

Microdispersion of Polyphenylene Ether in Polyphenylene Sulfide/Polyphenylene Ether Alloy Compatibilized by Styrene-*co*-Glycidyl Methacrylate

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ABSTRACT: The polyphenylene sulfide/polyphenylene ether (PPS/PPE) alloy is desired for use as an engineering plastic. In this case, microdispersion of PPE in the PPS matrix is preferable. We have developed a new method for the preparation of a PPS/PPE alloy that has microdispersed PPE in the PPS matrix. The reactive processing of PPS with PPE gave a PPS/PPE alloy with a microdispersed PPE in the PPS matrix, using styrene-*co*-glycidyl methacrylate copolymer (SG) as a compatibilizer. Although the general properties of the PPS/PPE alloy did not depend on the PPE particle

size, tensile strength at the weld part is found to be strongly dependent on PPE particle size. Only the finely dispersed PPE system gave tensile strength at the weld part comparable that of PPS. The PPS/PPE alloy shows superior property to PPS at elevated temperature and, moreover, attains the advantage of precise molding. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3030–3034, 2002

Key words: alloys; compatibilization; reactive processing

INTRODUCTION

Polyphenylene sulfide (PPS) is a linear polymer having the phenylene group combined with sulfide at the 1,4 position. PPS is a crystalline polymer with glass transition temperature of 88°C and melting point of 285°C,¹ and this compound reinforced with glass fiber is a representative specialty polymer. PPS has the advantage of excellent thermal and mechanical properties, chemical resistance, and flame retarding, and thus PPS is mainly used in industrial and precise molding parts. PPS has the further advantage of excellent flowability, and thus is also used in small precise molding parts. However, PPS suffers the disadvantage of flash that occurs during injection molding.

On the other hand, polyphenylene ether (PPE), that is, poly(2,6-dimethyl-1,4-phenylene ether), is a linear polymer having a 2,6-dimethylphenylene group combined with oxide at the 1,4 position. PPE is a thermostable polymer with glass transition temperature of 207°C and melting point of 262°C.² However, as its melt is difficult to crystallize, PPE is generally treated as an amorphous polymer. Poly(*p*-phenylene ether),

which has no substituted group, has a melting point of 262°C, similar to that of PPE, and has a glass transition temperature of 90°C, which is much lower than that of PPE having a dimethyl substituted group, and is similar to that of PPS.³ As PPE has high glass transition temperature of 207°C, its pure component is difficult to process; thus, PPE is usually alloyed with polystyrene and converted to a modified PPE, which is sold as a general-purpose engineering plastic.

As PPE has a chemical structure similar to that of PPS, the PPS/PPE alloy is expected to show the potential to be an excellent polymer alloy. As the PPE itself has excellent thermal and mechanical properties, various properties of the PPE/PPS alloy are expected to be equal to those of PPS. As the glass transition temperature of PPE is high, the PPS/PPE alloy is expected to be superior to PPS at elevated temperature.

In general, in the case of a noncompatible polymer alloy, a highly dispersed phase in the matrix is desired. Thus, the key feature of the PPS/PPE alloy is the highly dispersed PPE particles in the PPS matrix.

Although there are several reports of the PPS/PPE alloy in patents,⁴ there is no scientific report on PPS/PPE as far as the authors know. Only one report is known for the formation of toughened PPS from PPS and the hydrogenated styrene-butadiene-styrene triblock copolymer (SEBS), in which the addition of a small amount of PPE to the PPS/SEBS system was tried.⁵

Against the above background, this report is concerned with the PPS/PPE alloy produced by adding

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finely dispersed PPE to the PPS matrix. Furthermore, improvement in the properties of the alloy at elevated temperature and the precision moldability were checked.

We have already reported the formation of elastomer-toughened PPS by the reactive processing of diphenylmethanediisocyanate (MDI)-treated PPS and an elastomer having a functional group.^{6,7} The combination of MDI-treated PPS and an elastomer with a functional group was found to be widely applicable to give an elastomer-toughened PPS. However, during these studies, it was found that by using the elastomer of ethylene-*co*-glycidyl methacrylate, MDI treatment of PPS is not necessary to give the toughened PPS. This fact suggests that the "glycidyl" group can be strongly reactive with the —SH end group of PPS. Based on findings, and considering the fact that the glycidyl group is compatible with PPS and polystyrene is compatible with PPE, we devised a polymer alloy system of PPS/PPE compatibilized by styrene-*co*-glycidyl methacrylate (SG).

