Effect of different processing methods on PES/PPS melt blends

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ABSTRACT

Blends of polyether sulfone (PES) and polyphenylene sulfide (PPS) with different weight ratios (10/0, 7/3, 5/5, 3/7, 0/10) were prepared by melt extrusion using a twin-screw extruder. In this work, the thermal stabilities of blends were evaluated by TGA and the dynamic mechanical properties were investigated by means of DMA. The fracture surfaces were observed with a scanning electron microscopy. In addition, the mechanical property tests were also carried out to find out the effect of melt blending method on PES and PPS blends.

Keywords: PES, PPS, blends, twin-screw extruder, melt blending

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[1]. Thus it has attracted more and more attention among researchers in recent years.

Melt blending refers to a process that two or more kinds of polymeric materials, inorganic materials and modifying agent mix mechanically at a certain temperature**,** and eventually form a kind of new materials with mechanical, thermal, optical, and other performance improved[2]. By using this way we can integrate and optimize the performance of the original polymer, making blends system have more excellent and more comprehensive performance that in line with the required function. Modification of polymer blends is an important way to achieve polymer materials with composite and diversification performance and develop new varieties[3,4].

Both PES and PPS are the special engineering plastics that currently are applied, Chen Yang and Hanmin Zeng have studied their blends[5-8], but they did report it in detail. In this article, we aim to find out the effect of different melt method on PES and PPS blends.

Blend preparation

PES, PPS and their blends were first pre-mixed with a high-speed mixer respectively. The polymers were dried in a vacuum oven at 90 °C for 10 h before processing. And then the pre-dispersion mixture was blended by using a mini-Haake co-rotating twin-screw extruder at a screw speed of 80 rpm.

Characterization methods

Thermal gravimetric analysis

Thermal analysis was carried out in a TA instrument TGA Q2050 under N_2 atmosphere in the temperature range of 100 °C to 810 °C at a rate of 10 °C min^{-1}. The mass of samples was 5-10 mg.

Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was recorded on a TA Instruments DMA Q800 range from 50 °C to 300 °C at a frequency of 1 Hz and a heating rate of 5 °C min^{-1} in the tensile mode.

Microscopy

The fracture surfaces etched with DMAC for 8 h were observed with A SHIMADZUSSX-550 scanning electron microscopy, operating at a 15 KV accelerating Voltage. The surfaces were then gold-sputtered before scanning.

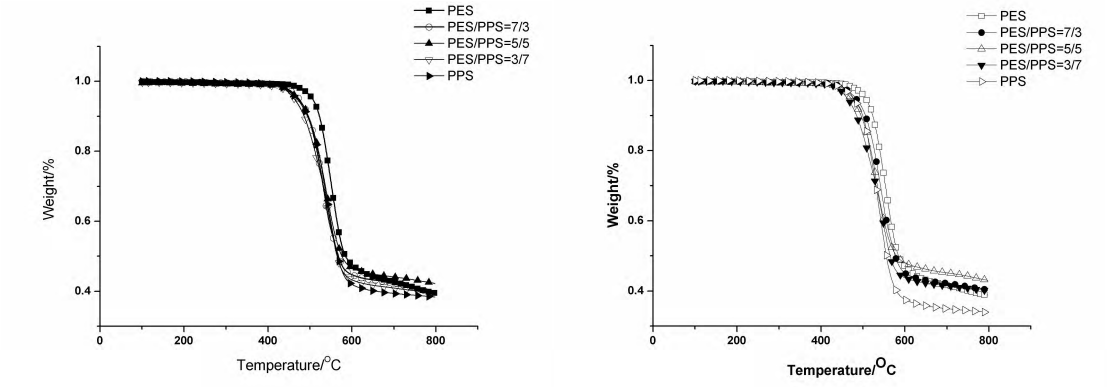
Mechanical testing

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^{-1}, respectively. Impact strength was tested using a Izod impact testing machine (Impact energy is 2.5 kJ m^{-2}) with a method of GB/T1843-2008. 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 Fig1a and b and the relevant data were listed in Table 1. Since the main chain of PES and PPS composed by 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°C and 523°C, while the T_{d5}% and T_{d10}% of quenched PPS were 469 ℃ and 494°C, respectively. The T_{d5}% and T_{d10}% of quenched PES/PPS blends decreased with increasing content 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°C for all samples and T_{d10}% remained above 480℃



