Grafting of Maleic Anhydride onto Isotactic Polypropylene in the Presence of Supercritical Carbon Dioxide as a Solvent and Swelling Fluid

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ABSTRACT: Grafting of maleic anhydride (MA) onto isotactic polypropylene (iPP) was carried out by thermal decomposition of dicumylperoxide (DCP) using supercritical carbon dioxide ($scCO_2$) as a solvent and swelling fluid. Provided that the initial concentration of anhydride dissolved in $scCO_2$ is higher than 1% w/w, the grafting occurs without significant molecular weight modification of the polymer, and with a proper selection of the operative conditions, a grafting level higher than 0.5% w/w with respect to the polymer mass was obtained. The amount of grafted MA was determined by FT-IR spectroscopy and polymer degradation was monitored by dynamic mechanical tests in the melt state. The effect of MA and DCP concentration, of the $scCO_2$ density, and of the reaction time on the grafting yield and on the melt flow behavior was studied. Maleic anhydride homopolymerization during the grafting is suggested by FTIR spectra. The home-synthesized maleated iPP was used as effective compatibilizing agent in the preparation of iPP/Nylon-6 blends.

Introduction

Modification of polypropylene (PP) by polar monomers has always been an object of great interest as it offers an effective route to address such a low cost commodity polymer to higher added value applications. By this route, new potential markets can be opened to such a petrochemical production that, in the medium term, is planned to be shifted into less mature productive areas of the planet owing to inadequate return of investment in the economic context of the more industrialized countries. By functionalization, it is possible to obtain an improved compatibility of the polyolefin with hydrophilic systems, because of the increased polarity and reactivity the functionality imparts to the polymer. In this way polypropylene can be used as adhesion promoter to bond polymers with other polar materials such as glass and metals, in the preparation of multilayer films (food industry) and composites (such as PP and mineral reinforcements to improve mechanical properties), and as a compatibilizer in the formulation of polymer blends. Maleic anhydride (MA) is a monomer widely used to graft onto polypropylene matrixes, and the maleated macromolecule is mainly used in the compatibilization of blends of PP with engineering thermoplastic polymers such as polyamide (PA), polycarbonate, and linear polyesters. Compatibilization is assured by a graft copolymer formed in situ by nucleophilic ring opening of the cyclic anhydride carried out by the amide or ester group of the thermoplastic compound. An amphipatic copolymer is thus generated which is mainly located at the interface between the two polymer phases and behaves as a sort of solid-state surfactant promoting mechanical interlocking through interpenetration and entanglements.[1−3]

The grafting of MA onto isotactic polypropylene (iPP), usually initiated via thermal decomposition of organic peroxides, can be performed both in the melt state by reactive extrusion[4−6] and in the presence of liquid solvents.[7−11] The latter suffers from the problem of removing the organic solvent from the modified polymer, the former exhibits molecular degradation of the polymer owing to the high operating temperature. Furthermore, the anhydride has a low solubility in the molten polyolefin, thus leading to a limited degree of maleation (generally lower than 0.5% w/w).

Supercritical carbon dioxide ($scCO_2$) has been an object of relevant interest as a medium for polymer processing.[12] The origin of such a plethora of research efforts is the capability of CO_2 to swell and plasticize amorphous domains of macromolecular materials. As a consequence of this ability, the free volume of the polymer is increased, and this leads to enhancement of the diffusion rate of low molecular weight molecules in the polymer matrix and reduction of viscosity for polymer extrusion and blending. Owing to the aforementioned mass transfer acceleration effect, $scCO_2$ has been extensively studied as a solubilizing and carrier agent to transport small molecules inside polymer materials.[13,14] At a properly chosen value of the density, $scCO_2$ can dissolve low polar compounds and interact with the polymer, both plasticizing and swelling the matrix; upon release of pressure, precipitation of the finely dispersed solute into the polymer structure occurs thus allowing impregnation of the substrate.[14]

If the solute is a reactive monomer, the $scCO_2$-assisted infusion can be followed by polymerization, and through this route, it is possible to prepare a massive composite[15−21] or a surface-modified organic polymer compound[22−24] or to induce grafting of suitable polar monomers onto the polymer backbone.[25,26]

Our research group has previously investigated the modification of iPP with maleic anhydride by using supercritical CO_2 as a solvent and carrier agent to deliver the monomer into the bulk polymer, performing an ex situ γ radiation initiated grafting of the solubilized

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MA in mild conditions ($T = 25$ °C, $P = 1$ atm). The main drawback of this method is the occurrence of polypropylene molecular degradation induced by the extremely high energy γ-photons.[27]

To overcome this disadvantage we have investigated the possibility of grafting MA onto isotactic polypropylene in a one-step process, performing the infusion of the cyclic compound in the presence of dicumyl peroxide (DCP) at a temperature high enough to allow thermal decomposition of the peroxide with the initiation of the grafting process in the heterogeneous supercritical system.

Experimental Section

Materials. The polymers used were an isotactic polypropylene (iPP) Stamylan P13E10 ($M_w = 500$ kg/mol, density $= 0.903$ g/mL) and, for the home-preparation of blends with iPP grafted in scCO$_2$, polyamide 6 (PA6), Akulon K 123 ($M_w = 25\,000$ g/mol). Both polymers were kindly supplied by DSM.

SOL 4.8 carbon dioxide, 99% MA and 98% DCP both from Aldrich, were used as received.

Phase Behavior. To study qualitatively the phase behavior of the CO$_2$/MA/DCP mixture in the adopted reaction conditions, a constant volume view-cell was assembled. A stainless steel high-pressure view cell having a volume of 14.5 mL, equipped with two 1 cm thick sapphire windows with a 180° orientation and 5 cm optical length was used.

After addition of the selected amounts of the condensed compounds (MA and DCP), the system was carefully washed with gaseous CO$_2$, and then the proper quantity of CO$_2$ was delivered by an ISCO model 500D syringe pump to reach the selected nominal density. The total amount of CO$_2$ introduced is measured by weighing the vessel with an electronic scale (Mettler PM34 maximum 30 kg, precision 0.1 g). Then the cell was placed in a homemade electronically controlled temperature bath, using water contained in a transparent polycarbonate tank as heating liquid, and it was heated until system homogeneity was attained. The pressure inside the view cell was measured by means of a pressure transducer. The cell was subjected to a thermal cycle consisting of a progression of stepwise increase of temperature over the transition value and a similar gradual cooling to room condition. In all experiments, the amplitude of the temperature variation was 1 °C. After each step, the attainment of equilibrium was awaited before acquisition of the pressure and temperature values inside the cell. Blank experiments with pure CO$_2$ demonstrated that the equilibrium condition is reached within 3 min from the thermal perturbation.

