polymer

Phase equilibria of CO_2–PET–phenol system and generation of PET powders by supercritical CO_2 anti-solvent

Dan Li, Zhimin Liu, Guanying Yang, Buxing Han[*], Haike Yan

Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

Received 14 July 1999; received in revised form 21 September 1999; accepted 28 September 1999

Abstract

Phase equilibria of CO_2–Phenol–Poly(ethylene terephthalate) (PET) ternary system were investigated at 318.15 and 326.15 K and at pressures ranging from 6 to 17 MPa. The results show that the solubility of CO_2 in PET/phenol solution increases with pressure, and decreases with temperature. The solubility of PET in phenol (on CO_2-free basis) decreases significantly with pressure at pressures lower than 10 MPa at 318.15 K and 11 MPa at 326.15 K, but increases slightly with pressure at higher pressures. On the basis of the phase behavior studied, PET powders were produced by the gas anti-solvent (GAS) process, and the morphology of the precipitated PET was examined using scanning electron microscopy. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Supercritical CO_2; Poly(ethylene terephthalate); Phenol

1. Introduction

It is well known that poly(ethylene terephthalate) (PET) is a high melting compound which has exceptional value as a fiber and film-making material, and which currently dominates the whole field of linear polyester substances. However, the high viscosity and limited solubility in liquid solvents restrict its processing to powders and hence the range of applications of such a polymer. Traditionally, crushing, mechanical grinding, ball milling and precipitation from solution are methods for producing powders. The first three ones inevitably change the property of materials. The last one is carried out on the basis of the application of an anti-solvent to decrease the solubility of a material that is dissolved in solution, in which we must separate the product and the solution of solvent/anti-solvent that is always very difficult and expensive.

Using a gas or a supercritical fluid as a gas anti-solvent (GAS) in polymer solutions has been studied by different authors [1–14]. The GAS process is based on the observation that the dissolution of a supercritical fluid in a liquid solvent is frequently accompanied by large expansion of the liquid phase. This causes the solution power of the solvent to reduce significantly and dissolved solute to precipitate. Therefore a major advantage of GAS over those based on

conventional liquid anti-solvent is that, by a suitable choice of supercritical fluid and operating conditions, the solvent can be extracted by anti-solvent and removed completely leaving behind a dry precipitate. Moreover, the GAS process uses common organic solvents in which a variety of polymers can be dissolved at ambient temperature. This technique opens a bright future for producing new types of polymer materials because the powder shape, size distribution, morphology and the rate of precipitation can be controlled by temperature, pressure and the concentration of polymer in solvent.

Both PET and CO_2 are soluble in phenol, and the dissolved CO_2 affects the solubility of PET in phenol. Thus it is expected that CO_2 can be used as an anti-solvent to produce PET powder by GAS process. Our goals are, first, to understand the phase behavior of the PET + phenol + anti-solvent ternary system and, second, to generate PET powders by GAS precipitation, relating their morphology to operating conditions.

2. Experimental

2.1. Materials

Air-quenched, melt-extruded PET granular supplied by Beijing Yanshan Petro-chemical Co. had an intrinsic viscosity $[\eta] = 0.67$ in C_6H_5OH/CCl_4 solution (1:1 by volume) at 45°C. Phenol (A.R. grade) produced by Beijing
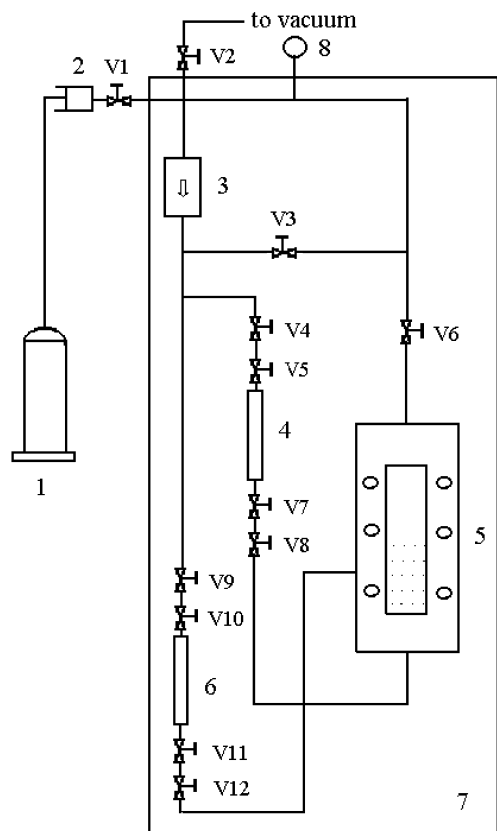

Fig. 1. High-pressure phase equilibrium system. (1) gas cylinder, (2) high pressure pump, (3) solenoid circulation pump, (4) vapor sample bomb, (5) optical cell, (6) liquid sample bomb, (7) constant temperature air bath, (8) pressure gauge, V1–V12 valves.

