

Characterization and Properties of sPS/PET/SsPS-K Engineering Plastic Alloys

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ABSTRACT: The compatibility, crystallization behavior, and mechanical properties of syndiotactic polystyrene (sPS)/polyester (PET)/potassium salt of sulfonated syndiotactic polystyrene (SsPS-K) were investigated. DMA results showed that all the alloys showed one T_g and the half-peak width of the sPS/PET/SsPS-K alloys became narrower compared with that of sPS/PET alloys, which decreased with an increasing content of the SsPS-K ionomer. The results of DSC showed that the T_m of sPS and PET of the alloys was similar to those of the pure materials and did not change with the content of the SsPS-K ionomer, while the initial crystallization temperature (T_0) and crystallization temperature at peak (T_p) increased. The crystallization velocity of PET increased with an increasing content of SsPS-K. The TMA results showed that the alloys could retain the perfect heat proof property of sPS. SEM micrographs showed that the addition of SsPS-K could reduce the PET domain dimen-

sion and enhance the adhesion between the PET domains and the matrix. With an increasing content of SsPS-K, the PET domain dimension was reduced continuously and dispersed more evenly. The ternary alloys had better mechanical properties and significantly higher unnotched Izod impact strength than those of the alloys without SsPS-K. When the weight ratio of sPS/PET/SsPS-K was 85/15/4, the impact strength reached a maximum of 11.5 kJ/m², which was about three times that of pure sPS, and still had a higher tensile strength, flexural strength, and storage modulus, which were 38.8, 54.2, and 1.55×10^4 MPa, respectively. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 656–661, 2002

Key words: potassium salt of sulfonated syndiotactic polystyrene ionomer (SsPS-K); engineering plastic alloy; ionomer; compatibility

INTRODUCTION

A polymer alloy is composed of more than two polymers, which not only has the properties of the components, but also has new and perfect properties through blending. Since the compatibility between most polymers is poor and the adhesion between the interfaces is less, which are the first destroyed domains, the properties of alloys will not reach our object. To improve the compatibility, a compatilization agent is added. Since ionomers have ion groups, which lead to special interactions between different polymers, the compatibility of components is improved and give alloys ideal properties.^{1,2}

Syndiotactic polystyrene (sPS) polymerized by a newly metalline catalyst is a crystal engineering plastic. sPS has a rapid crystallization velocity, better crystallization property, chemical causticity resistance, and so on, especially under high temperature; it can still keep the properties at room temperature, so it has wide utility.^{3–5} Because of the existence of the benzene ring in the sPS molecular chain and the perfect struc-

ture, it has a lower impact strength and its toughness needs to be improved.

Crystal polyester (PET) is a general engineering plastics and its production is only lower than that of PA. It has high strength and a soft temperature, while its crystallization velocity is lower and its processing property is poor. Because of the different polarities of sPS and PET, which leads to poor compatibility between them, the properties of sPS/PET alloys cannot be ideal and still have a lower impact strength. In this article, sPS/PET/SsPS-K engineering plastic alloys were made and their compatibility, crystallization behavior, mechanical properties, etc., were investigated.

EXPERIMENTAL

Materials

The sPS used in these studies was obtained from the Shanghai Petrochemical Institute (Shanghai, China).⁶ The syndiotactic unit of sPS was greater than 95 mol %, the average molecular weight was 32×10^4 g/mol, and the melting temperature was about 270°C. The content of β -sPS was more than that of α -sPS.

PET was obtained from the Shantou Polyester Factory (Shantou, China), which was vacuum oven-dried at 80°C for 1 week prior to use. Sulfonated syndiotactic polystyrene (SsPS-K) was prepared in our labora-

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tory. The degree of sulfonation used in these studies was 5.45 mol %.

Melt blending

An XSS-300 torque rheometer was used to prepare blends by molten mixing at 290°C and 32 rpm under 5 kg. PET and SsPS-K were first added, and after the torque was stable, sPS was added. All samples were blended for 10 min and kept at a constant torque for 3 min. IRGANOX1010 (0.1 wt %) was added as an antioxidant to minimize oxidative degradation during blending. The weight ratio of sPS/PET was 85/15 for all the alloys.

