Elastomer Toughened Polyphenylene Sulfide

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Abstract Elastomer toughened polyphenylene sulfide was developed. Polyphenylene sulfide (PPS) was chemically treated with diphenylmethandiisocyanate (MDI). By reactive extrusion processing of chemically treated PPS with olefinic elastomer having functional group such as carboxylic anhydride, epoxide, carboxylic acid, elastomer toughened PPS with high impact strength was obtained.

Introduction

Polyphenylenesulfide (PPS) features excellent mechanical properties, thermal stability, chemical resistance, flame resistance and precise moldability. However, PPS has a weak point of being a very brittle material. For use as electrical and electronic parts, automobile and mechanical parts, toughened PPS is desired. For these application, improving the toughness of PPS and developing an elastomer toughened PPS and related compounds are desired.

The targets of our development are as follows.

The first point is to maintain the advantages of PPS such as its thermal properties, mechanical properties, etc.

The second point is to improve the brittleness of PPS using the polymer alloy method.

Preparation of Toughened PPS

Material

The commercially available any PPS neat polymer (linear PPS, semi-linear PPS, cross-linked PPS) can be available. For example, the PPS neat polymer supplied by Tohprene Corporation (its trade name is "T-4" and this is the semi-linear type PPS) is suitable.

For the thermoplastic elastomer, one example is the commercially available olefinic elastomer composed of ethylene, acrylic ester and small amounts of maleic anhydride (~2 wt%). Another example is the ethylene propylene rubber(EPR) modified with maleic anhydride group. One more example is the olefinic elastomer having glycidyl group. These olefinic elastomers have the reactive functional group such as anhydride or epoxide group. A typical example of the elastomer is an olefinic copolymer composed of ethylene, acrylic ester and maleic anhydride, whose trade name is "Bondine" and supplied by Sumitomo Chemicals.

Chemical treatment of PPS

PPS was chemically treated to activate the reactivity of the PPS end-group with diphenylmethanediisocyanate (MDI, 2 wt% of PPS) using the method described in our patent [1]. PPS was mixed with MDI, and extruded in a molten state at 300 °C using a twin extruder.

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Reactive processing

The reactive processing of the MDI-treated PPS and an olefinic elastomer with a functional group such as carboxylic acid anhydride produced a toughened PPS [2]. Various twin extruders can be used for the reactive processing. For example, BT 40 of Plastics Kogaku Kenkyusho, PCM 30 of Ikegai Tekko, and ZSK 40 of the Werner & Pfleidere Corporation were used in our development.

Measurement

Transmission electromicroscope (TEM) was measured using Hitachi H-600 under the condition of 100 kV. Samples were prepared by ultra thin film method stained with RuO4. The mechanical properties of the toughened PPS were measured according to ASTM D 638.

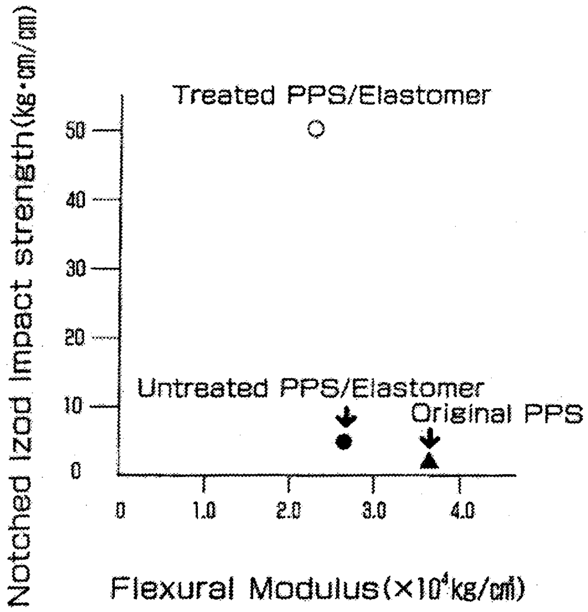

Fig. 1 Effect of chemical treatment on toughness of PPS/elastomer alloy.

