

## Thermal, morphology, and mechanical properties of polyphenylene sulfide/polyether sulfone binary blends

Dandan Li,<sup>1</sup> Guangtao Qian,<sup>2</sup> Changwei Liu,<sup>3</sup> Daming Wang,<sup>1</sup> Chunhai Chen,<sup>1</sup> Xiaogang Zhao<sup>1</sup>

<sup>1</sup>Department of Chemistry, Alan G. MacDiarmid Institute, Jilin University, Changchun, Jilin 130012, China

<sup>2</sup>Department of Chemistry, Jilin University, Changchun, Jilin 130021, China

<sup>3</sup>Institute of Petrochemistry, Heilongjiang Academy of Sciences, Harbin, 150040, China

Correspondence to: X. Zhao (E-mail: xiaogang@jlu.edu.cn)

**ABSTRACT:** Blends of polyether sulfone (PES) and polyphenylene sulfide (PPS) with different weight ratios (10/0, 8/2, 6/4, 4/6, 2/8, 0/10) were prepared by melt extrusion using a twin-screw extruder. In this work, the thermal stabilities of blends were evaluated by thermogravimetric analysis and the dynamic mechanical properties were investigated by means of dynamic mechanical analysis. The fracture surfaces were observed with a scanning electron microscopy. In addition, the mechanical property tests were also carried out and the impact strength of blends was improved by 110% compared to that of pure PPS. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41703.

**KEYWORDS:** blends; extrusion; morphology; thermogravimetric analysis (TGA)

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### INTRODUCTION

Nowadays, synthetic polymer has become an indispensable material to industrial and agricultural production and people's lives. However, facing the modern science and technology, people put forward to increasingly widespread and demanding requirements for polymeric materials. For example, we expect both high-temperature resistance and easy molding polymer materials with both excellent toughness and a relatively high hardness, which were not only good performance but also low price. For a variety of requirements, a single polymer is often difficult to meet. Polymer blending, also known as polymer alloy, is a long-standing issue in polymer science which makes it possible to achieve various properties in a more-effective way than in the case of synthesis of new polymers.<sup>1</sup> Thus it has attracted more and more attention among researchers in recent years.

Polyphenylene sulfide (PPS) is first commercialized by Philips Petroleum Co. in 1973 as a trade name of Ryton, and since then its application has been promoting. As we all know, PPS is mainly used in the manufacture connectors, switches, and coils and so on in the electrical and electronic fields, and in the automotive industry, PPS is primarily used to manufacture valves and engine parts, while PPS is mainly used for manufacturing case, pumps, cameras, and instruments in the machinery industry. With the development of economy, such as automotive and electronics industry's total demand for PPS will continue to expand. However, the brittleness of PPS, which is due to the rigid backbone and the crosslinking architecture, greatly restricts

its applications. To improve the impact toughness and reduce the cost, blending,<sup>2–7</sup> fiber reinforcing,<sup>3,4,8</sup> particle filling composite,<sup>9–13</sup> and liquid polymer composite<sup>14</sup> are usually used.

Polyether sulfone resin (PES) is an excellent overall performance thermoplastic polymer material developed by British ICI Company in 1972, which is one of the special engineering plastics that currently are applied. It has excellent heat resistance, mechanical properties such as impact toughness, and dielectric properties, which can maintain stable performance and other advantages especially those with continuous use at high temperatures and rapid temperature changes in the environment. In many areas, PES has been widely used in the fields such as electrical, electronic machinery, and automotive.