Dynamic mechanical analysis (DMA)

A TA Instru2ments DMA-2980 dynamical mechanical analyzer was used to study the dynamical mechanical properties of the alloys at a heating rate of 5°C/min, amplitude of 3 μm , and frequency of 1 Hz.

Thermal analysis

A Perkin-Elmer DSC-7 was used to study the thermal properties of the alloys under a nitrogen atmosphere. All samples were heated to 290°C and isothermally for 10 min and then cooled to 30°C, all at a rate of 10°C/min.

Thermal mechanical analysis (TMA)

A TA Instruments DMA-2980 dynamical mechanical analyzer was used to study the thermal mechanical properties of the alloys at a heating rate of 5°C/min and pressure of 9.8 N.

Scanning electron microscopy (SEM)

A Hitachi S520 scanning electron microscope was used to study the morphology of the surface of fractured samples and the surface was coated with gold.

Unnotched Izod impact strength testing

A VEB Werkstoffprüfmaschinen Leipzig Izod impact machine made in Germany was used to study the unnotched impact strength of the blends. All samples were equilibrated under an ambient condition (25°C) for at least 2 days before testing.

Flexural strength testing

An AG-1 10-kN electron pull machine made by Shimadzu of Japan was used to study the flexural strength of alloys. All samples were treated as above and the span was 30 mm. The rate was 50 mm/min.

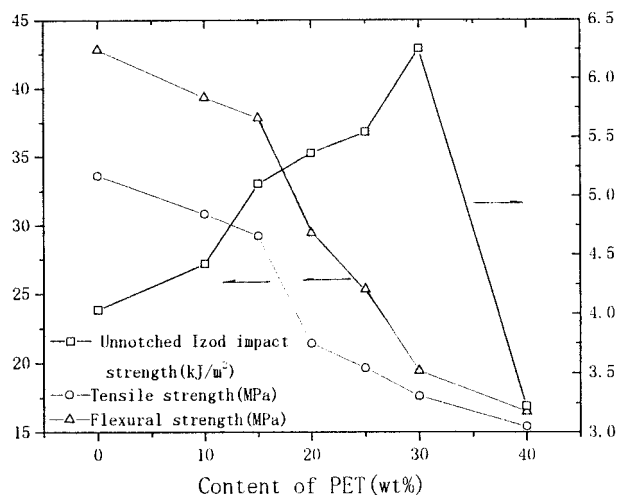


Figure 1 Mechanical properties of sPS/PET alloys.

Tensile strength testing

A LJ-500 tensile strength testing machine made by the Guangzhou Material Testing Machine Factory was used to study the tensile strength. The tensile rate was 50 mm/min.

RESULTS AND DISCUSSION

Mechanical properties of sPS/PET alloys

Figure 1 shows the impact strength, tensile strength, and flexural strength of sPS/PET alloys with different weight ratios of sPS/PET. With an increasing content of PET, the tensile and flexural strengths decreased continuously and the impact strength increased at first, reached a maximum, and then decreased. Results of Figure 1 are listed in Table I. When the weight ratio of sPS/PET was 70/30, the impact strength reached a maximum of 6.2 kJ/m², which is about 1.5 times that of pure sPS, while the tensile and flexural strengths were only 17.6 and 19.4 MPa, lower than one-half those of pure sPS. The storage modulus was 1.03×10^4 MPa. When the weight ratio of sPS/PET was 85/15, all the mechanical properties were improved and the impact strength reached 5.1 kJ/m² and other properties changed slightly compared with pure sPS.

Mechanical properties of sPS/PET/SsPS-K alloys

Figure 2 shows the mechanical properties of sPS/PET/SsPS-K alloys with different contents of SsPS-K. From Figure 2, one can see that the ternary alloys have better properties than those of binary alloys, and had the maximum values. The results of Figure 2 are listed in Table I. When the content of SsPS-K was 4 parts, both toughness and rigidity were improved. The impact strength was 11.5 kJ/m², which is about three times that of pure sPS, while the tensile and flexural

