Phase Behavior of Supercritical CO_2/Styrene/Poly(vinyl chloride) System and Synthesis of Polystyrene/Poly(vinyl chloride) Composites

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ABSTRACT: The phase behavior of the supercritical (SC) CO_2/styrene/poly(vinyl chloride) (PVC) system was studied at 40 °C in the pressure range from 80 to 160 bar. The styrene concentration in the fluid phase ranged from 0 to 0.4 mol/L. The mass uptakes of styrene in PVC films before and after depressurization were obtained. A considerable amount of styrene in the films was carried out by CO_2 in the venting process. When styrene contains 0.3 mol % initiator 2,2′-azobis(isobutyronitrile) (AIBN), the mass uptake is much higher than that in the absence of the initiator. The mass uptakes can be controlled by soaking time, pressure, and styrene concentration. PVC/polystyrene (PS) composites were prepared by the polymerization of styrene in PVC substrates. Scanning electron microscopy indicates that the original PVC grains are broken into the primary particles in the course of SC CO_2 swelling at the low temperature of 40 °C, and the PVC primary particles force the PS particles to be well dispersed between them. The mechanical measurements show that the addition of PS not only can toughen brittle PVC but also can reinforce it in the PS content range from 0.074 to 0.24 g/g.

Introduction

Supercritical fluids (SCFs), as alternative solvents, have tremendous potential for the modification and processing of polymers,[1] as they offer many advantages over conventional organic solvents.[2,3] The solvent strength of SCFs can be tuned over a wide range by changing temperature and pressure. Thus, the degree of polymer swelling and the partitioning of penetrants can be adjusted.[4−6] The gaslike viscosity of SCFs results in higher flow rates. The near-zero surface tension makes supercritical fluids essentially infinitely wetting. The above factors, coupled with high diffusion rate, enhance the kinetic absorption of penetrants. Near its critical point (31.1 °C and 72.8 bar), CO_2 has a solubility in many polymers which is as high as that of typical organic liquid-swelling agents.[7] The use of gaseous and liquid CO_2 to lower the glass transition temperature of various polymers has been extensively studied.[8−12] It has also been demonstrated that SC CO_2 has a strong plasticizing effect.[2,3,13] Finally, SCFs, such as SC CO_2, have clear environmental advantages over typical organic solvents.

Polymers can be impregnated with monomers and initiators with the aid of SC CO_2, and composites can be prepared by the polymerization of the monomers in the polymer substrates.[14−18] To control the composition and properties of the composites, the related phase behavior is very important. So we determined the phase behavior of the supercritical CO_2/styrene (with and without initiator)/poly(vinyl chloride) system in order to provide scientific basis for controlling the content of PS in PVC. In this work, we also prepared PVC/PS composites using SC CO_2 as swelling agent. Styrene and AIBN were sorbed into PVC films swelled by CO_2, and subsequent polymerization of the styrene in the films after releasing CO_2 yields PVC/PS composites. We also investigate the tensile properties, impact strength, and two-phase morphology of binary PVC/PS blends. On the basis of the results, we show the binary blend is toughened although there is not any compatibilizer in the system.

Experimental Section

Materials. Substrate PVC films were supplied by Beijing Plastics Factory with a thickness of 0.3 mm. Styrene supplied by Beijing Chemical Factory was vacuum distilled from calcium hydride. 2,2′-Azobis(isobutyronitrile) (AIBN) supplied by Beijing Chemical Factory was recrystallized twice from acetone. Carbon dioxide with purity of 99.9% was supplied by Beijing Huanxin Gas Co. and used as received.

Phase Behavior Apparatus. The apparatus for the phase behavior measurements was described in detail previously[19] and is shown schematically in Figure 1. Briefly, the apparatus consisted mainly of a gas cylinder, a syringe pump, a digital pressure gauge, a vapor sample bomb, a solenoid-operated pump, an optical cell, a constant temperature air bath, and valves and fittings of various kinds. The syringe pump was model SCF-8000 (Beijing Xiantong Scientific Instrument Co.), which was used to charge CO_2 into the system. The accuracy of the pressure gauge, which is composed of a transducer (IC Sensors Co., model 93) and an indicator, was ±0.05 MPa in the pressure range 0−20 MPa. The solenoid-operated pump was used to circulate the fluid phase. The constant temperature air bath was controlled by a main and a secondary controller. The fluctuation of the temperature in the bath was less than ±0.1 K, and the accuracy of the temperature measurement was ±0.1 K by a platinum resistance thermometer (Beijing Chaoyang Automatic Instrument Factory, model XMT). A Mettler PM1200 balance with a sensitivity of 0.001 g was used for weighing the sample bomb. The masses of the films were determined by a DT-100 balance with a sensitivity of 0.0001 g.