Based on the well performance of PES, researchers have interests in PPS and PES blends. Zeng and Yang studied the crystal morphology and texture,<sup>15</sup> the isothermal crystallization kinetics,<sup>16</sup> and the dynamical mechanical behavior of PPS and PES blends<sup>17</sup> using a method of physical blending. They also studied the behaviors of melting, crystallization, and phase separation of PPS and PES blends using the solution blending method.<sup>18</sup> After a few years, they researched the effect of coupling reagent on the behaviors of melting, crystallization, and impact performance of PPS and PES blends.<sup>19</sup> Shibata *et al.* continued to account for the behaviors of melting and crystallization theoretically.<sup>20</sup> Lai *et al.* also continued to do research on the thermal and dynamic mechanical properties of PPS and PES blends. Lai *et al.* investigated the effects of thermally crosslinkable

**Table I.** Code and Composition of PES/PPS Blends Used

Samples	PES (wt %)	PPS (wt %)	Melt temperature (°C)
PES	100	0	330
PES/PPS 8/2	80	20	320
PES/PPS 6/4	60	40	310
PES/PPS 4/6	40	60	300
PES/PPS 2/8	20	80	290
PPS	0	100	285

polymerization of monomer reactant–polyimide (POI) on the miscibility, morphology, and crystallization of partially miscible PES and PPS blends.<sup>21</sup> In these studies, PPS/PES blends show two glass transition temperatures and the results demonstrate PPS and PES have some compatibility, but no reports have been seen in detail on the relationship of the thermal, morphology, and mechanical properties.

In this research, we also prove some compatibility between PPS and PES, and illustrate the thermal properties of different processing (quenching and annealing) and the relationship of morphology and mechanical properties theoretically in detail. Moreover, we find that PES/PPS = 6/4 blends has the relative good mechanical and impact strength and solves the problem of high cost of PPS, which make PPS have a wide range of applications in the electrical, electronic, automotive, and precision molded article fields.

## EXPERIMENTAL

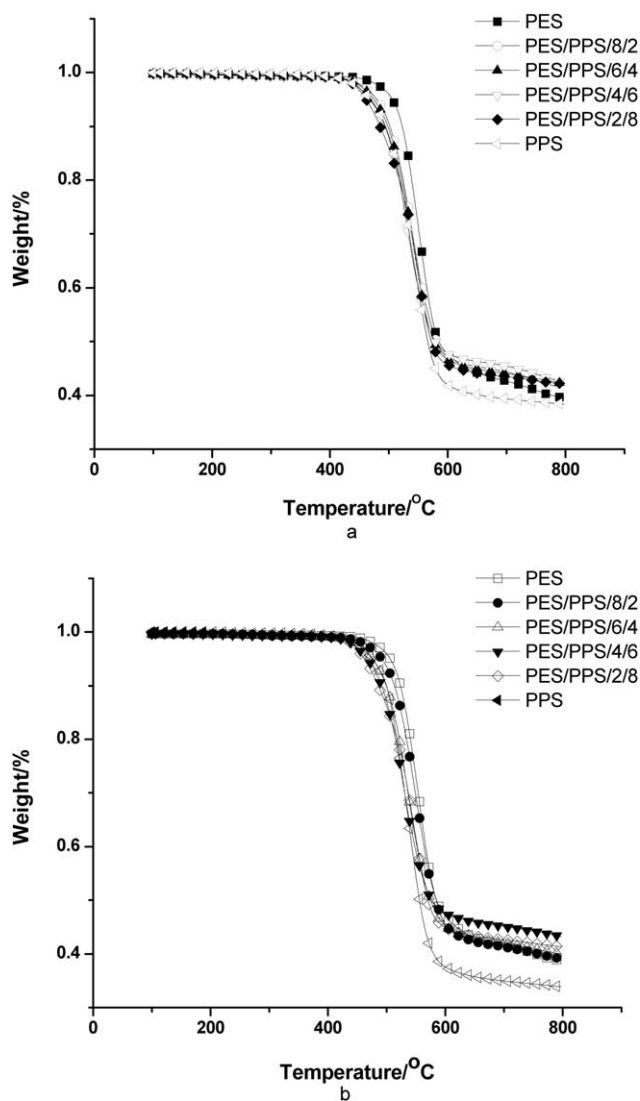
### Materials Used

PES powder was purchased from Special Plastic Engineering, Jilin University Research (Changchun, China). The inherent viscosity was 380 mL g<sup>-1</sup> at room temperature. PPS used was a commercial product manufactured by Sichuan Deyang Special New Materials Co.

