

Compatibilization of Ethylene/Maleic Anhydride/Glycidyl Methacrylate Terpolymer for Poly(phenylene sulfide)/Poly(amide-66) Blends

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ABSTRACT: In this article, a terpolymer of ethylene, maleic anhydride, and glycidyl methacrylate (EMG) was used to enhance the compatibilization between poly(phenylene sulfide) (PPS) and polyamide-66 (PA66). The mechanical properties, morphology, crystalline and melting behavior, and rheology of blends were discussed. The results showed that EMG was a good compatibilizer for PPS and PA66 through chemical reaction with them. The new generated polymer could prevent the aggregation of dispersed particles and reinforce the interface bonding. In addition,

it could not only act as a nucleating agent for PA66 to refine its spherulites and improve its crystallinity but also promote the apparent viscosity of blends and enhance the non-Newtonian behavior. The results will be useful to make high performance PPS/PA66 alloy with low cost and enlarge the application scope of PPS and PA66 resin. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 325–332, 2012

Key words: poly(phenylene sulfide); polyamide 66; compatibilizer; alloy

INTRODUCTION

On the chain of poly(phenylene sulfide) (PPS), the sulphur atom is attached to the contraposition of benzene ring which makes it rigid. Polyphenylene sulfide displays some special features. For example, polyphenylene sulfide has a high short-term heat distortion temperature of 260°C, and it is one of the thermoplastic plastics that own the best thermal stability. Furthermore, PPS has high stiffness and mechanical strength. Although it has perfect creep resistance and fatigue resistance, PPS still shows poor toughness and poor resistance to impact which need to be improved.

Regarding the weaknesses of PPS, there have been papers on the properties of PPS, such as crystallization behavior,^{1–3} rheological properties in a melt^{4,5} state, and crystal structure.⁶ An effective method of modification is melt blending of PPS with other resin^{3,7–11} such as polyamide66 (PA66). Polyamide which is inexpensive is a known polymer with good mechanical properties. Especially, Polyamide 66 has excellent processing performance and high resistance to abrasion. In this study, polyamide 66 was added

into PPS matrix and expected to improve the friability of PPS and reduce cost. The compounding of these two polymers would provide an excellent alloy with combined properties. This alloy would be a good material for making storage tanks and chemical liquid handling pipeline.

In the past, the blending of PPS and PA66 were studied extensively. Lee and Chun¹² studied the mechanical properties and fracture morphology of the alloy and the effects of the content of PA66 on mechanical properties of the alloy. They found that when PA66 was under 30%, the alloy could keep the thermal stabilization. But when the content of PA66 is over 30%, the thermal stabilization dramatically decreased. The tensile strength got the minimum at the content of 30% PA66, and the impact strength significantly increased when the content of PA66 exceeded 30%. Jung and Toshiaki¹³ found that PPS and PA46 were immiscible thermodynamically, but they were partially compatible in certain ratio and shear rate. PPS and PA66 were immiscible thermodynamically,¹³ so an effective compatibilizer is necessary for the improvement of mechanical performance of this blend system. There were a few reports about the compatibilization of the system of PPS/PA66. Gleim et al.¹⁴ made a multilayer composite material which was made from polyphenylene sulfide, polyamide, and ethylene/glycidyl methacrylate (EGMA). This alloy had high strength, high chemical resistance, and low permeation to chemicals and gas. But they did not have a comprehensive interpretation about the compatibilization of EGMA. Zhang

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et al.¹⁵ added poly(ethylene-stat-methacrylate) into PPS/PA66 blends, and they expected to modify the interfacial interplay of the system. They discussed the crystallization of the system. But what a pity was that they did not study the mechanical properties and morphology. Tang et al.¹⁶ studied the toughening and compatibilization of PPS/PA66 blended with SEBS and maleic anhydride grafted SEBS triblock copolymers. They reported that PA66-co-SEBS-g-MA formed *in situ* during melt extrusion played a key role between interfaces.

In this article, a terpolymer of ethylene, maleic anhydride, and glycidyl methacrylate (EMG) was firstly used as a compatibilizer for PPS and PA66 system. In the melt blending process, the epoxy group of EMG can react with the -SH group in PPS, and both epoxy group and anhydride group of EMG can easily react with the carboxyl and amine groups on the chain of PA66. So EMG is expected to be an effective compatibilizer for PPS/PA66. In our work, the EMG was added into the blend system of PPS and PA66 with different ways, and some properties such as mechanical performance, morphology, crystalline and melting behavior,^{17,18} and rheology were systematically studied. The results will be useful to make high performance PPS/PA66 alloy with low cost and enlarge the application scope of PPS and PA66 resin.

