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Phase behavior of supercritical CO_2/Styrene/Poly(ethylene terephthlate) (PET) system and preparation of polystyrene/PET composites

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Abstract

Phase behavior of supercritical CO_2/styrene/poly (ethylene terephthlate) (PET) system was determined at 35°C and different pressures. The concentration of styrene in the fluid phase ranged from 0 to 1.3 mol/l. Styrene partitioned between the fluid phase and PET films, and significant amount of styrene was absorbed into PET matrix. When the styrene contained 0.3 mol% initiator azobis (isobutyronitrile) (AIBN), the mass uptake was higher than that of the styrene without the initiator because the AIBN initiated polymerization during the soaking period. It was found that considerable amount of styrene was carried out by CO_2 in the depressurization process. After the depressurization process, the PET films impregnated with styrene and AIBN were placed in a reactor and heated at 80°C for 4 h under the protection of N_2, and the PET/Polystyrene (PS) blends were obtained. The properties of the blends could be controlled by manipulating experimental conditions, such as soaking time, pressure and styrene concentration. The blends were characterized using IR, SEM, rheological measurement, and some mechanical properties were also determined. Rheometer study indicates that the presence of PS in PET can improve the mobility of PET.

Keywords: Poly(ethylene terephthlate); Azobis (isobutyronitrile); Styrene

1. Introduction

Supercritical fluids (SCFs) are a curious hybrid of liquid and gas. Like liquids, they have high density and can swell polymers [1–5]. Like gases, they have low viscosity and high diffusivity, which make it possible for SCFs to penetrate into amorphous polymers in a relatively short period of time and provide a better flow resulting in deep penetration and more even distribution of additives. Different from the conventional organic solvents, the properties of SCFs are continuously tunable by simply adjusting pressure and temperature. The degree of polymer swelling and partitioning of additives between SCFs and swollen polymers can be manipulated by adjusting the solvent strength of the SCFs via changes in temperature and pressure [6–8]. Supercritical (SC) CO_2 is widely used because it is readily available, inexpensive, nontoxic, nonflammable, environmentally more acceptable, and it has moderate critical temperature and critical pressure ($T_c = 31.1$°C, $P_c = 73.8$ bar). CO_2 is a gas at ambient condition, therefore it rapidly dissipates upon release of pressure, leaving most of the solutes in the substrates.

Recently, McCarthy and coworkers developed a new route to produce composites [9–12]. This 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. Comparing with traditional blending methods, such as mechanical mixing, this approach is more versatile and general, and the most intriguing feature is that blending can be carried out at temperatures well below T_m. Any polymer that is insoluble in SC CO_2, but can be swollen by it can be used as a substrate, and any monomer that is soluble in SC CO_2 and can be free radically polymerized can be used to prepare the modifier in the blend.

PET is a high performance engineering plastics offering excellent thermal resistance, chemical resistance and mechanical performance. However, it has high melt viscosity and therefore low mobility, which is a disadvantage for processing. One of the important approaches to solve this problem is to formulate composites of PET with polystyrene (PS). PET films can be swollen by SC CO_2 [13]. On the basis of this fact, we have prepared PET/PS composite films. The

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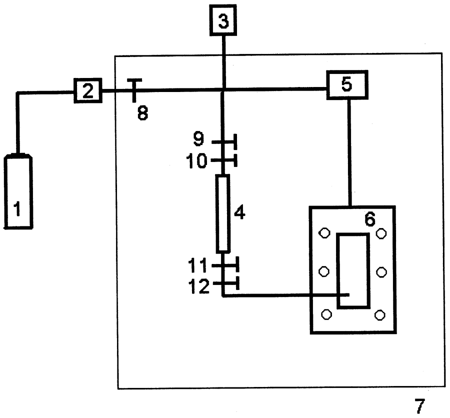


Fig. 1. Schematic diagram of the experimental apparatus (1) gas cylinder, (2) syringe pump, (3) digital pressure gauge, (4) vapor sample bomb, (5) circulation pump, (6) optical cell, (7) constant-temperature air bath, (8), (9), (10), (11) and (12) shut-off valves.