### Blend Preparation

Blends of PES powder and PPS powder were first pre-mixed with a high-speed mixer respectively with a speed of 18 r/min for 15 min. The mixed powder was dried in a vacuum oven at 90°C for 10 h before extrusion. And then the polymer powder was blended by using a mini-Haake co-rotating twin-screw extruder at a screw speed of 80 rpm in the temperature range between 310 and 350°C and the pellets were obtained by a Granulator. The codes and conditions of blends used are detailed in Table I.

Quenching and annealing samples preparation for thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA): the pellets after extrusion of PES, PPS, and their blends were dried in a vacuum oven at 90°C for 10 h to prevent bubbles during tableting process, then the pellets were pressed into a sheet in the pressing machine with the temperature of the upper plate and the lower plate between 330 and 350°C. Putting the samples directly into distilled water at room temperature was called quenching, while making the samples cool to room temperature naturally was called annealing.

**Figure 1.** (a) TGA curves of quenched PES and PPS blends; (b) TGA curves of annealed PES and PPS blends.

## Characterization Methods

**Thermal Gravimetric Analysis.** Thermal analysis was carried out in a TA instrument TGA Q2050 under N<sub>2</sub> atmosphere in the temperature range of 100–810°C at a rate of 10 °C min<sup>-1</sup>.

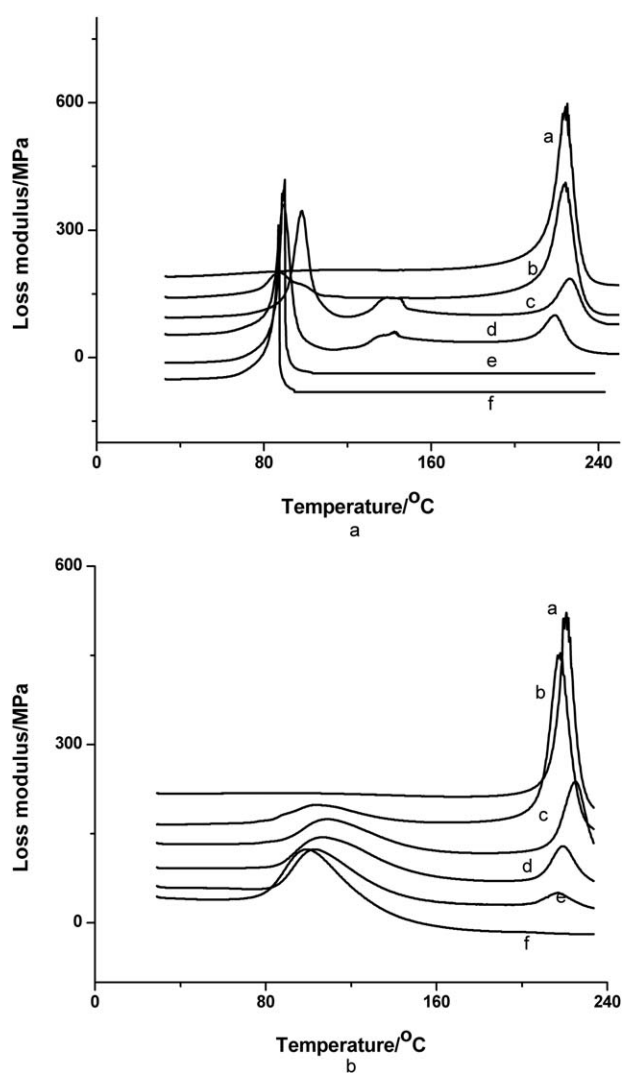
**Table II.** Thermal Stability of PES/PPS Blends