Grafting Procedure. Polypropylene sheets (about 80 μm thick) were prepared from pellets by compression molding in a laboratory press: the pellets were kept at 180 °C under a pressure of 12.5 MPa for 10 min, and then they were cooled to room temperature by cold water running through the press plates.

The maleation reaction was carried out in a high pressure PARR reactor, with a total free volume of 102 mL, equipped with a magnetic stir bar. The reactor was charged with the polypropylene films (0.5 g ca.) and the desired amount of MA and DCP. After sealing, it was repeatedly washed with gaseous CO$_2$ to purge atmospheric air and filled at room temperature, using an ISCO model 500D syringe pump, with a weighed amount of liquid CO$_2$ to reach the planned value of density. The total amount of CO$_2$ introduced is measured weighing the autoclave with the aforementioned Mettler PM34 electronic scale. The charged reactor was placed into an electronically controlled silicon oil bath and heated to the reaction temperature, which was controlled with an accuracy of ±0.1 °C. At the end of the reaction time, the system was quenched with cold water and slowly vented. The iPP film was rinsed with acetone at room temperature in order to remove the excess MA and DCP from the surface of the polymer sample.

To remove the not-grafted compounds present inside the sample, the films were continuously extracted with scCO$_2$ in an ISCO extractor at $T = 80$ °C and $P = 24$ MPa (CO$_2$ density 0.69 g/mL as estimated from the Bender equation of state[28]) for at least 5 h.

A double loading procedure was performed on the sample with the best MA grafting yield. After the first supercritical extraction and characterization the film was treated again with MA and DCP in scCO$_2$ with the same procedure previously described and it was analyzed again.

Characterization of Grafted iPP. An estimation of the amount of grafted MA in the polymer film was made by infrared (IR) spectra recorded on a Perkin-Elmer Spectrum 2000 Explorer FTIR with an averaging of 16 scans at a resolution of 1 cm^{-1} using a near-IR fast recovery deuterated tryglicine sulfate detector. The determination was made by calculating the ratio of the absorbance of the 1785 cm^{-1} band (A_{SA}), corresponding to the symmetric stretch of the carbonyl group in the grafted cyclic anhydride, to the absorbance of the methyl group band at 1165 cm^{-1} (A_{Me}), which was used as the internal reference in the normalization of the different spectra. The reported values were obtained, averaging at least five measurements in different points of the sample, using a calibration curve derived from standard samples supplied by DSM.

Horizontal attenuated total reflectance analyses (HATR) were carried out using the Perkin-Elmer Spectrum 2000 Explorer. A 45° zinc selenide (ZnSe) crystal with a total number of 12 reflections was used for the HATR measurements. The values of equipment parameters were the same ones adopted for transmission measurements.

Dynamic mechanical tests in the melt state were carried out through a RDA2 Rheometrics analyzer 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 1×10^{-1} to 5×10^{2} rad/s.

Calorimetric analysis was done through a Perkin-Elmer DSC7 calorimeter. To prepare a suitable sample (weight $= 5-15$ mg) from the specimens, several disks having the same diameter as the DSC sample pan were punched from the original polymer film and stacked into the pan. An aluminum lid was placed over the polymer and this assembly was pressed slightly with a metal plunger. Then the sealed pan was placed in the DSC holder under N$_2$ atmosphere. The sample was heated from 30 up to 200 °C, cooled to room temperature, and then heated again up to 200 °C. Both the heating and cooling rates were 10 °C/min.

Polyamide/Grafted-iPP Blends Preparation. Both the polypropylene and polyamide raw materials were in the form of pellets. The polyamide pellets were dried at 110 °C under vacuum for 24 h.

The blends were prepared by mixing the well-dried pellets of PA6 and iPP thoroughly, followed by melt mixing in a Brabender Plasticorder model PLE 330, operating at 240 °C, with a screw speed of 64 min^{-1} for 5 min. After the mixing procedure, the blends were chopped up and put in a vacuum oven for 12 h.

Blend Characterization. Dynamic-mechanical tests in the melt state were carried out with the same experimental setup previously described.

For tensile properties, blend sheets were prepared by compression molding, keeping the samples at $T = 240$ °C and $P = 50$ bar for 3 min. Then they were cooled by cold water running through press plates. Tensile properties were evaluated at room temperature (about 25 °C) by an INSTRON machine model 1122. The fust-shaped test specimens were prepared from polymer sheets by cutting them using a guide mold. The initial deformation rate was 1.67×10^{-3} s^{-1}. The reported results are the average of eight tests.

Blend morphology was analyzed and imaged with a Philips scanning electron microscope (SEM). First the samples were cut under liquid nitrogen to obtain an undistorted view representative of bulk material, and then they were subjected to selective extraction of polypropylene phase by boiling xylene

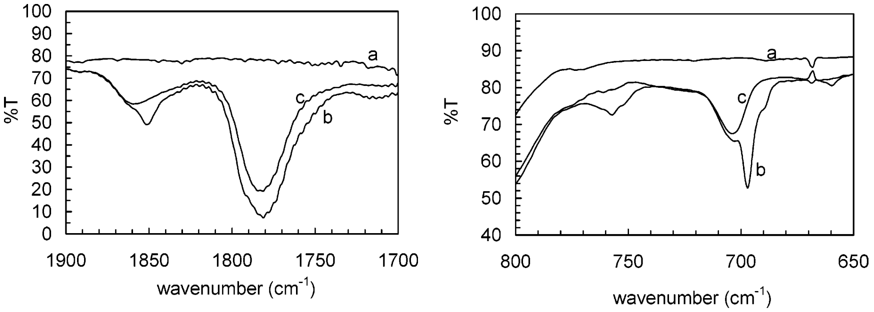

Figure 1. IR spectra of iPP: (a) virgin polymer, (b) iPP maleated in scCO$_2$ at 120 °C and 0.5 g/mL; (c) sample b extracted with scCO$_2$ at 24 MPa and 80 °C for 5 h.

for 20 h. After the extraction procedure, the samples were dried and sputter-coated with gold to a thickness of 200 Å.