Results and Discussion

Elastomer Toughening [2-8]

Figure 1 shows how PPS is toughened by elastomer alloying. The horizontal axis shows the flexural modulus of PPS and the vertical axis shows the notched Izod impact strength.

The original PPS has a notched Izod impact strength of about 1 to 2 kg·cm/cm, while elastomer-blended chemically, untreated PPS has a notched Izod impact strength of about 6 kg·cm/cm. In these cases, elastomer blended PPS is thought not to be toughened.

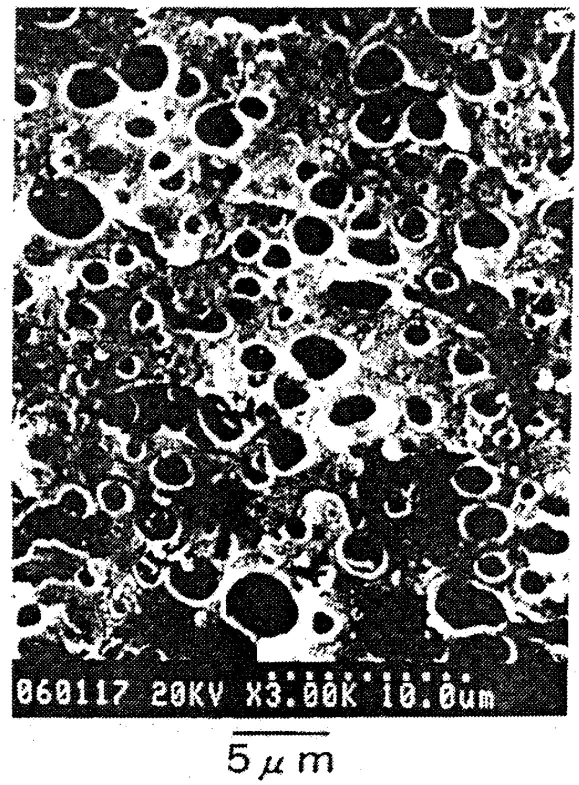

Fig. 2 A notched fracture surface of elastomer-blended, untreated PPS.

Using MDI-treated PPS and an olefinic elastomer with a functional group of maleic anhydride, elastomer toughened PPS using the reactive processing method was developed.

The elastomer alloy of the chemically treated PPS has a notch Izod strength value of about 50 kg·cm/cm [2]. Though the notched Izod impact strength of the original PPS is about 1 kg·cm/cm, the elastomer toughened PPS has a notched Izod impact strength around 50 kg·cm/cm.

A notched impact fracture surface of PPS is observed using a scanning electron microscope. Figure 2 shows the notched impact fracture surface of elastomer blended untreated PPS. The elastomer of the fracture surface is extracted with chloroform. The diameter of the extracted hole is about 1 μm. A scanning electron photograph of a notched impact fracture surface for a brittle PPS~elastomer blend shows a brittle surface.