Phase Behavior Procedures. Before doing the experiment, the system was washed thoroughly using different solvents and then dried under vacuum. PVC films were packed in the optical cell. A desired amount of styrene or styrene/initiator solution was added to the CO_2-purged sample bomb and then connected to the system, as shown in Figure 1. The valves of the sample bomb were closed, and the air in the system was removed by vacuum. The valve at the top of the sample bomb was opened. CO_2 was charged into the system

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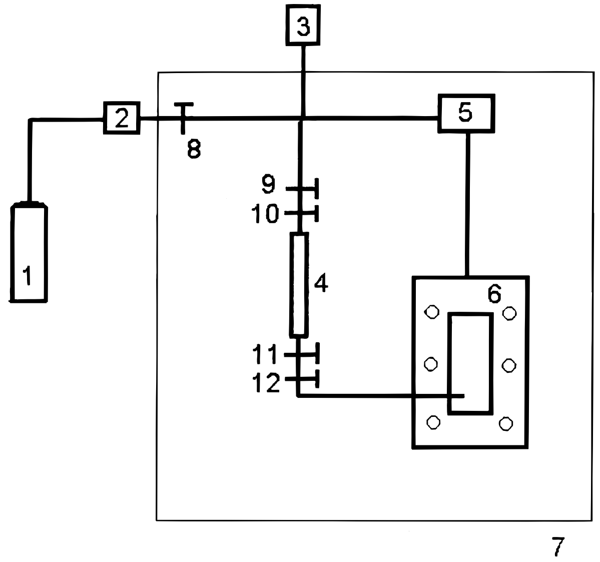


Figure 1. Schematic diagram of the experimental apparatus: (1) gas cylinder, (2) syringe pump, (3) digital pressure gauge, (4) vapor sample bomb, (5) circulation pump, (6) optical cell, (7) constant-temperature air bath, (8)–(12) shut-off valves.

at fixed temperature until the desired pressure was reached. The valve at the bottom of the sample bomb was also opened, and the fluid was circulated to pass through the solid phase and the vapor sample bomb. After a desired soaking time, the sample bomb was removed for composition analysis. The fluid in the optical cell was released. The time required to release the CO_2 was about 5 min, and the films were taken out for determining the mass uptake after venting and for blend synthesis. In the beginning, the mass of the films decreased with time since CO_2 in the films diffused out and then remained unchanged with time after about 24 h. The mass uptake of styrene in PVC after venting can be easily calculated on the basis of the masses of the films before and after soaking the styrene.

To determine the mass uptake before venting, the sample bomb was weighed and then refrigerated at −20 °C for several hours. Most of CO_2 in the bomb was liquefied after this procedure. The needle valve at the top of the sample bomb was opened slightly to release the CO_2 in the sample bomb slowly. After this process, the needle valve was closed. The quantity of the styrene in the sample bomb was determined by the gravimetric method. The mass uptake before venting was easily calculated from the following equation

$$\text{mass uptake before venting} = \frac{W_t - kW_s}{W_f} \qquad (1)$$

where W_t and W_s stand for total mass of styrene in the system and that in the sample bomb, k is the ratio of total volume to that of the sample bomb, and W_f denotes the mass of the PET films in the system. It is obvious that the mass uptake before venting is the mass (in grams) of styrene absorbed by 1 g of PVC film before releasing the CO_2 in the system. The accuracy of the data for mass uptake is better than 3%.

Blend Synthesis. PVC films impregnated with styrene and initiator obtained by above procedures were sealed in a stainless steel vessel of 20 mL. The vessel was vacuumed to remove the air and heated at 80 °C for 4 h under the protection of N_2. Then the vessel was cooled and opened and the specimen were taken out for characterization by different techniques.

Characterization. Infrared (IR) spectroscopy experiments were performed using a Perkin-Elmer 180 instrument under standard operating conditions.