I II

Fig.1 TGA curves of PES/PPS blends(I: quenched, II: annealed)

Table 1 Thermal stability of PES/PPS blends

Samples	Quenched		Annealed	
	T_{d5} (°C)	T_{d10} (°C)	T_{d5} (°C)	T_{d10} (°C)
10:0	506	523	506	524

7:3	486	509	483	506
5:5	471	496	471	495
3:7	462	485	462	485
0:10	469	494	477	500

Dynamic mechanical analysis

Glass transition temperature

To confirm the compatibilization of PES and PPS, the variation of tanδ as a function of temperature of the PES/PPS blends was measured, as shown in Table 2. Tg of PES- matrix in blends compared with pure PES decreased in both quenched and annealed samples, due to 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 Tg contrast with that of pure PPS increased slightly. Above all, Tg1 and Tg2 of blends shifted to the middle compared to pure PES and PPS which showed some compatibility between them. In addition, Tg in the quenched samples were a little lower than that in the anneal ones owing that annealing had a relatively long time to be constant temperature which made products have enough time to crystallize so that the structure of samples were more regular and Tg was much higher.

Table 2 Tg of PES/PPS blends

Samples	Quenched		Annealed	
	T_{g1} (°C)	T_{g2} (°C)	T_{g1} (°C)	T_{g2} (°C)
10:0	225	--	227	--
7:3	221	85	220	104
5:5	223	92	221	108
3:7	224	92	221	107
0:10	--	87	--	106

Loss modulus

Fig2 presented the loss modulus of each blending composites. it was 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 closed to each other to a certain extent. Furthermore, the quenched curve of neat PPS had the most sharp peak for the sake of Tg 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.

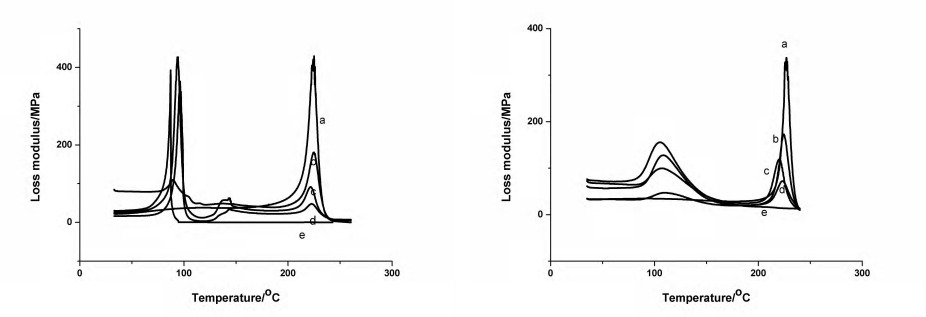


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Fig.2.a. Variation of Loss modulus for PES/PPS blends(I: quenched, II: annealed). (a: 10:0 ; b: 7:3; c: 5:5; d: 3:7; e: 0:10;)

Storage modulus

The temperature dependence on dynamic storage modulus of pure PES and PPS along with PES/PPS blends were shown in Fig3. The storage modulus of quenched neat PES was higher than that of neat PPS. 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=3/7 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 Tg 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.

