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Modification of isotactic polypropylene film by grafting of acrylic acid using supercritical CO_2 as a swelling agent

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Modification of isotactic polypropylene (iPP) film was carried out by grafting of acrylic acid (AA) onto its backbone using supercritical (SC) CO_2 as a solvent and swelling agent. The iPP film was impregnated with the monomer AA and benzoyl peroxide initiator using SC CO_2 at 308.15 K, followed by thermal polymerization of AA within SC CO_2-swollen iPP film, resulting in iPP-g-PAA composites. The degree of grafting can be controlled by variation of the soaking time, pressure, concentrations of monomer and initiator in the fluid phase, reaction temperature, and time. The morphology and structure of the products were characterized by Fourier transform infrared spectroscopy, scanning electron microscopy, differential scanning calorimetry, and wide angle X-ray diffraction.

1 Introduction

As one of the most commonly used plastics, isotactic polypropylene (iPP) has many valuable qualities, such as low cost and versatility.[1] However, iPP is limited in its applications in some important technological fields because of its lack of chemical functionalities, low surface energy, difficulty to dye, poor hygroscopicity, low impact strength, poor compatibility with other polymers, and sensitivity to photo- or thermal oxidation. In order to overcome these disadvantages, a great deal work has been carried out on the modification of iPP, *e.g.* chlorination,[2] hydroperoxidation,[3] hydrogen abstraction from tertiary carbons, followed by ozonolysis,[1] and graft copolymerization[1]. Among these methods, graft copolymerization onto iPP[4–7] offers an effective approach.

Grafting of iPP with water-soluble vinyl monomers leads to an appreciable improvement in its properties. A major advantage of this modification is that the surface becomes hydrophilic, although the bulk properties of PP are retained. The altered surface properties lead to PP that can be printed on much more easily, can adhere better to other materials, can provide more comfortable fabrics, and can be more easily dispersed in non-solvents. In addition, surface modification with hydrophilic monomers can provide specific functionalities to allow further modification. Grafting of water-soluble compounds onto iPP using conventional methods has been studied by a variety of techniques.[1,8] Unfortunately, the conventional methods suffer from several drawbacks. For example, the solvent must be removed from the final product and additional waste streams are usually produced, furthermore, melting of the graft may result in decomposition of the substrate polymer.

Supercritical fluids (SCFs) have some unique properties. For example, the density, dielectric constant, solubility parameter, and diffusivity can be tuned by altering the pressure. Therefore, it is possible to optimize operating conditions by conveniently altering the pressure without the need for harsh chemical changes.[9,10] SC CO_2 is most attractive because it is non-toxic, non-flammable, cheap, and environmentally more acceptable. It can dissolve small organic molecules, and can swell most polymers. SC CO_2 has near-zero surface tension and large diffusion coefficient. Therefore, it can be used to impregnate polymer matrix with different organic molecules. This principle has been used to modify different polymers.[7,11–22] SC CO_2 has been used to impregnate monomers and initiators into polymer substrates, and following thermal free radical polymerization of monomer within the polymer substrates, polymer composites have been prepared.[7,12–16] Recently, Spadaro and coworkers charged maleic anhydride (MA) and dicumyl peroxide (DCP) into polypropylene matrices using SC CO_2 at 80 °C, and successfully grafted MA into polymer chains through gamma irradiation in a CO_2 atmosphere (0.1 MPa, 25 °C).[23] The effects of swelling due to SC CO_2, maleic anhydride grafting, and gamma irradiation on the molecular structure and molecular weight of the modified polypropylene were investigated by differential scanning calorimetry (DSC) and dynamic mechanical tests in the molten state.

In this work, we selected acrylic acid (AA) as a hydrophilic monomer to provide polar functional groups. AA and BPO were charged into the iPP matrix using SC CO_2 at low temperature (35 °C) and in the pressure range 8.0–15.0 MPa. AA in the matrix was initiated to graft onto the iPP substrate at higher temperatures. We systematically studied the effects of various factors, *i.e.* the soaking time, pressure of SC CO_2, monomer and initiator concentrations, reaction time, and reaction temperature on the grafting percentage. Then, the morphology and structure of the grafted substrates were examined using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and wide angle X-ray diffraction (WAXD).

