

# Supercritical CO<sub>2</sub>-Assisted Synthesis and Characterization of a Polystyrene/Thermal Polyurethane Blend

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Received 27 May 2004; accepted 2 September 2004

DOI 10.1002/app.21646

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** A blend of polystyrene and thermal polyurethane (PS/TPU) was prepared using supercritical (SC) CO<sub>2</sub> as a substrate-swelling agent and monomer/initiator carrier. The SC CO<sub>2</sub>/styrene/TPU ternary system was studied. Virgin TPU and synthesized blends were characterized through differential scanning calorimetry, infrared spectroscopy,

rheometric measurements, and SEM. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 2016–2020, 2005

**Key words:** supercritical CO<sub>2</sub>; polystyrene; thermal polyurethane; synthesis; blends

## INTRODUCTION

Recently, the community of polymer research investigators have become increasingly interested in supercritical fluid (SCF)-assisted polymer modification and blend synthesis. The high solubility, diffusivity, and plasticizing behavior of CO<sub>2</sub> in polymers make it a unique plasticizer to accelerate the impregnation of small molecules into polymer substrates. Although supercritical (SC) CO<sub>2</sub> is a weak solvent for most polymers, it is a desirable swelling agent for polymers and can dissolve many small molecules.<sup>1–4</sup> One of the most intriguing features of SCF is that its density and solvent strength can be adjusted by changing the pressure and temperature of the system. As a result, the degree of swelling in the polymer and the mass of small molecular impregnation can be easily manipulated.<sup>5–8</sup>

The SC CO<sub>2</sub>-assisted synthesis of blends, developed extensively by McCarthy and coworkers,<sup>9–16</sup> is generally applicable and has proved uniquely successful for the preparation of certain types of polymer blends, for example, if one or two polymers are incompatible, infusible, and high purity is required, or if one component has already been processed to a desired shape.

Polystyrene and thermal polyurethane (PS/TPU) blends, which have excellent performance, have been applied in many areas.<sup>17,18</sup> PS and TPU are immiscible

polymers. It is difficult to mix them, with a fine homogeneous domain in the range of molecular-meter size, by using the conventional method.

The use of SC CO<sub>2</sub> as a means of improving the miscibility level is of major environmental importance, although it is a synthetic challenge.

This article reports preliminary results regarding the synthesis of a PS/TPU blend by SCF-swollen substrates described above. The partially miscible PS/TPU blends were obtained, and we achieved an extremely high mass gain (g/100 g TPU) of PS in TPU by means of the SC CO<sub>2</sub> method. Furthermore, the blend was characterized by means of infrared spectroscopy (IR), scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and rheometric measurements. The chief purpose of the study was to explore the potential of better performance for the composite.

## EXPERIMENTAL

### Materials

CO<sub>2</sub> (purity of 99.9%) was obtained from Zhengzhou Sanfa Gas Co. (China). Thermal polyurethane (TPU) was obtained from Zhengzhou Chemical Factory (China) in the form of transparent light-yellow pellets. After being dried under vacuum at 30°C for 24 h, the pellets were processed to 1 ± 0.1 mm-thick sheets on the press vulcanizer (Model QLB-D, made in China). Styrene (AR grade), purchased from Tianjin First Chemical Agent Factory (China), was distilled under reduced pressure. Azobis(isobutyronitrile) (AIBN, supplied by Shanghai Sanpu Chemical Co. Ltd., China) was recrystallized twice from methanol.

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Contract grant sponsor: Henan Natural Science Foundation; contract grant number: 0411020900.

Contract grant sponsor: The Prominent Youth Science Foundation of Henan Province.

### Synthesis of PS/TPU blends

Reactions were run in a 21.4-mL high-pressure stainless steel reactor. A high-pressure syringe pump (DB-80; Beijing Satellite Manufacturing Factory, China) was used to charge CO<sub>2</sub> into the reaction vessel and attached to the reactor by a coupling and high-pressure tubing. A pressure gauge, consisting of a transducer (Model 93; IC Sensors, division of Measurement Specialties, Inc., Fairfield, NJ) and an indicator (XS/A-1; Beijing Tianchen Automatic Instrument Factory, China) with an accuracy of  $\pm 0.05$  MPa, was also connected to the reactor. In the experiments, the reactor was placed in a constant-temperature circulator consisting of a temperature control module (C10; Thermo Haake, Haake, Bersdorff, Germany) and a bath vessel (P5; Thermo Haake). The fluctuation of temperature in the bath was less than  $\pm 0.1^\circ\text{C}$ . All sample sheets were weighed on a Shanghai (China) 328A electrobalance with a sensitivity of 0.1 mg.

