

Impact Modification of Engineering Thermoplastics

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SYNOPSIS

Impact modification was studied for a variety of engineering thermoplastics to determine if notched Izod data obtained at various temperatures and modifier concentrations could be correlated with particle size or surface-to-surface interparticle distance of the modifier. Elastomers evaluated were characteristic of those used in commercial blend systems for those polymers, and both functionalized and nonfunctionalized materials were studied. For the single matrix polymer/elastomer-modified blend systems studied [poly(phenylene sulfide) (PPS), polyoxymethylene (POM), poly(butylene terephthalate) (PBT)], elastomer interparticle distance provides a better correlation to brittle-tough transition temperature than does particle size, as predicted by the Wu model. In POM, the dispersion morphology of the samples used was not adequate to achieve the critical interparticle distance required for supertoughening at room temperature. In this study, the critical interparticle distance has been shown to depend on the degree of crystallinity (PPS) and the modulus of the impact modifier relative to the matrix (PBT). Actual adhesion of the polymer to the matrix (variation of functionality levels) was not found to have a strong influence (PBT). In POM, the increase in impact at the brittle-tough transition was dependent on the molecular weight of the base resin. This is examined with respect to the ratio of the molecular weight (M_n) to the entanglement molecular weight (M_e), which determines the critical molecular weight necessary to achieve useful physical properties. In polyester (PET)/polycarbonate (PC)/elastomer blends, the molecular weight of the primary matrix resin (PET) determined impact properties within the molecular weight range of the resin studied. This was again related to the M_n/M_e ratio for PET and PC. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

A number of models have been developed to describe the toughening of plastics by a dispersed elastomeric phase. For toughening of brittle matrices, some models have focused on the ability of rubber particles to initiate and terminate crazes in the matrix.^{1,2} Other models have invoked mechanisms of rubber particle tearing or cavitation of the rubber phase as other means of energy dissipation by the rubber.^{3,4} Plastics in which shear yielding is the major mode of energy dissipation during fracture are often referred to as pseudoductile matrices.^{5,6} Polyesters and polyamides are examples of pseudoductile matrices.⁵ A recent model describes the toughening of matrices that undergo shear yielding in terms of the thickness

of ligaments between rubber particles.^{5,7} In this model, the transition from brittle to ductile (tough) failure occurs when the average distance between rubber particles is below a critical value. Wu demonstrated that this model correctly describes the impact behavior of nylon/rubber blends.⁷

This study attempted to extend this model to describe the impact of blends of elastomer-toughened poly(phenylene sulfide) (PPS), polyoxymethylene (POM), and poly(butylene terephthalate) (PBT). These materials would be expected to be pseudoductile in nature based on the high ratio of unnotched to notched impact values or based on the criteria outlined by Wu for these polymers.^{5,8}

Other questions that have been explored include the following:

- The effect of crystallinity on the impact model (amorphous vs. crystallized PPS).

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- The effect of adhesion or functionalization of the rubber particle (PBT).
- The effect of modulus of the impact modifier (PBT).
- The effects of a second blend component (PC/PET).

Oshima and Sasaki⁹ showed that in the case of PBT/rubber blends that functionalization of a core shell impact modifier with epoxide can lead to more efficient impact modification without altering the basic dimensions of the impact modifier in the PBT. This would suggest that a good interfacial adhesion is essential for achieving impact in contrast to the Wu model where only minimal interfacial adhesion is necessary where shear yielding is a predominant mechanism.

EXPERIMENTAL

The PPS used in this study is a linear polymer sold by Hoechst Celanese Corp. under the trademark Fortron® (registered trademark of Fortron Industries) PPS. Three grades were used: one with a melt viscosity of 3000 poise at 1000 reciprocal seconds and 316°C (MV3000 or Fortron W300), another with a viscosity of 1400 poise at 1000 reciprocal seconds and 316°C (MV1400 or Fortron W214), and the third with a viscosity of 500 poise under the same conditions (MV500 or Fortron W205). These viscosities were measured using a Kayeness Galaxy V capillary rheometer. The elastomers used are hydrocarbon-based rubbers with varying levels of a functionality that is reactive with the PPS matrix. Blends of PPS containing these impact modifiers were found to exhibit torque increases during mixing bowl experiments, indicating the reaction of PPS and impact modifier. The identity of the elastomers is proprietary, so they will simply be referred to as modifiers A, B, and C.

Physical properties of the elastomers are shown in Table I, along with physical properties of PPS. Although the elastomers are chemically all in the same class of hydrocarbon copolymers, some variation of chemical structure and molecular weight exists from one elastomer to another. Modifier B is a graft copolymer. Thus, the physical properties of the elastomers are not simply a function of the weight percent of the reactive functionality. For instance, the T_g and flexural modulus of modifier B, with 10% reactive functionality, do not fall between

Table I Selected Properties for Poly(phenylene sulfide) (PPS) with Modifiers

| Compound | Wt % Reactive Group | T_g (°C) | Density (g/mL) |
|------------|---------------------------|------------|-------------------|
| Modifier A | 5 | -17 | 0.935 |
| Modifier B | 10 | 5 | 0.977 |
| Modifier C | 15 | -10 | 0.944 |
| PPS | — | 110 | 1.35 |

those of modifiers A and C, which have 5 and 15% reactive functionality, respectively.

The POM was of the formaldehyde/ethylene oxide copolymer type supplied by Polyplastics Co. under the name of Duracon (registered trademark in Japan) POM with melt flow rates equal to 2.5, 9.0, 27, and 45 (M25, M90, M270, and M450). An ether-based thermoplastic polyurethane (TPU) from Nippon Miractran Co. was used as the elastomer.

The PBT compositions were made with Duranex (registered trademark in Japan) PBT supplied by Polyplastics Co. with melt flow rates equal to 3.2 (800FP), 15 (600FP), and 52 (400FP) at 235°C (intrinsic viscosities [I.V.] of approximately 1.2, 0.9, and 0.7 dL/g, respectively). Impact modifiers included N-Tafmer® MP0620 (high maleic anhydride [high MAH]) and MP0610 (low maleic anhydride [low MAH]) ethylene propylene rubbers from Mitsui Petrochemicals. Tafmer® P0280 (unfunctionalized, no MAH) was used as a control. These are collectively denoted as EOR (ethylene olefin rubber) elastomers in the charts. Kraton® 1901, a styrene-ethylene-butylene-styrene copolymer (SEBS) that has been grafted with maleic anhydride, was also used and contrasted with the EOR elastomers.