Samples	Quench		Anneal	
	T <sub>d5%</sub> (°C)	T <sub>d10%</sub> (°C)	T <sub>d5%</sub> (°C)	T <sub>d10%</sub> (°C)
PES	506.1	522.7	506.1	523.5
PES/PPS 8/2	492.6	514.7	491.7	513.3
PES/PPS 6/4	474.4	498	475.2	499
PES/PPS 4/6	467.2	493.1	467.2	491
PES/PPS 2/8	460.9	484.4	461.9	485.4
PPS	469.1	494.3	476.7	500.1

**Table III.**  $T_g$  of PES/PPS Blends

Samples	Quench		Anneal	
	$T_{g1}$ (°C)	$T_{g2}$ (°C)	$T_{g1}$ (°C)	$T_{g2}$ (°C)
PES	225	-	226.7	-
PES/PPS 8/2	223	83.6	223.7	103.6
PES/PPS 6/4	222.4	90.8	223.2	106.9
PES/PPS 4/6	221.6	90.8	221.6	106.9
PES/PPS 2/8	-	90.9	221.2	107.7
PPS	-	87.2	-	105.5

The mass of the samples was 5–10 mg. The samples were obtained by pressing into a sheet in the pressing machine, then quenching and annealing, respectively.

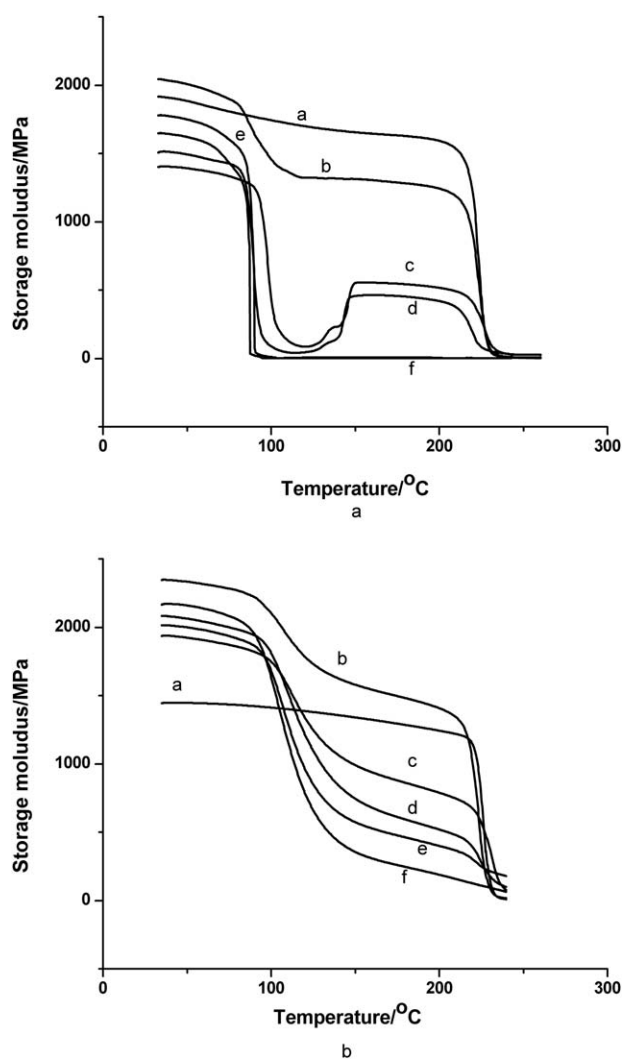


**Figure 2.** (a) Variation of loss modulus for quenched neat PES, PPS, and PES/PPS blends. (a) Neat PES, (b) PES/PPS/8/2, (c) PES/PPS/6/4, (d) PES/PPS/4/6, (e) PES/PPS/2/8, (f) Neat PPS; (b) variation of loss modulus for annealed neat PES, PPS and PES/PPS blends. (a) Neat PES, (b) PES/PPS/8/2, (c) PES/PPS/6/4, (d) PES/PPS/4/6, (e) PES/PPS/2/8, (f) Neat PPS.