2 Experimental

2.1 Materials

Substrate samples were obtained from Beijing Yanshan Petrochemicals Company and Soxhlet-extracted using acetone for 24 h, then dried in a vacuum oven at 80 °C. The thickness of the film was about 0.08 mm. Acrylic acid (AA, Beijing Chemical Reagent Center, A.R. grade) was vacuum distilled. BPO (Beijing Chemical Plant) was recrystallized twice from methyl alcohol. Ethanol (Beijing Chemical Reagent Center, A.R. grade) was used as received. CO_2 of 99.95% purity was provided by Beijing Analytical Instrument Factory and used as received.

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2.2 Grafting procedure

The preparation of iPP-g-PAA was composed of two steps: the soaking process and the thermal reaction process. During the soaking process, the monomer and initiator were infused into the SC CO_2-swollen iPP substrates. A suitable amount of BPO–AA solution (0.3 mol% BPO) was placed into a stainless steel high pressure vessel, together with about 0.3 g iPP substrate. After replacing the air with CO_2, the vessel was put into a water bath at 35.0 °C, controlled using a HAAKE D3 temperature controller with an accuracy of ± 0.1 °C. Then, the vessel was charged with CO_2 to the desired pressure. The CO_2 was released after the required soaking time had elapsed. The samples were then put into another vessel, heated up to the requisite reaction temperature, and kept at this temperature for the desired reaction time under a protective atmosphere of nitrogen gas. After the thermal treatment, the samples were removed from the vessel and weighed on an electronic balance (Shanghai 100) to an accuracy of 0.1 mg.

In order to investigate the degree of grafting of AA onto the iPP substrate, iPP–PAA composites were Soxhlet-extracted using hot ethanol for 24 h to remove any AA homopolymers. After drying, the extracted iPP–PAA composites were weighed and then re-extracted. These procedures were repeated until the weight was constant, indicating that unreacted monomer and any homopolymers had been completely removed.

The grafting percentage (G) was calculated from eqn. 1,

$$G\,(\text{wt\%}) = (W_1 - W_0)/W_0 \times 100 \qquad (1)$$

where W_0 stands for the weight of the as-prepared iPP–PAA composite and W_1 for the weight of the iPP-g-PAA after removal of homopolymers and unreacted AA.

2.3 Characterization

A Perkin-Elmer 180 IR spectrometer was used to determine the IR spectra of the composites. The phase morphological characteristics of the samples were observed by means of SEM (Hitachi S-530) in the normal secondary electron imaging (SEI) mode.

The thermal properties of the iPP–PAA composites were measured using a differential scanning calorimeter (Perkin-Elmer DSC-7). Samples of about 6 mg were heated from 60 to 190 °C, and then cooled down to 60 °C under an atmosphere of dry nitrogen. Both heating and cooling rates were 10 °C min^{-1}. The melting temperature T_m and the apparent enthalpies of melting (ΔH_m) were obtained from the maximum and the area of the melting peak, respectively. Similarly, the crystallization temperature (T_c) and crystallization enthalpy (ΔH_c) were obtained from the cooling plots. The apparent crystallinity (C_a) of the iPP and the grafted iPP were calculated from eqn. 2,

$$C_a\,(\%) = \Delta H_m/\Delta H^\circ \times 100 \qquad (2)$$

where ΔH° is the heat of fusion per gram of 100% crystalline iPP. Brandrup and Immergut[24] reported that ΔH° was 209 J g^{-1} for iPP. Because crystallization of the grafted iPP occurs in the iPP portion, the crystillinity of this part in the grafted copolymer (C_{iPP}) can be expressed as shown in eqn. 3,

$$C_{iPP} = C_a/W_{iPP} \qquad (3)$$

where W_{iPP} is the weight fraction of iPP in the grafted copolymer.

WAXD analysis of the iPP and iPP-g-PAA copolymers was carried out with an X-ray diffractometer (Rigaku D/MAX.RB) using Cu-Kα_1 radiation ($\lambda = 0.154056$ nm) at a generator voltage of 45 kV and a generator current of 300 mA. A standard sample was employed to determine the instrumental broadening.

