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Preparation of nanometer dispersed polypropylene/polystyrene interpenetrating network using supercritical CO_2 as a swelling agent

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Abstract

Nanometer dispersed polypropylene/polystyrene (PP/PS) interpenetrating networks (IPNs) have been prepared by the radical polymerization and crosslinking of styrene (St) within supercritical (SC) CO_2–swollen PP substrates. In this method, monomer St, crosslinking agent divinyl benzene (DVB), and the initiator benzoyl peroxide were first impregnated into PP matrix using SC CO_2 as a solvent and swelling agent at 35.0 °C, and then the polymerization and crosslinking were carried out at 120 °C. The composition of the IPNs can be controlled by SC CO_2 pressure, concentrations of St and DVB in the fluid phase. Transmission electron microscopy shows that the PS is homogeneously dispersed in the IPNs and its phase size is in the range of 20–30 nm. The impact strength, tensile strength, and elongation-at-break of the PP/PS IPNs increase with increasing PS percentage in the IPNs. © 2002 Published by Elsevier Science Ltd.

Keywords: Polypropylene/polystyrene interpenetrating network; Supercritical CO_2; Swelling agent

1. Introduction

In recent years, there has been a great deal of interest in using supercritical carbon dioxide (SC CO_2) as a solvent and/or a swelling agent for polymer processing [1–17]. SC CO_2 is a good solvent for many small molecules [4], and is also a good swelling agent for most polymers. However, it is a very poor solvent for most polymers even at extremely high pressure [5,6]. The density of supercritical fluids (SCFs) and thus their solvent strength is continuously tunable from gas-like to liquid-like by changing pressure and temperature. This provides them the ability to control the degree of swelling of polymers as well as the partitioning of small molecule penetrates between a swollen polymer phase and the fluid phase [7,8]. The low viscosity and near zero surface tension of SCFs allow for fast mass transfer of penetrates into a swollen polymer. SC CO_2 has been used to impregnate polymers with different additives [5]. Since CO_2 is a gas at ambient conditions, the removal and recovery of the solvent from final product are extremely facile.

Using SC CO_2 as a swelling agent, McCarthy and co-workers [9–14] reported a new method to produce polymer composites, which involves the SCF-assisted infusion of monomer and initiator into and subsequent polymerization within polymer substrates. We also prepared some polymer blends using this method [15–17].

Phase dispersion crosslinking synergism, or synthesis of interpenetrating polymer networks (IPNs) is an effective method to improve the properties of polymer materials. Preparation of different IPNs have been reported by conventional methods [18–24]. In this work, we synthesized polypropylene/polystyrene (PP/PS) IPNs using SC CO_2 as a solvent and swelling agent. Preparation of IPNs using SC CO_2 was not found in a literature survey. The method was similar to that of preparing polymer blends using SC CO_2 [9–14]. It involves impregnation of the solid PP substrate by the monomer styrene (St), initiator benzoyl peroxide (BPO), and crosslinking agent divinyl benzene (DVB) using SC CO_2. The system was vented to remove the SC solution and then heated to initiate polymerization and crosslinking. This work aims at: (1) preparing PP/PS IPNs with nanometer dispersion; (2) characterizing the thermal and mechanical properties of the IPNs; and (3) studying the features of the IPNs prepared by this method.

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2. Experimental section

2.1. Materials

PP substrate was supplied by Beijing Plastics Factory with a thickness of 0.4 mm, and its crystallinity was 39.8%. Monomer St and crosslinking agent DVB were washed successively with 5% aqueous NaOH and deionized water, dried over anhydrous Na_2SO_4, and then distilled under reduced pressure. BPO was purchased from Beijing Jinlong Chemical Reagent Company and was used after recrystallization in chloroform. CO_2 with purity of 99.95% was provided by Beijing Analytical Instrument Factory and used as received.

2.2. IPNs synthesis

In each experiment, 2.5 g PP sample, suitable amounts of monomer, initiator BPO, and crosslinker DVB were loaded into an optical cell of 30 ml. The cell was purged with CO_2 to remove the air, and then was placed in a water bath at 35.0 °C. After thermal equilibrium had been reached, CO_2 was charged into the cell by a syringe pump (Model SB-2, Beijing Xiantong Scientific Instrument Co.) until desired pressure was reached. After a suitable soaking time, CO_2 was released from the cell. The impregnated films were placed in another stainless steel cell of 30 ml, and the temperature was raised to 120 °C to initiate the polymerization and crosslinking under the protection of nitrogen.