The fracture topograph of the fractured specimen at the liquid nitrogen temperature was studied using SEM (s-530) in the normal secondary electron imaging (SEI) mode. The surfaces of the specimen were coated with gold to avoid charging under an electron beam.

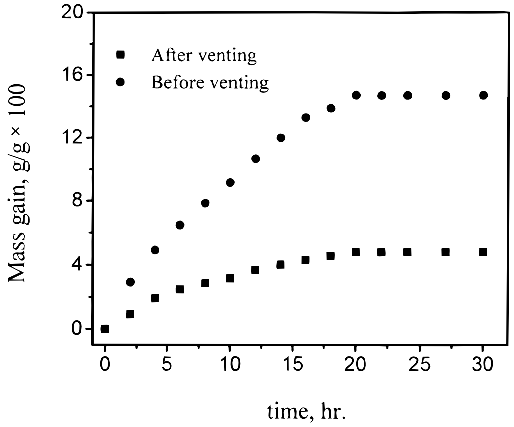


Figure 2. Mass uptake of PVC film as s function of soaking time at 40 °C, 100 bar, and styrene concentration of 0.237 mol/L without AIBN.

The tensile properties of the composites PVC/PS were carried on a universal tensile tester (Instron 1122). The load was 20 kg. The Young's modulus and the yield strength were measured at a crosshead speed of 5 mm/min; the fracture elongation and tensile strength were measured at a crosshead speed of 50 mm/min. The average of at least five tests was reported.

The notched Izod impact strength was measured with an impact-testing machine (CSI-137C) according to National Standard Testing Methods.

Results and Discussion

Phase Behavior. All experiments in this study were run under conditions at which CO_2 and styrene (with or without AIBN) were a single phase, which could be seen clearly through the optical cell. The solubility of CO_2 in PVC was determined by Berens et al.[7] They showed that the solubility of CO_2 in PVC was increased with pressure and could reach to 7% at 68 atm. Chiou et al.[8] reported the plasticization of PVC by CO_2, and the results showed that the glass transition temperature was decreased from 75 to 57 °C at low pressure of 20 atm. All these results mean that CO_2 is the swelling agent and the plasticizer for PVC.

PVC samples were soaked in styrene/CO_2 solution at 40 °C and 100 bar. The original concentration of styrene in CO_2/styrene solution was 0.237 mol/L. Figure 2 illustrates the mass uptake as a function of soaking time before and after venting. Before venting, saturate sorption of styrene was reached after about 20 h, and the absorption amount is 0.147 g/g. The data also show that the mass uptake before venting is much higher than that after venting; i.e., a significant amount of styrene is carried out by CO_2 during decompression. The reason is that both styrene and CO_2 exist in the PVC films. CO_2 comes out in the venting process, and some of the styrene is entrained by CO_2.

The effect of pressure on the absorption of styrene was studied at 40 °C in the pressure range from 80 to 160 bar with styrene concentration of 0.237 mol/L. The equilibration time was 20 h. The results are illustrated in Figure 3. The mass uptake before venting increases with pressure. The reason is that PVC films swell to a larger extent at the higher pressures. After venting, the amount of styrene absorbed increases with pressure at the lower pressures and decreases with pressure at the higher pressures. Therefore, there is a maximum at

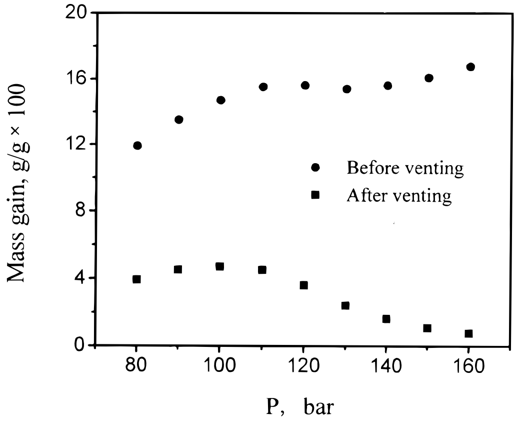


Figure 3. Mass uptake of PVC film as a function of pressure at 40 °C and styrene concentration of 0.237 mol/L without AIBN for 20 h.