Results and Discussion

Paulaitis and Alexander[29] investigated the phase behavior of the carbon dioxide−maleic anhydride binary system and they observed that a single phase is formed at *T* and *P* slightly higher than those corresponding to the critical point of CO$_2$. Anyway, those authors reported a portion of the phase diagram which corresponds to dilute solutions of MA in scCO$_2$ as already observed by Hayes and McCarthy.[25] These authors examined the phase behavior of the binary system in the presence of a higher MA molar fraction. When the concentration of anhydride used was 0.5 M, they found that the cloud point coordinate in the temperature−pressure scale are 85 °C and 240 atm. Under the experimental conditions adopted in this work, the maximum amount of MA inserted in the high-pressure reactor corresponds to 0.3 M concentration. The solvent power of supercritical carbon dioxide increases with the density, and to verify that the fluid system is homogeneous under grafting conditions, the phase configuration was investigated at the lower density and the highest MA concentration adopted in the modification experiments (i.e., 0.5 g/mL and 0.3 M) in a suitable view cell.

At room-temperature three phases can be observed inside the cell stratified according to their density: one at the bottom, rich in melt MA, one intermediate, rich in liquid CO$_2$, and the last in the upper portion of the view cell that we presume to be mainly constituted by gaseous CO$_2$.

When the temperature is raised, a threshold value is reached where opalescence is seen in the view cell and no meniscus can be detected. Moreover, for the analyzed concentrations, it was found out that a homogeneous solution is obtained at a maximum temperature of about 85 °C. A similar approach was used to investigate the solubility of DCP in scCO$_2$. Also at the highest concentration of DCP adopted in the grafting experiments, the fluid system is constituted by a homogeneous solution when a temperature higher than 80 °C is reached.

Effect of Maleic Anhydride Concentration. The infrared analysis is an analytical technique frequently adopted to follow the maleation reaction. In Figure 1, three spectra are shown; they are respectively referred to as the following: virgin iPP (spectrum a), iPP removed from the reaction vessel after maleation and simply rinsed with acetone (spectrum b), and this same sample after a scCO$_2$ extraction procedure (spectrum c). In spectrum b, additional bands appear in comparison to the spectrum a. They are in the range of wavenumbers where characteristic bonds of cyclic anhydride (1850 cm^{-1} with a shoulder at 1862 cm^{-1}; 1783 and 696 cm^{-1} with a shoulder at 704 cm^{-1}) and dicumyl peroxide (760 cm^{-1}) absorb energy. After the extraction treatment performed to eliminate the residual unreacted MA and DCP inside the polymer matrix, the only additional peaks are located at 1862, 1785, and 704 cm^{-1}. The first two bands correspond to the asymmetric and symmetric stretching of the carbonyl bond of the grafted anhydride. The latter one is due to the out of plane bending vibration of the C−H bonds in the anhydride ring. The carbonyl bands determined in this study are in good agreement with the IR response obtained by Hayes and McCarthy[25] in the maleation of poly(4-methyl-1 pentene) in scCO$_2$ (1864 and 1787 cm^{-1}).

To evaluate the distribution of grafted MA inside the polymer, maleated samples were also analyzed by HATR IR. To control that the grafting reaction is a bulk process, the absorbances of the 1785 cm^{-1} carbonyl symmetric stretching band, recorded both by transmission and HATR IR and normalized using the 1165 cm^{-1} band as internal reference, were compared as already described by other researchers.[25] The reason for this approach lies on the fact that the transmission spectrum collects information from the whole thickness of the film while the HATR IR spectrum detects only energy absorption in the outermost layer of the sample as the depth of penetration can be estimated less than 2 μm. As the normalized carbonyl peaks have both almost the same intensity, we can conclude that the MA grafting is a bulk reaction.

A controversial issue is the form under which the five-member cyclic anhydride is grafted onto the polymer backbone. NMR analyses[30] and mathematically deconvolved IR spectra[31,32] of melt or solution-maleated polymer samples indicate that the polar compound is present in the form of succinic units. More recently the chemical structure of iPP-*g*-MA prepared by melt reactive extrusion was studied by using electrospray ionization−mass spectrometery, and the authors proposed that maleic anhydride radicals always maintain their double bond after termination.[33]

The exact determination of the form of the grafted anhydride was behind the scope of the present investigation. Indeed, even if a mathematical elaboration of IR spectra could be of help in discriminating among the two cyclic forms, our spectroscopic analyses were performed only with the aim of evaluating the amount of cyclic carbonyl compound grafted to the polymer, as this method was proved to be more effective than acid group titration when the polymer is analyzed in the form of a film and is properly treated for removal of unreacted anydride.[34]

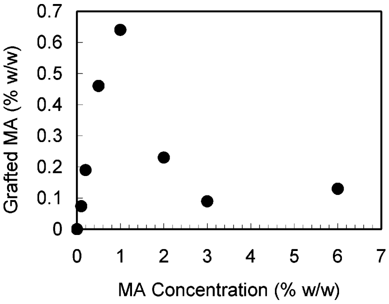

Figure 2. Effect of MA concentration (% w/w based on carbon dioxide) on the maleation of iPP in $scCO_2$. CO_2 density 0.5 g/mL, DCP concentration 50% w/w with respect to MA, 120 °C, reaction time 20 h.

A set of experiments was addressed to investigate the influence of the initial concentration of MA on the grafting process. In Figure 2, the weight percent (with respect to the polymer) of grafted MA is reported as a function of the amount of anhydride initially loaded in the reactor with the DCP/MA weight ratio fixed at 0.50.

Experiments were performed with a total density of the supercritical fluid solution of 0.5 g/mL at 120 °C, without any soaking period prior of the thermal activation of the peroxide decomposition, reaction time was always 20 h. When the initial concentration of cyclic anhydride was increased, an higher amount of grafted MA was measured up to a maximum value (about 0.65% w/w) in correspondence of an initial mass fraction in the fluid phase of 1% w/w. This behavior was already observed in the maleation of polyolefins both in conventional systems[33] and in $scCO_2$,[25] and it could be explained taking into account the fate of free radicals generated by the peroxide decomposition.

Alkoxyl radicals can add to free MA (Figure 3, route a) or abstract hydrogen atom from the iPP backbone, the tertiary carbon being kinetically favored owing to the higher stability of the radical formed on the macromolecule (Figure 3, route b). The formed macroradicals can evolve adding MA (Figure 3, route c) or undergoing β-scission with consequent reduction of the molecular weight. When a high concentration of anhydride is present in the system, scavenging of radicals by MA according to route a is favored, and a lower concentration of polymer macroradicals is generated, leading to a decrease in the grafting level despite the higher MA concentration dissolved inside the polymer matrix.