monomer of styrene and initiator were absorbed by PET film with the aid of SC CO_2, and then the monomer was polymerized to obtain binary blend films. To date many researchers have studied the impregnation of polymers using small molecules, and paid much attention to the amount of the small molecules trapped in the polymers after depressurization. It is very interesting to learn how many small molecules absorbed in the polymer matrix were carried out during the depressurization process. Thus, in this work, we investigated both of the mass uptakes before and after depressurization. The effect of PS on the mobility and mechanical properties of PET was also studied. Using this new method [9–12] to prepare PET/PS blends was not found in the literature survey.

2. Experimental section

Materials. Air-quenched, melt-extruded PET films (supplied by Yan Shan Petrochemical Co.) had an intrinsic viscosity $[\eta] = 0.64$ in C_6H_5OH/CCl_4 solution (1:1 by volume) at 45°C. The thickness of the film was 0.3 mm and was amorphous by density and infrared (IR) measurements. Its T_g was 81.6°C as determined by DSC with a heating rate of 20°C/min. CO_2 with purity of 99.9% was obtained from Beijing Huanxin Gas Co. Styrene (A.R. grade) supplied by Beijing Chemical Factory was vacuum distilled. Azobis (isobutyronitrile) (AIBN) supplied by Beijing Chemical Factory was recrystallized twice from acetone in our laboratory. It is well known that PET is quite hydrophilic and that the absorbed moisture has a plasticing effect. For this reason, all the samples were dried for 72 h in a vacuum oven.

Apparatus. The schematic diagram of the experimental apparatus is shown in Fig. 1. It consisted mainly of a gas cylinder (1), a syringe pump (2), a digital pressure gauge (3), a vapor sample bomb (4), solenoid-operated pump (5), optical cell (6), constant-temperature bath (7) 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 sample bomb was 120 ml. The principle of the apparatus is similar to those of the circulation apparatus reported previously [14,15].

The syringe pump (2) was model SCF-8000 (Beijing Xiantong Scientific Instruments Co.) which was used to charge the CO_2 into the system. The accuracy of pressure gage (3), which was consisted of a transducer (IC sensors Co., Model 93) and an indicator, was ±0.05 MPa in the pressure range of 0–20 MPa. The solenoid circulation pump (5) was used to circulate the fluid phase. The temperature of the air bath (7) 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 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 sample bomb.

Procedures. The system was cleaned thoroughly using suitable solvents and dried under vacuum. Four grams of PET films were placed in the high-pressure optical cell (6). The desired amount of styrene/initiator (0.3 mol%) solution was added to the CO_2-purged vapor sample bomb (4) by a syringe through valve 10. Then it was connected to the system as shown in Fig. 1. After the system had reached thermal equilibrium, the air in the other part of the system was removed; valves 10 and 11 were opened. Then the apparatus was charged with carbon dioxide until the desired pressure was reached. Valve 8 was then closed. The circulation pump (5) was started to circulate the fluid phase, which flow through vapor sample bomb (4). The PET films were swollen and some of the styrene and AIBN infused into the films. After a desired soaking period, valves 9 to 12 were closed. The sample bomb was removed to determine the composition of the fluid phase, which was used to calculate the mass uptake before depressurization. The fluid in the optical cell was released and the films were taken out for determining the mass uptake of styrene in PET after releasing CO_2 and for blend synthesis.