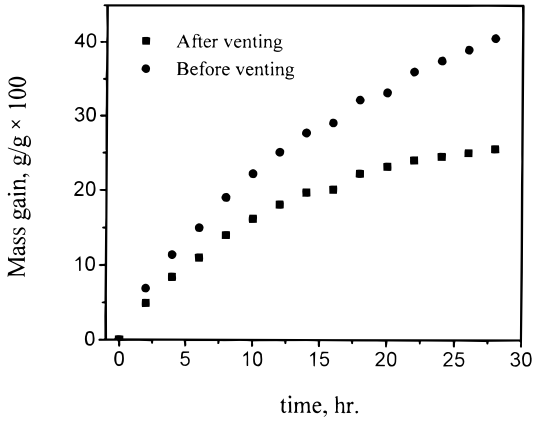


Figure 4. Mass uptake of PVC film as a function of soaking time at 40 °C, 100 bar, and styrene concentration of 0.237 mol/L with 0.3 mol % AIBN based on styrene.

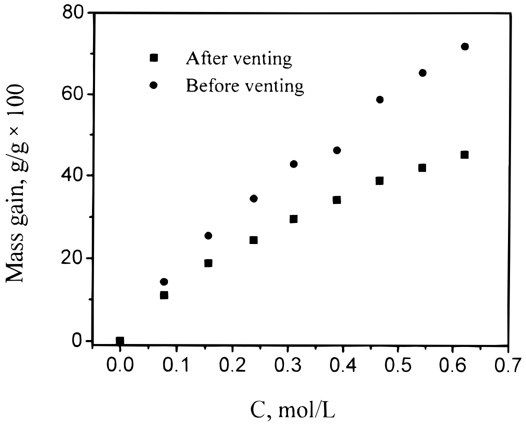


Figure 5. Mass uptake of PVC film as a function of styrene concentration at 40 °C and 100 bar with 0.3 mol % AIBN based on styrene with fixed soaking time of 20 h.

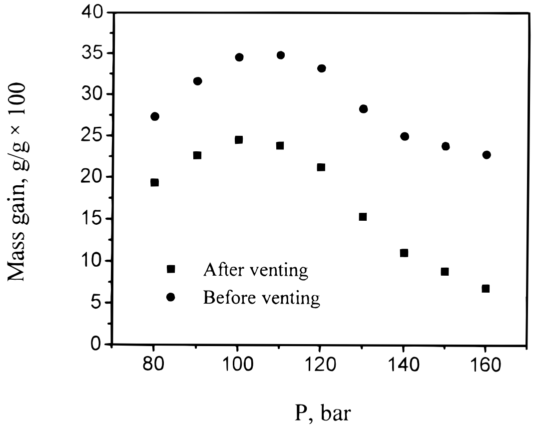


Figure 6. Mass uptake of PVC film as a function of pressure at 40 °C and styrene concentration of 0.237 mol/L with 0.3 mol % AIBN based on styrene with 20 h soaking time.

about 100 bar. There are two factors to affect the mass uptake after venting: the mass uptake before venting and the amount of styrene entrained by CO_2 from the films during venting. At the lower pressures the mass uptake before venting increases rapidly with pressure, as shown in Figure 3, and the first factor is dominant. At the higher pressures, the effect of pressure on the mass uptake before venting is very limited, but the amount of CO_2 in the film increases considerably with pressure, and more styrene is carried out by CO_2 in the venting process. Thus, the second factor becomes dominant, and the mass uptake after venting decreases with pressure.

The phase behavior in the absence of AIBN has been discussed in the above paragraphs. The phase behavior of CO_2/styrene (with 0.3 mol % AIBN)/PVC was also studied in this work. The effects of soaking time, pressure, and the concentration of styrene on the mass uptakes before and after venting were all examined at 40 °C.

Figure 4 shows the mass uptakes before and after venting as a function of soaking time. Comparing the data in Figures 2 and 4, one can find that the mass uptakes of styrene with and without AIBN are different in three aspects. First, the mass uptake of styrene without AIBN can reach saturate after 20 h, while that with AIBN cannot reach saturate even the soaking time is as long as 28 h. Second, the mass uptake with AIBN is much higher than that without AIBN. Third, the percentage of styrene entrained from PVC films by CO_2 during the venting process is smaller when styrene contains AIBN. All these indicate the polymerization of styrene in the PVC substrates in the course of soaking when AIBN exists in the system.