Chemical Factory, and purified in our laboratory by distillation was selected because of its high affinity to both PET and carbon dioxide. The purity of CO_2 was 99.9% supplied by Beijing Analytical Instrument Factory. Ethanol (A.R. grade) was produced by Beijing Chemical Factory with purity of 99.5%. The original concentrations of the polymer solution were 5 and 10 wt%.
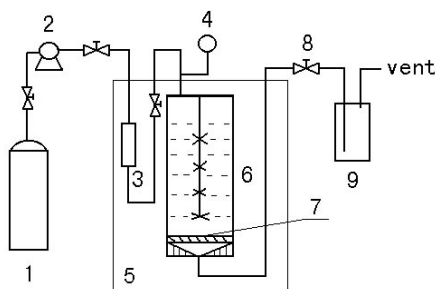

Fig. 2. Schematic diagram of the apparatus for precipitation of PET. (1) CO_2 cylinder, (2) syringe pump, (3) preheater, (4) pressure gauge, (5) water bath, (6) high pressure cell, (7) filter, (8) needle valve, (9) separator.

2.2. Apparatus and procedures for phase behavior measurements

The experimental apparatus is shown schematically in Fig. 1. It consisted mainly of a gas cylinder (1), syringe pump (2), solenoid circulation pump (3), vapor sample bomb (4), optical cell (5), liquid sample bomb (6), constant temperature air bath (7), pressure gauge (8), and valves (V1–V12). All the metallic parts in contact with the studied materials were made of stainless steel. The optical cell (5) and the sample bombs were placed in an air bath and a solenoid circulation pump (3) was installed to circulate the vapor phase. The temperature of the convective air bath (7) was controlled by a main and a secondary controller. The fluctuation of the temperature in the air 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). The fluid was pressurized using a syringe pump (2) (Beijing Xiantong Scientific Instruments Co., Model SCF-8000). The accuracy of the pressure gauge (8), which was composed of a transducer (IC Sensors Co., Model 93) and a indicator, was ±0.05 MPa in the pressure range of 0–20 MPa. A Mettler PM1200 balance with a sensitivity of 0.001 g was used for weight determination.

The system was washed thoroughly using different solvents and dried under vacuum. The PET solution (5 wt%) was charged into the optical cell. The air in the system was removed by vacuum. After the system had reached thermal equilibrium, CO_2 was compressed into the system until desired pressure was reached. The solenoid-operated circulation pump (3) was started to circulate the vapor phase which flowed alternatively through the vapor sample bomb (4) and the liquid sample bomb (6). Experiments showed that equilibrium could be reached in 6 h. In each experiment the equilibration time was at least 8 h. After equilibrium was reached, valve V12 was closed, and the precipitated PET was allowed to deposit at the bottom of the optical cell (5). Valves V3 and V12 was opened when the solution was completely clear. Some of the liquid solution in the optical cell began to flow into the liquid sample bomb (6), which was known by the falling of the liquid level in the optical cell (5). When the sample bomb (6) was full, and the liquid level in the optical cell (5) was unchanged with time, valves V4–V12 were closed. The vapor sample bomb and liquid sample bomb were removed and weighted for composition analysis. After the experiment, the pressure inside the cell was changed to the next value at the constant temperature by syringe pump.

The vapor 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 (5) at the end of the sample bomb was opened to release the CO_2 in the sample bomb slowly. After this process was finished, the needle valve was closed. The quantity of the phenol was determined by the gravimetric method.
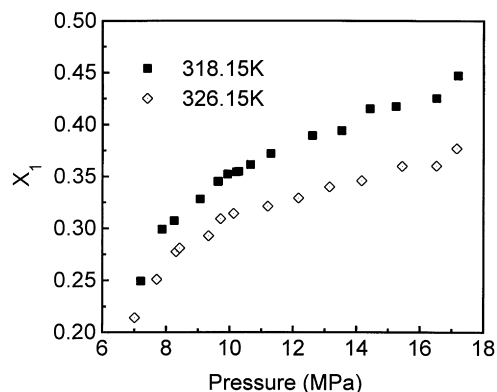
Fig. 3. Mole fraction of CO_2 (X_1) in the liquid phase.