TABLE I
Mechanical Properties of sPS/PET and sPS(85)/PET(15)/SsPS-K Polymer Alloys

sPS/PET/SsPS-K (wt %)	Unnotched Izod impact strength (kJ/m ²)	Tensile strength (MPa)	Flexural strength (MPa)	Storage modulus (10 ⁴ MPa)
100/0/0	4.1	33.6	42.8	1.89
90/10/0	4.4	30.8	39.3	1.10
85/15/0	5.1	29.2	37.8	1.06
80/20/0	5.4	21.4	29.4	—
75/25/0	5.5	19.6	25.3	—
70/30/0	6.3	17.6	19.4	1.03
60/40/0	3.2	15.4	16.5	0.91
0/100/0	13.9	50.3	68.7	1.91
85/15/2	8.2	41.5	55.4	1.53
85/15/4	11.5	38.8	54.2	1.55
85/15/6	6.6	36.5	45.5	2.33
85/15/8	4.9	31.2	41.3	1.52

strengths were 38.8 and 54.2 MPa, which are higher than those of pure sPS. The storage modulus was 1.55×10^4 MPa. While continuously increasing the content of SsPS-K, the mechanical properties of the alloy decreased and the impact strength was only 6.6 kJ/m² with 6 parts of SsPS-K.

Recently, studies on rigid polymer toughening indicated that, with proper dispersion phase dimension and concentration, adhesion between two phases was improved and could translate from brittleness to toughness.⁷⁻⁹ Since the SsPS-K ionomer could be compatible with the two components, and improved the compatibility of sPS and PET, it led to a higher interface adhesion and mechanical properties. With a higher content of SsPS-K, on the one hand, the composition of the interface changed and the thickness increased from tight to relaxed, which was not of benefit to stress translation. On the other hand, ion groups of the SsPS-K ionomer aggregated and formed multi-ion pairs or ion clusters, which was not of benefit to compatibility, and decreased the interface ad-

hesion again. The above two reasons both caused the mechanical properties of the sPS/PET/SsPS-K alloys to be poor.¹⁰

DMA analysis

The compatibility of the components of the alloys can be shown by the half-peak width and T_g . The DMA plots of the sPS/PET/SsPS-K alloys with different contents of SsPS-K are shown in Figure 3. All the alloys had one T_g and the results are listed in Table II. With an increasing content of SsPS-K, the half-peak width decreased slightly, while after addition of 6 parts of SsPS-K, it was wider, which indicated that the compatibility of the alloys improved with a lower content of SsPS-K, while it decreased with a higher content. Since ion aggregation decreased the interaction between SsPS-K and the components, with a high

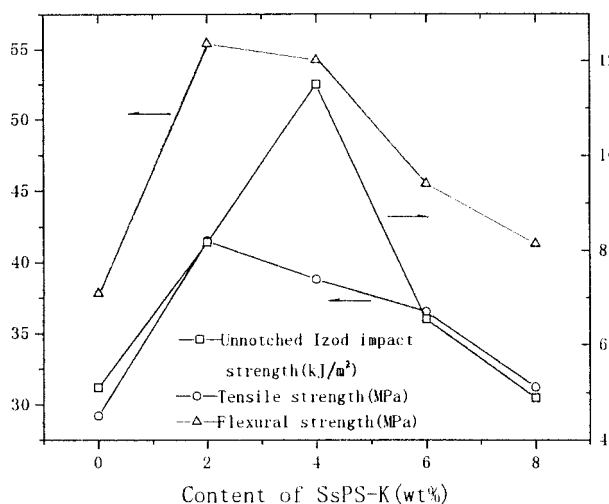


Figure 2 Mechanical properties of sPS/PET/SsPS-K alloys.