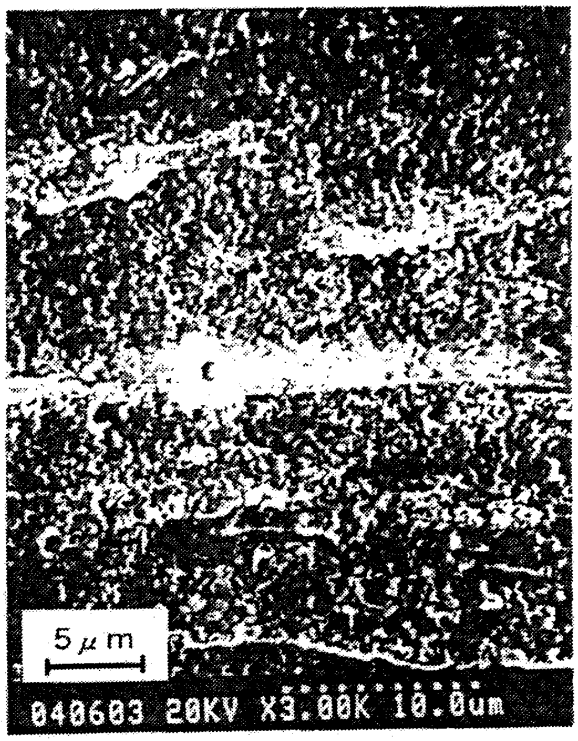

Fig. 3 A notched impact surface of elastomer-toughened, chemically treated PPS.

Figure 3 is a photograph of the notched impact surface of the elastomer-toughened, chemically treated PPS. The elastomer of the fracture surface of PPS was extracted with chloroform. The diameter of the extracted hole is about 0.3 μm. A scanning electron photograph of the notched impact fracture surface for the tough PPS~elastomer alloy shows a tough fracture.

Figure 4 is a transmission electron photomicrograph of a microtomed section of toughened PPS. This case contains 20% by weight of the elastomer with similar particle size, and well-dispersed particles.

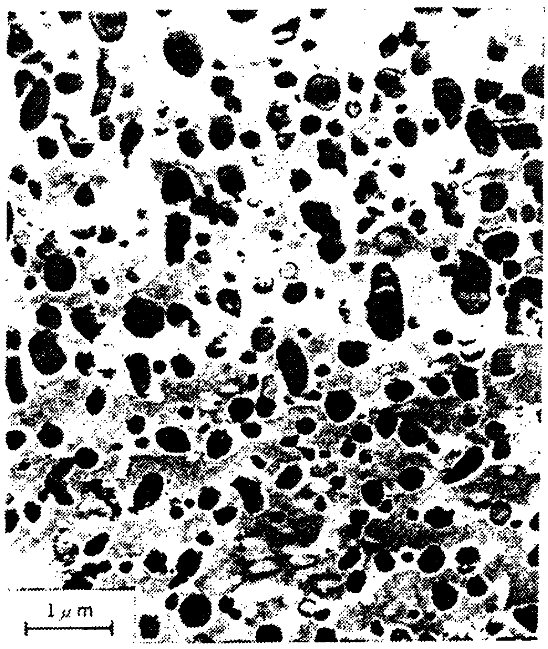

Fig. 4 Microtomed section of toughened PPS.

Properties

In the case of elastomer toughened PPS, there are two different application cases.

One case is unreinforced, and the other case is reinforced. Usually, we use our toughened PPS in the reinforced form.

The mechanical properties of unreinforced and glass fiber reinforced elastomer toughened PPS are shown in Table 1. Though the notched Izod impact strength of the general glass fiber reinforced PPS (Ryton R4) is about 7 kg·cm/cm, the glass fiber reinforced elastomer toughened PPS is about 22 kg·cm/cm.

Table 1 Properties of elastomer toughened PPS

PPS	Tensile strength (kg/cm^2)	Elongation at break (%)	Flexural strength (kg/cm^2)	Flexural modulus (kg/cm^2)	Notched izod impact strength (kg.cm/cm)	Heat deflection temperature[a] (°C)
Unreinforced	550	25	800	23,000	50	150
Glass fiber (40%) reinforced	1400	3	2200	110,000	22	>260
Ryton™ R4 (reference)	1300	1	2000	140,000	7	>260

Properties for Ryton R4 are from the catalog of the Dainippon Ink Corporation.
[a]At 4.6 kg/cm^2.

* Properties are cited from catalog of "Dainippon Ink Corporation (DIC)-PPS".

Elastomer toughened glass fiber reinforced PPS maintains its original thermal properties. Heat deflection temperature (HDT) is shown in the table at the same level of over 260□.

