

Impregnation of Polyethylene (PE) with Styrene Using Supercritical CO₂ as the Swelling Agent and Preparation of PE/Polystyrene Composites

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Impregnation of low-density polyethylene (LDPE) with styrene using supercritical (SC) CO₂ as the swelling agent was studied at 35 °C in a pressure range from 90 to 160 bar. The concentration of styrene in the fluid phase ranged from 0 to 1.668 mol/L. The soaking time varied from 4 to 36 h. In the presence of azobis(isobutyronitrile), the initiator, styrene polymerized to some extent in the soaking process, which results in an increase in the mass uptake. LDPE/polystyrene (PS) composites were prepared by the polymerization of styrene further in SC CO₂-swollen LDPE substrates at higher temperature. Using this method, the composition of the composites can be controlled by the soaking time, pressure, and styrene concentration in the fluid phase. Some of the PS molecules in LDPE/PS blends entangle with the polyethylene molecules, which causes significant improvement in the impact strength, the tensile strength, and the elongation at the break.

Introduction

Polymer blends play an important role in the modern polymer industry not only for the development of new materials but also for practical recycling.¹ Most of the polymer blends are incompatible, and the final performance of a polymer blend is determined by the polymer compatibility and the phase morphology. Both polyethylene (PE) and polystyrene (PS) are among the most commonly used polymers. However, when the two polymers are blended together by conventional methods, the resulting materials have poor mechanical properties. Therefore, it is highly desirable to develop new cost-effective ways of generating PE/PS blends with improved mechanical properties. One of the most commonly used methods to obtain these blends is the incorporation of a copolymer such as a block copolymer of PS and PE (PS-*b*-PE) as a compatibilizer.^{2–4}

Supercritical fluids (SCFs), as alternative solvents, are unique solvents for polymer processing. Among all of them, supercritical CO₂ (SC CO₂) is the most widely used because it is nonflammable, nontoxic, and relatively inexpensive. Moreover, the moderate critical conditions for CO₂ ($T_c = 31.1$ °C and $P_c = 72.8$ atm) make it a convenient fluid for experimentation.⁵ Except for some fluoropolymers and silicones, SC CO₂ is a very weak solvent for polymers.⁶ However, it is a good swelling agent for most polymers and will dissolve many small molecules.^{7–11} The solvent strength of a SCF can be tuned continuously from gaslike to liquidlike by manipulation of the temperature and pressure. This provides the ability to control the degree of swelling in a polymer^{7–13} as well as the partitioning of small molecule penetrants between a swollen polymer phase and the fluid phase.^{14–16} The low viscosity and zero surface tension of a SC CO₂ allow for fast mass transfer of penetrants into a swollen polymer. In addition, CO₂

is a gas at ambient pressure, so the removal of the solvent from the final product is facile.

Recently, McCarthy and co-workers have reported a method for producing polymer composite materials using SC CO₂ as the swelling agent.^{17–20} The method involved the soaking of the matrix polymer in a SC solution of monomer and thermal initiator at a temperature where the half-life of the initiator is hundreds of hours. The reaction is then initiated at a temperature at which the half-life of the initiator is much shorter. They have prepared a series of polymer blends using this method, including PE/PS.¹⁹ In comparison with the traditional blending method of mechanical mixing, this approach is more versatile and general, and the most intriguing feature is that the blend can be carried out at temperatures well below the melting temperatures of the polymers.

In this work, we investigated the effect of pressure, soaking time, concentration of styrene, and initiator on the mass uptake of PS on LDPE. Then we prepared LDPE/PS composites using the impregnated LDPE films.

Experimental Section

Materials. LDPE films supplied by Beijing Plastics Factory were 0.4 mm in thickness. CO₂ with a purity of 99.9% was obtained from Beijing Huanxin Gas Co. and used as received. Styrene (A.R. grade) supplied by Beijing Chemical Factory was vacuum distilled from calcium hydride. Azobis(isobutyronitrile) (AIBN) supplied by Beijing Chemical Factory was recrystallized from acetone twice in our laboratory.