Mass uptake of styrene in PET before depressurization. The sample bomb (4) was refrigerated at −20°C for several hours. Most of the CO_2 in the bomb was liquefied after this procedure. The needle valve 9 at the end of the sample bomb was opened slightly to release the CO_2 in the sample bomb slowly. After this process was finished, the needle valve was closed. The quantity of the styrene in the sample bomb was determined by gravimetric method. Experiments showed that the quantity of styrene entranced by CO_2 during this process was negligible, i.e. the styrene in the sample remains in the sample bomb after releasing the CO_2. The mass uptake of styrene before depressurization can be

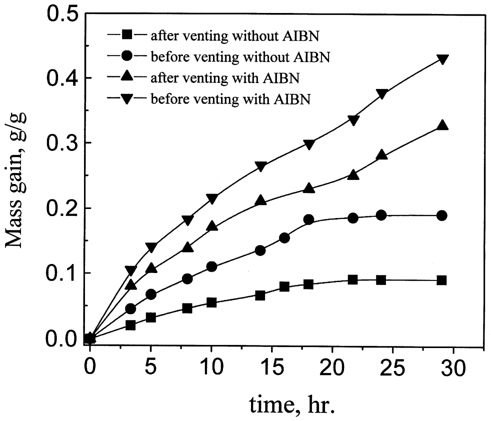


Fig. 2. Mass gain of styrene as a function of soaking time at 35°C and 100 bar with and without AIBN (styrene concentration = 0.387 mol/l).

calculated easily from the following equation:

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

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 depressurization is the mass (grams) of styrene absorbed by 1 g PET film before releasing the CO_2 in the system.

Mass uptake of styrene in PET after depressurization. After depressurization of the system, the films were taken out, the condensed styrene on the surface of the films was cleaned, and then the films were weighed. At beginning, the mass of the films reduced with time because CO_2 in the films diffused out, and then remained unchanged with time after about 20 h. The mass uptake of styrene in PET after releasing CO_2 can be easily calculated on the basis of masses of the films before and after soaking the styrene.

Blend synthesis. The PET films impregnated with styrene and initiator obtained by above procedures were placed in a stainless steel vessel of 20 ml. The vessel was vacuumed to remove the air and charged with N_2 and heated at 80°C for 4 h. Then the vessel was cooled and opened and the specimens were taken out to characterize by different techniques.

Blend characterization. IR spectroscopy experiments were performed using a Perkin–Elmer 180 instrument under standard operating conditions.

The freeze-fractured surfaces at the liquid nitrogen temperature of PET/PS blends were observed with a Hitachi S-530 scanning electron microscope (SEM). The surface was coated with gold and the accelerating voltage was 25 kV.

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 break were determined from the load-extension curves. All values are averaged from five measurements.

Rheology measurements were carried with a capillary rheometer (Instron 3210). The isothermal viscosity was measured at 270°C using capillaries with diameters of $d =$ 0.3 and 1.26 mm and length-to-diameter ratio $(L/d) = 3.8$ and 20.7. Before experiments, a series of experiments were performed using capillaries with $L/d = 5$, 10, 20 and 40 to calibrate the rheometer. It was found that, in the full range of shear rate (γ), the Bagley correction did not exceed 5%. As a result, the correction was subsequently neglected. All the samples were dried under vacuum for 12 h at 135°C and then stored in a vacuum oven to avoid water absorbing.

3. Results and discussion

3.1. Phase behavior

Mass uptake of styrene. In this work, all the experiments were conducted under the conditions at which CO_2, styrene, and AIBN exist as a single phase [16], which could also be seen clearly from the optical cell during the experiments. Some of the styrene absorbed by PET may be entrained by CO_2 during the depressurization process. Thus, mass uptake before venting may be higher than that after decompression. In this work we determined both mass uptakes before and after depressurization. The effects of pressure, soaking time, and concentration of styrene on the mass uptakes were also studied.

Effect of soaking time. Soaking time was varied from 3 to 30 h at 100 bar and 35°C. The concentration of styrene in CO_2/styrene solution is 0.387 mol/l. The mass uptakes of styrene without and with AIBN 0.3 mol% are shown in Fig. 2. Significant amount of styrene can be incorporated into PET films using this method.