PETs were supplied by Hoechst Celanese as Impet® PET (I.V. of 0.95 and 0.70 dL/g) and were blended with two Lexan® polycarbonates supplied by General Electric (I.V. of 0.45 and 0.3 dL/g) and a core shell acrylic/MBS modifier.

Unless otherwise noted, blends were compounded on a lab scale Haake twin-screw extruder. The barrel temperature and screw speed were set to the recommended processing values for each resin. In some cases, particle size was varied by controlling the extrusion conditions (barrel temperature and screw speed). Molded parts were made on a Boy 22 ton or equivalent injection-molding machine. Molded bars of $\frac{1}{8}$ and $\frac{1}{4}$ in. thickness were used for Izod impact testing according to ASTM D 256. The temperature

dependence of notched Izod impact strength at temperatures above or below room temperature were obtained by equilibrating the samples and the Izod impact testing machine at the temperature of interest for 1 h before testing. This was accomplished through the use of a thermostated cover that fit over the Izod impact tester.

Dynamic mechanical measurements were made using a Polymer Laboratory dynamic mechanical thermal analyzer (DMTA). For neat PPS and PPS blends containing the impact modifier, measurements were made using samples cut from annealed injection-molded flex bars. These bars were annealed for 5 h at 180°C prior to sample preparation. For each of the above DMTA experiments, the instrument was run in a dual cantilever mode. DMTA data on samples of modifiers A, B, and C were also obtained on calendered film that was approximately 3 mil thick. These experiments were run in a tensile deformation mode.

Samples were prepared for microscopy by immersing notched Izod impact test bars in liquid nitrogen and fracturing the specimen in an Izod impact testing machine. This procedure generally resulted in smooth fracture surfaces. Samples were then immersed in an appropriate solvent (xylene for PPS blends, tetrahydrofuran for POM blends, and chloroform for PBT blends) for an effective time and temperature in order to extract the impact modifiers. After drying, the specimens were gold-sputtered and imaged on a JEOL JSM-T200 or Hitachi S-800 scanning electron microscopes. The cavities left by the extracted impact modifier were easily distinguished.

RESULTS

Poly(phenylene sulfide) (PPS)

The T_g values reported in Table I for modifiers A, B, and C were taken as the temperature corresponding to the low-temperature peaks in the $\tan \delta$ curves from DMTA measurements. For each of the blends studied, the $\tan \delta$ peaks for the PPS and the elastomer were not shifted from the values for the pure components. This indicates that the blend components are essentially completely immiscible. The reaction of PPS and the elastomer, which presumably yields a graft copolymer at the elastomer-matrix interface, does not significantly affect the dynamic mechanical response of the blends.

Izod impact values as a function of temperature are shown in Figures 1-4. For most blends, a distinct brittle-tough transition region was observed. In general, blends exhibiting notched Izod impact values above 30 kg-cm/cm showed ductile-type failures, with the edges of the samples drawing inward at the point of fracture. Thus, for purposes of comparing the impact behavior of various samples, the temperature at which samples reached 30 kg-cm/cm is defined as the brittle-ductile transition temperature. To interpret the impact data in terms of the model presented by Wu, the interparticle distances of the samples were calculated as described below.

The impact modifier was extracted from selected blends as described in the Experimental section. The number-average particle areas for the cavities left by the extracted modifier were obtained from the SEM photographs with an optical analyzer. Although the

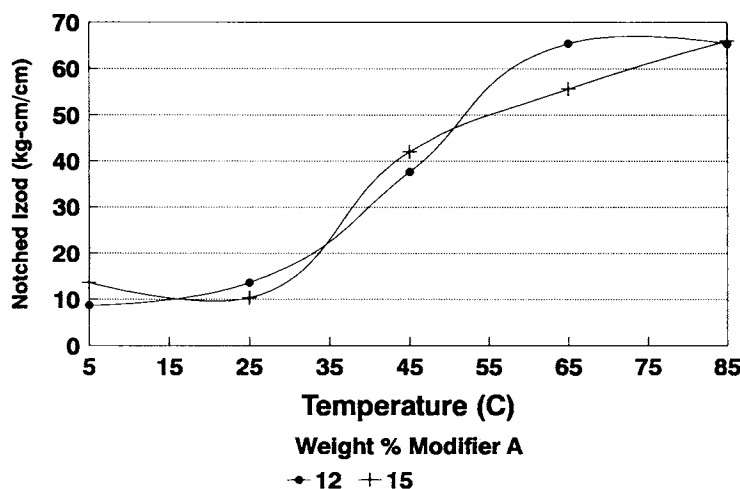


Figure 1 Notched Izod vs. temperature for PPS (M.V. = 1400 poise at 1000 s⁻¹) with modifier A.

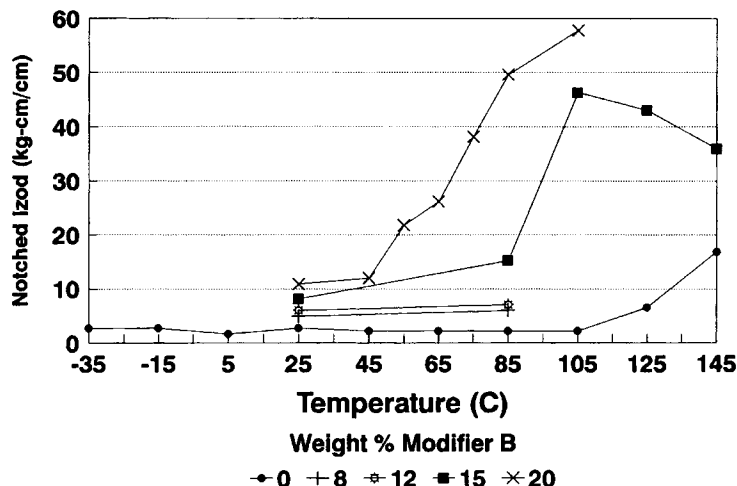


Figure 2 Notched Izod vs. temperature for PPS (M.V. = 500 poise at 1000 s⁻¹) with modifier B.