2.3. Characterization

The composition of PP/PS IPNs was determined gravimetrically and was calculated from the masses of initial PP and PP/PS IPNs after removal of all homopolymers by Soxhlet extraction in boiling xylene for 24 h. The experiments showed that the extractable homopolymers were not considerable (less than 10% of the total PS in the IPNs). In other words, most PS were crosslinked in the IPNs. The other properties were determined using the untreated samples.

The DSC data were obtained with a Perkin–Elmer DSC-7. The weight of the sample for each experiment was about 6 mg. Samples were scanned from 60 to 190 °C with a heating rate of 10 °C/min under an atmosphere of dry nitrogen. The observed T_m and the apparent enthalpies of melting (ΔH^*) were obtained from the maxima and the area of the melting peak, respectively.

The phase morphological characteristics of the samples were studied by means of transmission electron microscopy (TEM) (HITACHI, H-800). Prior to the examination, cryo-ultrathin sections were cut using an ultramicrotome and they were chemically stained in OsO_4 vapor for 24 h.

A dynamic mechanical analyzer, Perkin–Elmer DMA-7, was employed to measure the dynamic mechanical properties of PP/PS IPNs. The specimens were 3 mm wide by 10 mm long. The mode of force loading was three-point bending. The testing frequency, heating rate, and temperature scanning range were 1 Hz, 10 °C/min, and −100 to 100 °C, respectively.

The tensile properties of the PP/PS IPNs were investigated on a universal tensile tester (Instron 1122) using a load of 20 kg. The fracture elongation and tensile strength were measured at a crosshead speed of 50 mm/min. The average of five tests was reported. The notched Izod impact strength was measured with an impact-testing machine (CSI-137C).

3. Results and discussions

3.1. Effects of the soaking conditions on the mass uptake

All the soaking experiments were conducted at 35.0 °C, and the concentration of BPO in St/BPO/DVB mixtures was 3 wt%. To optimize the operation conditions, the effects of various parameters such as the soaking time, the pressure of SC CO_2, the concentrations of St and DVB were studied. During the soaking process, there was a PP solid phase and a fluid phase in the system, i.e. the fluid mixture was homogeneous (one phase) for all the experiments, which could be seen from the windows of the optical cell.

The effect of soaking time on mass uptake is shown in Fig. 1. The PP samples were soaked in St/BPO/DVB/CO_2 solution at 110 bar, and 4.5 g St/BPO/DVB mixture was charged into the high-pressure vessel. The concentration of DVB in the St/BPO/DVB mixture was 6.3 wt%. In this work, the mass uptake is defined as following:

$$\text{Mass uptake} = 100(W - W_0)/W_0 \qquad (1)$$

where W and W_0 stand for the masses of the IPNs and the substrate, respectively. The figure indicates that the mass uptake increases initially with soaking time, and is independent of soaking time after about 13 h, i.e. equilibrium can be reached in about 13 h. A soaking time of 14 h is used in the following studies.

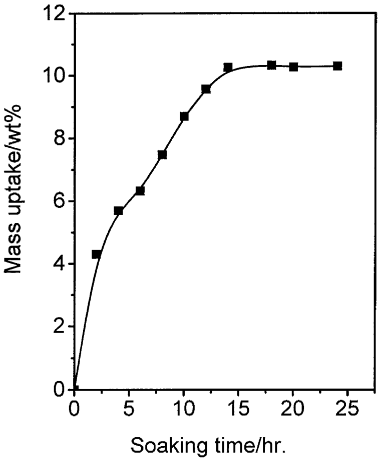

Fig. 1. Mass uptake as a function of soaking time at 35.0 °C and 110 bar.

To study the effect of soaking pressure on the mass uptake, the pressure was varied from 100 to 200 bar. The high-pressure vessel contains 2.5 g St/BPO/DVB mixture, and the concentration of DVB in the St/BPO/DVB mixture was 6.3 wt%. Fig. 2 shows the plot of PP/PS IPNs mass uptake vs. soaking pressure. A maximum is observed at about 140 bar. This phenomenon may be explained qualitatively.