Apparatus. The experimental apparatus consisted mainly of a gas cylinder, a syringe pump, a digital pressure gauge, a sample bomb, a solenoid-operated pump, an optical cell, a constant-temperature bath, and valves and fittings of different kinds. All of the metallic parts in contact with the studied chemicals were made of stainless steel. The apparatus was tested up to 30 MPa. The total volume of the system including the vapor

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sample bomb was 90 mL. The principle of the apparatus is similar to that of the circulation apparatus reported previously.^{21,22}

The syringe pump was model SCF-8000 (Beijing Xiantong Scientific Instruments Co.), which was used to charge the CO₂ into the system. The accuracy of the pressure gauge, which consisted of a transducer (IC sensors Co., model 93) and an indicator, was ± 0.05 MPa in the pressure range of 0–30 MPa. The solenoid circulation pump was used to circulate the fluid phase. The temperature of the air bath was controlled by main and secondary controllers. The fluctuation of the temperature in the bath was less than ± 0.1 K, and the accuracy of the temperature measurement was within ± 0.1 K by a platinum resistance thermometer (Beijing Chaoyang Automatic Instrument Factory, model XMT). A Mettler PM 1200 balance with a sensitivity of 0.001 g was used for weighing the samples.

Procedures. The system was cleaned thoroughly using suitable solvents and dried under vacuum. Suitable amounts of LDPE films were placed in the high-pressure optical cell. The system was purged with CO₂, and the desired amount of styrene or styrene + AIBN (0.3 mol %) solution was added to the system. After the system had reached thermal equilibrium, CO₂ was charged until the desired pressure was reached. The circulation pump was started to circulate the fluid phase. The LDPE films were swollen, and some of the styrene or styrene + AIBN solution infused into the films. After a desired soaking period, the fluid in the system was released and the films were taken out for determination of the mass uptake of styrene in PE and for blend synthesis.

Blend Synthesis. The LDPE films impregnated with styrene and initiator obtained by the above procedures were placed in a stainless steel vessel of 20 mL. The vessel was evacuated to remove the air, charged with N₂, and heated at 80 °C for 4 h. Then the vessel was cooled and opened, and the specimens were taken out for characterization by different techniques.

Blend Characterization. The fracture topographs of the fractured surfaces at the liquid-nitrogen temperature of LDPE/PS blends were observed with a Hitachi S-530 scanning electron microscope (SEM) in the normal secondary electron imaging (SEI) mode. The surface was coated with gold to avoid charging under an electron beam.

Samples of $55 \times 10 \times 0.4$ mm³ were used to measure the mechanical properties. Mechanical tests were performed at room temperature and at a crosshead speed of 5 mm/min using a universal tensile tester (Instron 1122). Young's modulus, tensile strength, and elongation at the break were determined from the load-extension curves. All values are averaged from five measurements. The notched Izod impact strength was measured with an impact-testing machine (CSI-137C).

Results and Discussion

1. Impregnation of PE. In this work, all of the experiments were conducted under the conditions at which CO₂, styrene, and AIBN exist as a single phase,²³ which could also be seen clearly from the optical cell during the experiments. The effects of the pressure, soaking time, and concentration of styrene on the mass uptakes were studied.

Effect of Soaking Time. The soaking time was varied from 4 to 36 h at 120 bar and 35 °C. The original

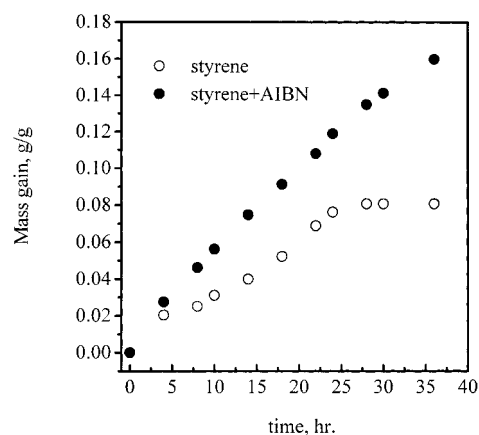


Figure 1. Mass gain of LDPE films as a function of soaking time with and without AIBN at 35 °C, 120 bar, and a styrene concentration of 0.632 mol/L.

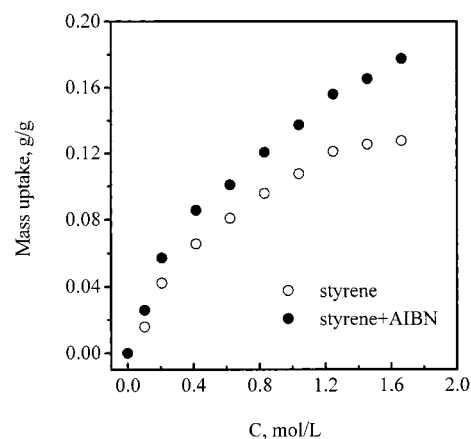


Figure 2. Plots of mass uptake vs styrene concentration with and without AIBN at 35 °C, 120 bar, and a soaking time of 24 h.

concentration of styrene in a CO₂/styrene solution (C) is 0.632 mol/L. The mass uptakes of styrene without and with 0.3 mol % AIBN are shown in Figure 1.