EXPERIMENTAL

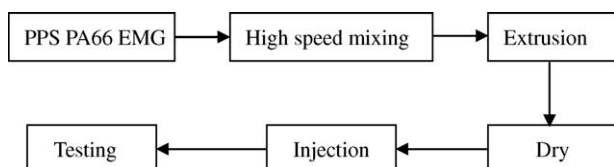
Materials

Polyphenylene sulfide in a powder form ($M_w = 48,000$) was purchased from Sichuan Deyang Chemical Co. (Sichuan, China) and polyamide-66 (EPR-27) ($M_w = 20,000$) was supplied by China ShenMa Group (Henan, China). Terpolymer of EMG (ethylene/maleic anhydride/glycidyl methacrylate = 86/8/6 terpolymer) was from Shenyang Ketong (Shenyang, China).

Preparation

Before blending, all resins should be fully dry, for example, PPS resin should be kept at 90°C for 6 h, PA66 and EMG should be kept at 80°C and 40°C for 12 h, respectively.

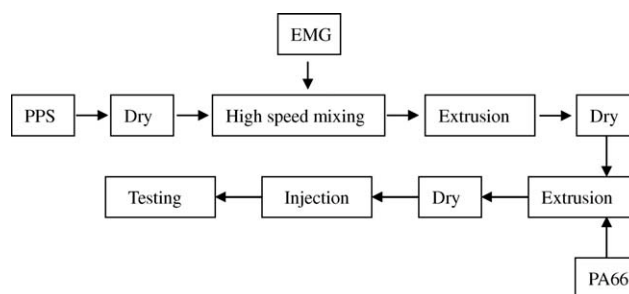
Two ways of blending were adopted, the first way was an one-step blending called method (1), which was shown as follows:



Therein, PPS, PA66, and EMG were together mixed in a high-speed mixer, and then melt blending was

conducted through a twin-screw extruder (SHJ-35, Nanjing Haote Machinery). The barrel temperatures were set at 220°C/235°C/250°C/265°C/280°C/290°C/295°C/295°C/300°C/300°C from hopper to die, and the screw speed was 150 rpm. The L/D ratio of the screws was 40, and $D = 25$ mm. The filaments obtained on extrusion were immediately quenched in water, and then cut into pellets by a pelletizer. After compounding, the blends were injection moulded into test bars using a PS40E5ASE injection moulding machine. The injection temperature was chosen as 280°C/290°C/290°C/290°C/285°C from hopper to nozzle.

The other way was a two-step refining called method (2) as follows:



where EMG and PPS were firstly blended and granulated. Then, the pellets were mixed with PA66 and extruded. The processing parameters of extrusion and injection were set as the same of method (1).

Mechanical property measurements

The measurement of tensile strength was according to GB/T 1040-2006, where the tensile rate was 10 mm/min; the notched impact strength was according to GB/T 1843-1996. The specimens were made using injection molding machine.

Scanning electron microscopy

The morphology of blends was observed using scanning electron microscope (SEM). The specimen was brittle fractured after dipping in liquid nitrogen for 15 min and then immersed in acid solvent to etch away the PA66 phase. The specimen was coated with gold and examined by an X-650 Hitachi SEM at 20 KV.

Differential scanning calorimetry

The sample was prepared by method (2). The weight of the sample which was surrounded in nitrogen atmosphere was 5–6 mg. It was heated from room temperature to 310°C (pure PA66 was 270°C) as a speed of 10°C/min, stayed 5 min to eliminate thermal history, and then cooled to 70°C as a speed of