Figure 5 plots the mass uptake as a function of styrene concentration at 40 °C and 100 bar with fixed soaking time of 20 h and styrene concentration of 0.237 mol/L with 0.3 mol % AIBN (based on styrene). The mass uptake of styrene increases continuously with the concentration of styrene. Figure 6 shows the effect of CO_2 pressure on the mass uptake at 40 °C in the pressure range from 80 to 160 bar; the original concentration of styrene in the fluid phase was 0.237 mol/L with 0.3 mol % AIBN, and the soaking time was 20 h. There is a maximum at about 110 bar. This is the competing effect of infusion rate and solvent strength. With increasing in pressure, PVC swells to a larger extent, which is favorable to increasing the mass uptake. However, the diffusion rate of the styrene in CO_2 decreases as pressure increases, and CO_2 is a better solvent for styrene, which is not favorable to increasing mass uptake.

Blend Synthesis. After determining the mass uptakes, the PVC samples impregnated with styrene and AIBN were placed in a constant air bath of 80 °C for 4 h to allow the styrene to polymerize under the protection of N_2. The reported half-life of AIBN at 80 °C is about 2 h.[14]

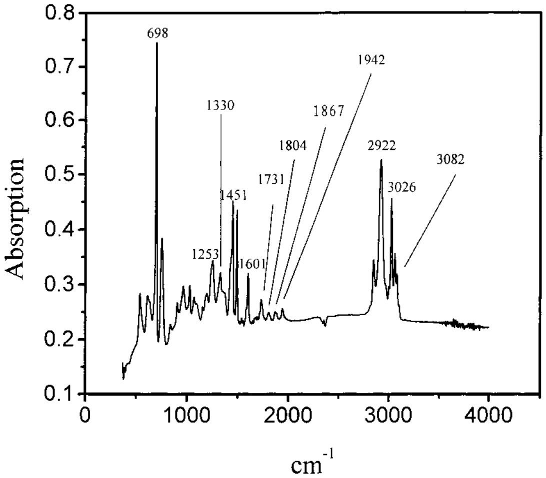


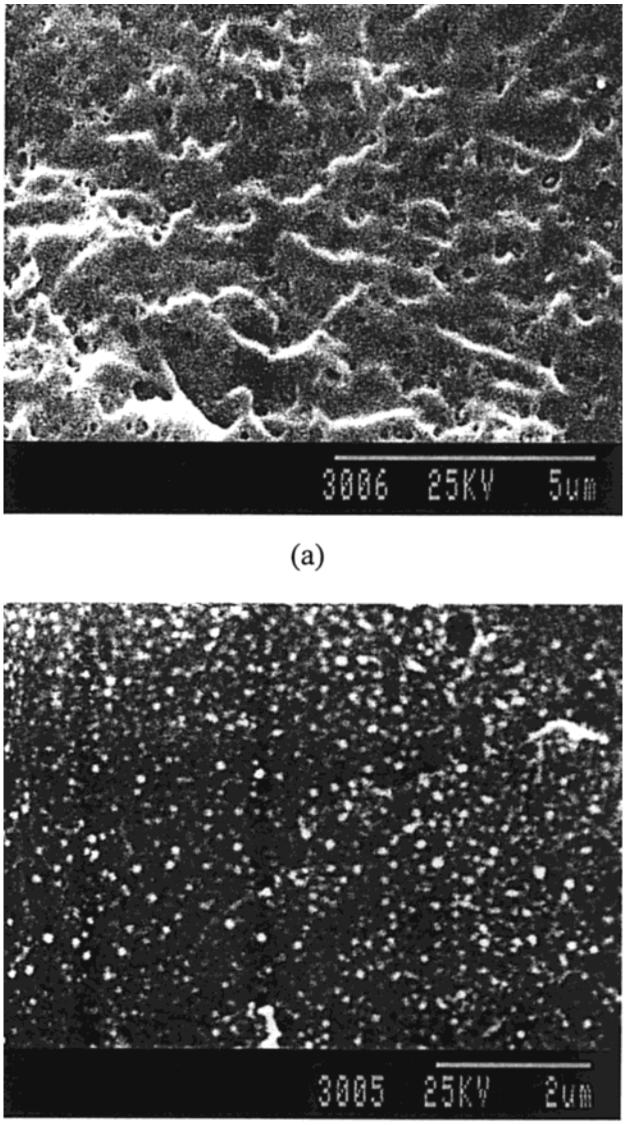
Figure 7. Infrared spectrum of PVC/PS (74/26) composite.