The monomers in the system are distributed between PP phase and CO_2-rich phase. The degree of the polymer swelling increases with increasing pressure of CO_2, which is favorable to increasing the mass uptake. On the other hand, CO_2 is a better solvent for the monomer at high pressures, which is not favorable to increasing the mass uptake because more monomers are dissolved in CO_2. The first factor is dominant at low pressures, and the second one becomes dominant at high pressures. The competition of these two opposite factors results in the maximum. The solvent power of CO_2 increases monotonously with its pressure. Therefore, the mass uptake decreases with increasing pressure after the maximum. There were also maxima on the mass uptake vs. pressure curves as PS/PVC and PS/PET blends were prepared using SC CO_2 as solvent and swelling agent [15,16].

The effect of monomer concentration on the mass uptake is also studied. The soaking process was conducted at 110 bar with various monomer concentrations. The original concentration of DVB in the St/BPO/DVB mixture was 6.3 wt%. As expected, the mass uptake increases with increasing concentration of the monomer, and to be, respectively, 2.8, 4.8, 6.7, 8.4, 10.4, and 12.6 wt% as the cell contains 1.3, 2.0, 2.5, 3.5, 4.5, and 6.0 g St/BPO/DVB mixture.

The concentration of DVB in St/BPO/DVB mixture (C_{DVB}) also influences the mass uptake. Fig. 3 shows the effect of DVB concentration in the St/BPO/DVB mixture on the mass uptake. The cell contained 2.5 g St/BPO/DVB mixture and the soaking experiments was carried out at 110 bar. The mass uptake increases with the increasing of the concentration of DVB, as can be seen from Fig. 3. The possible reason is that DVB is less volatile than St. Thus, PP matrix can absorb DVB more easily.

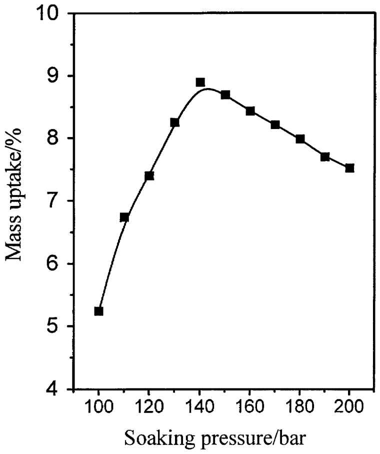

Fig. 2. Mass uptake as a function of soaking pressure at 35.0 °C.

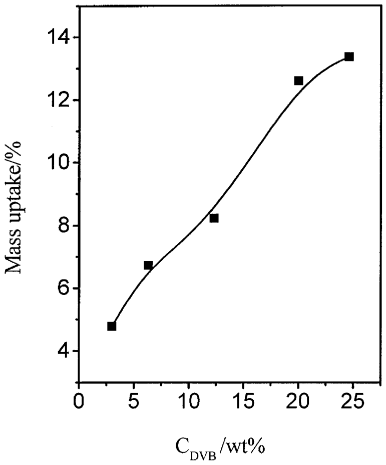

Fig. 3. Mass uptake as a function of DVB concentration in St/BPO/DVB mixture at 35.0 °C and 110 bar.

3.2. Characterizations

The morphology of the PP/PS IPNs was investigated by TEM of cryomicrotomed cross-sections. Fig. 4 displays TEM micrographs of the two samples with 6.3 wt% mass uptake (a) and 12.6 wt% mass uptake (b) at magnification of 150,000 times, respectively. These samples were prepared at the soaking conditions of 110 bar, and with 2.5 g St/BPO/DVB mixture containing 3 wt% BPO. The concentration of DVB in the St/BPO/DVB mixture was 6 wt% for preparing sample (a) and was 20 wt% for preparing sample (b). In Fig. 4, the dark portions in the micrographs are PS, and the light portions are PP. Clearly, the TEM micrographs shows the IPNs prepared by the method of this work have the following features. First, the phase boundary is relatively ambiguous. Second, the domain diameter of the dispersed