3 Results and discussion

3.1 Grafting

In this work, the soaking experiments were conducted under conditions at which CO_2, AA, and BPO exist as a single phase. In order to determine the optimal operation conditions, the effects of the soaking time, SC CO_2 pressure, monomer and initiator concentrations, reaction temperature, and reaction time on the degree of grafting were studied, and the results were shown in Fig. 1–6.

Fig. 1 shows the grafting percentage plotted as a function of soaking time at 35 °C and 11 MPa with a monomer concentration in the fluid phase of 0.433 mol L^{-1} (the concentration of BPO in AA is 0.3 mol%), followed by thermal reaction at 120 °C for 6 h. The plot shows that the grafting percentage reaches a constant value after a soaking period of about 12 h, although it initially increases rapidly. In other words, equilibrium can be reached within 12 h. It also implies that the swelling ability of SC CO_2 towards this iPP substrate has a limiting value.

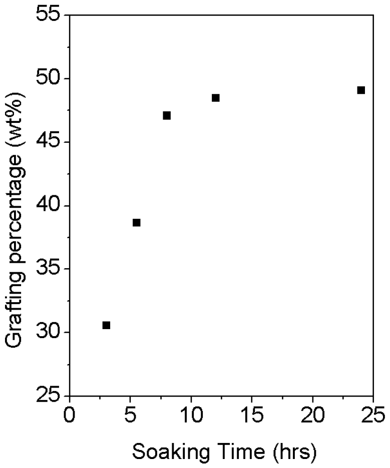

Fig. 1 Grafting percentage of iPP films as a function of the soaking time at 35 °C and 11 MPa. The concentration of AA with 0.3 mol% BPO added is 0.433 mol L^{-1}. Reaction time: 6 h; reaction temperature: 120 °C.

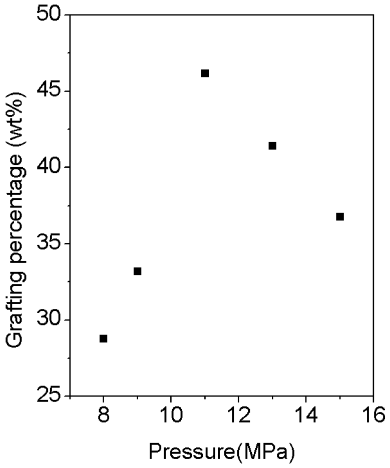

Fig. 2 Grafting percentage of iPP films as a function of pressure at 35 °C with a soaking time of 12 h. The other conditions are same as those in Fig. 1.

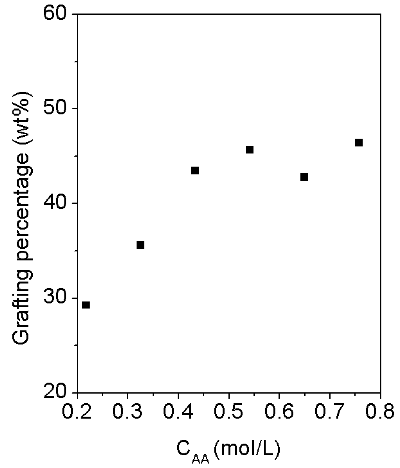

Fig. 3 Effect of the concentration of AA with 0.3 mol% BPO added on grafting percentage with a soaking time of 12 h. The other conditions are same as those in Fig. 1.

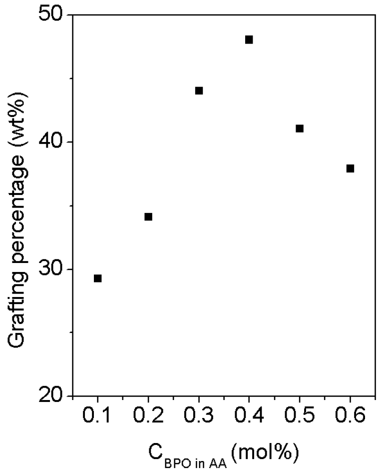

Fig. 4 Effect of the concentration of BPO in 0.433 mol L^{-1} AA solution on grafting percentage with a soaking time of 12 h. The other conditions are the same as those in Fig. 1.