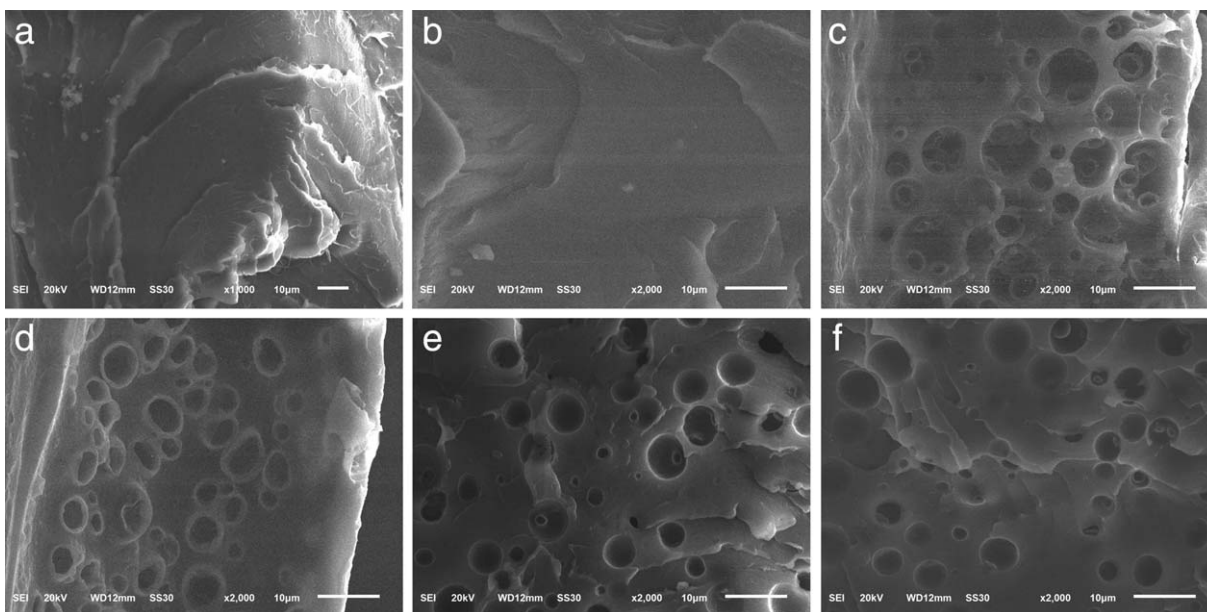
**Dynamic Mechanical Analysis.** DMA was recorded on a TA Instruments DMA Q800 in the temperature range of 50–300 °C at a frequency of 1 Hz and a heating rate of 5 °C min<sup>-1</sup> in the tensile mode. The samples were obtained by pressing into a sheet in the pressing machine, then quenching and annealing, respectively.

**Microscopy.** The fracture surfaces etched with DMAC for 8 h were observed with A SHIMADZUSSX-550 scanning electron microscopy, operating at a 20 kV accelerating voltage. The surfaces were then gold-sputtered before scanning.

**Mechanical Testing.** Three-point flexural and tensile tests were performed on a Shimadzu AG-1universal testing machine without a strain gauge type extensometer at room temperature. The rates for tensile and flexural tests were 5 and 2 mm min<sup>-1</sup>, respectively. Impact strength was tested using a Izod impact



**Figure 3.** (a) Variation of dynamic storage modulus with temperature for quenched neat PES, PPS, and PES/PPS blends. (a) Neat PES, (b) PES/PPS/8/2, (c) PES/PPS/6/4, (d) PES/PPS/4/6, (e) PES/PPS/2/8, (f) Neat PPS; (b) Variation of dynamic storage modulus with temperature for annealed neat PES, PPS, and PES/PPS blends. (a) Neat PES, (b) PES/PPS/8/2, (c) PES/PPS/6/4, (d) PES/PPS/4/6, (e) PES/PPS/2/8, (f) Neat PPS.