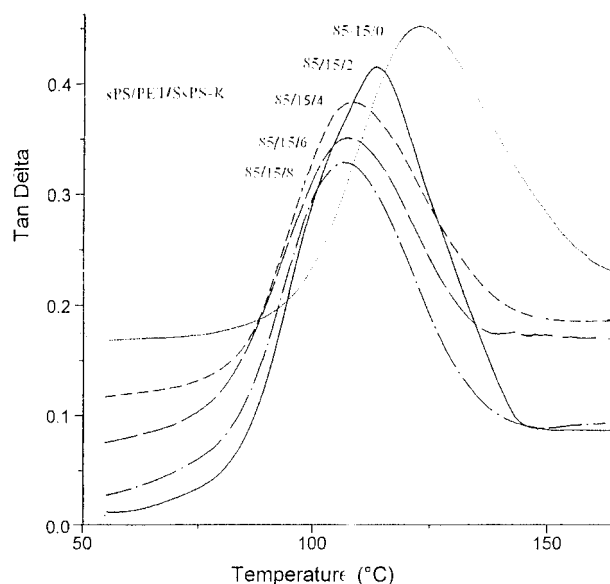


Figure 3 DMA plot of sPS(85)/PET(15)/SsPS-K polymer alloys.

TABLE II
DSC Values of sPS(85)/PET(15)/SsPS-K Polymer Alloys

sPS/PET/SsPS-K (wt %)	T_g (°C) ^a	T_{m_1} (°C)	ΔH_{m_1} (J/g)	T_{p_1} (°C)	T_{0_1} (°C)	T_{m_2} (°C)	ΔH_{m_2} (J/g)	T_{p_2} (°C)	T_{0_2} (°C)
85/15/0	120.6	271.2	24.24	238.3	242.9	247.7	28.29	191.3	198.6
85/15/2	112.0	268.2	14.46	247.5	253.3	245.9	13.92	198.2	204.3
85/15/4	107.0	269.8	17.59	250.5	255.6	246.9	10.51	197.6	204.6
85/15/6	105.8	269.9	20.04	249.6	254.8	246.4	9.31	198.1	205.3

^a Measured by DMA.

content of SsPS-K, ion aggregation was remarkable and led to poor compatibility.

DSC analysis

Figures 4 and 5 show the melting and cooling curves of the sPS/PET/SsPS-K alloys. The lower melting temperature and crystallization temperature belong to PET, and the higher, to sPS. Table II shows the results of Figures 4 and 5.

The T_{m_1} of sPS of the alloys was near to that of pure sPS. The initial crystallization temperature (T_{0_1}) and the crystallization temperature at peak (T_{p_1}) were higher than those pure sPS. T_{m_1} , T_{0_1} , and T_{p_1} were not affected by content of SsPS-K, indicating that SsPS-K could be the heterogeneous nucleator, which increased the crystallization property of sPS and made it crystallize at a higher temperature.¹¹ Moreover, the

value of $T_{0_1} - T_{p_1}$ was similar to that of pure sPS at a lower content of SsPS-K, retaining the good processing property of sPS.

The heat of melting (ΔH_{m_1}) of sPS increased with an increasing content of SsPS-K, indicating that the crystal degree of sPS was increased. Since the SsPS-K ionomer was the nucleator, crystallinity was controlled by the compatibility and nucleation. The better the compatibility, the lower the number of nucleators and the lower the crystallinity. With an increasing content of SsPS-K, the number of nucleators increased, which had more effect than did compatibility and led to higher crystallinity.

The melting temperature (T_{m_2}) of PET decreased slightly with an increasing content of SsPS-K. An enhanced compatibility hindered orderly molecular chain motion and pile, which led to a reduced crystallite dimension, imperfect crystal, and decreased T_{m_2} .

The initial crystallization temperature (T_{0_2}) and the crystallization temperature at peak (T_{p_2}) of PET were higher than those of pure PET and were not affected by the content of SsPS-K. This indicated that SsPS-K was the heterogeneous nucleator to PET and improved the crystalline property of PET. The value of $T_{0_2} - T_{p_2}$ decreased with an increasing content of SsPS-K, which proved that the aggregation of ions remarkably affected the polymer crystalline property. The addition of SsPS-K quickened the crystallization velocity of PET, which was important for PET to improve its processing property.

The heat of melting (ΔH_{m_2}) of PET was lower than that of pure PET, indicating that crystallinity decreased. With an increasing content of SsPS, ΔH_{m_2} decreased continuously.