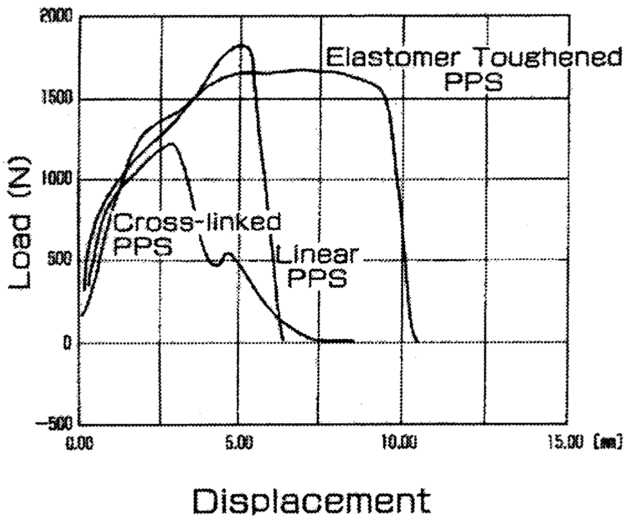

Fig. 5 Dart impact properties of glass fiber reinforced PPS.

Figure 5 shows the behavior of the dart impact strength of various glass fiber reinforced PPS's. The horizontal axis is displacement, and the vertical axis is load. The area is energy for dissipation. Dissipation energies increased in the following order:

cured and cross-linked PPS < linear PPS < elastomer toughened PPS.

Elastomer toughened glass fiber reinforced PPS has an impact strength value twice that of the linear PPS and four times that of the cross-linked PPS.

Effect of the Method of Reactive Extrusion Processing

We checked how the difference in the reactive extrusion processing method affects the elastomer dispersion. When PPS and olefinic elastomer were extruded without a chemical modifier (MDI), it gave a large elastomer particle size and brittle material (Fig. 6).

Fig. 6 TEM of chemically untreated PPS blend (core, parallel to the flow).

When PPS and olefinic elastomer were extruded with MDI (this reactive extrusion process is called the one-step extrusion), it gave a mixed combination of elastomer with large and small particle sizes and a tough material (Fig. 7).

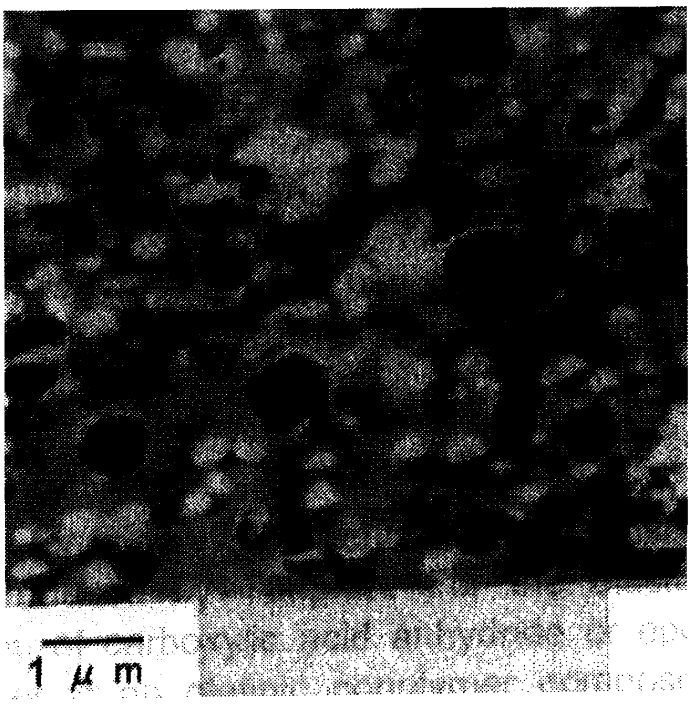

Fig. 7 TEM of reactive extrusion of elastomer MDI-PPS-elastomer alloy (core, parallel to the flow extrusion process: one-step reactive extrusion processing.