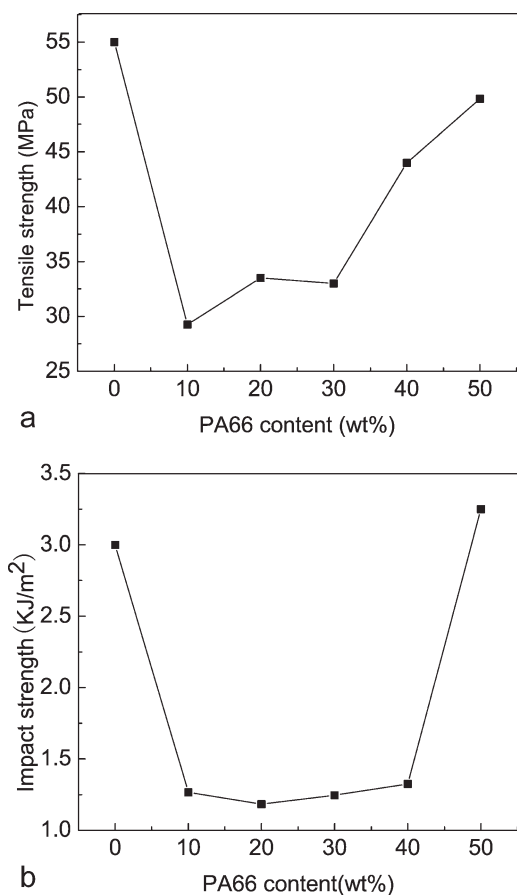


Figure 1 Effect of PA66 content on tensile strength (A) and impact strength (B) of PPS/PA66 blends without compatibilizer.

10°C/min. The heating and cooling curves were recorded simultaneously.

Rheological measurement

The rheological property was measured using a capillary rheometer (RHEOGRAPH2002 GOTTFERT, Germany). The diameter of the capillary was 0.1 cm and the L/D ratio of the capillary was 30. After a warming up period of 4 min, the melt was extruded through the capillary. The speed of extrusion, temperature, and apparent viscosity were recorded automatically by a recorder apparatus.

RESULTS AND DISCUSSION

Mechanical properties

The effects of PA66 content on mechanical properties of blends without addition of compatibilizer are investigated first. It can be seen from Figure 1 that both tensile strength and impact strength decrease in the beginning, and then increase with the content of PA66. When PA66 is less than 10 wt %, the two

show a significant downward trend. However, the tensile strength increases dramatically when PA66 is more than 30 wt % and the impact strength goes up when PA66 is more than 40 wt %. Combined with the SEM observation later, it can be attributed to the fact that the size of PA66 as a dispersed phase gets larger and larger with increasing PA66 content. There is a clear interface between these two immiscible phases, and it has destroyed the monolithic construction of PPS, so that the matrix cannot effectively transfer the outside stress loaded. However, as increasing PA66 content up to 50 wt %, PA66 phase becomes continue, and the blends display a co-continue morphology where two-phase interface gets the theoretically maximum area. Although there is poor compatibility between the two phases, stress can be transmitted effectively.^{19,20} As a consequence, the mechanical performance is improved again.

To investigate the compatibilization of EMG, the content of PA66 was kept at 40 wt %, and the blending was conducted by method (2) described in experiment section. The effects of EMG on mechanical properties are shown in Figure 2. It is illustrated

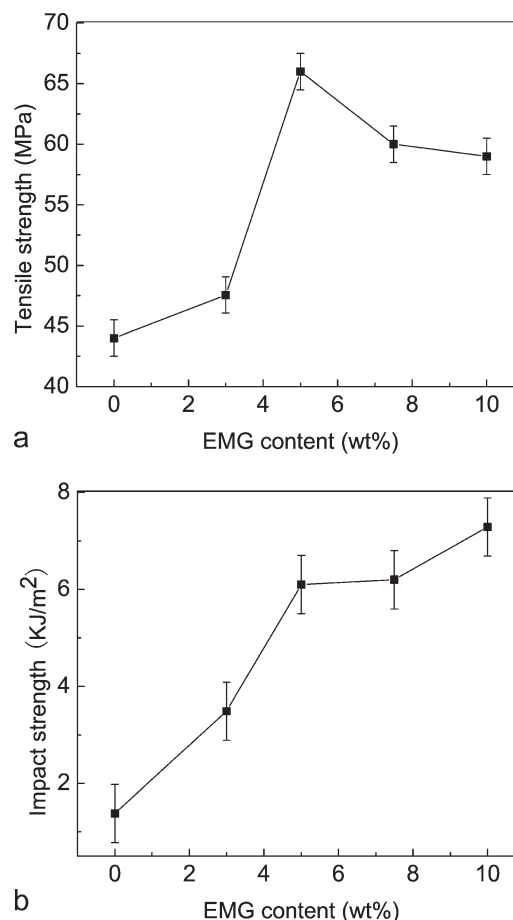


Figure 2 Effect of EMG content on tensile strength (A) and impact strength (B) of PPS/PA66 (content of PA66 is kept at 40 wt %).