TMA analysis

sPS has a high thermal deformation temperature and can be used at elevated temperatures. Figure 6 shows temperature-deformation curves of sPS/PET/SsPS-K alloys. From 110 to 120°C, there was a slight deformation from 20 to 30 μm , which was the glass transition temperature of sPS and PET and decreased with an increasing content of SsPS-K. Since sPS and PET are both crystal polymers the deformation was small. With an continuously increasing temperature, there

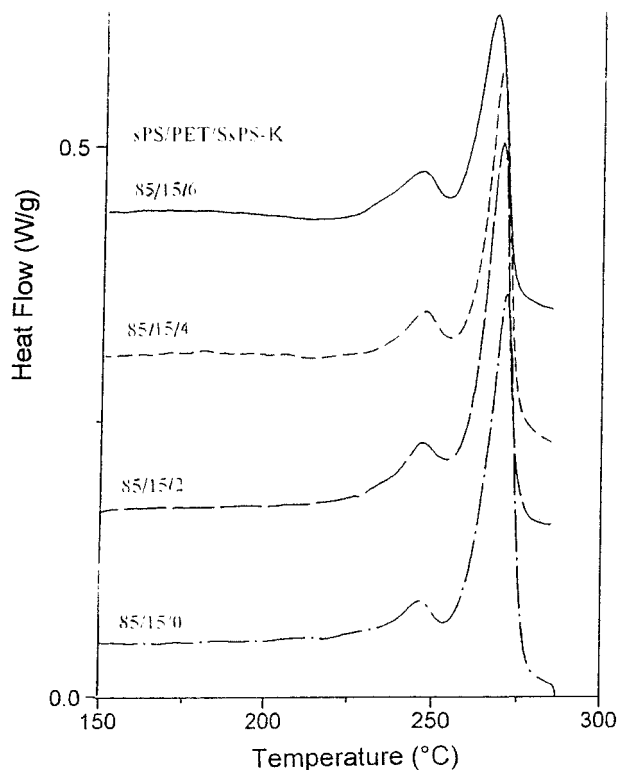


Figure 4 DSC heating curves of sPS(85)/PET(15)/SsPS-K polymer alloys.

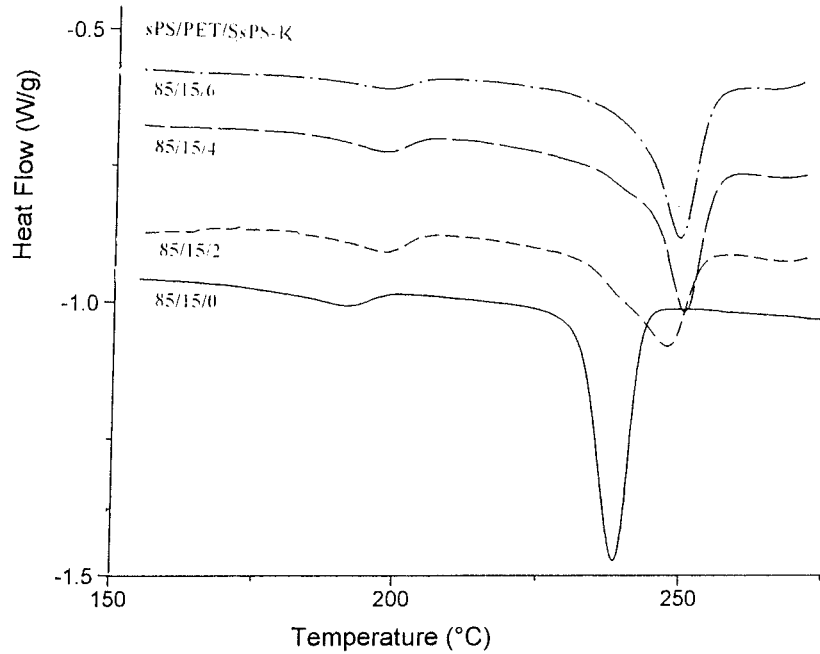


Figure 5 DSC cooling curves of sPS(85)/PET(15)/SsPS-K polymer alloys.

was a remarkable deformation of 400 μm at 170–210°C, which was due to the melting of PET but most of the crystal of sPS was not destroyed. When the temperature was higher than 260°C, sPS began to melt and the alloys could be processed at this temperature.