When MDI-treated PPS was extruded with olefinic elastomer (this reactive extrusion process is called the two-step extrusion), it gave a uniformly dispersed elastomer with a small particle size as shown in Fig. 4.

Considering the fact that both the reactive one-step extrusion and two-step extrusion methods gave a tough material with a same order, elastomer particles with a small size were thought to contribute to the toughness of PPS.

Mechanism of Elastomer Toughening

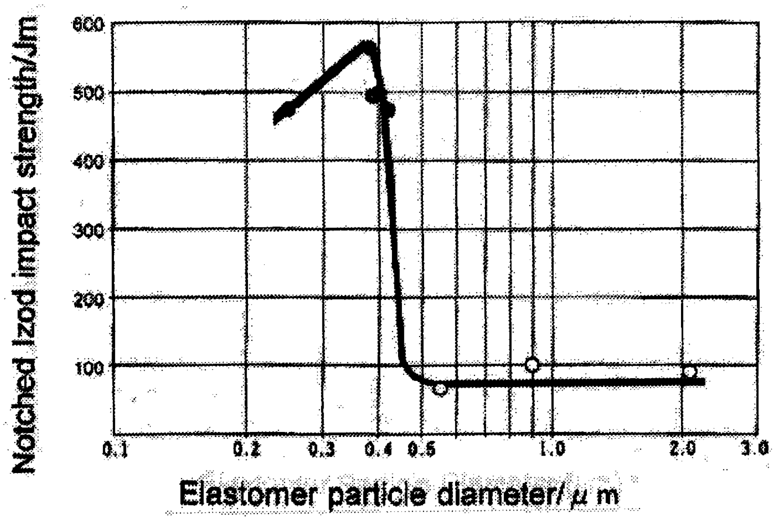

Fig. 8 Notched Izod impact strength vs. the number average particle diameter.
○ PPS/elastomer,
●MDI-treated PPS/elastomer

Fig. 8 shows the effect of the particle diameter on the Izod impact strength. Particle diameter was changed, first by the chemical treatment of PPS, and second by the extrusion conditions, such as rotation speed of the screw. The following relations were observed. When the elastomer particle diameter is large (particle diameter > 1 μm), the notched Izod impact strength is below 100 J/m. Around the particle diameter approximately 0.5μm, a brittle - tough transition was observed.

The mechanism for the toughening is attributed to the matrix PPS shear yielding. This may come from the chemical structure of PPS. The molecular structure of PPS is linear chain structure without side chain, main chain phenylene group is bonded at 1,4-position with sulfide, which is thought to be a some kind of free joint system, as shown in Fig. 9.

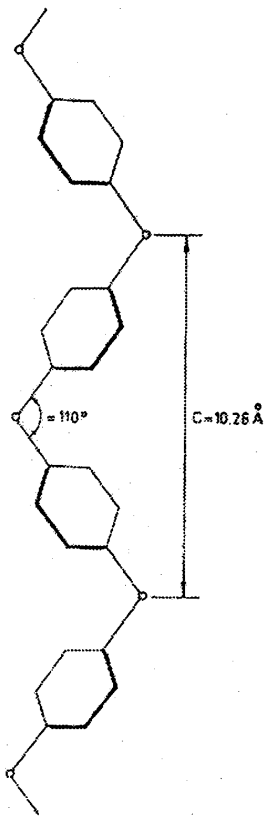

Fig. 9 Structure of PPS [14]

The interaction between PPS and the elastomer was checked. The PPS sheet and elastomer sheet were thermally pressed. Only the combination of the MDI-treated PPS and an olefinic elastomer with a functional group showed a strong adhesion. A strong interaction between the MDI-treated PPS and olefinic elastomer with a functional group was suggested.

The chemical reaction of PPS and an olefinic elastomer with a functional group was also discussed from the viewpoint of infrared spectroscopy.