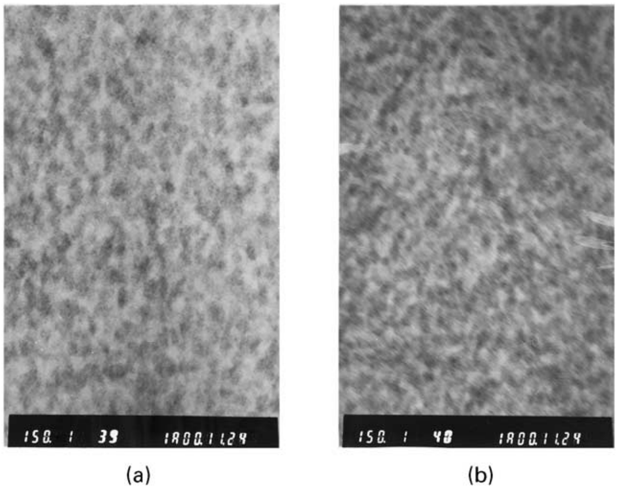

Fig. 4. TEM micrographs of PP/PS IPNs (a) 6.3 wt% mass uptake, (b) 12.6 wt% mass uptake.

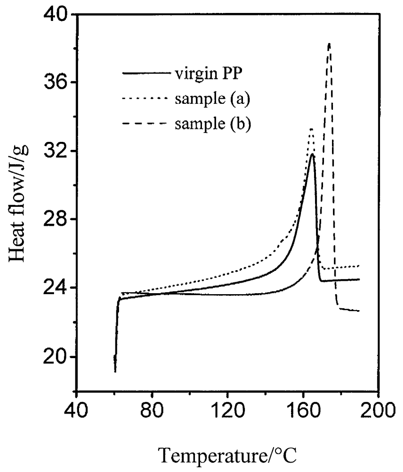

Fig. 5. DSC thermographs of virgin, PP/PS IPNs with 6.3 wt% mass uptake, and 12.6 wt% mass uptake.

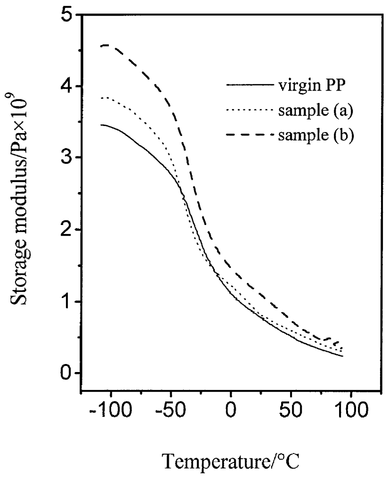

Fig. 6. Storage modulus (G') variation of virgin PP and PP/PS IPNs with 6.3 wt% PS and 12.6 wt% mass uptakes.

PS phase is in the range of 20–30 nm, which is very small. Third, the PS phase is uniformly dispersed. This can be attributed to the special properties of SCFs and can be explained as follows.

It is known that SCFs have high diffusivity and low viscosity on comparing with liquids, and near zero surface tension. Thus, the monomer and the initiator molecules can diffuse into any interchain space in the PP matrix with a faster rate provided the size of the space is larger than that of the molecules. Therefore, the monomers and the initiator are more uniformly distributed in the PP matrix before polymerization. Some of the St and DVB monomers are polymerized around PP molecules, and thus some polymer molecules in the IPNs may entangle with each other. Some of the PP and PS is crosslinked by DVB. SC CO_2 is a swelling agent for PP; however, it only swells the amorphous regions of the PP matrix. Because of the existence of crystalline domains in PP matrix, SC CO_2 cannot create large interchain space within the PP substrate, and it can only swell the polymer to some extent. Thus, the size of the PS phase polymerized within PP matrix is much smaller.

Thermal properties of the samples were measured by DSC. Fig. 5 shows the DSC thermograms of virgin PP, sample (a), and (b). The melting temperature T_m of the sample (a) is almost identical to that of the substrate, but that of sample (b) is 10 °C higher. One of the reasons may be that the crosslinking density in sample (b) is larger because the concentration of DVB is higher in the soaking process, and thus more DVB is absorbed in the process. The heat of fusion of virginal PP, sample (a), and sample (b) obtained from the integral areas are 83.1, 84.9, and 85.1 J/g, respectively. The heat of fusion for PP of 100% crystalline is known to be 209 J/g [25]. From the DSC results above, the unmodified PP substrates are 39.8% crystalline and the sample (a) and sample (b) are 40.6 and 40.7% crystalline, respectively. Considering the fact that PS should be amorphous, the crystallinity of PP portion of sample (a) and sample (b) should be, respectively, 43.3 and 46.6%. The reason for the slight increase in crystallinity may be that the added components act as nucleation agents for PP. In other words, the added components may induce crystallization of PP matrix more or less.