cavities were generally not spherical, the number- or weight-average particle diameters were calculated from the number- or weight-average areas as if the particles were spherical. The error that this produces in the calculation of interparticle distances was discussed by Wu.¹⁰ The main error introduced by this simplification is that the breadth of the distribution of ligament thicknesses is underestimated. Another factor that must be considered is the fact that the

observed radii of the cavities are smaller than the true radii since the fracture does not generally cut through the center of the particle. On average, for randomly dispersed spherical particles, the observed radius is smaller than the average radius by a factor of ($\pi/4$).⁷ This correction factor has been applied to the PPS data. For randomly dispersed spherical particles, the distance between the surfaces of adjacent particles τ is given by

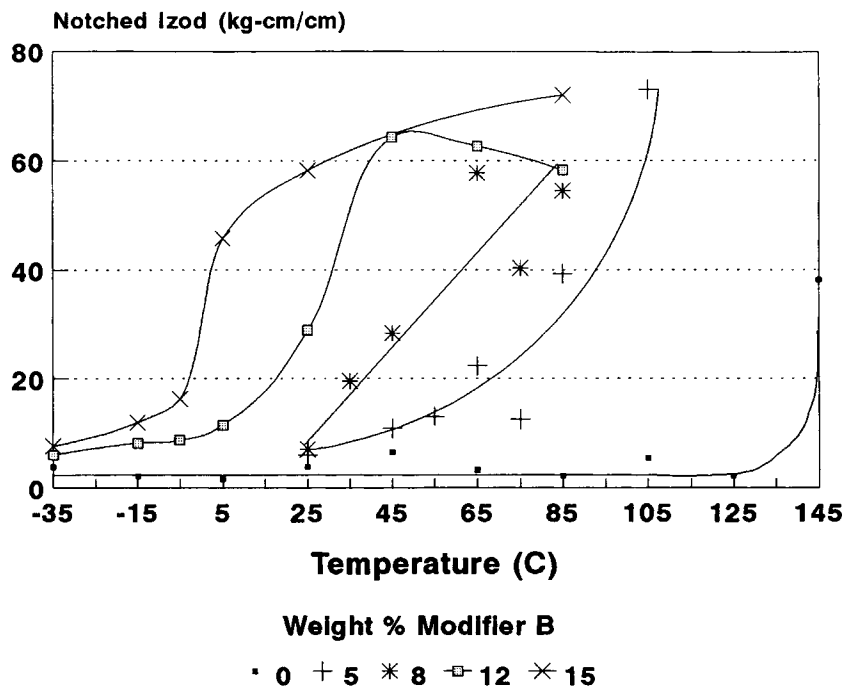


Figure 3 Notched Izod vs. temperature for PPS (M.V. = 1400 poise at 1000 s⁻¹) with modifier B.

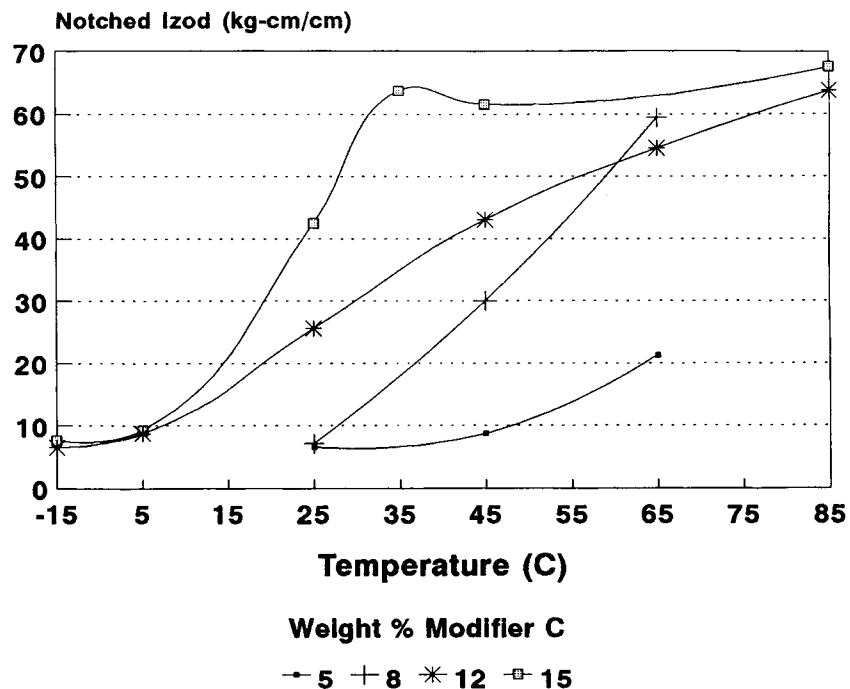


Figure 4 Notched Izod vs. temperature for PPS (M.V. = 1400 poise at 1000 s⁻¹) with modifier C.

$$\tau = [(\pi/6\phi)^{1/3} - 1]d \quad (1)$$

where d is the particle diameter, and ϕ , the volume fraction of the dispersed phase.⁷

Figure 5 shows notched Izod impact values at 25°C vs. interparticle distance. For each blend, the brittle-tough transition temperature was plotted against average particle size (Fig. 6) and interpar-