Blend Characterization. a. Infrared Spectroscopy. Figure 7 shows the IR spectrum of the PVC/PS composite. Clearly, it can be seen that, besides the characteristic absorption peaks of PVC at 698, 1253, 1330, 1451, and 2922 cm^{-1}, etc., the characteristic absorption peaks of polystyrene of the aromatic C$-$H stretching vibration at 3026 and 3082 cm^{-1} and the aromatic C$-$H bending vibration at 1601, 1731, 1804, 1867, and 1942 cm^{-1} appear, implying that PS indeed exists in the PVC matrix.

b. Morphology. The formation of the PVC/PS composite is able to influence its phase morphology. Figure 8 presents the SEM photographs of the matrix PVC and the cryogenically fractured surfaces for PVC/PS (74/26) composite.

The particulate nature of PVC is responsible for the morphologies of PVC/PS blends. It is well-known that PVC obtained by suspension polymerization can exhibit three types of particulate structure. The largest structure is the powder grain. The powder grains start to break down into primary particles at the lower processing temperatures. The primary particles are fused into large domains at the higher processing temperatures. From Figure 8a, we can see that the original morphology of PVC film is powder grain. After blending with PS, PS particles are well dispersed in between the PVC primary particles, which is effective in the PS toughing of PVC. Because of large difference in chemical structure, clear phase separation of the composite was also observed for the blend. The interfaces between PS particles and the PVC matrix are clear. Therefore, we can draw some conclusions; i.e., the PVC grains are broken into the primary particles in the course of SC CO_2 swelling at the low modification temperature of 40 °C, and the PVC primary particles force the PS particles to be dispersed between them. This dispersion is favorable to the toughing of the blends.

c. Mechanical Properties. Mechanical properties were obtained from stress$-$strain curves of original PVC and PVC/PS composites.



(a)

(b)

Figure 8. SEM microphotographs of the freeze-fractured surfaces of original PVC film (a) and PVC/PS (74/26) composite (b).

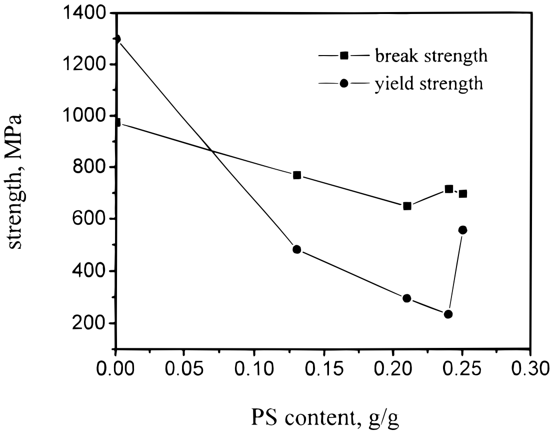


Figure 9. Plots of yield strength and break strength versus PS content for PVC/PS composites.

Figure 9 shows plots of yield strength (σ_y) and break strength (σ_b) versus PS content for PVC/PS blends. It is clearly seen that the σ_y of the PVC blend decreases at PS content of <0.237 g/g and then increases, whereas the σ_b decreases at <0.212 g/g PS content and then increases at >0.212 g/g PS content, which may be attributed to the thin-neck effect occurring during tensile testing. Moreover, it is apparent that σ_y and σ_b show interesting relations: at low PS content (<0.074 g/g), $\sigma_y > \sigma_b$; however, at high PS content, $\sigma_y < \sigma_b$. When $\sigma_y > \sigma_b$, blends are brittle; otherwise, blends are in the

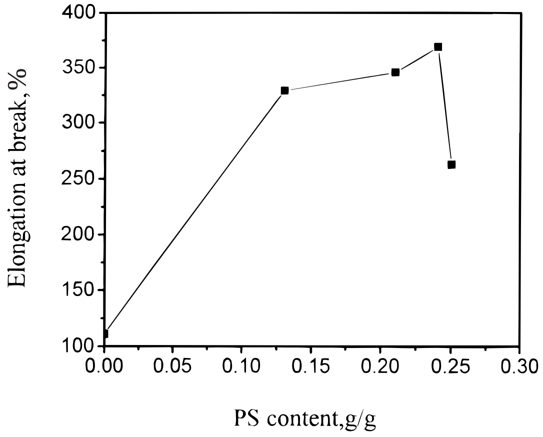


Figure 10. Plot of elongation at break versus PS content for PVC/PS composites.