From Fig. 2, we can see that in the absence of AIBN, the mass uptake of styrene reaches equilibrium after a soaking period of 20 h; when the styrene contains 0.3 mol% AIBN, however, equilibrium cannot be reached even if the soaking time is as long as 30 h. This indicates that styrene polymerizes in the PET matrix during the soaking process. Since styrene in the swollen PET films is consumed by polymerization, styrene in the fluid phase repartitions between the solid and the fluid phases. The polymerization thus induces a continuous absorption of styrene and resulting in the high PS content.

The mass uptake of the film before venting is higher than that after venting. Thus, an important conclusion can be obtained, i.e. significant amount of styrene absorbed was carried out by CO_2 during the venting process. In the absence of AIBN, about 50% styrene was entrained by CO_2. In the presence of AIBN, however, about 25% styrene was carried out. The main reason for the difference is that the amounts of oligmers or polymers entangle with PET molecules.

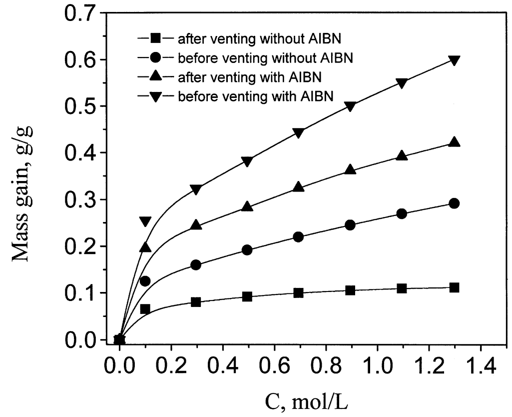


Fig. 3. Mass gain of styrene as a function of styrene concentration at 35°C and 100 bar with and without AIBN.

Effect of styrene concentration. A series of experiments were run with varying styrene concentrations and the soaking time was at least 24 h at 35°C and 100 bar. Fig. 3 gives the dependence of mass uptake of styrene without and with 0.3 mol% AIBN (based on the monomer) on the concentration of styrene in the fluid phase. The overall initiator concentration in the fluid phase varied with styrene concentration because the ratio of the monomer to AIBN is fixed. The mass uptake increases with 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 80 to 160 bar, and the concentration of styrene was 0.387 mol/l. The soaking time was 24 h.

Fig. 4 shows the dependence of mass uptake on pressure with and without AIBN. Equilibrium absorption can be reached without AIBN as can be known from Fig. 2. The mass uptake before venting decreases slightly with pressure at the lower pressures. At the higher pressures, however, pressure effect is very limited. The main reason may be that the density or solvent strength of CO_2 increases more significantly with pressure at the lower pressure [17]. Increase in solvent strength of the fluid is not favorable to the increase of mass uptake. The difference of the mass uptakes before and after venting becomes larger and larger with increasing pressure. There may be two reasons for this. First, the quantity of CO_2 in the swollen PET matrix increases with pressure. Second, CO_2 swells PET more sufficiently at the higher pressures. Thus more styrene was carried out in the decompression process.

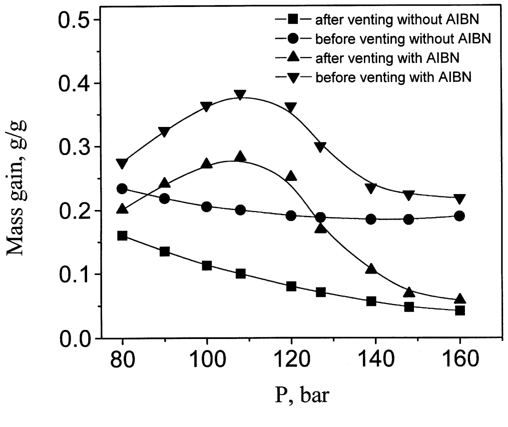


Fig. 4. Mass gain of styrene as a function of pressure at 35°C by a soaking time of 24 h with and without AIBN (styrene concentration = 0.387 mol/l).