Beside the grafting level, an important point for the control of the end use properties of the grafted polymer is the limitation of the structural modification that can occur during polyolefin maleation. In the case of iPP, the polymer degradation occurs mainly as a consequence of the aforementioned β-scission reaction.

To investigate this aspect, the melt flow behavior of maleated iPP was studied. In Figure 4 and Figure 5 the melt flow curves of samples modified with initial concentrations of MA respectively lower and higher than 1% w/w are shown.

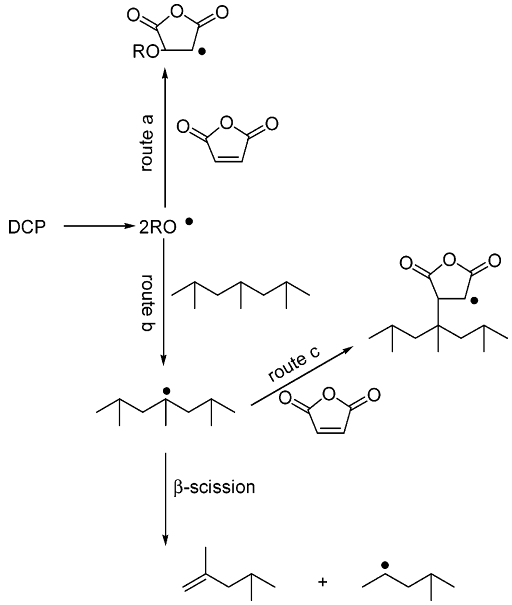

Figure 3. Grafting of MA onto iPP in $scCO_2$.

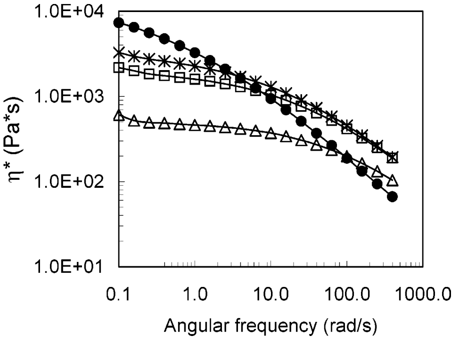

Figure 4. Melt flow behavior of iPP samples maleated at low initial concentration of MA. Initial MA concentration (% w/w based on CO_2): (●) untreated iPP; (∗) 0.1% w/w; (□) 0.2% w/w; (△) 0.5% w/w. Conditions: CO_2 density 0.5 g/mL; DCP concentration 50% w/w with respect to MA; 120 °C; reaction time 20 h.

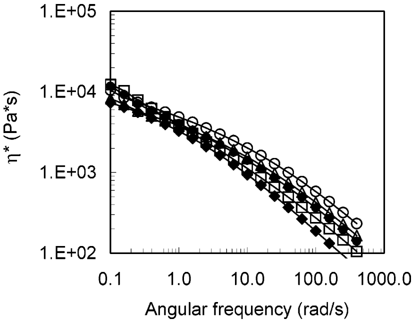

Figure 5. Melt flow behavior of iPP samples maleated at high initial concentration of MA. Initial MA concentration (% w/w based on CO_2): (◆) untreated iPP; (□) 1% w/w; (○) 2% w/w; (△) 3% w/w; (●) 6% w/w. Conditions: CO_2 density 0.5 g/mL; DCP concentration 50% w/w with respect to MA; 120 °C; reaction time 20 h.

When the initial anhydride concentration is low and then a low grafting level is achieved, molecular degradation of the polymer is indicated by the marked decrease of the zero shear complex modulus with respect to the curve of pure iPP. The extent of polymer degradation increases if the MA concentration in the $scCO_2$ is increased up to 0.5% w/w, but, quite interestingly, when polymer films were modified in the presence of higher cyclic carbonyl concentrations, a marked decrease of molecular degradation was observed when their rheological behavior is compared with that of virgin iPP.

To make more evident the interpretation of the melt dynamic analyses in term of polymer degradation we have plotted the crossover frequency of storage and loss moduli (i.e., the frequency ω_x where the equation $G'(\omega) = G''(\omega)$ is satisfied) as a function of the MA initial

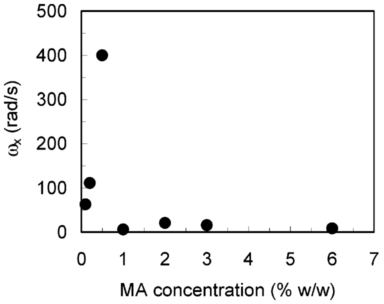

Figure 6. Modification of the crossover frequency ω_x with the MA initial concentration in the supercritical phase. Experimental conditions are as in Figure 2.

concentration (Figure 6). In the literature[6,35] it is reported that ω_x may be related to the weight-average molecular weight of the polymer (M_w) according to

$$\omega_x \approx (M_w)^b$$

where b is a negative exponent. On this basis the higher the value of the cross over frequency the lower M_w is. The trend obtained for ω_x confirms that chain scission is relevant at low initial MA concentration and that this phenomenon is inhibited by the presence of an high enough concentration of the unsaturated carbonyl compound.

Some considerations about the influence of unsaturated species present in the reaction media during polypropylene modification are reported in the literature.[4,6] It was observed that iPP degrades extensively during the functionalization process, but the presence of maleic anhydride can alleviate the scission reactions and the simultaneous presence of such molecule and a peroxide could also induce cross-linking of iPP. The rationale for these results can be given in term of the elementary reactions which are postulated to be active during the maleation process. Indeed a crucial bifurcation in the evolution of the polymer chain occurs after generation of the macroradical by hydrogen abstraction. As already reported, such species can evolve through intramolecular β-scission or can add an anhydride unit. Of course the higher the rate of MA addition the lower the portion of polymer chains undergoing the scission. It seems reasonable that when small amounts of maleic anhydride are present in the reaction medium, the addition kinetics is slow and the polymer degradation becomes the main evolution path for polymer radicals. When the concentration of MA in the reaction medium increases, the maleation will become faster as there is an high probability that a MA molecule in the polymer matrix is located near a reactive center generated on the polymer backbone. As a consequence of the addition reaction a succinic secondary carbon radical is formed which can terminate by combination or dismutation without the occurrence of chain fragmentation.

The onset of homopolymerization of maleic anhydride during the grafting of polypropylene is a controversial issue. From the literature, it can be deduced that the grafting mechanism, structure, and location of the grafted anhydride depend on the grafting method and the reaction conditions. For what concern MA homopolymerization, it is reported that the operative temperature adopted for melt grafting processes is higher than the ceiling temperature T_{ce} for anhydride polymerization.[36] Such argumentation suffers from the weak point that the ceiling temperature for a vinyl monomer polymerization depends on the local concentration of the unsaturated compound, and indeed De Roover et al.[37] observed the formation of free low molecular weight MA oligomers by size exclusion chromatography in a study of the homopolymerization of the anhydride during the melt-functionalization of iPP at 190 °C.