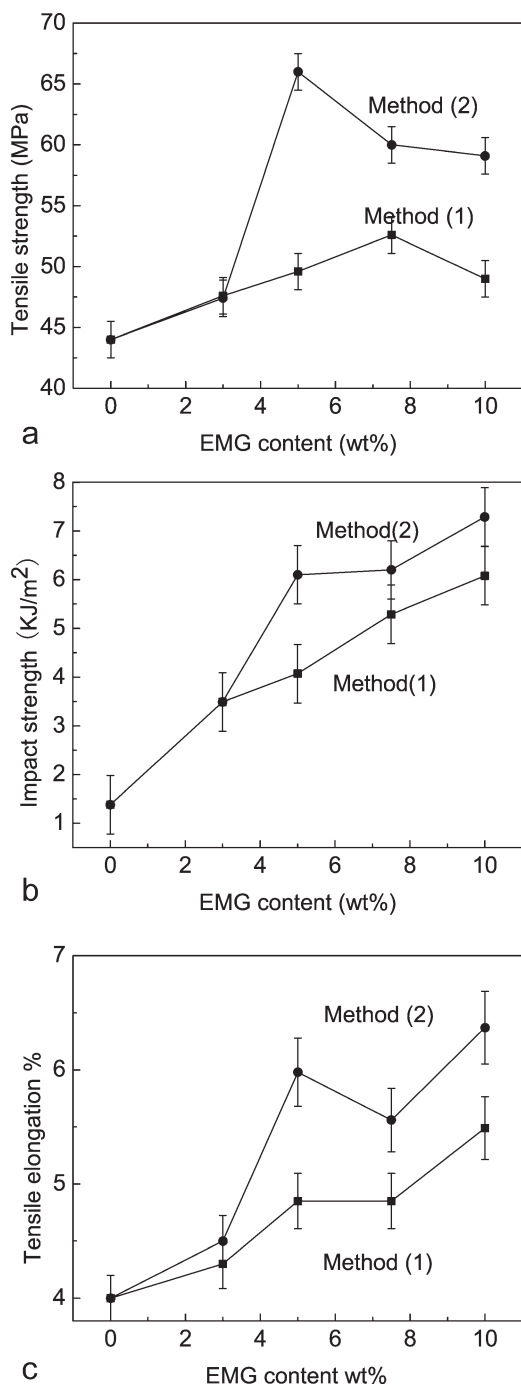


Figure 3 Effects of processing method on tensile strength (A), impact strength (B) and tensile elongation (C) of PPS/PA66 (content of PA66 is kept at 40 wt %).

that both tensile strength and impacted strength increase with EMG content compared with the blend without compatibilizer. Especially, the impact strength rises linearly with EMG content. When 10 wt % of EMG was added, the impact strength increased from 1.4 KJ/m² to 7.4 KJ/m². However, as far as the tensile strength, it can be seen from Figure 2(A) that the tensile strength did not always go up with EMG, that is, it reached the highest point at 5

wt % EMG and then dropped. So, 5 wt % of EMG is the best content for PPS/PA66 in our experiments. When it exceeded 5 wt %, EMG as a flexible polymer whose strength and modulus were much lower than PPS and PA66 would pull down the whole tensile strength of alloy.

The processing methods were compared in our work. It is illustrated in Figure 3 that whenever which one is used, the addition of EMG will always be beneficial to the improvement of mechanical properties. However, Figure 3 also obviously shows that the alloy by method (2) has higher mechanical performance than method (1) due to more evenly dispersion of EMG in blends through two-step process. Meanwhile, good dispersion of EMG will contribute to the reduction of compatibilizer, which is verified in Figure 3(A). Therein, the tensile strength of alloy through method (2) reaches the peak at 5 wt % EMG while that through method (1) gets the highest point at 7.5 wt % EMG. Different from the variation of tensile strength of alloy with EMG, the impact strength and elongation increase with the content of EMG as shown in Figure 3(B,C) by whatever method. EMG is not only a compatibilizer for PPS/PA66 but also a good elastomer. So, EMG can toughen PPS/PA66 effectively under the influence of strong interfacial interaction with PPS and PA66. If EMG did not act as a compatibilizer for PPS/PA66 system, it would usually lower the tensile strength as an elastomer. However, the result showed in Figure 3(A) negated the assumption.