EXPERIMENTAL

Materials

In this study, semilinear type PPS, which was supplied by Tohpren under the trade name T-4, with a weight average molecular weight of 21,000, was used. PPE, which was supplied by Asahi Kasei with reduced viscosity of 0.53 and molecular weight of 56,000, was used. Styrene-*co*-glycidyl methacrylate (SG) was supplied by Arakawa Chemical. SG is characterized as follows: molecular weight was 100,000 and glycidyl methacrylate content was 5 wt %. Glass fiber, which was supplied by Nihon Plate Glass under the trade name RES03X-TP10151F (diameter: 13 μm , length: 3 mm) was used.

Reactive processing

PPS, PPE, and SG were dry-blended in a Henshel mixer, and the mixture was fed to a twin-screw extruder by a weight-controlled feeder, and extruded at 300°C. At that time, the glass fiber was fed to the extruder by the side-arm method, while its feed rate was controlled by weight, and glass fiber reinforced pellets (glass fiber content was 40 wt %) were obtained.

Injection molding

Glass fiber-reinforced pellets were injection molded at 320°C, under the conditions of a mold temperature of 130°C and injection pressure of 100–110 MPa. Thus, the injection-molded samples for the measurement of properties were obtained. Notched Izod impact

strength was measured according to ASTM D256. Tensile strength and tensile elongation were measured according to ASTM D638 using a dumbbell sample. Weld tensile strength was measured using the sample obtained in the weld mold.

Observation by electron microscopy

The injection-molded sample from the reactive processing was observed using an SEM (scanning electron microscope). The SEM, JSM-5300 made by Nihon Den-shi, was used.

Measurement of PPE average particle diameter

A sample was cut transverse to the injection flow by a microtome, and the cut sample was extracted with chloroform to remove PPE from the surface; then the sample was observed using the SEM. The SEM photograph was processed by an image analyzer and the number-average particle diameter was calculated. The image analyzer, the IP-1000 made by Asahi Kasei, was used.

Measurement of "flash"

In general, during the injection molding of PPS, "flash" is easy to generate. "Flash" is the phenomenon that occurs when the polymer melt penetrates through the clearance of the mold during injection molding, thus forming an unfavorable thin film on the mold sample. In the present experiment, "flash," which was generated at the clearance of the gas vent (clearance: 30 μm) of the mold, was measured using a microscope.

RESULTS AND DISCUSSION

PPS/PPE blend

In Figure 1, an SEM photograph of the PPS/PPE blend is shown. The injection molded sample of the PPS/PPE blend did not show any "marble mark," which suggests a macrophase separation. PPE is uniformly dispersed in the PPS matrix. The maximum diameter of the observed particles was 5 μm . There were many particles around 2 μm , and some were below 1 μm , and the average particle diameter was 1.25 μm . The fact that the PPS/PPE alloy did not incur macrophase separation maybe due to the similarity in the chemical structures between PPS and PPE.

However, our former study on toughened PPS from the PPS/elastomer alloy system, suggested that to obtain the toughened PPS, the elastomer particle should be below 0.4 μm .⁶ Accordingly, a more finely dispersed PPE in the PPS matrix may be desired.

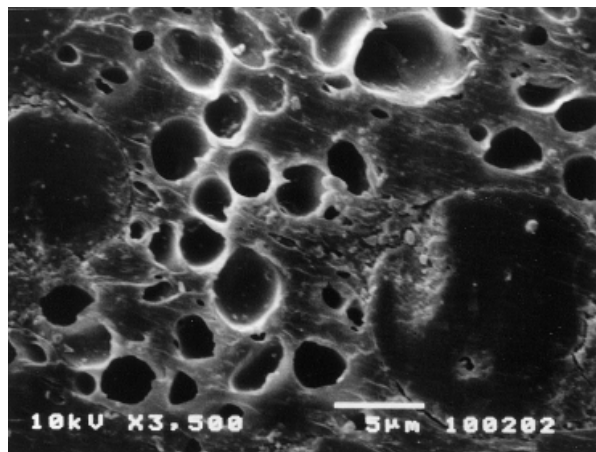
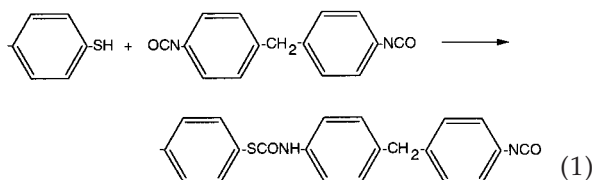


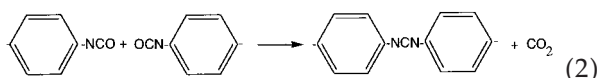
Figure 1 SEM photograph of the PPS/PPE blend; 40 wt % grass fiber reinforced. Weight ratio of PPS/PPE = 70/30.