From Figure 1, we can see that, in the absence of AIBN, the mass uptake of styrene reaches equilibrium after a soaking period of 24 h. When the styrene contains 0.3 mol % AIBN, however, equilibrium cannot be reached even if the soaking time is as long as 36 h. This indicates that styrene polymerizes in the LDPE matrix during the soaking process. Because styrene in the swollen LDPE films is consumed by polymerization, styrene in the fluid phase repartitions between the solid and fluid phases. The polymerization thus induces a continuous absorption of styrene, resulting in the high PS content.

Effect of Styrene Concentration. A series of experiments were run at 35 °C and 120 bar with different styrene concentrations. The soaking time was 24 h. Figure 2 gives the dependence of the mass uptake of styrene with and without 0.3 mol % AIBN (based on the monomer) on the concentration of styrene in the fluid phase. The mass uptake increases with the styrene concentration in the range studied.

Effect of Pressure. A series of experiments were performed to determine the effect of pressure on the mass uptake of styrene at 35 °C in the pressure range from 90 to 160 bar, and the original concentration of styrene was 0.632 mol/L. The soaking time was 24 h. Figure 3 shows the dependence of the mass uptake on the pressure without and with 0.3 mol % AIBN (on the

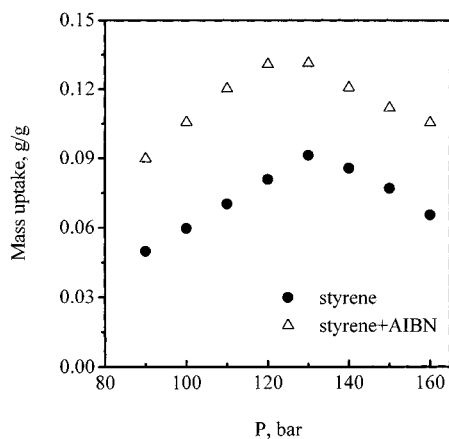


Figure 3. Effect of pressure on the mass uptake of PS at 35 °C, a styrene concentration of 0.623 mol/L, and a soaking time of 24 h.

styrene basis). The mass uptake increases with increasing pressure when the pressure is lower than 130 bar for both cases. This can be explained qualitatively in the following.

The solvent power of SC CO₂ increases with pressure,¹⁴ which is not favorable to increasing the mass uptake. LDPE swells to a large extent at the higher pressures, which is favorable to the increase of the mass uptake. The effect of the pressure depends on which factor is dominant. The first factor is dominant at the lower pressures, and the second one becomes dominant at the higher pressures.

2. Blend Synthesis and Characterization. Blend

Synthesis. Kung et al. prepared a PS/high-density PE blend using CO₂ as the swelling agent.¹⁹ In their experiments, the PE samples were first soaked in styrene/CO₂/*tert*-butyl perbenzoate solutions for 5 h at 80 °C and 240 atm, and the reaction vessel was placed in a 100 °C constant-temperature bath for various durations, vented, then refilled with nitrogen, and maintained at 100 °C for 6 h.

As discussed above, we obtained the LDPE films impregnated with styrene and AIBN at 35 °C, and the styrene polymerized to some extent when AIBN exists in the system. However, the polymerization is not sufficient because the half-life of the initiator AIBN is hundreds of hours¹⁷ at the soaking temperature of 35 °C. To get the LDPE/PS composites, the impregnated PE films were sealed into a stainless steel reactor and the air in the reactor was replaced by N₂. Then the reactor was maintained at 80 °C for 4 h to allow the polymerization to take place further. The mass loss results from the vaporization of the styrene monomer or oligomer are negligible during this process.

Characterization. Figures 4–6 show the mechanical properties of PE/PS blends with the PS content varying from 0 to 18%.