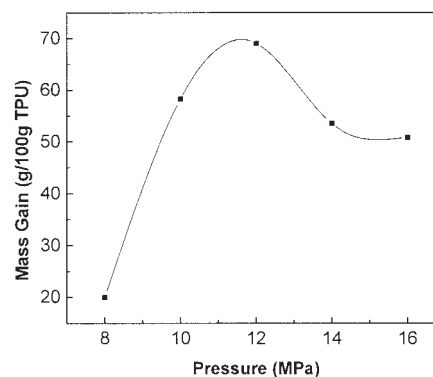
The initiator AIBN (0.3 mol %, based on additive) was dissolved in a certain amount of the additive, and the solution was charged to the bottom of the reactor. Then some glass wool was inserted, upon which polymer samples were placed. After being purged with CO<sub>2</sub> and then filled with CO<sub>2</sub> to 5 MPa, the reactor was equilibrated in a  $40 \pm 0.1^\circ\text{C}$  water bath and repressurized to the desired pressure. After 4 h of treating, the reactor was depressurized for 1 h. The samples were removed and wiped using clean filter paper. Variations of this procedure involved changing the pressure from 8 to 16 MPa (the concentration of additive was fixed at 30 wt %) and the concentration of additive was changed from 5 to 50 wt % (the pressure was controlled at 12 MPa). At 20 min after impregnation, the additive-impregnated samples were transferred to another (identical) reaction vessel. The vessel was then subjected to vacuum and heated at a higher temperature under the protection of N<sub>2</sub> for 4 h.

Based on our previous study, both CO<sub>2</sub> and additive are absorbed by substrates to some degree during the impregnation period. Moreover, the absorbed CO<sub>2</sub> is totally released during subsequent polymerization; thus the mass gain of substrate after polymerization is equal to the incorporated amount of additive. All sample sheets were weighed on a Shanghai 328A electrobalance with a sensitivity of 0.1 mg.

### Characterization

Differential scanning calorimetry (DSC) measurements were conducted on a Netzsch 204 DSC apparatus (Netzsch-Gerätebau GmbH, Bavaria, Germany) under N<sub>2</sub> atmosphere at a heating rate of  $10^\circ\text{C}/\text{min}$  in the temperature range of  $-90$  to  $300^\circ\text{C}$ .

The blend was observed with a JSM-5600 scanning electron microscope (SEM; JEOL, Tokyo, Japan). Each



**Figure 1** Mass gain of TPU as a function of impregnation pressure (impregnation conditions: 30 wt % PS/SC CO<sub>2</sub> for 4 h at  $40^\circ\text{C}$ , polymerization at  $80^\circ\text{C}$  for 4 h).

specimen surface was coated with graphite and the accelerating voltage was 20 kV.

IR spectroscopy experiments were performed using Nicolet 460 FTIR equipment (Nicolet Instrument Technologies, Madison, WI) under standard operating conditions.

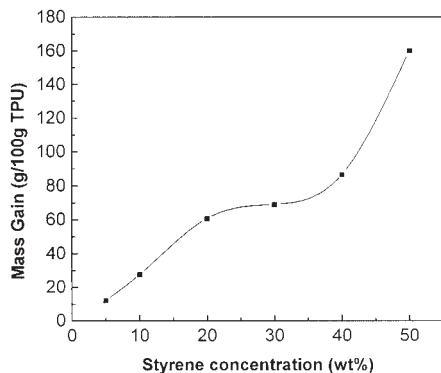
A Haake RS-150 parallel-phase rheometer was used to carry out the rheological experiments of the PS/TPU blend. The RS-150 was fixed at the controlled rate mode, which applies shear stresses to a test sample by means of higher inertia. The controlled shear rate varied from 0 to  $200\text{ s}^{-1}$  at  $200^\circ\text{C}$ .