PPS/PPE alloy compatibilized with SG

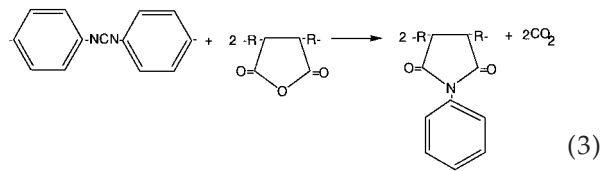
We have already studied the reactive processing of the MDI chemically treated PPS and the elastomer with a functional group to obtain toughened PPS.⁶ In that case, as the functional group of the elastomer, carboxylic anhydride, epoxide, and carboxylic acid were suitable for obtaining the finely dispersed elastomer in the PPS matrix. For the alloy system of the MDI-treated PPS/elastomer with carboxylic anhydride, we have already reported the reaction of MDI with the —SH end group of PPS, and the reaction of the carboxylic anhydride with polycarbodiimide, which was generated by the MDI chemical treatment of PPS.⁷ The isocyanate group of MDI will react with —SH of the PPS end-group to form —SCONH bond;⁸ and, furthermore, this group may be assumed to be bonded with polycarbodiimide. That is to say, the carbodiimide, which is combined with the PPS macromolecular chain end, may react with carboxylic anhydride,^{9,10} which is bonded to the elastomer, thus, giving rise to chemical bonding between PPS and the elastomer. From these observations, it is suggested that chemical bonding between PPS and the elastomer is necessary for obtaining finely dispersed elastomer in the PPS matrix. The reaction schemes concerning reactive blending processes are shown as follows: the reaction of the —SH end group with MDI:



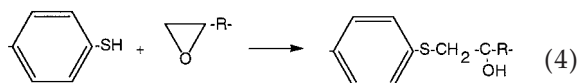
Formation of carbodiimide



The reaction of carbodiimide with carboxylic anhydride to the formation of imide



On the other hand, in the studies on elastomer-toughened PPS it was found that by using an elastomer with a glycidyl group, MDI-treated PPS is not necessary for obtaining the elastomer-toughened PPS. This fact strongly suggested that the glycidyl group can be reacted with the —SH end group of PPS. For this reaction, following scheme may be valid:



Thus, as the compatibilizer for manufacturing the PPS/PPE alloy, we selected the glycidyl group as the reactive group to react with the —SH end group of PPS. Then, considering the fact that polystyrene is completely miscible with PPE, polystyrene was selected as the compatible group with PPE. Thus, SG was selected as the compatibilizer for the PPS/PPE alloy.

Figure 2 shows an SEM photograph of the alloy system of PPS/SG/PPE using SG as the compatibilizer. It is obvious that PPE is finely dispersed in the PPS matrix. The number average particle diameter is 0.26 μm .

From this observation, in the PPS/SG/PPE alloy system, it is strongly suggested that the glycidyl group of SG reacts with the —SH end group of PPS, and the polystyrene part in SG is miscible with PPE. This

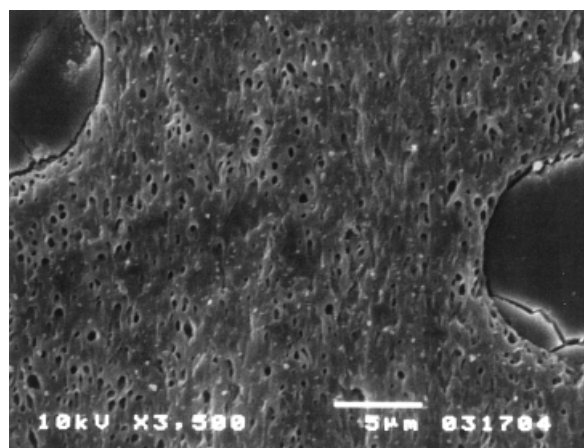


Figure 2 SEM photograph of the PPS/SG/PPE alloy; 40 wt % grass fiber reinforced. Weight ratio of PPS/SG/PPE = 70/10/20.