Morphology

Figure 4 shows the morphology of impact fractured surfaces of PPS/PA66 blends without etched by method (2). It is illustrated from Figure 4(A) that the PA66 got a spherical dispersed phase distribution in PPS matrix, two-phase interface was clear, and the dispersed particles had an obvious shedding phenomenon which indicated they were not compatible. The alloy did not get a good interface adhesion and there was almost brittle fracture.

When EMG was added, different morphology occurred. The two-phase interface became blurred with the content of EMG increased. There was hardly any shedding phenomenon of dispersed particles. Fracture occurred in the continuous phase which was consistent with mechanical properties analysis. The phenomena turned more obvious with the content of EMG increased.

Figure 5 shows the morphology of PPS/PA66, where the holes represent the PA66 particles etched by acid. It can be seen from Figure 5(A) that the minor phase distributed randomly in the form of particle in matrix without compatibilizer and the average particle size was some large (about 1 μ m).

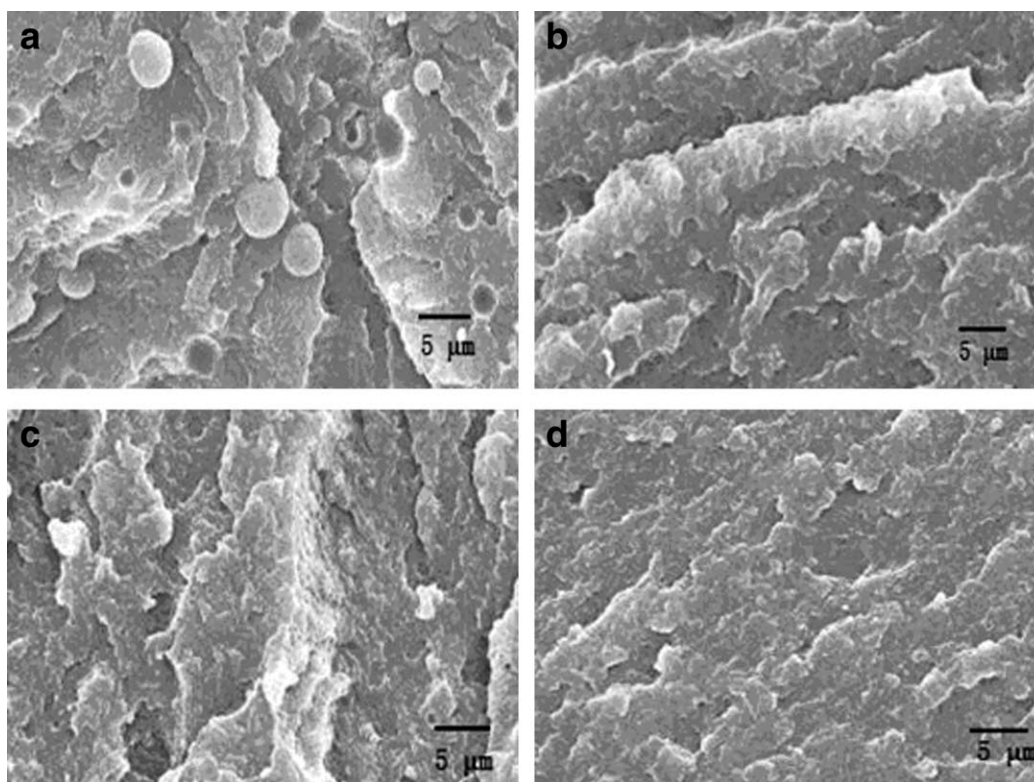


Figure 4 SEM of PPS/PA66 with different content of EMG (no etched).