The glass transition temperature (T_g) of the PS in the PP/PS IPNs is not reflected in Fig. 5. The reason may be that the PS is well dispersed in the IPNs and crosslinked. It does not have the T_g of the homopolymer PS.

The variation of the storage modulus (G') with temperature is shown in Fig. 6. The temperatures at which the values of G' reaches 3.25×10^9 are, respectively, -81.2, -60.1, and -42.1 °C for virgin PP, sample (a), and sample (b). The increase in the temperature shows that the presence of PP and PS networks increases the rigidity of PP. The temperature of sample (b) is higher because its crosslinking density is higher, as discussed above.

Mechanical properties were obtained from stress–strain curves of virgin PP and PP/PS IPNs with different PS contents, as shown in Figs. 7–9. The soaking process was

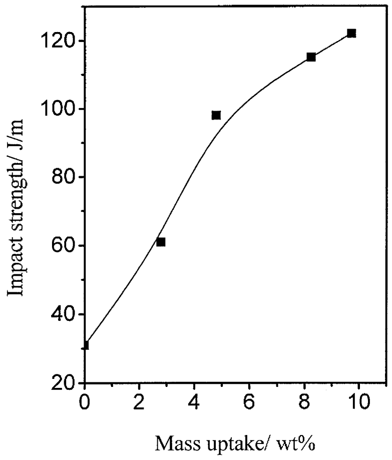

Fig. 7. Effect of mass uptake on notched Izod impact strength of PP/PS IPNs.

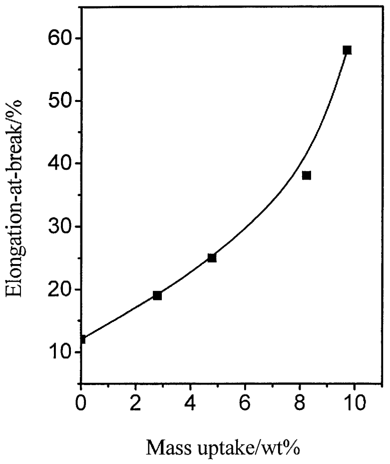

Fig. 8. Effect of PS content on elongation-at-break of the IPNs.

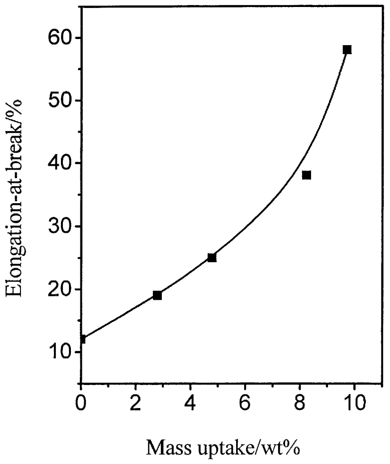

Fig. 9. Effect of PS content on tensile strength of the IPNs.

conducted at 110 bar with various monomer concentrations. The original concentrations of DVB in the St/BPO/DVB mixture was 6.3 wt%. The results indicate that the impact strength, elongation-at-break, and tensile strength of IPNs prepared in our work increase significantly with increasing mass uptake. It is known that strong interfacial adhesion in multiphase structural blends gives rise to an increase of impact strength [26]. Therefore, the significant increase in the impact strength and the elongation-at-break is attributed to the crosslinking between PP and PS and the increased interfacial adhesion.

4. Conclusions

PP/PS IPNs can be prepared using SC CO_2 as a solvent and swelling agent to impregnate monomer St, crosslinker DVB, and initiator BPO into PP matrix, followed by the radical polymerization and crosslinking of St within the matrix. The composition of the IPNs can be controlled by SC CO_2 pressure, concentrations of St and DVB in the fluid phase. The PS is uniformly dispersed in the IPNs and its phase size is in the range of 20–30 nm. The impact strength, tensile strength, and elongation-at-break of the PP/PS IPNs increase with increasing PS content.

Acknowledgments

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