In our study, one must moreover consider that the grafting process is performed using supercritical carbon dioxide as a solvent and swelling agent at pressure higher than 20 MPa. In principle, high pressure can have effect on the thermodynamics and reversibility of a polymerization reaction.

This means that the value of the ceiling temperature can be modified with respect to processes performed at low pressure. This effect can be made evident considering the origin of T_{ce}. This can be defined[38] as the temperature at which the propagation reaction of the chain polymerization becomes reversible; i.e., it must be written as an equilibrium reaction:

$$P_n^\bullet + M \underset{k_{dp}}{\overset{k_p}{\rightleftharpoons}} P_{(n+1)}^\bullet \tag{1}$$

k_p and k_{dp} respectively being the rate constant of the propagation and its reverse reaction termed depolymerization or depropagation.

In the frame of dynamic description of equilibrium condition, when the reaction temperature is increased a value T_{ce} (ceiling temperature) is reached when the propagation and depropagation rates are equal and the net rate of polymer production is zero. Obviously the position of the monomer–polymer equilibrium depends on the value of the equilibrium constant K whose variation as a function of pressure is given by the differential equation

$$\left(\frac{\partial \ln K}{\partial P}\right)_T = -\frac{\Delta V}{RT} \tag{2}$$

where ΔV is the reaction volume (the difference in the volume between products and reactants).

For $T = T_{ce}$, it is possible to write the following equation:

$$-RT_{ce} \ln K = \Delta G^0 = \Delta H^0 - T_{ce}\Delta S^0 \tag{3}$$

and solving with respect to T_{ce}

$$T_{ce} = \frac{\Delta H^0}{\Delta S^0 - R \ln K} \tag{4}$$

The variation of the ceiling temperature with pressure takes the form[38]

$$\frac{\partial T_{ce}}{\partial P} = \frac{T_{ce}\Delta V}{\Delta H} \tag{5}$$

From this equation, it can be deduced that, as ΔV and ΔH for the propagation reaction are negative, an increase of pressure leads to an increase in the ceiling temperature so that it could be possible the synthesis of polymers at temperatures above that they would normally decompose.[39]

When applied to our research, these considerations sustain the consciousness that, under adopted operative conditions, the occurrence of MA homopolymerization cannot be discarded on the basis of T_{ce} considerations. For this reason, we tried to investigate whether the MA-

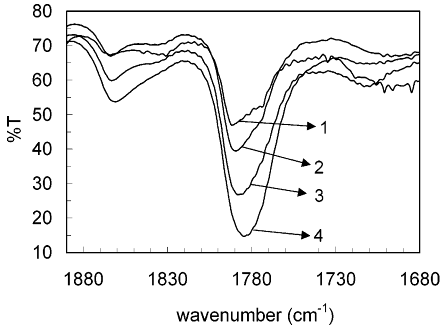

Figure 7. IR spectra of iPP sample maleated in scCO$_2$ with different initial MA concentration (% w/w based on CO$_2$). Key: spectrum 1, MA 0.1%; spectrum 2, MA 0.2%; spectrum 3, MA 0.5%; spectrum 4, MA 1%. Conditions: CO$_2$ density 0.5 g/mL; DCP concentration 50% w/w with respect to MA; 120 °C; reaction time 20 h.

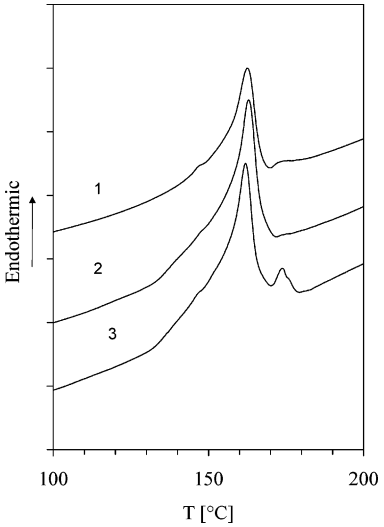

Figure 8. DSC thermographs for the heating of virgin iPP (graph 1), iPP-*g*-MA with 0.33% w/w grafted MA loading (graph 2), and iPP-*g*-MA with 0.64% w/w grafted MA loading (graph 3).

modified polypropylene chains bring single anhydride rings or not by using the results of IR analyses as suggested by De Roover et al.[31] These authors observed that the symmetric stretching of carbonyl group of a single moiety of MA absorbs energy at 1792 cm^{-1} while in the case of poly(MA) the band is located at 1785 cm^{-1}.

In Figure 7, the spectra of samples processed with different initial concentration of maleic anhydride are reported in the pertinent wavenumber's range. A shift toward lower wavenumbers is observed with the increase of MA amount. It seems reasonable to associate this behavior to the formation of poly(maleic anhydride) chains which becomes gradually more significant when the concentration of the carbonyl compound in the reaction medium increases.

To verify if the modification process induces changes in the crystallinity of polypropylene calorimetric analyses were carried out. In Figure 8, the curves relative to the heating run for virgin iPP and iPP with 0.33 and 0.64% w/w of grafted MA are shown. From their comparison, it can be deduced that maleation in scCO$_2$ medium alters the crystalline phase of the polymer. In fact even if the melting points of iPP-*g*-MA samples are quite close to that of virgin iPP, a higher melting enthalpy can be measured in the case of the functionalized samples as testified by the higher area under the peaks. Observing the shape of the three curves, it is worth noting that in the case of maleated samples the melting onset is located at lower temperatures probably as a consequence of a wider distribution of regularity of the crystalline domains in the presence of grafted anhydride. For the sample with 0.64% w/w of grafted MA, a small peak after the main one appears. It could be attributed to the formation of new more regularly packed crystalline domains under the experimental conditions used.

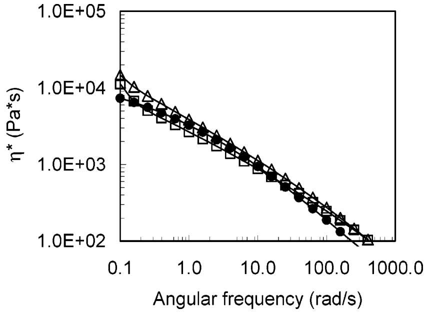

Figure 9. Comparison of melt flow behavior of iPP samples treated with a double MA loading: (●) untreated iPP; (△) iPP-*g*-MA-g 0.64% w/w MA (first treatment); (□) iPP-*g*-MA 1.30% w/w MA (same sample after second treatment). In both cases, $T = 120$ °C, CO$_2$ density 0.50 g/mL, reaction time 20 h, MA initial concentration 1% w/w based on CO$_2$, and DCP 50% w/w based on MA.