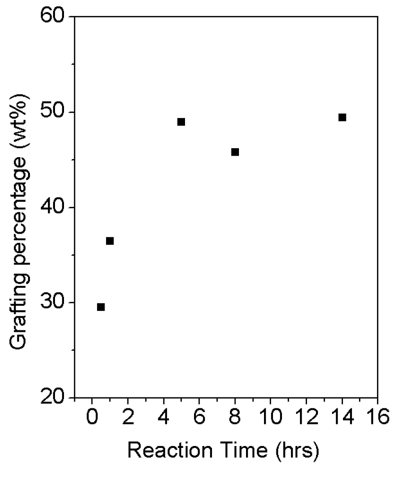

Fig. 5 Effect of reaction time on grafting percentage with a soaking time of 12 h. The other conditions are same as those in Fig. 1.

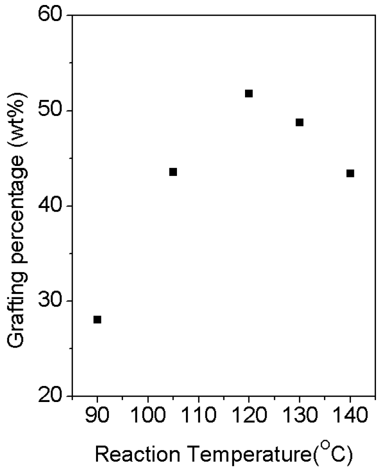

Fig. 6 Effect of reaction temperature on grafting percentage with a soaking time of 12 h. The other conditions are same as those in Fig. 1.

Fig. 2 shows the dependence of grafting percentage on pressure with the soaking time of 12 h. The other conditions are the same as those in Fig. 1. The mass uptake of iPP reaches maximum at 11 MPa. Higher CO_2 pressure induces a greater degree of swelling in the PP substrates, which is favorable for increased mass uptake. On the other hand, the stronger solvent power of CO_2 at higher pressures makes the absorption of AA and the initiator on the iPP matrix more difficult. The competition between these two opposite factors results in the observed maximum. In the following (Fig. 3–6), the results with a soaking pressure of 11 MPa are discussed.

Fig. 3 shows the effect of monomer (AA) concentration on the mass uptake with a soaking time of 12 h. The other conditions are the same as those in Fig. 1. It can be seen that the grafting percentage increases initially with the concentration of the monomer, and then reaches a constant value. Obviously, the greater the monomer concentration, the more monomers will be impregnated into the matrix. However, the amount of homopolymers increases with monomer concentration, and the homopolymers have been removed *via* the extraction process. It can be deduced that all the active sites on the iPP substrate can be grafted if the concentration of the monomer is high enough.

The effect of the concentration of BPO in the AA on the grafting percentage with a soaking time of 12 h is plotted in Fig. 4. The other conditions are the same as those in Fig. 1. It can be seen that as the concentration of BPO is increased, the grafting percentage initially increases and passes through a maximum. The initial increase in the degree of grafting is caused by the increased availability of free radicals for the chain transfer to the polymer backbone. But when the concentration of the initiator exceeds around 0.4 mol%, the average molecular weight of the side chains is reduced and the degree of homopolymerization is increased. Both of these result in reduction of the grafting percentage. Hence, the appearance of the maximum shown in Fig. 4.

Fig. 5 shows the effect of reaction time on the grafting percentage with a soaking time of 12 h. The other conditions are the same as those in Fig. 1. Clearly, the degree of grafting increases initially with reaction time and reaches a plateau after 5 h. This is easy to interpret because all the BPO initiator will be consumed and/or all the monomer will be polymerized after a certain reaction time.

The effect of reaction temperature on the grafting percentage with a soaking time of 12 h is shown in Fig. 6. The other conditions are the same as those in Fig. 1. At lower temperatures the initiator cannot decompose completely, and mass uptake increases with increasing temperature. At 120 °C the

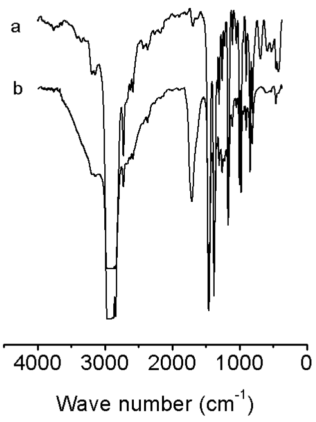

Fig. 7 FTIR spectra of pure iPP (a) and iPP-g-PAA (27 wt%) (b).