The amount of CO_2 in the liquid sample bomb (6) was determined by the PVT method [15]. The PET and phenol in the sample was washed into a beaker using ethanol, and then the ethanol and phenol was removed in a vacuum oven at 120°C. The weight of PET in the beaker was known by weighing. The amount of phenol in the liquid sample was easily calculated on the basis of total weight of the liquid phase sample, the weight of CO_2, and the weight of PET.

2.3. Apparatus and procedures of GAS process

The experimental apparatus for the GAS process is shown schematically in Fig. 2. It was mainly composed of a gas cylinder (1), a syringe pump (2), a preheater (3), a pressure gauge (4), a constant temperature water bath (5), a high-pressure cell of 30 ml (6), a filter of 0.2 μm (7), and valves and fittings.

In a typical experiment, 10 ml solution was put in the high pressure cell (6). The CO_2 was charged into the cell from the top of the cell until the desired pressure was reached. The stirrer in the cell was started. The dissolution of the carbon dioxide in the liquid phase causes the expansion of the solution and polymer nucleation [2]. After a sufficient quantity of polymer was precipitated (about 1 h), the stirrer was stopped and the needle valve (8) was opened.
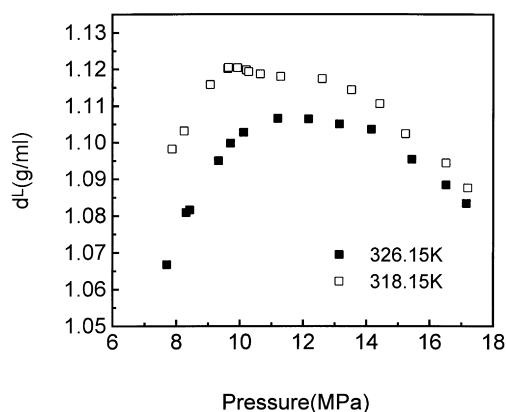

Fig. 4. Dependence of liquid density (d^L) on temperature and pressure.

The liquid was released slowly from the bottom of the cell through the filter. Additional carbon dioxide was injected from the top of the cell to compensate for pressure drop due to the draining. The dry PET powders were obtained after this procedure, and the morphology and the dimension of the precipitated PET were examined by scanning electron microscopy (SEM; Hitachi, s-530).

3. Results and discussion

3.1. Phase behavior

At the equilibrium conditions of this work there are three phases in the system—vapor phase, liquid phase and PET solid phase.

There are only CO_2 and phenol in the vapor phase because PET is not soluble in supercritical CO_2. The mole fraction of phenol increases from 0.003 to 0.03 as pressure is increased from 7 to 17 MPa.

3.1.1. Mole fraction of CO_2 in the liquid phase
Fig. 3 shows the effect of temperature and pressure on the mole fraction of CO_2 in the liquid phase (X_1). X_1 increases with pressure and decreases with temperature, as can be seen from Fig. 3.

3.1.2. Density of the liquid phase
Fig. 4 illustrates the dependence of liquid phase density (d^L) on temperature and pressure. It is interesting to notice that d^L increases with pressure at pressures below 10 MPa, but decreases with pressure at pressures above 10 MPa at 318.15 K and 11 MPa at 326.15 K. The main reason may be that some of the CO_2 molecules dissolved form a hydrogen bond with phenol because phenol is a Lewis acid and CO_2 is a Lewis base [16]. The distance between molecules should be reduced when the hydrogen bond is formed. Therefore, the hydrogen-bonded CO_2 is favorable to increasing the density, and the free one results in decreasing of the density. The percentage of CO_2 molecules that form the hydrogen bond should decrease with the concentration of CO_2 in the liquid phase. The solubility of CO_2 in the liquid phase is lower at lower pressures, as shown in Fig. 3. The percentage of the CO_2 forming hydrogen bond is higher at lower pressures, and density increases with pressure. At higher pressures, the percentage of CO_2 that forms the hydrogen bond is smaller because the solubility is high, and so the density decreases with pressure.