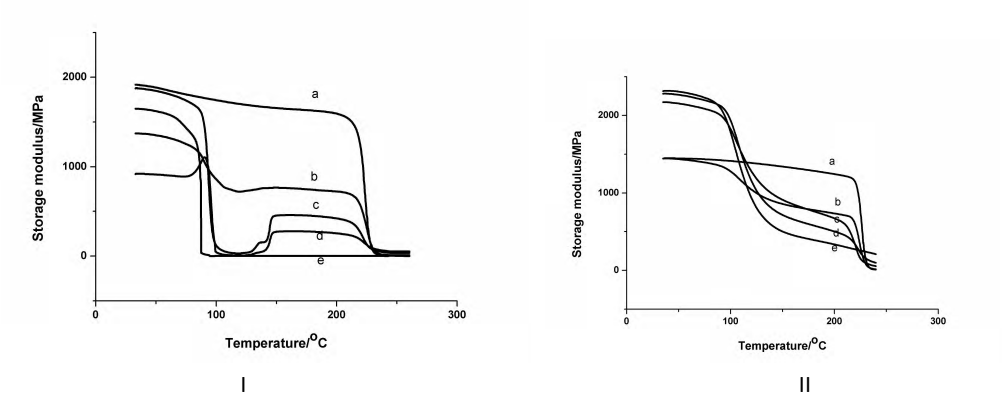

Fig.3 a. Variation of dynamic storage modulus with temperature for PES/PPS blends(I: quenched, II: annealed). (a: 10:0 ; b: 7:3; c: 5:5; d: 3:7; e: 0:10;)

Morphology

Fig.4 showed the 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 were shown in Fig.4 (a) and (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[9]. It was shown from Fig4(d)、(e) 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. But for Fig4(c) , PES was the continuous phase.

Moreover, the PES domain size was decreased with the increasing content of PPS. But the spherical morphology of PES in PES/PPS=5/5 blends (Fig4.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[10]. 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 favouring 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.