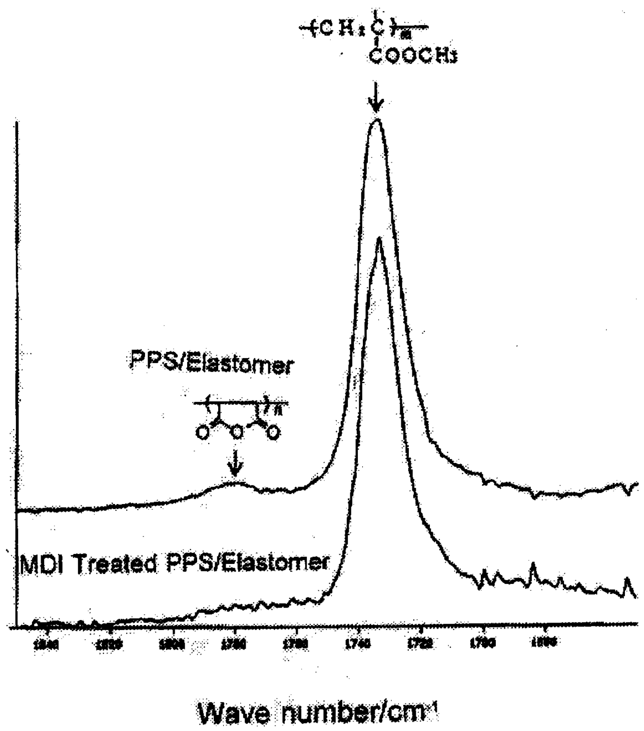

Fig. 10 Infrared spectra of acid anhydride absorbance.

Fig. 10 is the infrared spectra of the combination of PPS and olefinic elastomer. The combination of the chemically-untreated PPS and an olefinic elastomer showed the absorption of the carboxylic anhydride at around 1780 cm^{-1}, while for the combination of the chemically-treated PPS and olefinic elastomer, this band disappeared. This fact suggested a chemical reaction between the chemically-treated PPS and olefinic elastomer.

Fig. 11 shows the infrared spectra of MDI-treated PPS. MDI-treated PPS showed the carbodiimide band [2], while this band disappeared for the combination of MDI-treated PPS and an olefinic elastomer.

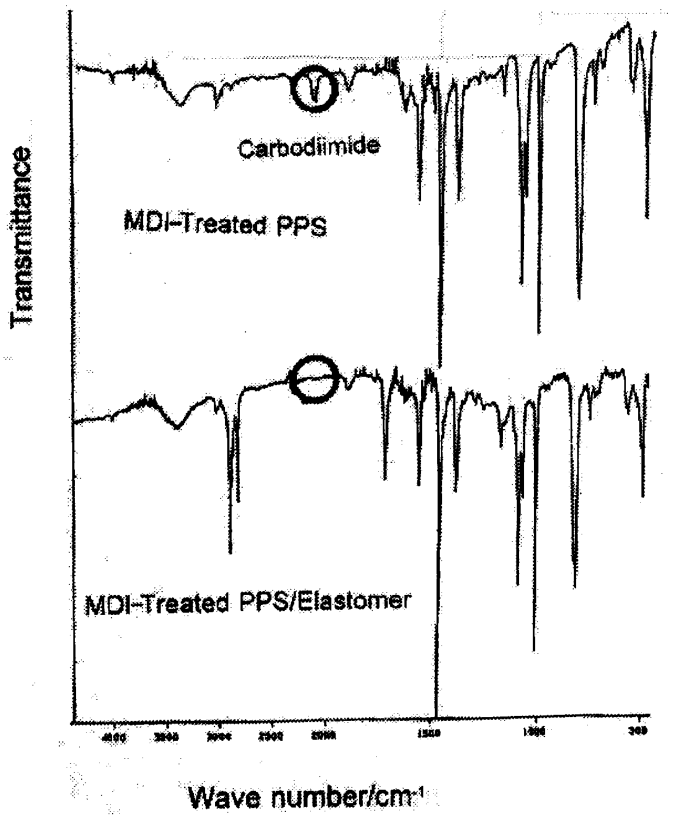

Fig. 11 Infrared spectra of carbodiimide absorbance.