**Figure 4.** SEM images of (a) PES; (b) PPS; (c) PES/PPS/8/2 etched; (d) PES/PPS/6/4 etched; (e) PES/PPS/4/6 etched; (f) PES/PPS/2/8 etched.

testing machine (Impact energy is  $2.5 \text{ kJ m}^{-2}$ ) with a method of GB/T1843–2008. Samples of flexural, tensile, and impact were obtained by Haake-Minijet under the pressure of 900 bar in the temperature range between 310 and  $350^\circ\text{C}$ . From stress–strain curves, we can directly obtain the tensile strength, flexural modulus, flexural strength, and impact strength. The data reported were the mean from five determinations.

## RESULTS AND DISCUSSION

### Thermal Stability

The thermal stabilities of pure polymers and different blend compositions were investigated by TGA shown in Figure 1(a,b) and the relevant data are listed in Table II. The test samples were first dried in a vacuum oven at  $90^\circ\text{C}$  for 10 h before processing so that we could observe stable curve without decline curve of water loss weight. Since the main chain of PES and PPS is composed of phenyl ring, they had excellent thermal stability. The heat resistance of PES was better than that of PPS. For quenched PES, the  $T_{d5\%}$  and  $T_{d10\%}$  were  $506.1^\circ\text{C}$  and  $522.7^\circ\text{C}$ , and the  $T_{d5\%}$  and  $T_{d10\%}$  of quenched PPS were  $469.1^\circ\text{C}$  and  $494.3^\circ\text{C}$ . The  $T_{d5\%}$  and  $T_{d10\%}$  of quenched PES/PPS blends decreased with increasing content of PPS accordingly. When the content of PPS exceeded 50%, the thermal stability of blends was less than the

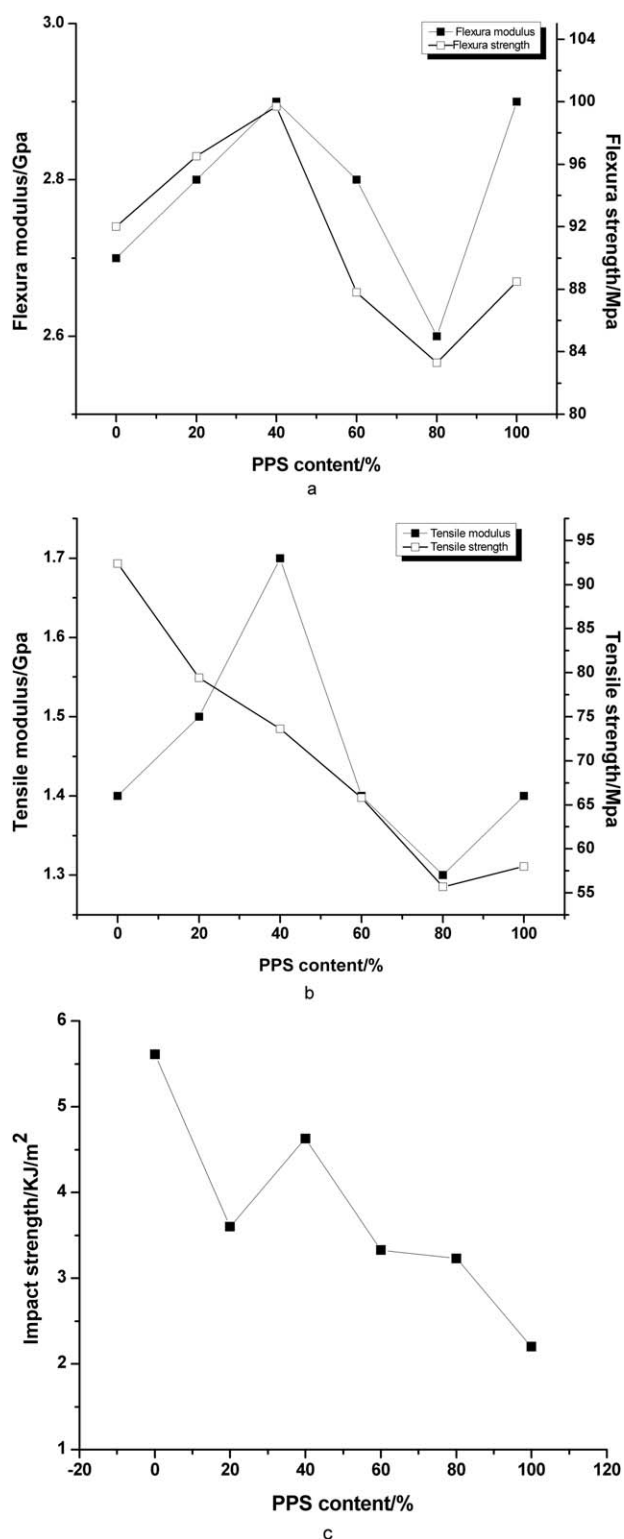
pure PPS, and the same phenomenon of annealed blends was also observed. In short, the incorporation of PES had a certain impact on the inherent thermal stability of PPS and the overall weight loss ( $T_{d5\%}$ ) remained approximately above  $460^\circ\text{C}$  for all samples and  $T_{d10\%}$  remained above  $480^\circ\text{C}$ .