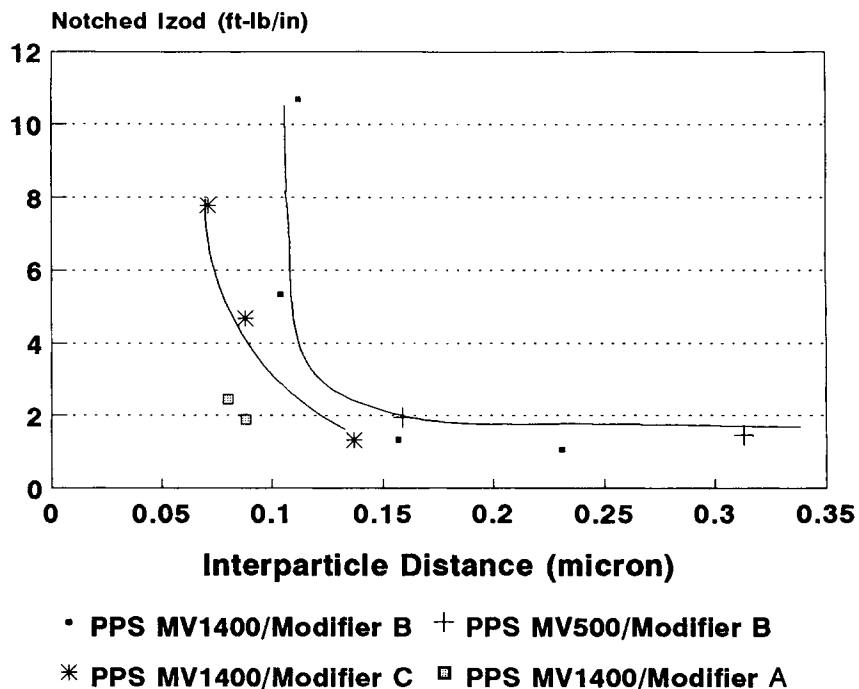


Figure 5 Notched Izod vs. interparticle distance for PPS with modifiers.

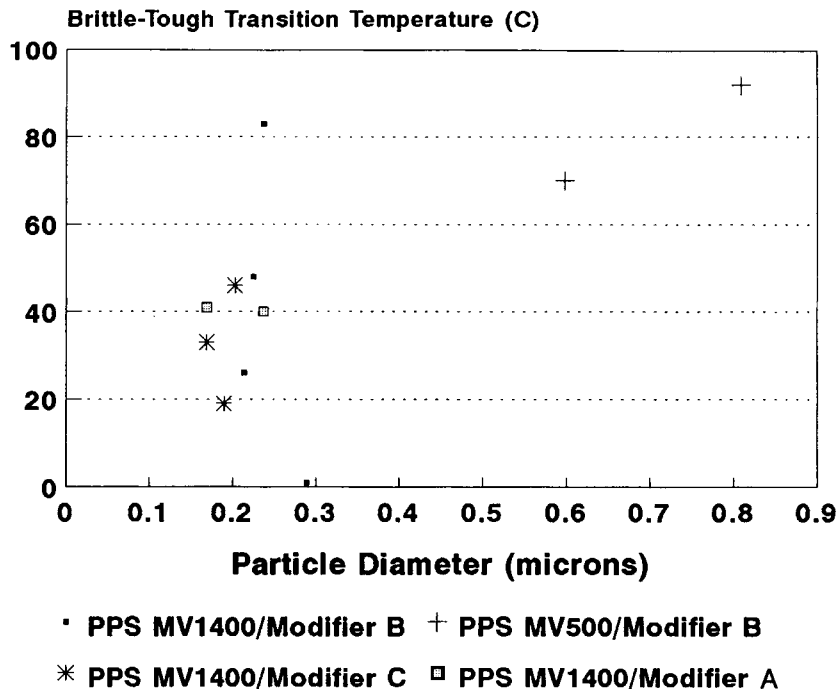


Figure 6 Brittle-tough transition temperature vs. average particle diameter for PPS with modifiers.

ticle distance (Fig. 7). In spite of the differences observed with different modifiers in Figure 5, Figure 7 shows a clear trend toward lower brittle-tough

transition temperature with smaller interparticle distance. Particle size alone does not provide an adequate correlation (Fig. 6). Figure 7 shows that the

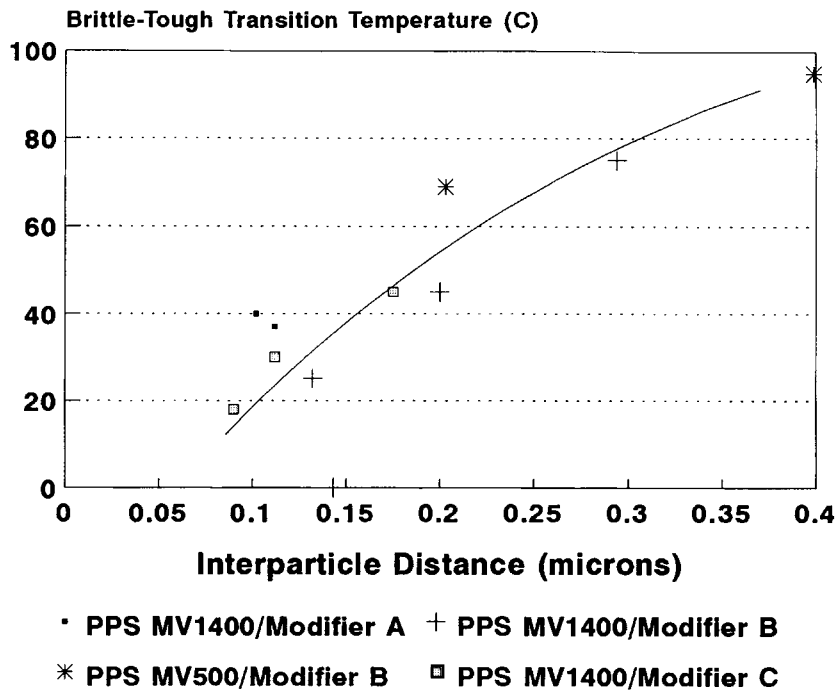


Figure 7 Brittle-tough transition temperature vs. interparticle distance for Forton with modifiers.

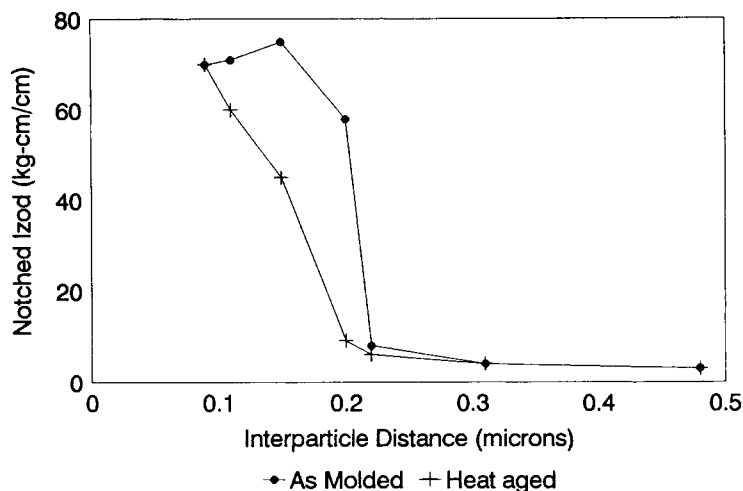


Figure 8 Notched Izod vs. interparticle distance for PPS with modifier B (annealed vs. unannealed).

interparticle distance gives a useful parameter for describing the impact behavior of toughened PPS within a given class of impact modifiers. It is significant that the data in Figure 7 encompass not only different modifier concentrations, but also different molecular weight PPS. This result indicates that the model of Wu^{5,7} does provide a useful parameter for correlation of impact data on samples containing various particle sizes and concentrations.