## RESULTS AND DISCUSSION

It has been reported that carbon dioxide significantly accelerates the absorption of many low molecular weight additives into a number of polymers.<sup>19</sup> The effect is mainly attributed to the high diffusivity, solubility, and plasticizing action of compressed CO<sub>2</sub> in polymers. The amount of additive absorbed can be determined from the plateau weight of the sample after most of the CO<sub>2</sub> has escaped.

### Effect of pressure

Figure 1 shows a plot of mass gain versus soaking pressure. A peak is clearly obtained at about 12 MPa. The phenomenon, in effect, amounts to the partitioning of the additive between the CO<sub>2</sub>- and polymer-rich phases. These profiles exhibit the maximum in PS content, and this maximum is readily explained: CO<sub>2</sub> is a very poor solvent to sufficiently swell TPU to permit rapid infusion of styrene at low pressure. At high pressure, TPU is readily swelled; on the other hand, however, CO<sub>2</sub> is a much better solvent for styrene, and the partitioning of styrene in the fluid phase is enhanced. We can thus conclude that, at some in-



**Figure 2** Mass gain of TPU as a function of monomer concentration (impregnation conditions: 12 MPa for 4 h at 40°C, polymerization at 80°C for 4 h).

intermediate pressures, these competing effects balance and a maximum is observed.<sup>20</sup>

### Effect of styrene concentration

Figure 2 shows the dependency of mass gain on the styrene concentration. The effect of styrene concentration on the mass gain increases with concentration from 5 to 50 wt %. As can be seen, an extremely low increasing rate between 20 and 30 wt % is observed, which may be explained, in part, by the hard segment and soft segment forming the physical crosslinked structure in the TPU. Before the physical crosslinked structure is destroyed, the maximum volume of aperture gap in the polymer molecule is constant. The mass gain increases in the aperture gap of TPU with increasing concentration of styrene. Above 30 wt % the concentration of styrene is so high that the crosslinked structure can be easily destroyed, and the volume of aperture gap in the polymer is also substantially enlarged. As a result, a higher mass gain can be obtained freely without restraint, and so we can obviously observe the rate faster than before.

### Characterization

#### IR spectroscopy measurement

By analogy with the studies reported using conventional processes through FTIR analysis, we can expect that the blend of PS/TPU can be unambiguously confirmed. Figure 3 shows the IR spectra of virgin TPU and PS/TPU blends obtained by SC CO<sub>2</sub> at 313.15 K and 12 MPa.

The spectra of virgin TPU shows stretching bands at 1735 cm<sup>-1</sup> for the C=O group and at 1534 cm<sup>-1</sup> for the N—H group. The spectra of PS/TPU blend indicate significant polystyrene incorporation by the presence of the spectral features of polystyrene (aromatic and aliphatic C—H stretching at 3100–2850 cm<sup>-1</sup>; ar-

omatic C—C stretching at 1601 and 1493 cm<sup>-1</sup>; and aromatic C—H out-of-plane bending at 698 cm<sup>-1</sup>), indicating that the PS has been impregnated into the TPU pellets.<sup>20</sup>