In the presence of 0.3 mol% AIBN, equilibrium absorption cannot be reached in 24 h, which is shown in Fig. 2. The effect of pressure on the mass uptake is more complicated. The mass uptake increases with pressure in the range from 80 to 110 bar, and then decreases with pressure, i.e. there is a maximum at 110 bar. It is very difficult to give an exact explanation on this. Fig. 4 indicates that the difference in mass uptakes of styrene with and without AIBN is not significant at the higher pressures. One of the reasons may be that the pressure affects the polymerization of the monomer during the soaking period.

3.2. Blend synthesis

As discussed above, in the process of determining the phase behavior, we also obtained the PET films impregnated with styrene and AIBN, 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 hours [9] at the soaking temperature (35°C). In order to get the PET/PS composites, the impregnated PET films were sealed into a stainless steel reactor, and the air in the reactor was replaced by N_2. Then the reactor was maintained at 80°C for 4 h to allow the polymerization taking place further. Experiments showed that the mass loss of the impregnated PET was negligible during the blend synthesis process.

3.3. Characterization

IR spectroscopy. Using the method described by Watkins and McCarthy [10], some of the composites prepared in this work were analyzed by IR measurement. Fig. 5 gives the IR spectra of virgin PET and PET/PS (90/10) blend. In the spectrum of the PET/PS (90/10) blend, the spectral features of PS (aromatic and aliphatic C–H stretching at 3100–2900 cm^{-1}, aromatic C–C stretching at 1614 cm^{-1} and aromatic C–H out-of-plane bending at 700, 1954 cm^{-1}) clearly show that there exists PS in the PET matrix.

Morphology. Both THF and toluene are good solvents for PS, but PET is not soluble in them. The extraction of PS from the blends was carried out using these two solvents at room temperature for 24 h. The blends were then dried at 60°C in a vacuum oven and weighted. Experiments showed that the PS extracted by the solvents from the blends was not considerable. The possible reason for this is that at least a part of PS molecules in the blends was entangled with the PET molecules, so they are forming quasi-network

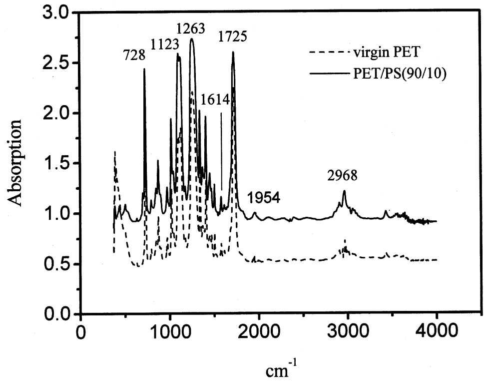


Fig. 5. IR spectra of virgin PET and PET/PS (90/10) composite.

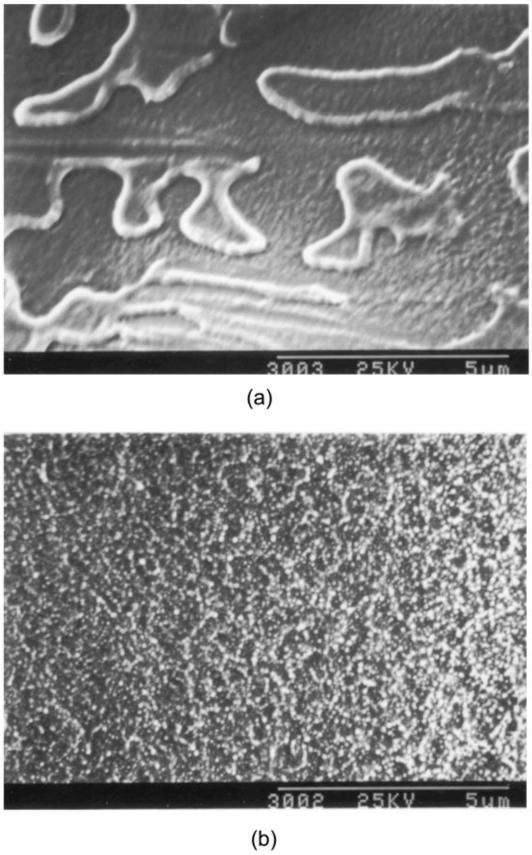
structure. The mechanism to form this kind of structure can be deduced. Before polymerization, distribution of the monomers in the matrix is relatively even. A large number of monomers joint together crossing some PET molecules in the polymerization process.