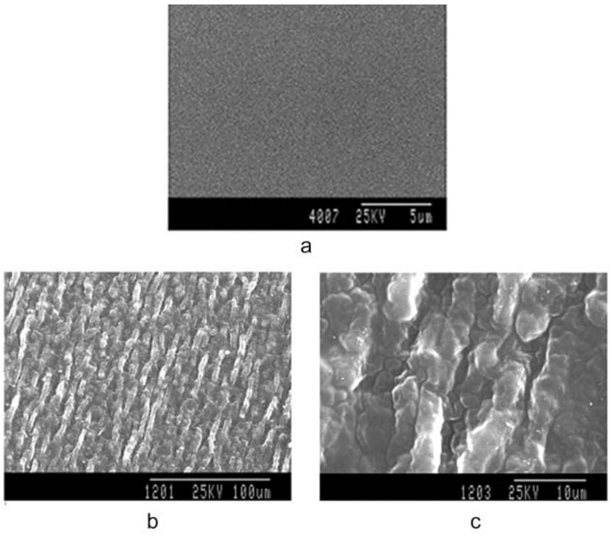

Fig. 8 Scanning electron micrographs of virgin iPP film (a), iPP-g-PAA (27 wt%) film (low magnification) (b), and iPP-g-PAA (27 wt%) film (high magnification) (c).

decomposition rate is compatible with the polymerization rate, so AA can be grafted onto iPP efficiently. However, the decomposition rate of the initiator will exceed the polymerization rate when the temperature is too high, which decreases the efficiency of the polymerization, so the mass uptake is reduced.

3.2 Characterization

3.2.1 Infrared spectroscopy. The presence of AA grafted onto the iPP film was confirmed by FTIR analysis. The IR spectra of virgin iPP and the grafted polymer iPP-g-PAA (27 wt%) are shown in Fig. 7. The presence of a band at 1730 cm^{-1} in the spectrum of the grafted polymer (characterizing the carbonyl group of AA), which is absent from the spectrum of the original substrate, indicates that AA has been grafted onto iPP.

3.2.2 Scanning electron microscopy. The surfaces of the original iPP and the grafted iPP films were examined by SEM and the results are shown in Fig. 8. The morphology of grafted iPP is significantly different from that of virgin iPP substrate. The grafted surface shows a markedly bumpy texture, while the pure iPP surface is very flat. The bumpy surface of the grafted layers can be explained by the difference in the swelling ability of SC CO_2 for amorphous and crystalline sites on the iPP substrate, resulting in different degrees of grafting in the amorphous and crystalline regions of iPP. Fig. 8 also indicates that the grafted molecules are uniformly distributed in the iPP matrix.

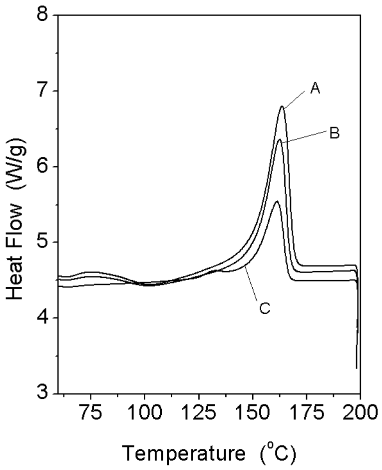

Fig. 9 DSC thermographs (heating) for pure iPP (a), SC CO_2-treated iPP (b), and iPP-g-PAA (27 wt%) samples (c).

3.2.3 Differential scanning calorimetry. DSC measurements were carried out for virgin iPP, iPP processed with SC CO_2 at 308.15 K and 11 MPa for 12 h, and iPP-g-PAA samples with grafting percentages of 27 and 68 wt%. The melting and crystallization behaviors of the samples are shown in Fig. 9 and 10.