These facts suggest the chemical reaction between the functional group of the elastomer (acid anhydride) and the carbodiimide group of the MDI-treated PPS [3].

The chemical reaction between the MDI-treated PPS and olefinic elastomer with a functional group will combine the PPS and elastomer, thus reducing the surface tension between PPS and the elastomer. Reducing the surface tension between the matrix PPS elastomer will produce finely dispersed elastomer particles. Due to these finely elastomer particles, PPS is thought to be toughened. Thus, the key point for toughening is the chemical reaction between the matrix PPS and elastomer.

Conclusion

We developed elastomer toughened PPS. Since this toughened PPS maintains the advantages of PPS, that is, thermal properties, mechanical properties, chemical properties and dimensional stability, toughened PPS has been in market development in the fields of electrical and electronics, automobile and mechanical applications, and good results have been obtained.

References

1) J. Masmoto, T. Nakamoto and K. Kubo, US Pat. 5,191,020 (1993), assigned to Asahi Chemical.

2) J. Masamoto and K. Kubo, "*Benibana" International Symposium on "How to Improve the Toughness of Polymers and Composite?*", p.21-24 (1990).

2) J. Masamoto and K. Kubo, *Am. Chem. Soc. Polym. Prepr.* 32(2), 215-216 (1991).

3) J. Masamoto, K.Kubo, T. Nakamoto and M. Yokoyama, *Rep. Prog. Polym. Phys. Jpn.*, 38, 355-359 (1995).

4) J. Masamoto and K. Kubo, *Polym. Eng. Sci.*, 36, 265-270 (1996).

5) J. Masamoto, J. Masamoto, "Polyphenylene Sulfide (Elastomer Toughened)" in *Polymeric Material Encyclopedia*, Ed. by Joseph C. Salamone, CRC Press Inc. 8, 6503 - 6506 (1996).

6) J. Masamoto, *The 16th International Conferences "Additives '97", New Orleans, Louisiana,* Feb 3 - 5, pp. 1 - 11 (1997).

7) J. Masamot and K. Kubo, *37th IUPAC International Symposiium on Macromolecules*, pp. 446 (1998).

8) J. Masamoto, "Poly(*p*-phenylene sulfide)" in *Polymer Data Handbook*, Ed., by James E. Mark, Oxford University Press, pp. 714-721 (1999).

9) J. Masamoto and K. Kubo, *Sen'i Gakkaishi*, 54, 562-567 (1998).

10) J. Masamoto and K. Kubo, *Rep. Prog. Polym. Phys. Jpn.*, 42, 211-212 (1999).

11) K. Kubo and J. Masamoto, *Kobunshi Ronbunshu*, 56, 426-433 (1999).

12) K. Kubo, M. Yokoyama and J. Masamoto, *Rep. Prog. Polym. Phys. Jpn.*, 42, 295-296 (1999).

13) J. Masamoto, *6th Annual International Conferenece on Composites Engineering* (ICCCE/6), Florida, July 27-June 3, pp. 555-556 (1999).

14) H. Kanai, V. Sullivan and A. Auerbach, *J. Appl. Polym. Sci.*, 53, 227 (1994).

15) I. A. Karchev, A. V. Bratchikov and Y. M. Budunitskii, *Plast. Massy*, 1992, 48 (1992).

16) J. Goto, K. Sasaki and K. Ashida, Polyurethane, 94, Proc. Polyurethane Conf. (1994), p. 346, Soc. Plast. Ind. Polyurethane Div., New York, N. Y.

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