Fig. 6 gives SEM photographs of cryogenically fractured surfaces for PET matrix and PET/PS (67/33) blends. The appearance of the composite film was obviously different from that of the matrix film. The PS molecules are well distributed in the PET matrix, as can be seen from Fig. 6, which supports the fact that PS in the matrix cannot extracted by liquid solvents. If large PS phase existed in the blends, the PS could be extracted by suitable solvents. SEM study was also performed on CO_2-treated films. The results showed that treatment using CO_2 did not affect the morphology of the films noticeably.

Mechanical properties. Some mechanical properties of PET and its blend are measured under static loading conditions at a constant strain rate of 5 mm/min. The results are summarized in Table 1.

These results suggest that the effect of blending is to increase the tensile strength and to cause the toughness of the samples. This supports the statement that PET and PS form quasi-network structure as discussed above.

Rheological measurement. Fig. 7 presents the dependence of shear stress (τ) on shear rate (γ) of the pure PET and PET/PS composites with different PS contents at 270°C, which is about 15°C higher than the melting temperature. The shear stress decreases with the content of PS in the composites. This is easy to understand because the readily deformable PS in PET reduces the shear stress.



(a)

(b)

Fig. 6. SEM photographs of cryogenically surface for virgin PET film (a) and PET/PS (67/33) composite film (b).

Fig. 8 shows a plot of apparent viscosity (μ_a) vs. PS content at different shear rates at 270°C. Qualitatively, in the full range of shear rate investigated, the blends have lower viscosity than pure PET.

The μ_a was employed to estimate the activation energy of flow, E_a:

$$E_a = R[d\ln \mu_a/d(1/T)] \tag{2}$$

where R and T are the gas constant and absolute temperature, respectively. For comparison, the relationship between

Table 1
Mechanical data of PET and its blends at strain rate of 5 mm/min

Material	PS content g PS/100 g PET	Young's modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
PET	0	1.7	39	40
PET/PS-1	5	2.0	46	43
PET/PS-2	12	2.1	48	44
PET/PS-3	18	2.2	48	44
PET/PS-4	26	2.4	51	46
PET/PS-5	33	2.9	68	51

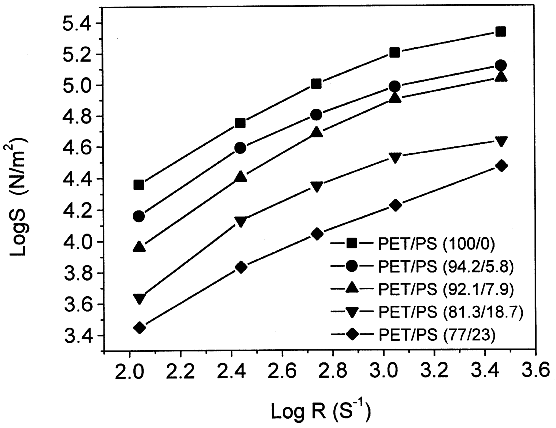


Fig. 7. Rheological properties of virgin PET and PET/PS composites at 270°C.

apparent viscosity μ_a and temperature at a shear rate of 2951 (S^{-1}) are shown in Fig. 9. E_a calculated from the plots are shown in Table 2. The E_a value for pure PET agrees quite well with that reported by Utracki et al. [18], which verified our experimental method. As expected, E_a decreases with the increase of temperature. Fig. 9 also indicates that E_a decreases considerably with the PS concentration. Thus blending can improve the mobility of PET.