### Dynamic Mechanical Analysis

**Glass Transition Temperature.** To confirm the compatibilization of PES and PPS, the variation of  $\tan \delta$  as a function of temperature of the PES/PPS blends was measured, as shown in Table III.  $T_g$  of PES-matrix in blends compared with pure PES decreased in both quenched and annealed samples; because of the addition of PPS, the free volume of the molecular chains of PES increased, which made the intermolecular forces between PES weakened. For PPS-matrix in blends, the  $T_g$  contrast with that of pure PPS increased slightly. Above all,  $T_{g1}$  and  $T_{g2}$  of blends shifted to the middle compared to pure PES and PPS which showed some compatibility between them. In addition,  $T_g$ 's in the quenched samples were a little lower than that in the annealed ones because annealing had a relatively long time to be in constant temperature which made products have enough time to crystallize so that the structure of samples were more regular and  $T_g$  was much higher.

**Table IV.** Mechanical Properties of PES/PPS Blends

Samples	Flexural modulus (GPa)	Flexura strength (MPa)	Tensile modulus (GPa)	Tensile strength (MPa)	Impact strength ( $\text{kJ m}^{-2}$ )
PES	2.7	92.0	1.4	92.4	5.61
PES/PPS 8/2	2.8	96.5	1.5	79.4	3.6
PES/PPS 6/4	2.9	99.7	1.7	73.6	4.63
PES/PPS 4/6	2.8	87.8	1.4	65.8	3.33
PES/PPS 2/8	2.6	83.3	1.3	55.7	3.23
PPS	2.9	88.5	1.4	58	2.2



**Figure 5.** (a) The curve of flexural strength and flexural strength of the blends with different contents of PPS; (b) the curve of tensile strength and tensile strength of the blends with different contents of PPS; (c) the curve of impact strength of the blends with different contents of PPS.

**Loss Modulus.** Figure 2 presents the loss modulus of each blending composites. It is clear that there was only one peak in the curves of neat PES and near PPS. For the blends, two peaks

were observed and they were close to each other to a certain extent. Furthermore, the quenched curve of neat PPS had the sharpest peak for the sake of  $T_g$  of PPS-matrix and the peaks were leveling off with the increase of PES content. There was also a sharp peak in quenched curve of neat PES and the peaks of PES-matrix in the curves of blends were leveling off with the decrease of PES content. For the annealed curve, the peaks of PPS-matrix were gentle because PPS had been partially crystallized during processing, strengthening the rigidity of the molecular chain.