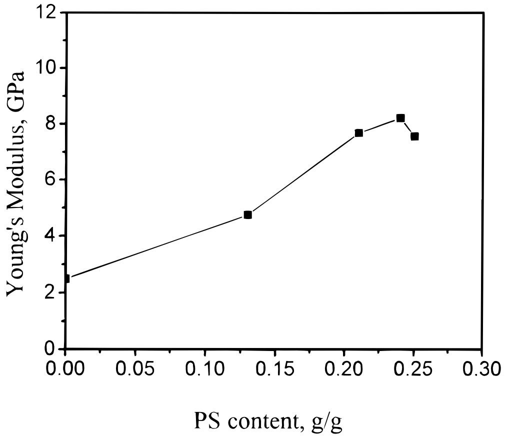


Figure 11. Plot of Young's modulus versus PS content for PVC/PS composites.

tough mode. The condition of brittle−tough transition is $\sigma_y = \sigma_b$ at a PS content of 0.074 g/g.

Figure 10 shows the elongation at break versus PS content for the PVC/PS blends. It is interesting that the elongation at break increases with increasing PS content of lower than 0.238 g/g. This means that PVC is toughened by PS at PS content lower than 0.238 g/g.

Figure 11 shows a plot of Young's modulus versus PS content. It can be seen that modulus increases gradually with increasing PS content at PS content lower than 0.24 g/g, which is caused mainly by the addition of PS with a relatively high modulus. It is well-known that the main shortcoming of toughening is the significant reduction of the rigidity of polymer blend. In our work, we obtained the blends exhibiting both reinforcing and toughening effects. This may be attributable to a strengthening of the interface between the PVC grains by PS. Before polymerization the styrene molecules distribute in the PVC matrix. It is easy to imagine that some of the styrene molecules polymerize across some PVC molecules; i.e., some polystyrene molecules entangle with PVC molecules in the interface between the PVC grains.

The effects of PS content on notched Izod impact strength of PVC/PS blends are shown in Figure 12. It is well-known that PVC belongs to a brittle polymer that has a low notched Izod impact strength of 25.8 J/m. The incorporation of PS greatly improves the notched Izod impact strength. In PVC/PS blends, the impact strength increases with the concentration of PS at PS content lower than 0.25 g/g. The largest impart strength is about 64.5 J/m, which is about 2.5 times that of pure PVC. As a brittle polymer, PS has very low elongation at break, but it has certain toughening ability when filled in the PVC matrix.

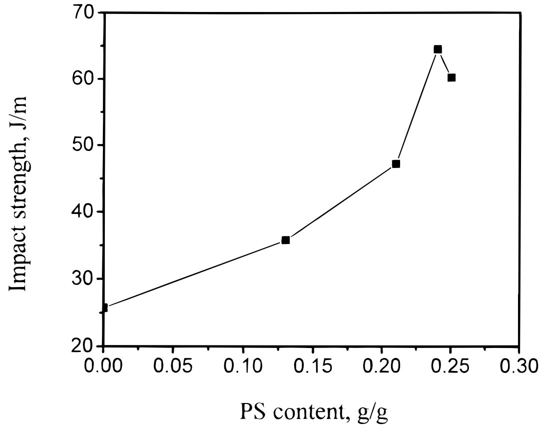


Figure 12. Effects of PS content on notched Izod impact strength of PVC/PS composites.

Conclusions

SC CO_2 can be used as a swelling agent in the modification of PVC films, and interesting composites can be obtained by polymerization of styrene in the PVC matrix. According to the phase behavior studied, the content of PS in blend can be conveniently controlled by soaking time, pressure, and styrene concentration. The polymerization of styrene in the course of soaking results in a high amount of PS incorporated. It is no doubt that morphology imposes a significant influence on the toughening efficiency of PVC/PS blends. In this work, PS particles are well dispersed between the PVC primary particles. We obtained the blend exhibiting both reinforcing and toughening effects by mechanical measurements. Brittle ductile transitions have been observed in PVC/PS blends by plotting strength against PS content. The incorporated PS significantly improves the notched Izod impact strength of PVC so as to reach a tough mode. A brittle−tough transition takes place in the PS content from 0.074 to 0.24 g/g, which can be controlled by experimental conditions.

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