The effect of crystallinity on the critical interparticle distance was examined with the use of a high molecular weight PPS. When the material is molded with a cold mold (80°C), an amorphous product is obtained. Subsequently heating the test bars significantly increased the level of crystallinity. This material was then impact-tested to determine the brittle-tough transition and the critical interparticle distance. As can be seen from Figure 8, the interparticle distance shifted from 0.2 to 0.15 as a result of crystallizing the sample. This is consistent with Wu's analysis that crystallinity can alter the critical interparticle distance by varying the critical molecular weight ratio (M_n/M_e) necessary for supertough behavior.⁸

Polyoxymethylene (POM)

Similar data were obtained for POMs of differing molecular weights compounded with a polyurethane. Differing particle diameters were obtained upon extrusion of the compositions as a result of the difference in shear and temperature. The correlation between particle diameter and impact strength (notched izod) is shown in Figure 9 for POM having

a melt index of 2.5 g/10 min. Poor correlation was obtained in these cases. When the same data are plotted vs. interparticle distance, the data points fall on the expected line (Fig. 10). This again indicated the broad applicability of the Wu model. By varying the molecular weight of the POM, it is possible to obtain a broad range of particle sizes. This can be seen very clearly in Figure 11. Plotting the impact strength (subtracting the control) vs. the particle size yields a very poor correlation (Fig. 12), but

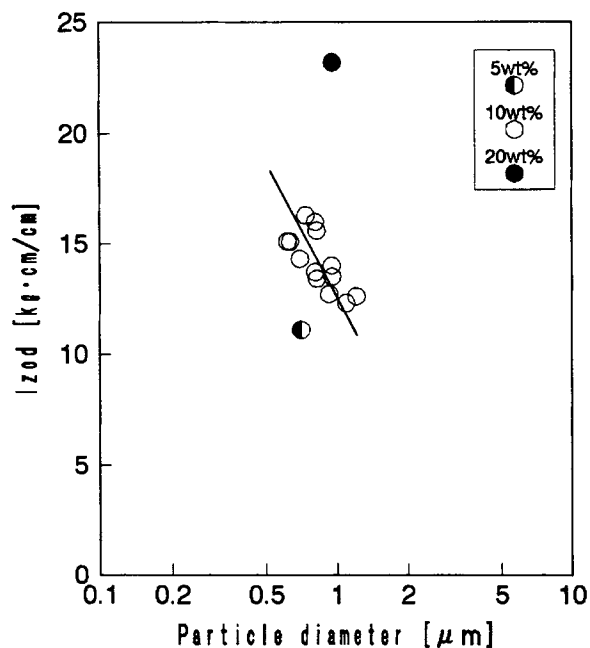


Figure 9 Notched Izod vs. particle diameter for POM (M.I. = 2.5) with thermoplastic urethane.

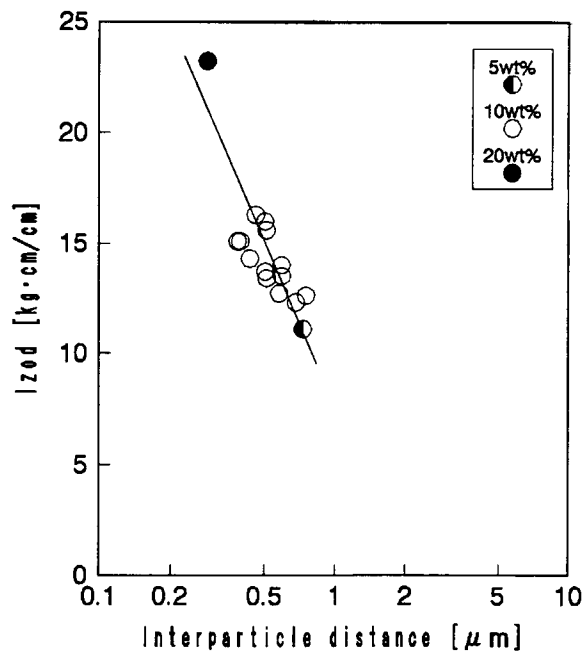


Figure 10 Notched Izod vs. interparticle distance for POM (M.I. = 2.5) with thermoplastic urethane.

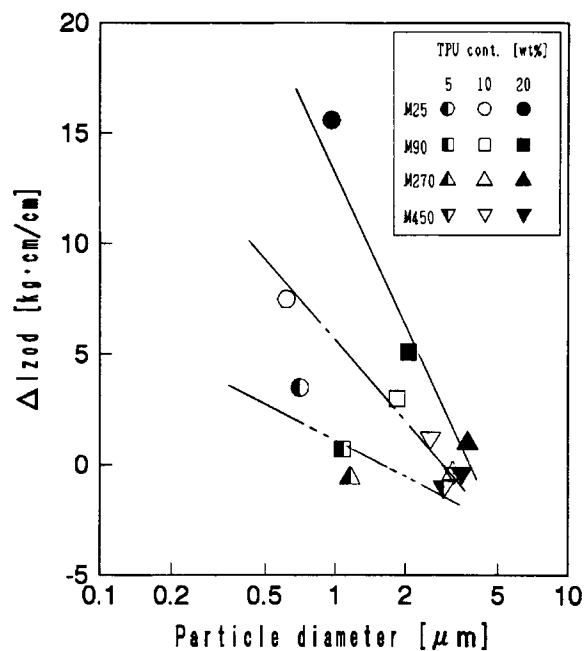


Figure 12 Notched Izod vs. particle diameter for POM (M.I. = 2.5, 9.0, 27.0, 45.0) with thermoplastic urethane.

compared to the interparticle distance, a clear break is observed for tough behavior (Fig. 13). The impact vs. interparticle distance curve is independent of the molecular weight of POM. In the case of POM, supertough behavior was not observed at room tem-

perature. At elevated temperatures (Fig. 14) very clear transition to supertough behaviors are found.