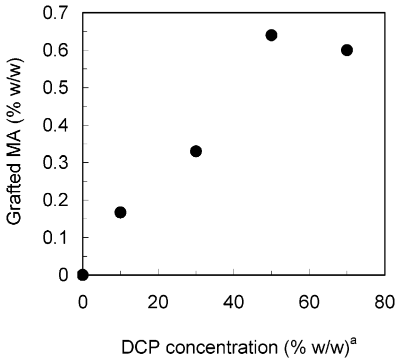

Figure 10. Effect of DCP concentration (% w/w based on MA) on the maleation of iPP in scCO$_2$. Conditions: CO$_2$ density 0.5 g/mL; MA concentration 1% w/w with respect to CO$_2$; 120 °C, reaction time 20 h.

In a single batch experiment, the gradual decrease of initiator and MA concentration sets an intrinsic limit to the amount of grafted anhydride. For this reason, we have tested the possibility of increasing the loading of polar compound in the macromolecular matrix by performing two repeated batch maleations on the same polymer sample. This experiment is particularly relevant because it can demonstrate the possibility of achieving an high grafting level by a semicontinuos maleation process where the concentration of MA and DCP is maintained at a suitable steady value.

The amount of grafted maleic anhydride is almost doubled (1.3 wt %) with respect to simple treatment; moreover, no evidence of enhancement in the chain scission of the polymer as a consequence of the second treatment sample was observed from the comparison of the dynamic rheological curves (Figure 9).

Effect of Dicumyl Peroxide Concentration. The effect of DCP concentration on the percentage of grafted MA was also investigated. The results are reported in Figure 10.

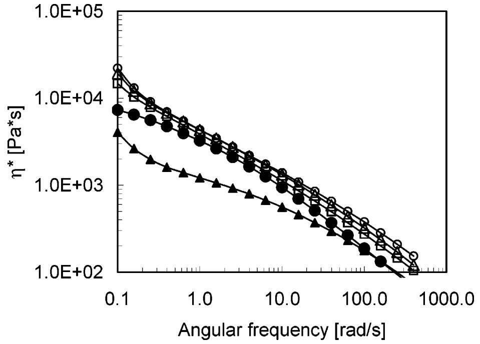

Figure 11. Effect of DCP concentration on the melt flow behavior of iPP samples maleated in $scCO_2$. DCP concentration (% w/w based on MA): (●) virgin iPP; (▲) 10%; (△) 30%; (□) 50%; (○) 70%. Other experimental conditions are as in Figure 10.

Experiments were performed with 20 h reaction time at 120 °C and total density of the supercritical fluid solution of 0.5 g/mL, with fixed initial MA concentration (1% w/w with respect to CO_2) and variation of the DCP concentration from 0 to 70% w/w with respect to MA.

In the absence of DCP, no grafting occurred. As expected, the amount of grafted MA increased when the initiator concentration was increased up to 50% w/w; further increment behind this value did not lead to an improvement in the amount of grafted anhydride. This result could have different explanations: a possible justification is the achievement of saturation concentration in the partitioning of the peroxide between the supercritical solution and the CO_2 swollen polypropylene matrix; one different possibility is that when high concentrations of DCP are added to the system, the rate of generation of free radical species reaches such an high value that the homopolymerization of MA becomes a significant sink of the unsaturated compound thus depressing the grafting process.

Molecular modifications of the polymer after thermal maleation were studied through dynamic-mechanical tests in the melt state. In Figure 11, the melt flow curves of iPP-*g*-MA samples processed in the presence of different amounts of DCP are reported. Only in the case of the polymer grafted at 10% w/w DCP concentration, a decrease in the zero shear viscosity, attributable to a decrease in the molecular weight of the polymer, was observed. These results can be explained considering that, with low peroxide concentration, the chain transfer and β-scission reactions are more favorable with respect to recombination reactions as the local concentration of radical species is low. If the peroxide concentration increases, a faster rate of generation of free radical is obtained, and this leads to a prevalence of bimolecular coupling reactions vis a vis chain scission.

Effect of CO_2 Density. When a chemical process is carried out in the presence of a supercritical fluid, a relevant parameter that can be used to influence its performances is the density of the fluid phase. By a proper modification of this intensive quantity, it is possible to change the physicochemical and transport properties of the reaction medium. This possibility can become an additional instrument that the process engineer can adopt to optimize the process. In this perspective we have studied the effect of the CO_2 density on the performances of the maleation of iPP. The experiments were carried out at three different density values (0.50, 0.57, and 0.65 g/mL) with a constant initial amount of MA loading in the vessel and two different concentrations of DCP (50 and 70% with respect to MA).

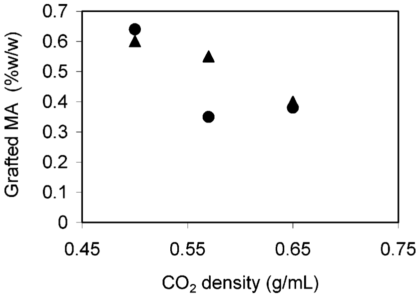

Figure 12. Effect of CO_2 density on the maleation of iPP in $scCO_2$. Conditions: $T = 120$ °C; reaction time 20 h; MA 1% w/w based on CO_2 at 0.5 g/mL. DCP concentration (% w/w based on MA): (●) 50%; (▲) 70%.

Table 1. Solubility Parameters of Supercritical Carbon Dioxide at Different Densities Compared with that of Maleic Anhydride

component	ρ_1 (g/mL)	δ_1 (MPa$^{1/2}$)
$scCO_2$	0.50	6.8
	0.57	7.8
	0.65	8.9

component	δ_2 (MPa$^{1/2}$)
MA	25.2

Whatever the concentration of the initiator, the highest grafting values were obtained at 0.50 g/mL (Figure 12). When more dense fluid phases were adopted, a decrease in the amount of grafted MA was observed.

Among the tunable properties of a supercritical fluid, it is possible to mention the solvent power, which increases by enhancing the density of the fluid; this effect can be made quantitative by referring to the concept of the Hildebrand solubility parameter δ extended by Allada[40] to supercritical fluids.