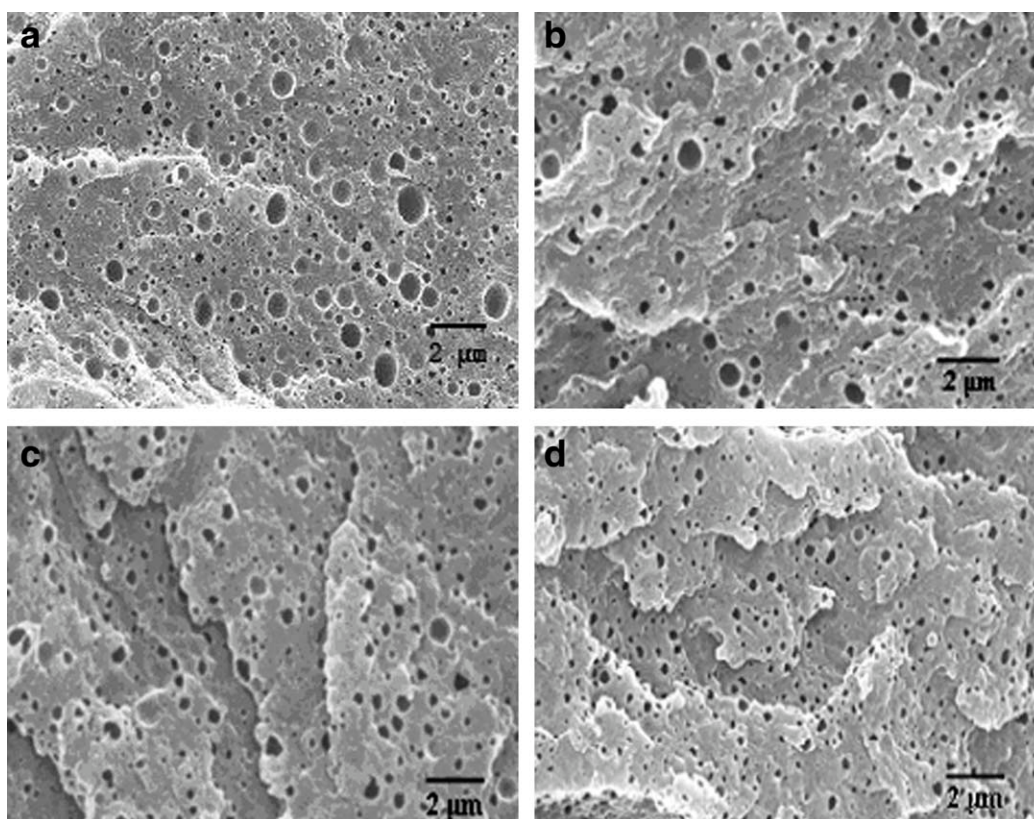


Figure 5 SEM of PPS/PA66 with different content of EMG (etched).

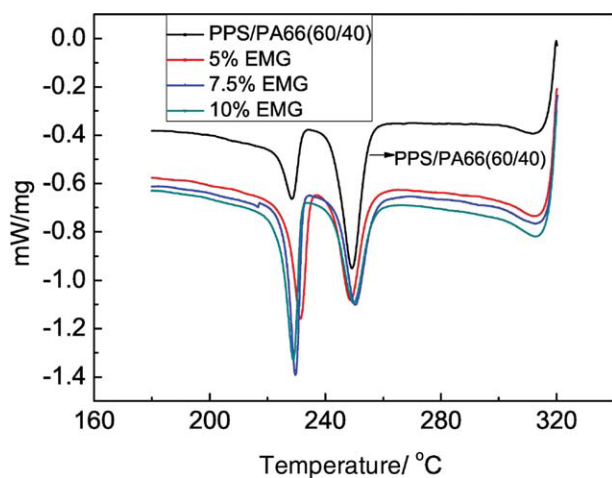


Figure 6 Crystallization curves of alloy with different content of EMG [Color figure can be viewed in the online issue, which is available at www.onlinelibrary.wiley.com].

With the addition of EMG, the compatibilizer reduced the surface tension of dispersed phase, so the particles broke more easily, and the size decreased. Because of the spatial stabilizing role of compatibilizer, it can prevent the aggregation of dispersed particles and further reduce the size of dispersed phase illustrated in Figure 5(B–D). The sizes of dispersed particles become smaller and smaller and distributed more uniformly which can inhibit the crack growth effectively.¹⁸

Both mechanical property and morphology indicate that EMG is a good compatibilizer in PPS and PA66 system. The obscure interfaces observed from Figure 4 indicate that good compatibility can be achieved between PPS and PA66 with the addition of EMG. This is owed to the special structure of EMG. A few studies about the reaction of the system have been reported. The maleic anhydride group of EMG can react with the terminal amino group of PA66 during processing.¹⁶ On the chain of EMG, the epoxy group can react with the -SH group in PPS.²¹ In addition, it is known that epoxy group can easily react with terminal amino group of PA66. So, a new polymer PPS-EMG-PA66 may be generated in the process of blending and enhance the interface bonding force between PPS and PA66. The reactions are shown as follows:

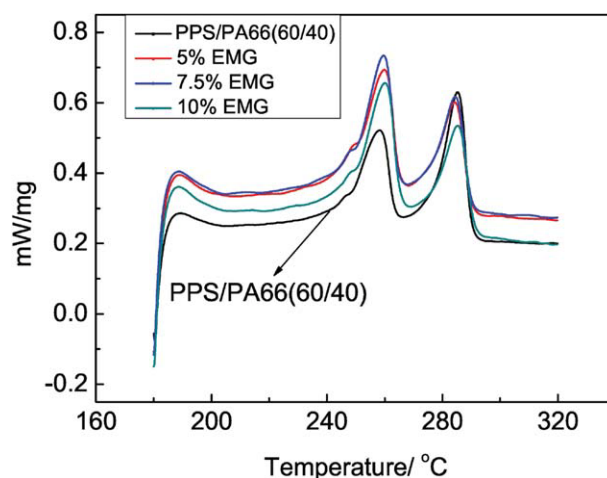
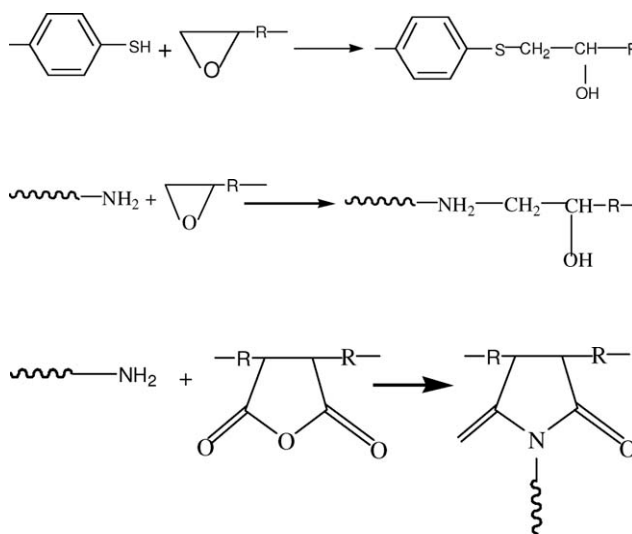


Figure 7 Melting curves of alloy with different content of EMG [Color figure can be viewed in the online issue, which is available at www.onlinelibrary.wiley.com].



Crystalline and melting behavior

PA66 and PPS are crystalline polymers, so the compatibilizer or new generated polymer may affect the crystalline behavior of PA66 and PPS. Figure 6 records the crystallization curves of blends. Detailed crystallization parameters are listed in Table I. The enthalpies were calculated from the integration on the curves. The enthalpy of unit mass was the ratio of the integration calculated by the software of NETZSCH and the weight listed as above about 5–6 mg.

It can be seen that with the addition of EMG, the crystallization temperature (T_c) and crystallinity (crystallization enthalpy ΔH_c) of PA66 have increased, particularly the increase of crystallinity is obvious. The crystallization enthalpy of PA66 increases from 23.69 J/g to 54.63 J/g, meaning a

TABLE I
Crystallization Parameters of the Alloy with Different Content of EMG

	T_c (°C)		ΔH_c (J/g)	
	PA66	PPS	PA66	PPS
PPS/PA66(60/40)	229.5	251.2	23.69	45.58
EMG (5%)	231.4	248.7	44.7	39.82
EMG (7.5%)	230.2	250.3	53	43.47
EMG (10%)	229.9	249.7	54.63	43.96

TABLE II
Melting Parameters of the Alloy with Different Content of EMG

	T_m (°C)		ΔH_m (J/g)	
	PA66	PPS	PA66	PPS
PPS/PA66(60/40)	258.5	285.3	45.68	41.10
EMG (5%)	259.9	284.3	59.35	29.16
EMG (7.5%)	259.6	284.5	59.55	31.35
EMG (10%)	260.2	285.4	63.63	31.72

more than doubled increase in crystallinity. The EMG or new generated polymer from the system of PPS/EMG/PA66 may act as a nucleating agent for PA66 which can promote the nucleation and crystallinity,^{1,2,22,23} and many small spherulites are generated. On the contrary, with the addition of EMG, the crystalline temperature and crystallinity of PPS have decreased a little. It indicated that the compatibilizer had prevented PPS from crystallizing.