3.1.3. Volume expansion of solution
In this paper, the volume expansion coefficient (α) of the PET−phenol solution is defined by the following equation:

$$\alpha = (V - V_0)/V_0 \tag{1}$$

where V_0 and V, respectively, are the volumes of 1 g of PET−phenol solution before and after dissolution of CO_2. α
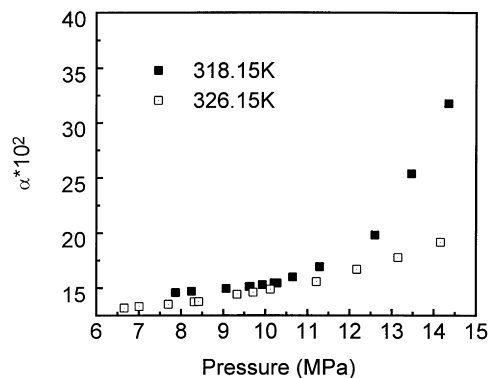
Fig. 5. Dependence of volume expansion coefficient (α) on temperature and pressure.

can be easily calculated on the basis of the volume of the liquid sample bomb (6), the weight of the PET and the phenol in the liquid sample, and the density of the PET–phenol solution (CO_2-free) at the experimental temperature and concentration, which was determined in this work by the gravimetric method.

Fig. 5 shows the dependence of α on temperature and pressure. α increases slowly with pressure at the lower pressures, but increases rapidly with pressure when pressure is higher than about 10 MPa at 318.15 K and 11 MPa at 326.15 K. This is easy to understand considering the results shown in Figs. 3 and 4.

3.1.4. Concentration of PET in the liquid phase

In this work, the concentration of PET (C_{PET}) in the liquid phase (wt% of PET) is defined on CO_2-free basis

$$C_{PET} \, (wt\%) = W_{PET}/(W_{PET} + W_P) \tag{2}$$

where W_{PET} and W_P stand for the weight of PET and the weight of phenol in the liquid sample, respectively.

Fig. 6 illustrates the dependence of C_{PET} (wt%) on pressure at 318.15 and 326.15 K. The figure shows clearly that the solubility of PET is reduced by the dissolution of CO_2. Thus phenol and CO_2 can be used in the GAS process
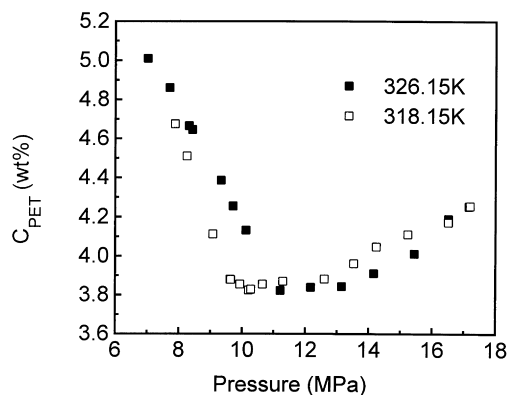

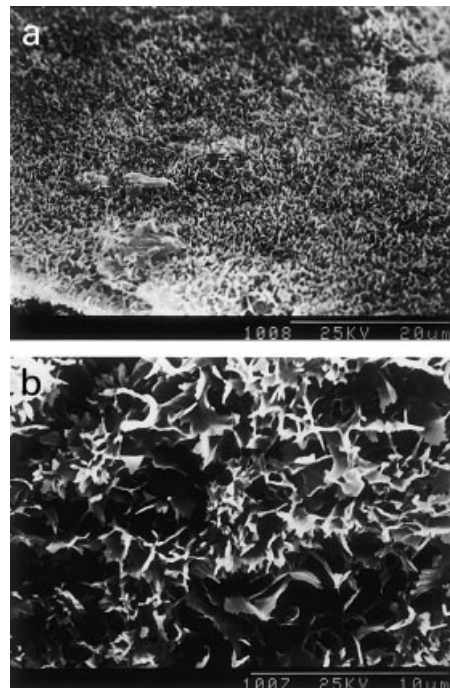Fig. 6. Dependence of concentration of PET (C_{PET}) on temperature and pressure.