In Table 1 are reported the values of δ for $scCO_2$ (δ_1) and maleic anydride (δ_2). In the case of the supercritical fluid, the values of the Hildebrand parameter were estimated, as noted by Giddings, according to vdW theory[41]

$$\delta_1 = \frac{a^{1/2}}{v_1}$$

where the constant a is the energy parameter in vdW equation of state and v_1 is the molar volume of $scCO_2$.

In the case of the cyclic compound the value of δ was estimated according to its definition from the heat of vaporization and the density[42]

$$\delta = [(\Delta H_{\mathrm{ev}} - RT)\rho_2]^{1/2}$$

We see that the fluid phase becomes an increasingly better solvent for MA and DCP when the density is increased and this shifts the equilibrium partitioning of the solutes toward the fluid phase. This means that, if higher densities are adopted, a lower local concentration of carbonyl compound is available in the amorphous domains of the iPP, and this could justify the observed trend in the grafting level as a function of density.

As mentioned when the effect of MA loading was discussed, we have observed that an higher concentration of the unsaturated compound alleviates the polymer degradation, presumably as a consequence of the addi-

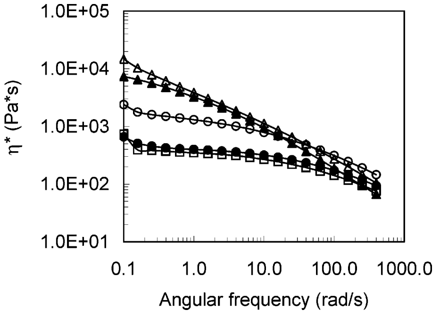

Figure 13. Effect of the density on the rheological behavior of iPP-*g*-MA. Conditions: $T = 120$ °C; reaction time 20 h; DCP 0.5% w/w based on CO_2. Density of CO_2 and MA concentration (% w/w based on CO_2): (▲) untreated iPP; (○) 0.50 g/mL, MA absent; (△) 0.50 g/mL, MA 1%; (□) 0.65 g/mL, MA absent; (●) 0.65 g/mL, MA 1%.

tion of the cyclic anhydride to the polymer macroradicals before the occurrence of the β-scission.

Indeed, dynamic mechanical tests performed in the melt state on polymer samples maleated with a fixed MA weight fraction (1% w/w) have shown evidence of significant molecular degradation only in the case of the polymer grafted into the more dense systems (Figure 13).

On the basis of this result it should be postulated that, despite the decreased equilibrium partition of the DCP, the number of polymer radicals generated inside the matrix is still high enough to induce significant β-scission. This result could be justified by a lower extent in the decrease of the partition coefficient of DCP compared with MA when CO_2 density is increased. The hypothesis is confuted when the rheological behavior of polymer soaked with DCP in the absence of MA is considered. When flow curves are compared, it is possible to determine a more significant degradation in the polymer swollen with $scCO_2$ at the highest investigated density. The frequency of the crossover point, ω_x increases with the density, and such behavior confirms the occurrence of the M_w decrease.

In our opinion, a more sound interpretation of the experimental frame can be given considering that when the solubility parameter increases an higher swelling of the polymer is reached, and this induces an enhancement of the diffusion coefficients of the species inside the polymer. This must be valid also for free radicals generated by the thermal decomposition of the peroxide in the fluid phase that can be efficiently scavenged by the matrix, thus becoming an additional source of macroradicals which evolves through β-scission reactions with a consequent decrease of the molecular weight.

Effect of Reaction Time and Temperature. The influence of reaction temperature and time was also object of investigations. Under the adopted experimental conditions, at a fixed reaction time, an higher grafting level was obtained when the temperature was increased (Figure 14), but in our opinion, taking into account the high complexity of the kinetic scheme of the process, no sound interpretation can be proposed for this experimental evidence. In fact, quite obviously, when the temperature is increased the rate of generation of free radical species is made faster owing to the faster decomposition of the initiator. Anyway, the effect of temperature cannot be interpreted only in this perspective as a significant number of elemental reactions can play a role in the process, and moreover, an effect on the mass transfer kinetics of both the anhydride and the peroxide inside the swollen polymer cannot be excluded.

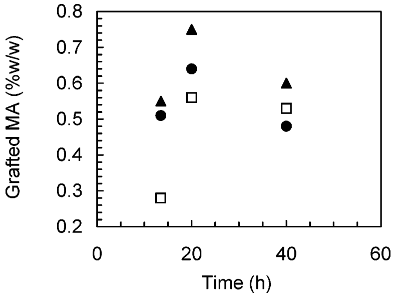

Figure 14. Effect of reaction time and temperature on the maleation of iPP in $scCO_2$. Conditions: CO_2 density 0.50 g/mL; MA concentration 1% w/w (based on CO_2). DCP 50% w/w (based on MA): (□) 110 °C; (●) 120 °C; (▲) 130 °C.

Table 2. Composition of the Home-Prepared IPP/PA6 Blend

blend	PA6[a] (% w/w)	iPP[b] (% w/w)	iPP-*g*-MA[c] (% w/w)	MA loading[d] (% w/w)
1	80	20	0	0
2	80	15	5	0.19
3	80	15	5	0.64
4	80	18	2	0.19

[a] Weight fraction of polyamide in the blend. [b] Weight fraction of polypropylene in the blend. [c] Weight fraction of the compatibilizer. [d] Maleation level of the compatibilizer as estimated from IR calibration curve.

Concerning the effect of the reaction time, we have observed that at fixed temperature the grafting level initially increases with the time and then the percentage of grafted MA levels off or decreases (Figure 14).

Such behavior was observed with an initial concentration of MA of 1% w/w. When a lower concentration of maleic anhydride was charged in the reactor, the enhancement of the reaction time (from 20 to 40 h) did not correspond to significant variations in the percentage of grafted anhydride. In the case of low initial loading of MA, the depletion occurring during the batch process can be so high in the first 20 h as to make useless any further continuation of the treatment.

Use of iPP-*g*-MA as a Compatibilizing Agent. A further part of our study was oriented to evaluate the end-use properties of the grafted iPP as a compatibilizing agent. To this purpose we have prepared, as model systems, blends of iPP and nylon-6,6 polyamide, whose compositions are reported in Table 2.