The results in Figures 4–6 indicate that the mechanical properties of the blends are enhanced significantly, although there is no compatibilizer. In particular, the impact strength and the elongation at the break increase dramatically when the concentration of PS increases. We believe that the significant increase in the impact strength and the elongation at the break is attributed to the special structure of the blend. Distribution of the monomers in the matrix is relatively even before polymerization, and a large group of monomers joined together cross some LDPE molecules in the

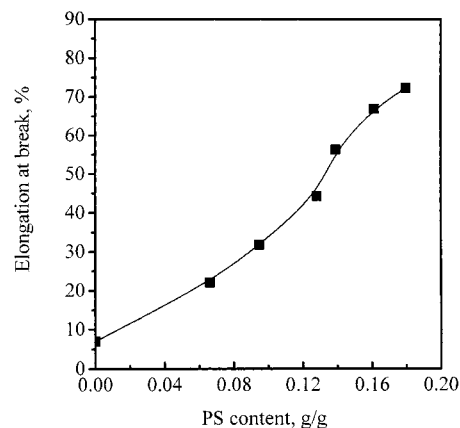


Figure 4. Tensile strength of the LDPE/PS blends as a function of PS concentration.

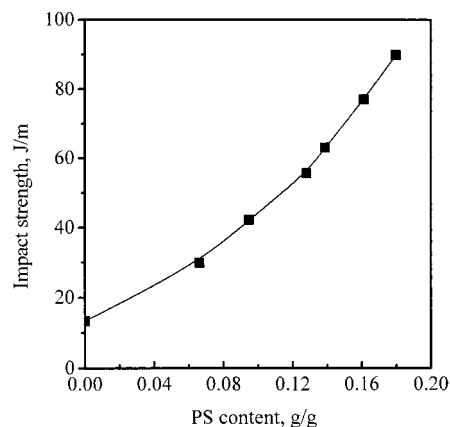


Figure 5. Elongation at the break of the LDPE/PS blends as a function of PS concentration.

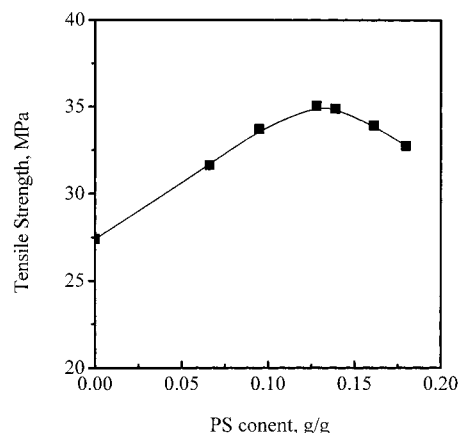
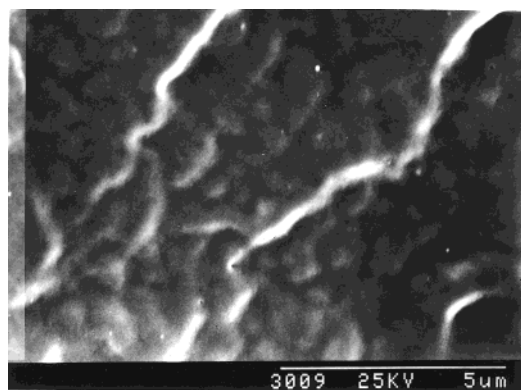


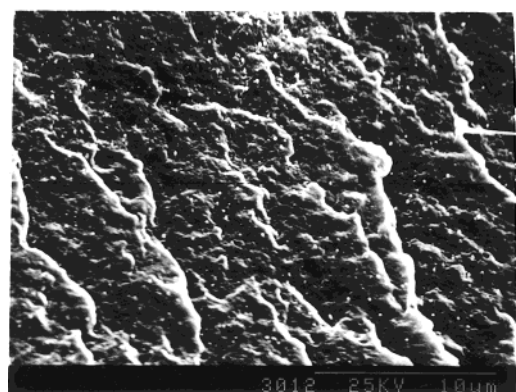
Figure 6. Impact strength of the LDPE/PS blends as a function of PS concentration.

polymerization process; i.e., some PS molecules entangle LDPE molecules. The tensile strength of the blend also increases as a function of the PS concentration up to 12 wt % and then decreases on further increases of the PS concentration. In this work, we obtained the blend exhibiting both reinforcing and toughening effects.

Figure 7 gives SEM photographs of the cryogenically fractured surfaces for PE and LDPE/PS (86/14) blends. It can be easily identified in the SEM micrograph that some PS exists as a discrete phase in the PE matrix. However, the amount of PS in the form of the discrete phase is much less than 14%. This supports the statement of the entanglement structure mentioned above.



(a)



(b)

Figure 7. SEM photographs of cryogenically fractured surfaces for a virgin LDPE film (a) and a LDPE/PS (86/14) composite film (b).

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