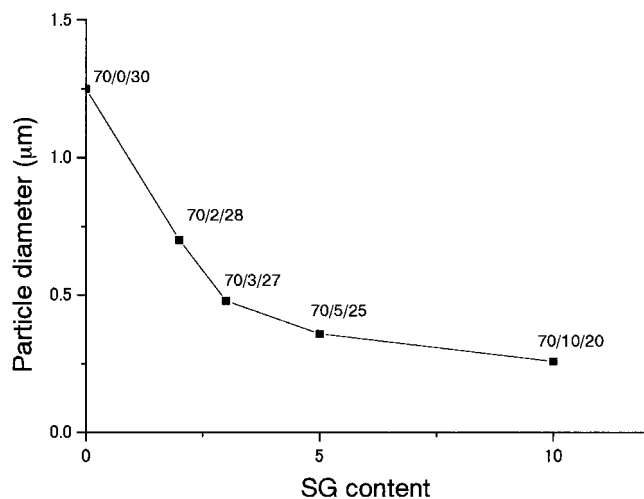


Figure 3 Effect of SG content on particle diameter. 40 wt % glass fiber reinforced. Numbers in the figure are the weight ratio of PPS/SG/PPE.

compatibilizer, SG, will reduce the surface tension between the PPS and PPE phases, and then finely dispersed PPE in the PPS matrix will be obtained.

Figure 3 shows the effects of SG content on the dispersed particle diameter of PPE in the PPS matrix. With the increase of the SG content, the dispersed particle diameter of PPE was decreased gradually.

Properties of pps/ppe alloy

In the alloy system of PPS/SG/PPE using SG as the compatibilizer, it was found that finely dispersed PPE in the PPS matrix was obtained. We compared the mechanical properties of the PPS/PPE alloy with those of PPS. Usually, PPS was used in the glass fiber-reinforced form and we measured the mechanical properties of the compound containing 40 wt % glass fiber.

In Table I, miscellaneous properties of the PPS and PPS blend are shown. In every case, general mechanical properties such as tensile strength, flexural strength, notched Izod impact strength and deflection temperature of the PPS/PPE blend were independent

TABLE I
Miscellaneous Properties of PPS/PPE Blend

| | PPS | PPS/PPE | PPS/SG/PPE |
|------------|--------|---------|------------|
| TS (MPa) | 140 | 125 | 130 |
| FS (MPa) | 260 | 230 | 238 |
| FM (MPa) | 12,800 | 12,000 | 10,900 |
| NIIS (J/m) | 80 | 65 | 72 |
| HDT (°C) | 270 | 264 | 257 |

40 wt % glass fiber to the composition. PPS/PPE = 70/30 weight ratio. PPS/SG/PPE = 70/10/20 weight ratio. TS: tensile strength, FS: flexural strength, FM: flexural modulus, NIIS: Notched Izod impact strength, HDT: heat deflection temperature.

of the PPE particle size, and these values are almost the same as those of the PPS single component (PPS single component is composed of 60 wt % PPS and 40 wt % glass fiber).

However, in general, the polymer blend is said to be sensitive to the weld strength in the part of the weld. The weld is the part where the two polymer flows, which were cooled in the mold, meet, and it is said the reduction in the mechanical strength occurs here. In Figure 4, the weld strength of each polymer blend is shown. With increase in the PPE particle diameter, the weld strength is reduced. That is to say, the weld strength is found to be dependent on the particle diameter.

The weld strength of the PPS/SG/PPE alloy, which had the finely dispersed PPE in the PPS matrix, showed weld strength of 74 MPa, which was nearly equal to the value of 81 MPa of the PPS single component. This fact showed that in practical usage, weld strength is needed; thus, the PPS/SG/PPE alloy is desirable, which showed the finely dispersed PPE particles.

The T_g of PPE is 208°C, which is much higher than that of PPS (88°C); thus, the polymer alloy from PPS and PPE is assumed to show superior properties in the high-temperature region to those of the PPS single component. To qualify this assumption, we compared the temperature dependence of the flexural modulus of the glass fiber reinforced PPS/SG/PPE alloy with the glass fiber-reinforced PPS compound. The result is shown in Figure 5. For both PPS and the PPS/SG/PPE alloy compounds, from room temperature to the T_g of PPS (88°C), the flexural modulus showed a constant value. However, over the T_g of PPS, the PPS single component showed an abrupt reduction in flexural modulus, while the PPS/SG/PPE alloy compound showed a gentle reduction. Especially, in the temper-