By plotting the interparticle distance vs. the brittle-tough transition temperature for various POMs,

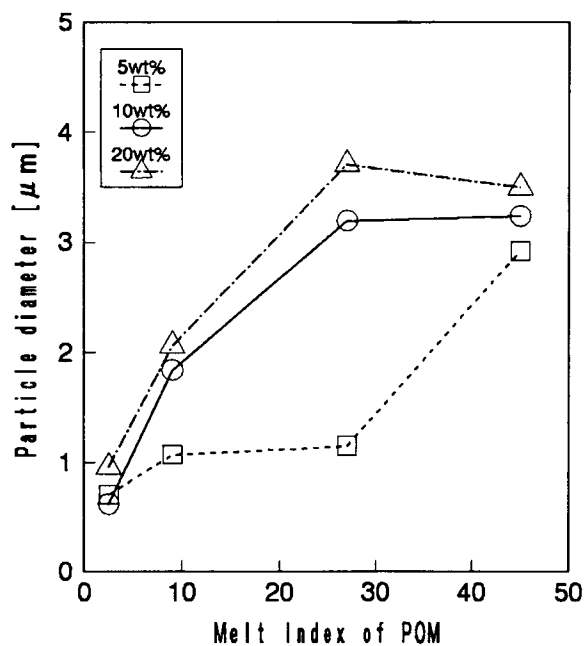


Figure 11 Particle diameter vs. melt index for POM with thermoplastic urethane.

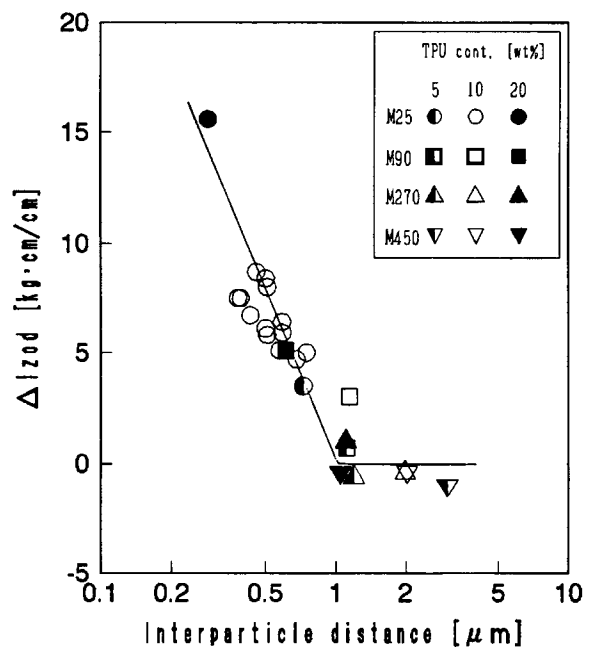


Figure 13 Notched Izod vs. interparticle distance for POM (M.I. = 2.5, 9.0, 27.0, 45.0) with thermoplastic urethane.

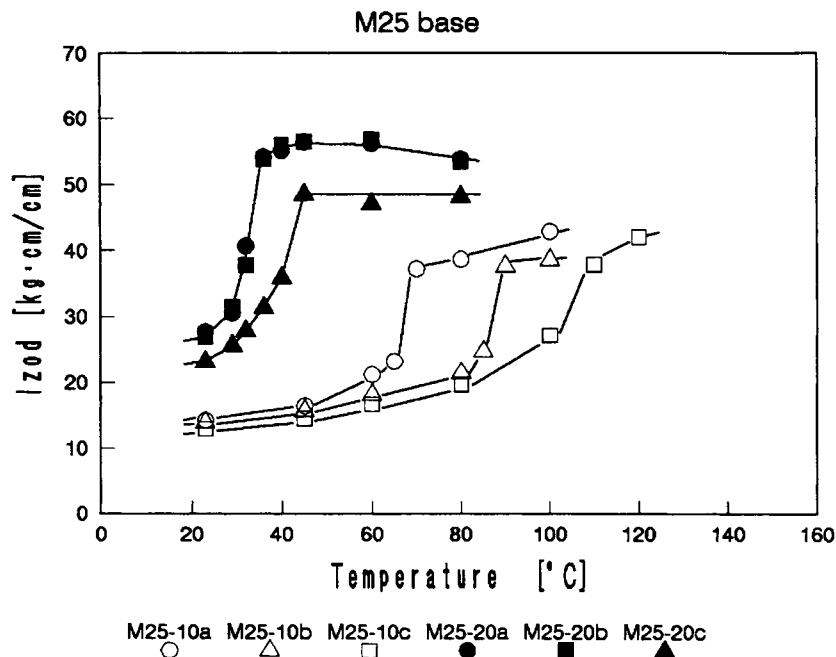


Figure 14 Notched Izod vs. temperature for POM (M.I. = 2.5) with thermoplastic urethane.

it can be seen that an interparticle distance of 0.18 microns would be needed to obtain supertough behavior at room temperature (Fig. 15). This inter-

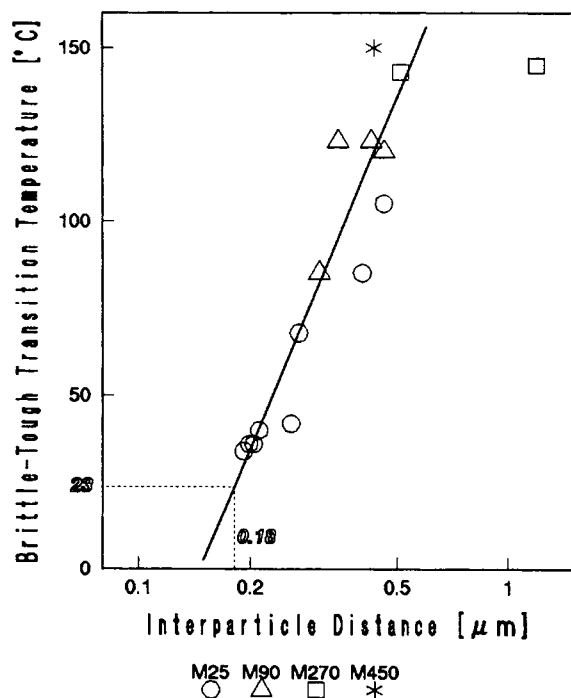


Figure 15 Brittle-tough transition temperature vs. interparticle distance for POM with thermoplastic urethane.

particle size is not readily achievable using the indicated experimental modifier and extrusion equipment at less than 30% impact modifier concentrations. Ductile samples have been obtained in POM at concentrations greater than 30%.¹¹ Figure 16 presents a typical brittle-tough transition curve for POM at 60°C having different melt indices and concentration ranges.