4. Conclusions

Phase behavior of supercritical CO_2/styrene/poly (ethylene terephthlate) (PET) system was determined at 35°C in the pressure range from 80 to 160 bar. Significant amount of

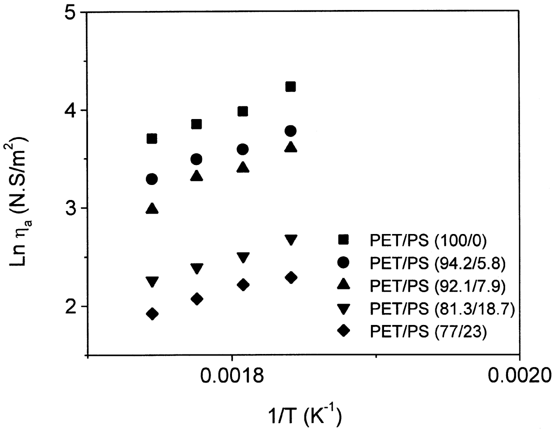


Fig. 9. Effect of temperature on the apparent viscosity (μ_a) at constant shear rate of 2951 S^{-1} for virgin PET and PET/PS composites with different PS contents.

styrene was carried out by CO_2 in the depressurization process. When the styrene contained 0.3 mol% AIBN, less styrene absorbed by PET matrix was entrained by CO_2 during the venting process because the AIBN initiates polymerization of styrene during the soaking period, and the polymerization of styrene during the soaking period also results in higher mass uptake.

The PET/PS blend was obtained by polymerization of the styrene in the CO_2-swollen PET matrix at 80°C for 4 h. The properties of the blends can be controlled by manipulating experimental conditions, such as soaking time, pressure, and styrene concentration. In the blends at least part of the PS molecules entangle with PET molecules. The blends have lower apparent viscosity and higher mobility than pure PET,

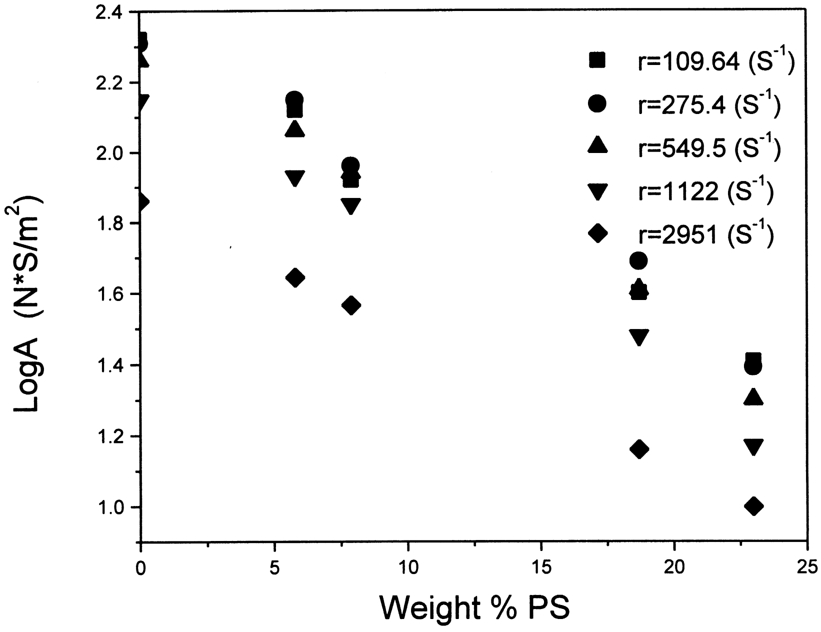


Fig. 8. Effect of PS content on the apparent viscosity (μ_a) at different shear rate (γ) at 270°C.

Table 2
Activation energy of flow E_a of PET and its blends at shear rate of 2951 S^{-1}

Materials	PS content g PS/100 g PET	E_a (kJ/mol)
PET	0	18.298
PET/PS-6	5.8	16.418
PET/PS-7	7.9	15.422
PET/PS-8	18.7	11.410
PET/PS-9	23	9.854

and the activation energy of flow decreases considerably with the PS concentration.

Acknowledgements

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