The melting behavior of alloy further confirms above judgment. It can be seen from Figure 7 and Table II that the melting temperature (T_m) of PPS changed little but the melting enthalpy (ΔH_m) decreased significantly from 41.10 J/g to 31.72 J/g with the addition of EMG, indicating that the crystallinity of PPS decreased and EMG prevented PPS from crystallizing. The melting enthalpy of PA66 increases from 45.68 J/g to 63.63 J/g with the addition of EMG, which again confirms the nucleation of EMG or new generated polymer from PPS/EMG/PA66 for PA66.

Rheology

The relationship between apparent viscosity and shear rate at a certain temperature (295°C) is shown in Figure 8. PPS/PA66/EMG alloy, like most of polymer fluid, is non-Newtonian fluid and shows

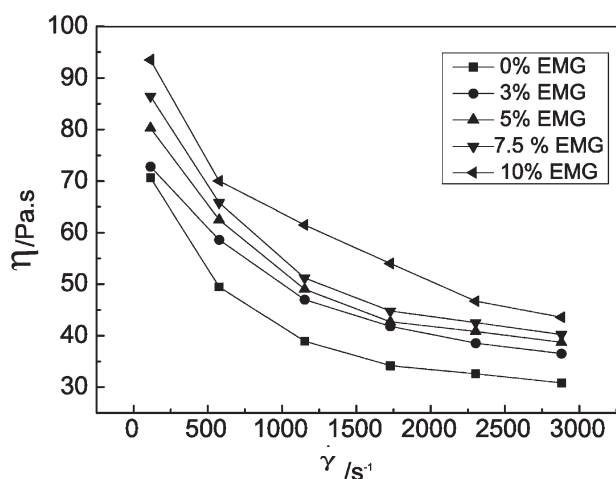


Figure 8 Viscosity curve of alloys with different content of EMG at 295°C.

TABLE III
Variation of Non-Newtonian Index with the Content of EMG

Content of EMG (wt %)	0	3	5	7.5	10
Non-Newtonian index (n)	0.72	0.68	0.64	0.64	0.61

pseudoplastic rheological properties, that is, its apparent viscosity increases with decreasing shear rate. However, in different shear rates, this change will have a very different trend. In the relatively low shear rate, the “shear thinning” is very significant, and when the shear rate is greater than a certain value, the “shear thinning” phenomenon will be reduced to some extent.

In addition, it can also be seen from Figure 8 that at the same temperature (295°C), the viscosity of blends will be significantly increased after the addition of compatibilizer. It can be explained in two ways: on the one hand, the compatibilizer will be distributed at the interface between PPS and PA66, and react with them to improve the interface bonding. So, the flow of polymer alloy becomes more difficult, and the viscosity increases. On the other hand, the compatibilizer with the chemical reaction between PPS and PA66 will play a similar role to improve the molecular weight of PPS and PA66, which will enhance the viscosity of the blend.^{24,25}

Non-Newtonian index is very useful to describe the viscoelasticity of polymer. Generally, the larger the viscoelasticity of polymer is, the smaller its non-Newtonian index is. As shown in Table III, with the addition of EMG, the non-Newtonian index is gradually reduced, indicating that the non-Newtonian behavior has been enhanced by EMG. Shear stress and shear rate is further from the linear relationship. The EMG has enhanced the viscoelasticity of alloy by chemical reaction with PPS and PA66.

CONCLUSION

PPS and PA66 were immiscible thermodynamically, so a terpolymer of EMG was used to enhance the compatibilization between PPS and PA66. The results showed that a little content of EMG, i.e., 5 wt %, could improve the mechanical properties of blends greatly. The SEM also indicated that the compatibilizer prevented the aggregation of dispersed particles and further reduced the surface tension and the size of the dispersed phase which made the particles get a uniform distribution. EMG was a good compatibilizer in the PPS/PA66 system.

EMG could react with PPS and PA66 and got a new grafted polymer, which could not only act as a nucleating agent for PA66 to refine its spherulites and improve its crystallinity but also promote the

apparent viscosity of blends and enhance the non-Newtonian behavior.

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