**Storage Modulus.** The temperature dependence on dynamic storage modulus of pure PES and PPS along with PES/PPS blends are shown in Figure 3. The storage modulus of quenched neat PES was higher than that of neat PPS. Among all the blends, PES/PPS = 8/2 had the highest storage modulus at the temperature region less than 87°C. For the quenched samples, there was a sharp decrease of storage modulus due to the cold crystallization of PPS in the range of 90–145°C, and PES/PPS = 2/8 had the biggest extent of decline because of the maximum content of PPS resulting in a significant decrease of modulus. After 150°C, the storage modulus of blends enhanced slightly because of the presence of PES. Additionally, at above 225°C, it appeared a second drop of the storage modulus attributed to the  $T_g$  of PES. For the annealed blends samples, there were two steps of decrease and no rebound because of the crystallization of PPS during annealing process.

### Morphology

Figure 4 shows the scanning electron microscopy (SEM) micrograph of cryogenically fractured surface of PES/PPS binary blends with different weight ratios. To distinguish the PPS from PES, PES on the fracture surface was etched by DMAc before the SEM test was taken. The morphology of neat PES and PPS are shown in Figure 4(a,b) for comparison with blends. It appeared that PES was spherical or ellipsoidal in shape in the blends. PES spherical domains were dispersed in the PPS matrix because of the much higher melt viscosity of PES than PPS.<sup>22</sup> It is seen from Figure 4(c–f) that the PES domain size distribution was large and the PES particles were nonuniformly dispersed in the PPS matrix, which was due to the poor compatibility between PES and PPS phases. Moreover, the PES domain size was decreased with the increasing content of PPS. But the spherical morphology of PES in PES/PPS = 6/4 blends [Figure 4(d)] were relatively structured which made its impact properties much higher. The chemical nature of the components and the characteristics of the mixer used were two important factors that exert a significant influence on the morphology of the investigated blends.<sup>23</sup> PPS was a semi-crystalline thermoplastic resin while PES was an amorphous thermoplastic resin. On this basis, it was reasonable to assume that the interfacial tensions that were obtained in PES/PPS binary blends were large because of the different chemical nature of the blends components, which made interpolymer polar interactions across phase boundaries much harder, thus favoring a bad-dispersed morphology. On the other hand, although we used a parallel twin-screw extruder that was more suitable for processing powder, the interfacial tension was still not reduced.

### Mechanical and Impact Properties

Table IV shows the value of mechanical properties of blends. From Figure 5(a,b), we could observe that the flexural strength value for the pure PES sample was 92 MPa, while it gradually increased to a value of 99.7 MPa for composite with 40 wt % PPS content and then fell down to 83.3 MPa with the decreasing content of PES, the trend of flexural modulus value first increased then decreased with the increasing of PPS. The flexural modulus and flexural strength of PES/PPS = 6/4 blends were higher than that of others over the entire composition range. On the other hand, tensile strength gradually reduced with the increasing of PPS content and tensile modulus of PES/PPS = 6/4 blends (1.7 GPa) had a significant improvement compared to other components of the blend.

The impact strength of the neat PES, PPS, and PES/PPS blends are shown in Figure 5(c). Apparently, the impact strength of PPS was lower than that of both neat PES and PES/PPS blends. When the PES content was 60 wt %, the impact strength of blends was enhanced by 110% from 2.2 to 4.6 kJ m<sup>-2</sup> compared to that of neat PPS which could explain by SEM.

### CONCLUSION

In this work, the PES/PPS binary blends with different weight ratios were prepared by a parallel twin-screw extruder and subsequent injection molding, and their thermal stabilities, dynamic mechanical properties, morphology, and mechanical properties behavior were compared. The TGA experiments indicated that PES/PPS blends had excellent thermal stabilities with the  $T_{d5\%}$  above 460°C and the  $T_{d10\%}$  beyond 480°C both for quenched and annealed samples. The DMA curves and the SEM photographs evidenced that PES and PPS had some compatibility. Moreover, PES/PPS blends exhibited excellent mechanical properties, especially when PES/PPS = 6/4 where impact strength could be obviously improved by 110% and the thermal stability of PES/PPS = 6/4 blends was very outstanding. Besides, this weight ratio of blends also had excellent chemical resistance, dimensional stability, and processability.

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