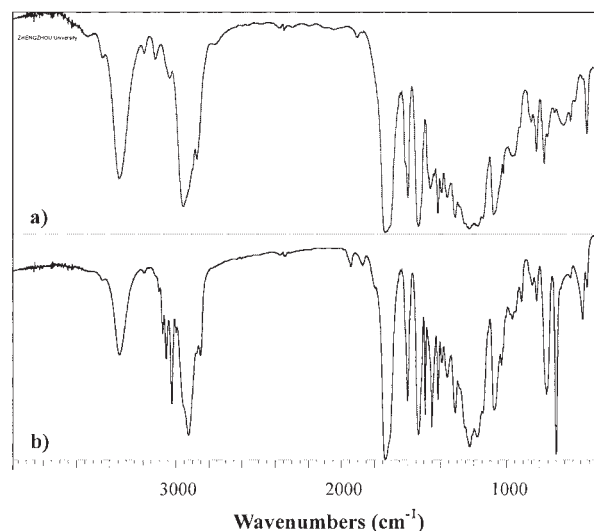
#### SEM measurements

Scanning electron microscopy was performed on several blends. As shown in Figure 4, SEM studies of PS/TPU blends of varying concentrations demonstrate the homogeneous dispersion of PS in the TPU matrix. Moreover, SC CO<sub>2</sub>-assisted blends exhibit phase separation throughout the entire sample, which seems to form a network within the TPU matrix and is probably attributable to the entanglements that occur between PS and TPU during the polymerization of styrene. However, considering the high incompatible level of the two substrates, this special microstructure can form only at a partially miscible level, a phenomenon that can also be verified by means of DSC.

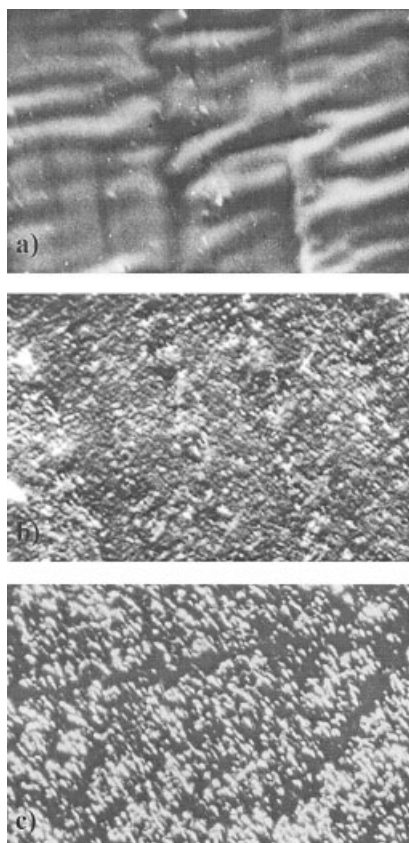
#### DSC measurements

Homogeneous polymer mixtures show only one glass transition ( $T_g$ ) positioned between the glass transitions of the pure components, and truly heterogeneous polymer mixtures, in contrast, possess a series of single glass transitions, one for each component.<sup>21</sup>

All the samples, including virgin TPU and PS/TPU blends of different mass gains, were analyzed by means of DSC (see Table I). Each blend has two glass transitions, and the first  $T_g$  comes close with increasing PS content in the blends. The first  $T_g$  at -21.9 to -33.5°C, corresponding to TPU, and the second at



**Figure 3** IR spectra of (a) virgin TPU and (b) PS/TPU blend; both samples were extracted with water followed by drying in vacuum.

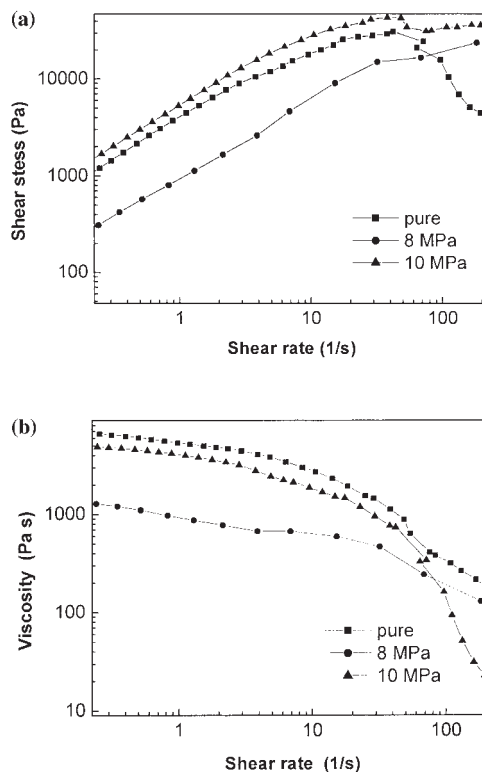


**Figure 4** SEM micrographs ( $\times 2000$ ) of (a) virgin TPU; (b) PS/TPU, impregnation conditions: 40°C, 12 MPa, 4 h; 20 wt % of monomer concentration; and (c) PS/TPU, impregnation conditions: 40°C, 12 MPa, 4 h; 40 wt % of monomer concentration.