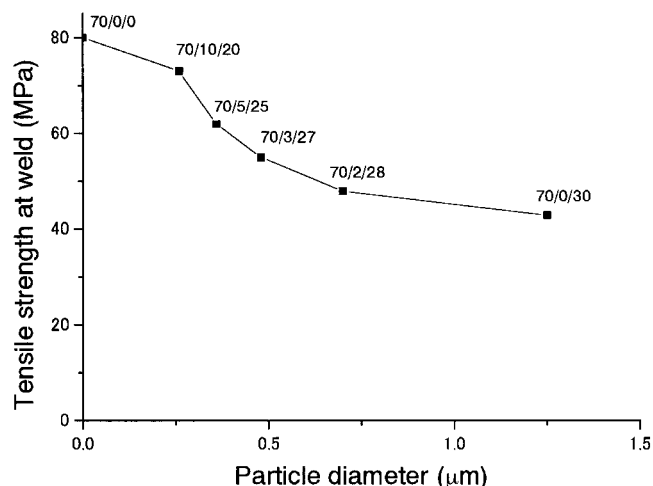


Figure 4 Relationship between particle size diameter and tensile strength at weld; 40 wt % glass fiber reinforced. Numbers in the figure are the weight ratio of PPS/SG/PPE.

ature range of 120 to 150°C, it showed a very gentle reduction. At the temperature of 150°C, the PPS/SG/PPE alloy compound showed 1.2 times the flexural modulus of the PPS single component. This phenomenon may be hypothetically attributed to the fact that as the end group of PPS is connected to the PPE through SG, the molecular motion of the PPS main chain may be restricted by the glassy state of PPE, whose T_g is 207°C, which is much higher than that of PPS of 88°C.

During the precise injection molding of PPS, one problem is the appearance of "flash." In Figure 6, "flash," which appeared during the injection molding, was compared between the PPS/SG/PPE alloy compound and the PPS compound. As shown in Figure 6, the PPS/SG/PPE alloy compound showed much less flash than the PPS compound. It may be suggested that in the PPS/SG/PPE alloy system, the molten PPS molecular chain end might be fixed during the cooling stage by the PPE glass phase, which has a high glass temperature; thus the penetration of PPS into the clearance of the mold might be impeded. This phenomenon is partly due to the strong interaction between the PPS and PPE macromolecular chains.

CONCLUSION

The reactive processing of the PPS/PPE compatibilized with SG PPE gave a PPS/SG/PPE alloy with

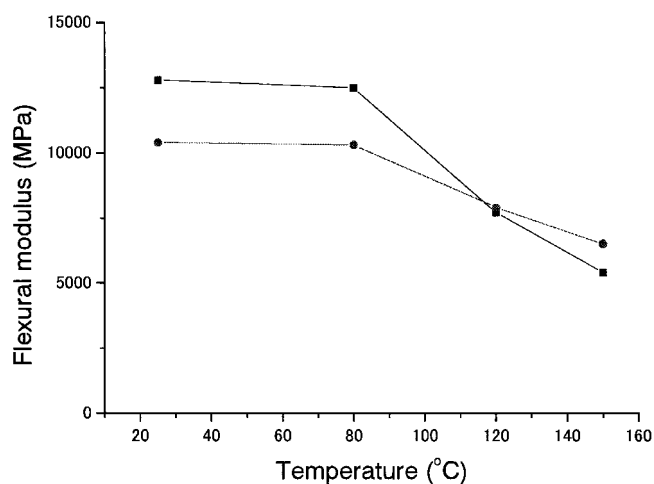


Figure 5 Effects on temperature on flexural modulus; 40 wt % glass fiber reinforced. ■ PPS, ● PPS/SG/PPE; weight ratio of PPS/SG/PPE = 60/10/30.

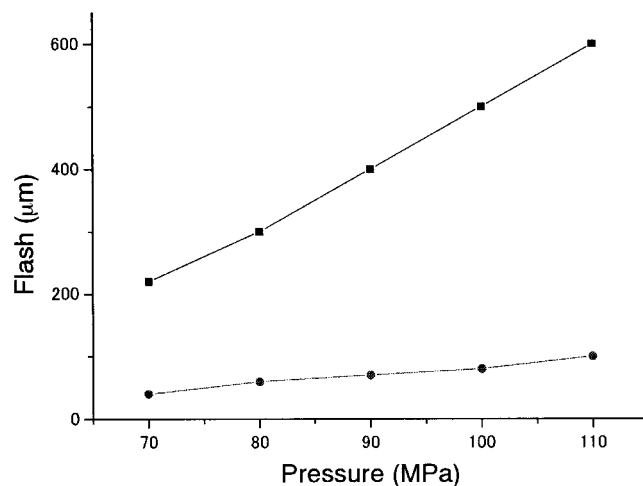


Figure 6 Flash properties of PPS and the PPS/PPE alloy; 40 wt % glass fiber reinforced. ■ PPS, ● PPS/SG/PPE; weight ratio of PPS/SG/PPE = 70/10/20.

microdispersed PPE in the PPS matrix. The PPS/SG/PPE alloy showed mechanical properties superior to those of PPS at elevated temperature (150°C) and also showed precision molding ability superior to that of PPS.

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