The T_m, T_c, ΔH_m, ΔH_m, C_a, and C_{iPP} values obtained from DSC curves in Fig. 9 and 10 are listed in Table 1. It can be seen from these data that the properties of the SC CO_2-treated and untreated iPP film are nearly the same. However, the grafting results in considerable changes in these properties. Grafting of AA onto iPP film reduces the heat of fusion, and the larger the grafting percentage is, the larger the effect is. The heat of fusion is proportional to the amount of crystalline iPP in the sample. Thus, the apparent crystallinity (C_a) decreases with increasing grafting percentage. However, the crystallinity of the iPP portion of the film (C_{iPP}) almost remains unchanged, mainly because the AA monomer is mostly grafted onto the amorphous part of the iPP substrate. This suggests that the grafting process does not affect the properties of the crystalline portion.

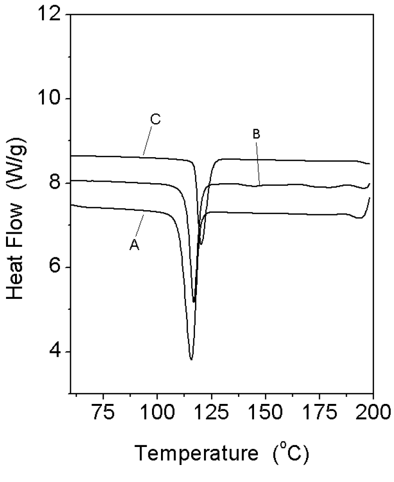

Fig. 10 DSC thermographs (cooling) for pure iPP (a), SC CO_2-treated iPP (b), and iPP-g-PAA (27 wt%) samples (c).

Table 1 Thermal parameters of iPP and iPP-g-PAA obtained by DSC

Samples	T_m/°C	T_c/°C	ΔH_m/J g^{-1}	ΔH_c/J g^{-1}	C_a (%)	C_{iPP} (%)
iPP	163.5	115.7	77.02	91.06	36.9	36.9
iPP (CO_2 processed)	163.0	115.8	75.31	90.89	36.0	36.0
iPP-g-PAA (27 wt%)	160.7	121.8	60.52	58.78	28.9	36.7
iPP-g-PAA (68 wt%)	164.9	132.0	46.38	48.05	22.2	37.3

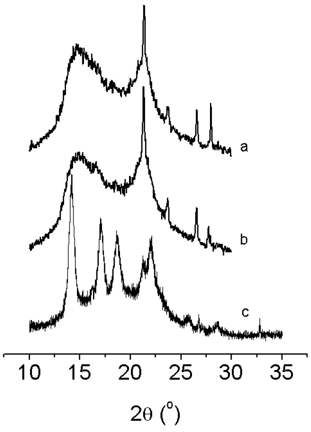

Fig. 11 WAX diffractograms for pure iPP (a), SC CO_2-treated iPP (b), and iPP-g-PAA (27 wt%) samples (c).

The data in Table 1 also indicate that the T_m of the original iPP, the CO_2-treated iPP, and the grafted iPP are nearly the same. This is understandable considering the fact that the grafting process does not change the crystalline portion of iPP considerably, as discussed above. However, the T_c of the iPP-g-PAA increases with the grafting level. The observed increase in crystallization temperature can be attributed to the AA acting as a nucleating agent.

3.2.4 Wide angle X-ray diffraction. In order to investigate the crystallization behavior of the grafted iPP obtained, a WAXD study was performed. Typical WAX diffractograms of pure iPP and iPP-g-AA films are shown in Fig. 11. The samples of iPP and the CO_2-treated iPP show diffraction peaks whose angles are characteristic for the crystal structure of the β form of polypropylene, while the iPP-g-PAA shows peaks due to the α form. This means that the grafting can induce changes in crystalline form.

4 Conclusion

iPP-g-PAA graft copolymer can be prepared by free radical polymerization within a swollen iPP matrix, using SC CO_2 both as a solvent for AA and BPO and a swelling agent for the iPP matrix. The grafting polymerization mainly occurs at the amorphous parts of the iPP substrate, and the grafting procedure does not destroy the crystalline phases of iPP. The melting temperature of the grafted copolymer changes little from that of pure iPP. However, the crystallization temperature increases with increasing grafting percentage. The grafting results in changes in the crystallization form from the β to the α form, although the change in crystallinity of the iPP portion of the grafted film is very limited.

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