The increment of notched Izod increase at the brittle-tough transition, relative to room temperature, was plotted vs. transition temperature (Fig. 17). The increment is determined by the molecular weight of the POM. Since the increment is independent of the transition temperature, it is expected to be the same at room temperature. As per the above discussion, the impact vs. interparticle distance curve can be predicted (Fig. 18). This discussion implies that there may be a critical molecular weight to achieve supertough properties. The mechanical properties of polymers are known to depend on molecular weight (e.g., tensile strength). Wu indicated that supertoughness can only be obtained when the molecular weight of the matrix is at least seven times the entanglement molecular weight (M_e). Ratios up to 20 times may be necessary, however, depending on the crystallinity of the sample. The entanglement molecular weight can be defined as the molecular weight of an entanglement strand between two adjacent entanglement junctions along a chain. Table

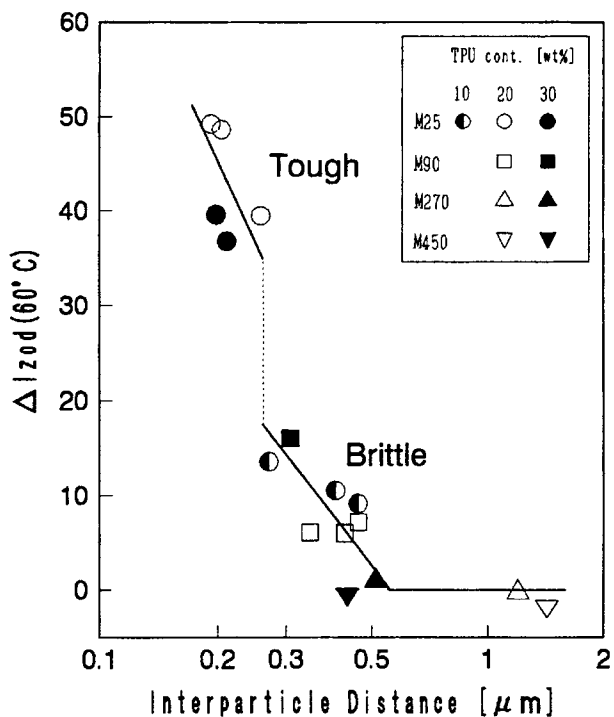


Figure 16 Notched Izod vs. interparticle distance for POM (M.I. = 2.5, 9.0, 27.0, 45.0) with thermoplastic urethane at 60°C.

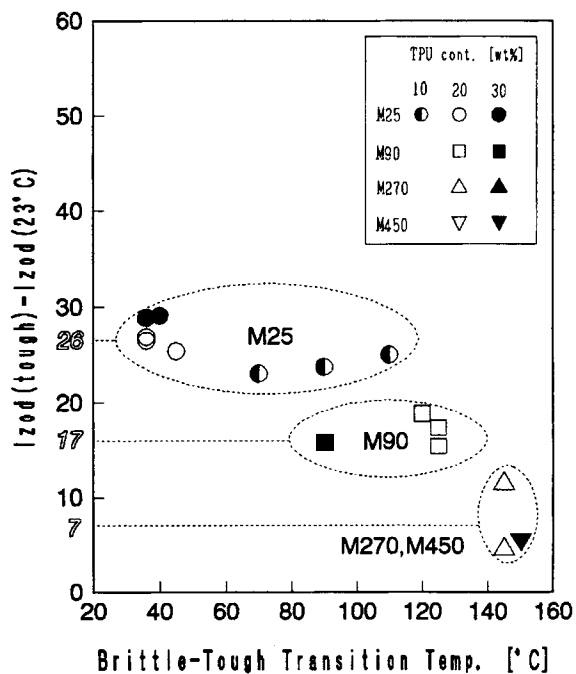


Figure 17 Notched Izod (relative to room temperature Izod) vs. brittle-tough transition temperature for POM (M.I. = 2.5, 9.0, 27.0, 45.0) with thermoplastic urethane.

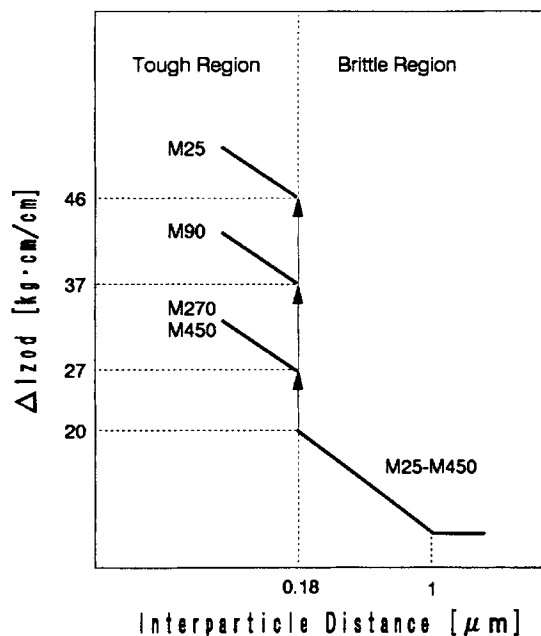


Figure 18 Model of impact vs. interparticle distance for POM with thermoplastic urethane.

II lists the molecular weight (M_n), the entanglement molecular weight, and the M_n/M_e ratio. In the ratio ranges indicated (11–16 times), it would be expected that in a highly crystalline sample such as POM that some dependence of impact on molecular weight would be observed.

Poly(butylene terephthalate) (PBT)

Three different types of modifiers were used in the study of this polymer:

- Ethylene-olefin rubber (EOR) (Figs. 20 and 21).