49.2–95.6°C, representing that of PS, could be found. For comparison, a blend that was prepared by the conventional method was also analyzed by DSC. We can observe the apparent advantage of preparing the blend of two immiscible polymers by means of SC CO<sub>2</sub>. The reason for this property may be the thermal conditioning and homogeneous dispersion of PS in the TPU matrix.

#### Rheological properties

An elastic behavior of melts, as observed for the PS/TPU blend, was previously reported for other rubber-



**Figure 5** Flow behavior curves of virgin TPU and PS/TPU blends: (a) flow curves displayed the relationship between the shear stress ( $\tau$ ) and shear rate ( $\dot{\gamma}$ ); (b) viscosity curves correlated changes in viscosity ( $\eta$ ) with the shear rate at fixed temperature.

modified thermoplastics.<sup>22–27</sup> To obtain the complete flow curve and viscosity curve, a parallel-phase rheometer was used. The representative flow behavior curves and viscosity curves for different shear rates are shown in Figure 5. The flow curves display the relationship between the shear stress ( $\tau$ ) and shear rate ( $\dot{\gamma}$ ) [Fig. 5(a)]. The viscosity curves [Fig. 5(b)] correlate changes in viscosity ( $\eta$ ) with the shear rate ( $\dot{\gamma}$ ) at constant temperature.

Both panels in Figure 5 indicate that virgin TPU and the blend experienced shear thinning with increasing shear rate at fixed temperature. The viscosity curves in Figure 5(b) reveal that the effect of shear rate on the flow behavior of virgin TPU and blend is more pronounced at higher shear rate than its effect at lower

**TABLE I**  
Comparison of Glass Transitions of Virgin TPU and PS/TPU Blends of Different Mass Gain

| Sample                    | Method             | $T_{g(1)}$<br>(°C) | $T_{g(2)}$<br>(°C) | $\Delta T_g$ [ $T_{g(1)} - T_{g(2)}$ ]<br>(°C) |
|---------------------------|--------------------|--------------------|--------------------|--|
| 1 Virgin TPU              | None               | -21.9              | —                  | —  |
| 2 PS/TPU blend (12.3/100) | SC CO <sub>2</sub> | -33.5              | 49.2               | 82.7   |
| 3 PS/TPU blend (86.7/100) | SC CO <sub>2</sub> | -32.0              | 54.3               | 86.3   |
| 4 PS/TPU blend (148/100)  | Conventional       | -23.4              | 95.6               | 119.0  |



rate. The blend prepared at 8 MPa showed an extremely low viscosity behavior. One of the explanations for this phenomenon is the supermolecular structure in the blends. If two immiscible polymers are mixed, one of which is low in content, a supermolecular structure tends to emerge. Correspondingly, the viscosity of the blend decreases substantially.<sup>28</sup> However, the blend prepared at 10 MPa does not demonstrate the same behavior as that of the blend prepared at 8 MPa. The main reason for this difference is explained by the physical cross section of two components. The solvent power of SC CO<sub>2</sub> at low pressure is weak, so at 8 MPa the PS with low content in the blend is more uniformly dispersed. At high pressure, CO<sub>2</sub> is capable of creating large interchain spaces, and thus more styrene is impregnated into the TPU matrix and the rigid segment of PS and the TPU chain forms a high degree of physical crosslinking. This structure contributes to the flow-resisting force and to the melt viscosity. However, further investigation is necessary to elucidate the relationship between this complex structure and the morphology of the blend.

### CONCLUSIONS

A blend of PS/TPU can be prepared by infusion of styrene into and radical polymerization within TPU using supercritical CO<sub>2</sub> as a carrier. The content of incorporated polymers can be controlled by adjusting the reaction conditions. Moreover, SEM characterization shows that the prepared PS/TPU blend has homogeneous dispersion, and the supermolecular structure of the blend was revealed through rheological study.

The authors are grateful for the financial support of the Henan Natural Science Foundation (Grant 0411020900) and The Prominent Youth Science Foundation of Henan Province.

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