When the blend was prepared in the absence of the functionalized polypropylene (Figure 15a) the morphology of the mixture, analyzed by SEM after dissolution of the polyolefin phase, was typical of a noncompatible system formed by inhomogeneous discrete iPP domains, having sizes of 10−80 μm, embedded in the nylon continuous phase. When a small amount of iPP-*g*-MA was added to the mixture (blend 2, Figure 15b), a strong "compatibilizing effect" was detected. In fact an almost uniform distribution of very small spherical particles having sizes between 0.5 and 1.5 μm was observed. This result was considered as an evidence that during the reactive mixing the MA end group in iPP-*g*-MA reacts with the chain end NH_2 groups in nylon to form a diblock copolymer which in situ acts as a "compatibilizer" between the two components.

It is worth noting that when iPP-*g*-MA samples with an higher grafting level were used, no appreciable

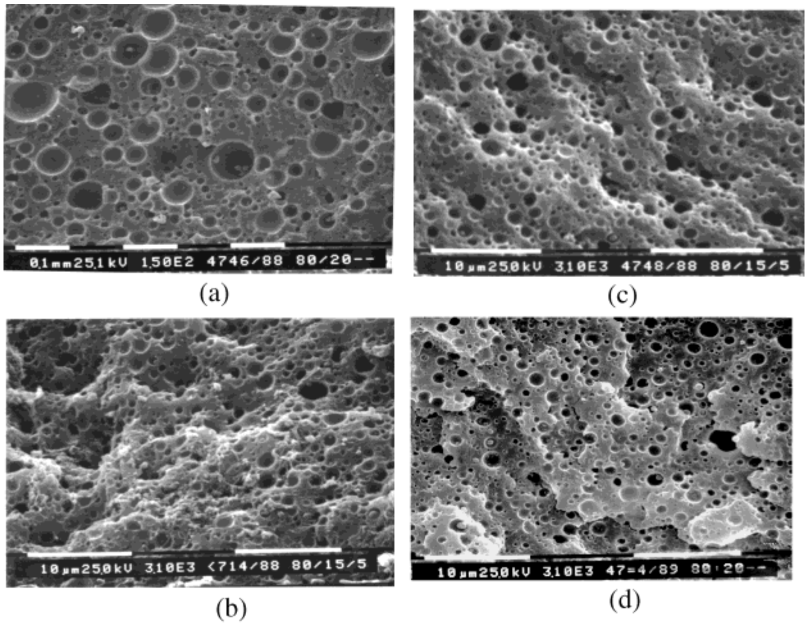

Figure 15. SEM micrographs of home-prepared compatibilized blends. Referring to the blends described in Table 2: (a) blend 1 (no iPP-*g*-MA added); (b) blend 2; (c) blend 3; (d) blend 4.

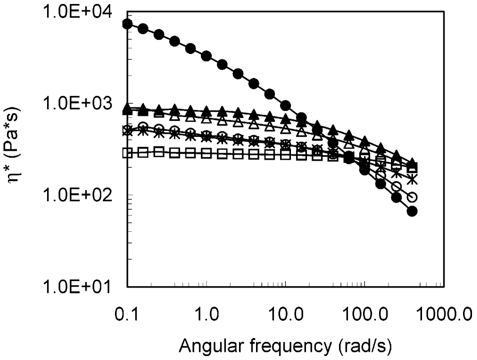

Figure 16. Flow curves of polymer samples constituted by the following: (●) pure iPP; (□) pure PA6; (∗) blend 1 in Table 2; (○) blend 2 in Table 2; (▲) blend 3 in Table 2; (△) blend 4 in Table 2.

Table 3. Tensile Properties of Virgin Materials and PA6/IPP Blends

sample	Young modulus (MPa)	stress at break (MPa)	elongation at break (%)
iPP	1054	23	600
PA6	1747	55	44
blend 1	1520	34	5
blend 2	1720	43	6
blend 3	1924	53	9
blend 4	1445	45	11

modification in the morphology was observed (Figure 15c). This result is consistent with the spectroscopic suggestion that in the presence of high levels of grafted MA, under our experimental conditions, the carbonyl compound is involved in homopolymerization reactions. In fact, in the presence of grafted poly(maleic anhydride), the number of polypropylene chains participating in the compatibilization process decreases.

Prepared blends were analyzed by dynamic-mechanical tests in the melt state, and the recorded melt flow behavior is shown in Figure 16. The flow curve of the system prepared in the absence of compatibilizer is comprised between the flow curves relative to the pure polymers. The increase of melt viscosity for blend 3 is a clear evidence of the compatibilizing effect. This effect is also present for blend 2, where the increase of melt viscosity is hidden by the lower melt viscosity of the iPP-*g*-MA used for this blend. Such a consideration is supported by the flow curve for blend 4, which contains a lower amount of the same iPP-*g*-MA with respect to blend 2. A SEM micrograph of blend 4 is shown in Figure 15d, and no differences relative to the analogous blend 2 can be observed.

In Table 3, the tensile properties of virgin materials and blends are reported. It can be observed that mechanical properties of blend prepared in the absence of the compatibilizer are rather poor according to the incompatible morphology which was observed in the micrographs. On the other hand the addition of iPP-*g*-MA induced an increment of stress and elongation at break.

Conclusions

The thermal grafting of maleic anhydride, delivered inside isotactic polypropylene swollen by $scCO_2$ in the presence of DCP, was successfully controlled by varying the initial concentration of the organic peroxide, the anhydride, and the density of the supercritical fluid. HATR analyses of the modified polymers confirmed that the process proceeds in the bulk of the material and is not limited to the external portion of samples exposed to the supercritical phase. Quite interestingly dynamic mechanical tests in the melt state have given evidence of limited molecular weight decrease of the maleated polymer when the initial MA concentration is higher than 1% w/w with respect to CO_2. This result confirms the positive role of the cyclic compound in the depression of β-scission reactions which are the main responsible of iPP degradation in the case of conventional MA grafting processes.

By a proper selection of the operative conditions, grafting levels higher than 0.5% w/w were obtained even if the occurrence of homopolymerization of maleic anhydride is suggested by the analyses of FTIR spectra of maleated samples.

Melt blending of PA6 and iPP in the presence of the iPP-*g*-MA synthesized in this study results in a wellcompatibilized system with a uniform particle size distribution. The amount of grafted maleic anhydride in the functionalized polypropylene used seems to have a minor influence on the compatibilizing effect, probably because part of the unsaturated compound is incorporated in pendant chains of poly(MA).

The whole experimental picture suggests that maleation of iPP in $scCO_2$ can be successfully carried out at temperature considerably lower than that adopted for reactive extrusion, thus allowing the achievement of a high grafting level in the presence of limited molecular degradation of the polymer.

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