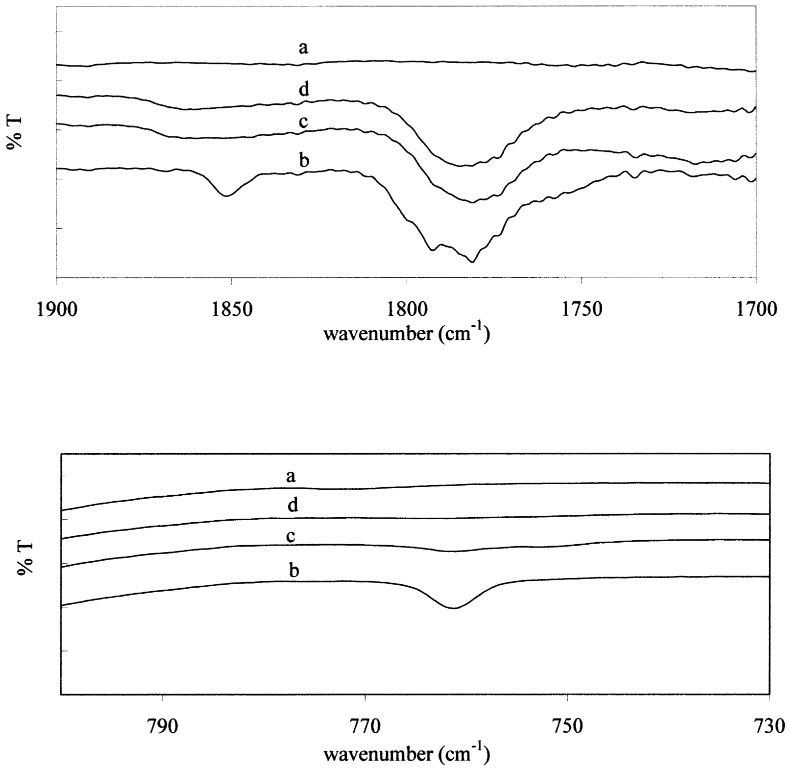

Fig. 1. FT-IR spectra: a-iPP, b-iPP + MA + DCP, c-iPP + MA + DCP 85 kGy, d-iPP + MA + DCP 85 kGy and thermal treatment.

thermal treatment, the first peak (1850 cm^{-1}) disappears, whilst the other two peaks of MA transform in one broader peak at about 1785 cm^{-1}. This indicates that the irradiation in these experimental conditions grafts MA into iPP chains with the formation of succinic anhydride. These results are confirmed by other independent tests; in fact the FT-IR spectra of samples obtained by reprecipitation or $scCO_2$ extraction procedures described in Section 2 still show the presence of the characteristic peaks. The presence of DCP appears to be significant; when grafting occurs its absorption peak decreases its intensity.

Quantitative results are reported in Table 1; at a fixed irradiation dose the grafted MA amount increases with the increase of the initial amount of MA and DCP in the polymer matrix. In the presence of MA alone a net decrease in the grafting yield is observed.

The influence of grafting through irradiation on molecular weight was studied by dynamic-mechanical tests in the melt state. The flow curves are reported in Fig. 2. Grafting process causes a decrease in molecular weight. A comparison with pure iPP subjected to the same irradiation conditions shows more marked degradation phenomena for the

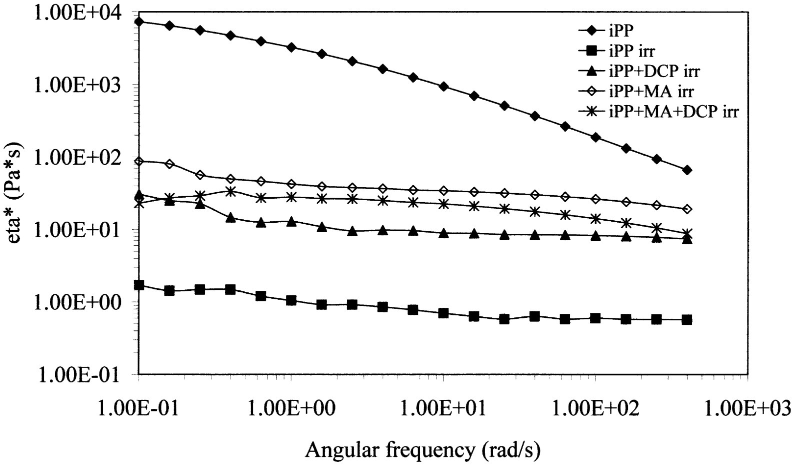

Fig. 2. Flow curves.

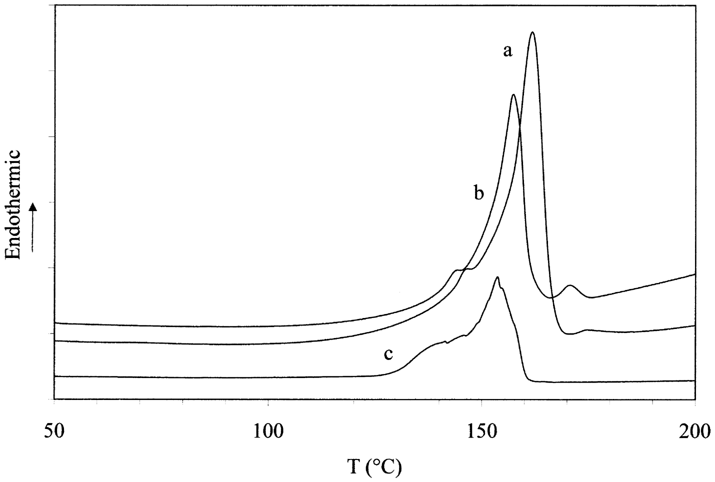

Fig. 3. Calorimetric curves: a-iPP, b-iPP 85 kGy, c-iPP + MA 0.33%.

pure sample, thus suggesting that the presence of the carried species limits the extent of degradation. In fact both DCP and MA have a positive influence in limiting the extent of molecular degradation as shown by flow curves of iPP irradiated in presence of DCP or MA alone. This can be related to the radical scavenger activity of DCP and MA towards the iPP macroradicals generated by gamma rays, thus limiting β-scission reactions [18].

The thermograms in Fig. 3, relative to the second heating run, for non-irradiated, irradiated without grafting and irradiated and grafted iPP samples are reported. A general influence of irradiation and grafting on melting behaviour is observed: both processes influence, adversely, the regular domains of the crystalline phases. The temperature of the main peak decreases and a less regular melting behaviour is observed.

4. Concluding remarks

In this work the preliminary results about the charging of MA and DCP into solid polypropylene through $scCO_2$ and the subsequent radiation induced grafting of MA into the polymer chains are reported.

FT-IR analysis shows that $scCO_2$ is apt to carry MA into the polypropylene matrix and that relevant amounts of the carried anhydride is fixed to the polymer chains through gamma radiation.

Dynamic-mechanical tests in the melt state indicate that the molecular degradation of the polypropylene due to gamma radiation is reduced by the presence of both DCP and MA.

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