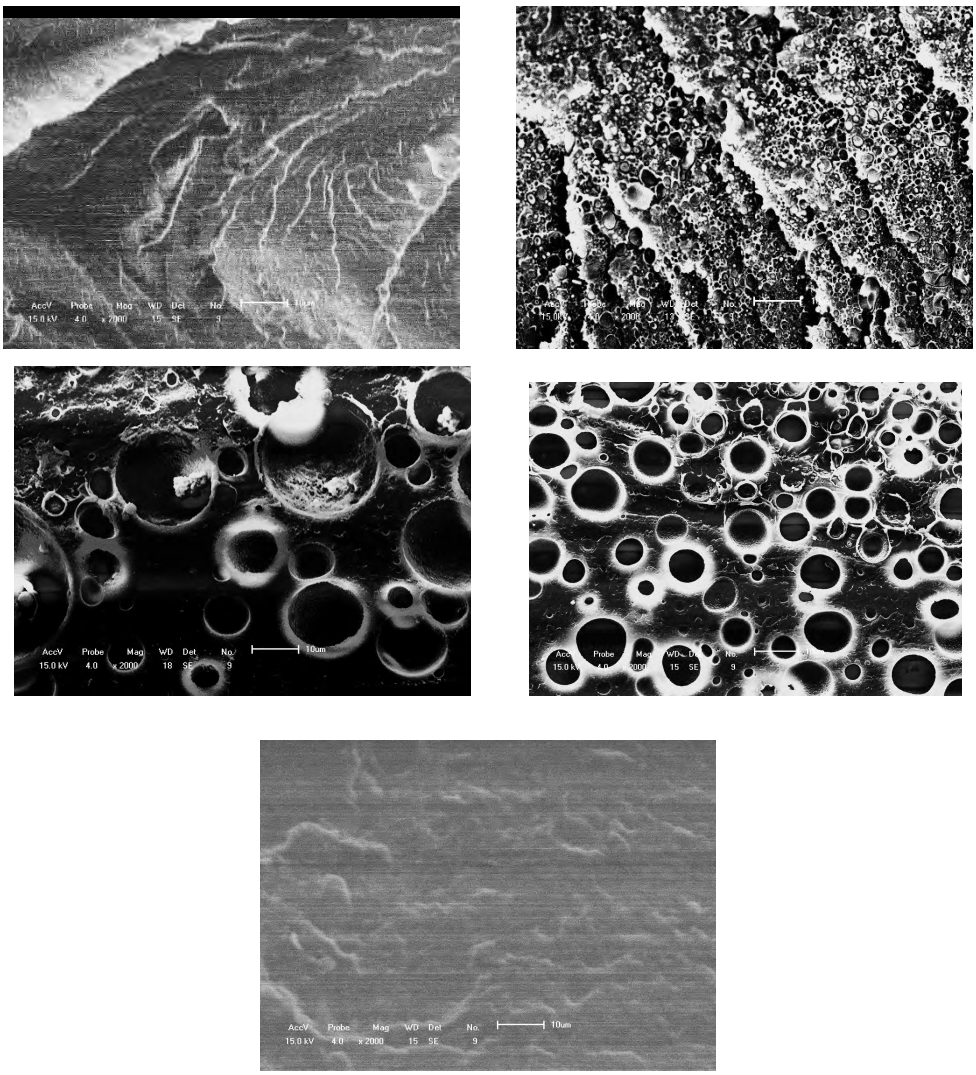

Fig.4 SEM images of etched PES/PPS blends (a: 10:0 ; b: 7:3; c: 5:5; d: 3:7; e: 0:10;)

Mechanical and impact properties

Table 3 showed the value of mechanical properties of blends. We could observe that the flexura strength value for the pure PES sample was 92 MPa, while it gradually decreased to a value of 89.2 MPa for composite with 70 wt% PPS content, the trend of flexural modulus value increased with the increasing of PPS. The flexural modulus and flexura strength of PES/PPS=5/5 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=5/5 blends (1.7 GPa) had a significant improvement compared to other components of the blend.

From the value of impact strength of the neat PES, PPS, and PES/PPS blends we could find the impact strength of PPS was lower than that of both neat PES and PES/PPS blends. When the PES content was 50 wt %, the impact strength of blends was enhanced by 60% from 2.2 to 3.5 kJ m^{-2} compared to that of neat PPS which could explain by SEM.

Table 3 Mechanical properties of PES/PPS blends

Samples	Flexural modulus (GPa)	Flexural strength (MPa)	Tensile modulus (GPa)	Tensile strength (MPa)	Impact strength (KJ/m^2)
10:0	2.7	92.0	1.4	92.4	5.6
7:3	2.9	90.0	1.5	78.3	3.3
5:5	3.0	92.6	1.7	70.5	3.5
3:7	3.0	89.2	1.4	63.7	3.3
0:10	2.9	88.5	1.4	58.0	2.2

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 stability, dynamic mechanical properties , morphology and mechanical properties behavior were compared. The TGA experiments indicated that PES/PPS blends had excellent thermal stability 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 have some compatibility. Moreover, PES/PPS blends exhibited excellent mechanical properties. We are also doing melt blending with other method, but for some reason we can not report it in this article.

REFERENCES

[1].J Choi and S. Lim. Studies of an epoxy- compatibilized poly(phenylene sulfide) /polycarbonate blend. J. Polymer .1997(38): 4401–4406.

[2].黄玉东. 聚合物表面与界面技术[M]. 北京: 化学工业出版社,2003: 94 - 95.

[3]. Li Zhaohui, Zhang X M. The Interfacial Tension and Morpholgy of Reactive Polymer Blends[J] . Materials Letters, 2001, 48(2) : 81.

[4]. Beshay A D, Kokta B V, Danesult C. Use of wood fibers in thermoplastics composites Ⅱ: Polyethylene [J] . Polymer Composites,1985(6) : 261- 271.

[5]. H.M. Zeng and C. Yang. The crystalline morphologies of polyphenylene sulfide and its blends with polyether sulfone. J. Acta Polym. Sinica, (Chin.) 1989(4):409-414..

[6]. H.M. Zeng and C. Yang. Investigation on the crystallization kinetics of polyphenylene sulfide and its blends with polyether sulfone. J. Acta Polym. Sinica, (Chin.) 1989(5):538-543.

[7]. Chen Yang and HanMin Zeng. Study on PPS/PES blends prepared by coprecipitation technique. J. Polymeric materials science and engineering. (Chin.)1992(4):81-87

[8]. Chen Yang and HanMin Zeng. Study on the interface modification of PPS/PES blends. J. Aerospace material process. (Chin.)1993(8):19-22

[9].Y. Li. Novel morphologies of poly(phenylene oxide) (PPO)/polyamide 6(PA6) blend nanocomposites. J. Polymer. 2004(45):7381-7388.

[10]. Ramiro Dell'Erba. Immiscible polymer blends of semicrystalline biocompatible components: thermal properties and phase morphology analysis of PLLA/PCL blends. J. Polymer. 2001(42):7831-7840.