Fig. 7. (a) SEM micrograph of PET powders by CO_2 from 5 wt% PET solution at 318.15 K and 14.5 MPa; (b) Sample (a) at a higher magnification.

for generating PET powders. It is interesting to notice that a minimum can be observed in each C_{PET} (wt%) vs pressure curve. This is understandable considering the fact that C_{PET} is expressed on the CO_2-free basis, as can be known from
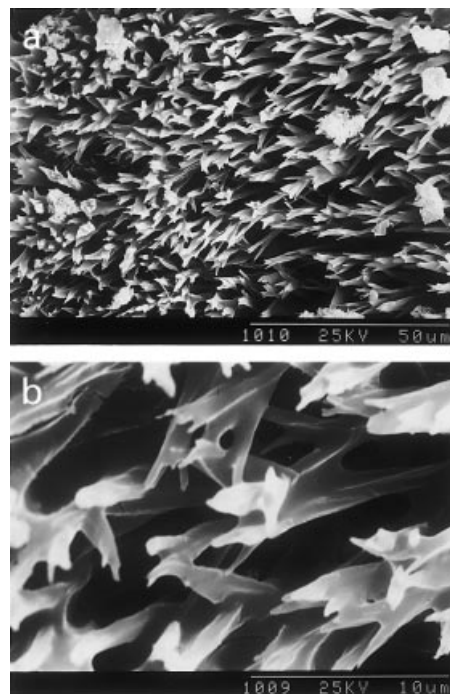

Fig. 8. (a) SEM micrograph of PET powders by CO_2 from 5 wt% PET solution at 326.15 K and 14.5 MPa; (b) Sample (a) at a higher magnification.
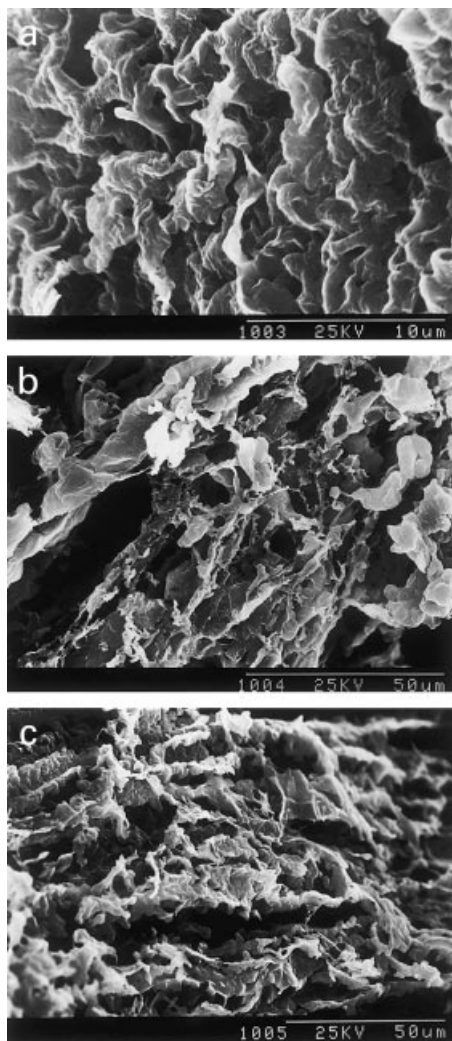
Fig. 9. SEM micrographs of PET powders by CO_2 from 5 wt% PET solution at 326.15 K: (a) 7.0 MPa; (b) 8.5 MPa; (c) 11 MPa.

Eq. (1). It should be pointed out that the volume concentration of PET in phenol/CO_2 decreases monotonously with increasing pressure.

3.2. Morphology study

The results shown in Figs. 3–6 allow us to select suitable operating conditions for the GAS process. In this work, experiments were performed at 7.0, 8.5, 11.0, 14.5 MPa, and at 318.15 and 326.15 K for solutions of different concentrations to produce PET powders. Figs. 7–10 show the SEM micrographs of the products.

3.2.1. Effect of temperature

To examine the effect of temperature on polymer morphology, experiments were performed at constant pressure. Figs. 7 and 8 show SEM micrographs of PET powders precipitated in the GAS process at 14.5 MPa and at 318.15 and 326.15 K by adding SC CO_2 to 5 wt% PET solution. The results show an increment of powder size with

increasing of temperature. Larger powder size may result from the accelerated movement of molecules in the solution at higher temperature.