SEM analysis

Figure 7 shows SEM micrographs of the surfaces fractured in liquid nitrogen of the sPS/PET/SsPS-K alloys. Since the weight ratio of sPS/PET was 85/15, the

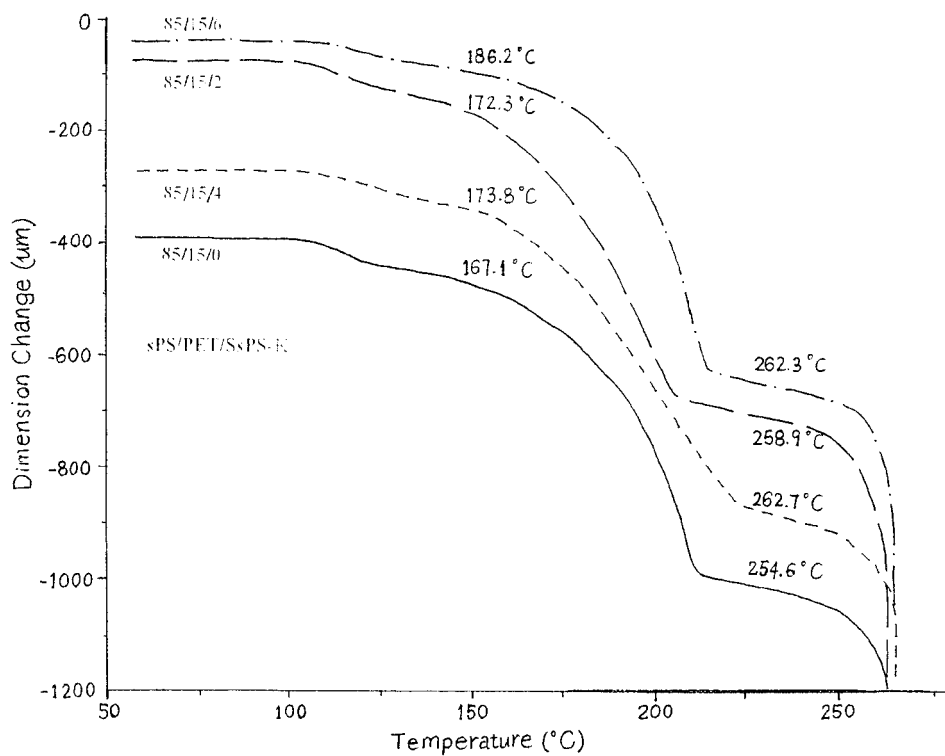


Figure 6 Temperature-deformation curves of sPS(85)/PET(15)/SsPS-K polymer alloys.

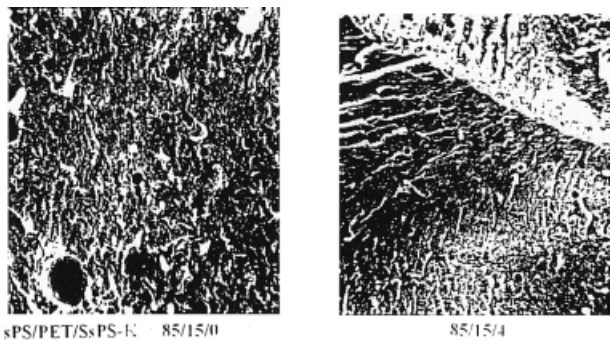


Figure 7 SEM micrograph of fracture surface in liquid N₂ of sPS(85)/PET(15)/SsPS-K polymer alloys.

white dispersion phase was PET and the black continuous phase was sPS.

The surface of the sPS/PET alloy showed a typical morphology of an immiscible blend. PET domains had a well-defined spherical shape with a very broad diameter distribution from 4 to 10 μm . Since the adhesion of sPS and PET was poor, the interface between the sPS matrix and PET appeared very smooth and clear and there were some holes left by the PET spheres.

With the addition of SsPS-K, the dimension of the PET domains decreased remarkably and the dimension distribution was even. Since adhesion between

the two phases improved, the number of holes was clearly reduced and the interface became rough, suggesting an enhanced compatibility. With an increasing content of SsPS-K, the dimension of PET domains decreased continuously, indicating that the compatibility increased. With the addition 2 parts of SsPS-K, the dimension of the PET domains was 2–4 μm , and with the addition of 4 parts, it decreased to 2 μm .

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