3.2.2. Effect of pressure

The effect of the pressure on the powder structure was studied at a constant temperature of 326.15 K. Figs. 8 and 9 show SEM micrographs of PET powders precipitated at 7.0, 8.5, 11 and 14.5 MPa. Benedetti et al. and Schmidt et al. reported that the pressure did not seem to have much effect on the properties of the products for other polymers [17,18]. Figs. 8 and 9 indicate that the PET powder size decreases when the operating pressure is increased. The smallest micropowders were made at 14.5 MPa and have a relatively good distribution (Fig. 8). The microstructure has the appearance of a flake and the polymer arranges loosely not being coalesced into larger powders. At a constant temperature, the powder size increases considerably as the pressure is decreased to 11 MPa (Fig. 9c). This trend becomes even more evident when the pressure is decreased to 7.0 MPa (Fig. 9a), in which the powders are agglomerated and the microstructure has a cobweb-like appearance. It is likely that the tendency for the PET micropowders to flocculate is increased with the decrease of pressure. From the experiments, we found that pressure is an important variable for controlling morphology and the mechanism for powder formation is very complicated. However, this effect may be explained from three facts. First, at higher pressure, the diffusion in both directions of SC CO_2 to solution and phenol to SC CO_2 is higher relative to a lower pressure [1], and thus nucleation is rapid. The formation of many nuclei favors the production of a larger number of very small micropowders. In addition, the rapid drying of micropowder due to rapid diffusion of phenol out of solution helps to prevent the coarsening of the micropowders during solidification. Second, the larger volume expansion of the solution at higher pressure is favorable for the formation of nonconnected powders because the solution contains more CO_2. If the expansion is not sufficient, more phenol exists between the powders and longer drying time is required, which may result in connected powders. The same happened at intermediate expansion values, and the powders are connected loosely. Third, when the operating pressure is increased, the CO_2 solubility in the solution increased, as shown in Fig. 3, and then the higher supersaturation concentration of PET is reached. Thus a violent nucleation occurs and a lot of smaller PET powders are formed. To sum up, the higher pressure will be suitable for preparing smaller powders and the reasonable operation pressure can be determined according to the required size.

3.2.3. Effect of concentration

The concentration of PET solution is an another important variable for controlling morphology. The previous results have been for 5 wt% PET in phenol. Increasing the
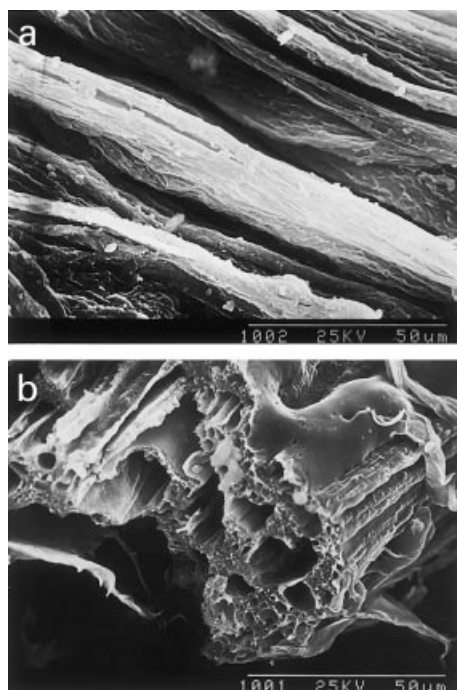
Fig. 10. (a) SEM micrograph of PET fibers by CO_2 from 10 wt% PET solution at 326.15 K and 14.5 MPa; (b) Cross-section of sample (a).

concentration to 10 wt% leads to hollow fiber formation, as shown in Fig. 10. The fibers in Fig. 10 are not uniform. To obtain a photograph of the fiber cross-section, a fiber was immersed in liquid nitrogen, removed, and immediately cut with a new razor blade. It was attached to a SEM stage, and the result indicates that the fibers are hollow with skin on the surface. The main reason for the fiber formation appears to be the increased viscosity. There is significant chain entanglement in the solution. It is likely that the viscoelastic force in the polymer solution causes CO_2 mass transfer rates into the liquid larger than the phenol transfer rates out. The rapid mass transfer of CO_2 and phenol from the surface lead to rapid precipitation and formation of a dense skin. CO_2 diffuses through this dense skin faster than phenol. As more and more CO_2 diffuses into the solution, the interior of the skin remains rich in phenol. Therefore, the polymer rich domains will remain plasticized allowing the CO_2 rich voids to grow. These voids may coalesce with sufficient time. This growth and coalescence will lead to a hollow structure.

4. Conclusions

Supercritical carbon dioxide is an effective anti-solvent and can be used to produce PET powder which is difficult to form by the physical phase separation technique and conventional liquid anti-solvent. The phase behavior for the CO_2 + phenol + PET ternary system was measured and used to explain the morphology formed in the GAS process. The experimental investigations in this study have led to following conclusions:

- The GAS process can be used to produce PET powder.
- We have investigated the phase behavior, which can be used to determine the operating conditions.
- The morphology of PET powder could be varied by temperature, pressure and solution concentration. The reasonable conditions can be determined by the required powder size.

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