Table II Polyoxymethylene (POM) Molecular Weight (M_n), Entanglement Molecular Weight (M_e), and Ratios (M_n/M_e)

| | Melt Index | | | |
|----------------------|------------|------|------|------|
| | 45.0 | 27.0 | 9.0 | 2.6 |
| $M_n \times 10^{-3}$ | 28 | 30 | 36 | 40 |
| $M_e \times 10^{-3}$ | 2.54 | 2.54 | 2.54 | 2.54 |
| M_n/M_e | 11 | 12 | 14 | 16 |

- EOR functionalized with an anhydride (Figs. 19–21).
- Styrene–ethylene–butylene–styrene copolymer (SEBS) having a maleic anhydride graft (Fig. 22).

The modulus of the EOR was much lower than the SEBS (82 vs. 220 kg/cm²) and can be compared to the matrix modulus of 28,000 kg/cm² (340 and 127/1, respectively). The molecular weight of the PBT was varied in order to vary also the size of the dispersed phase. It can be seen in Figure 19 that plotting the impact strength vs. the particle diameter did not yield any meaningful relationship, whereas plotting impact strength vs. interparticle distance yielded a relationship similar to previous studies (Fig. 20). A critical interparticle distance of approximately 0.4 microns was obtained for PBT/EOR blends. It can be seen from Figure 21 that functionalization (degree of functionalization is 0, low, and high) of the rubber allowed for a range of interparticle distances; however, all points fell on the line of impact strength vs. interparticle distance. In Figure 22, it can be seen that the SEBS-modified PBT had an critical interparticle distance of 0.16 microns as contrasted to 0.4 microns for the EOR,

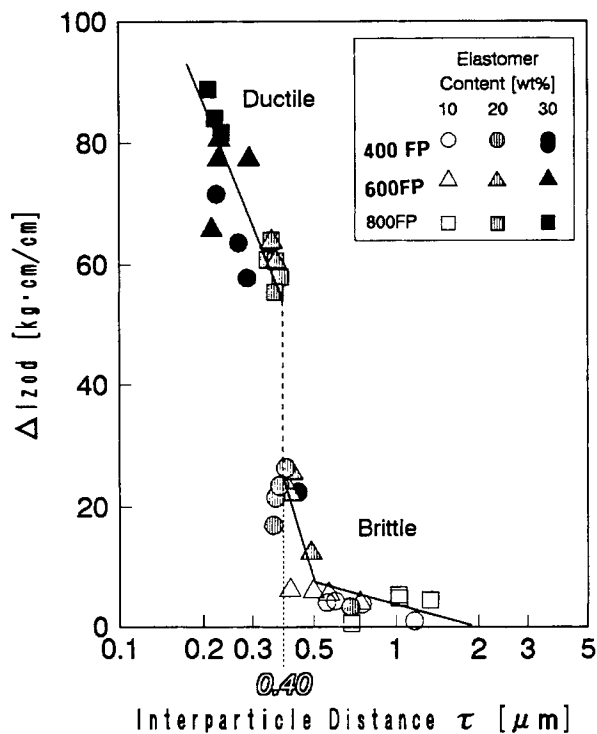


Figure 20 Notched Izod vs. interparticle distance for PBT with EOR (high MAH).

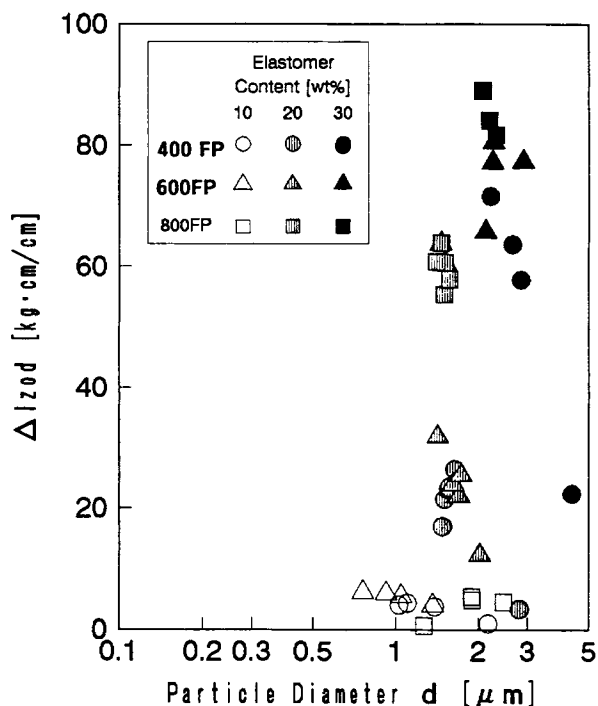


Figure 19 Notched Izod vs. particle diameter for PBT with EOR (high MAH)

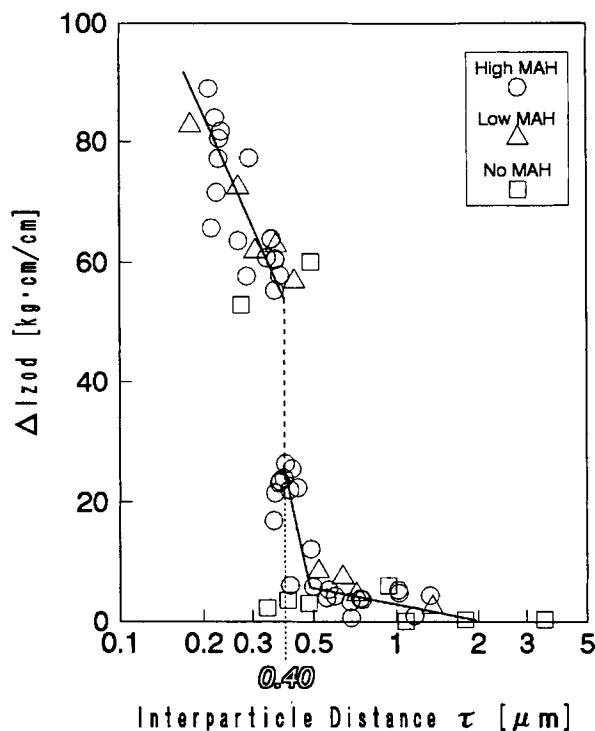


Figure 21 Notched Izod vs. interparticle distance for PBT with EOR (high, low, and no MAH).

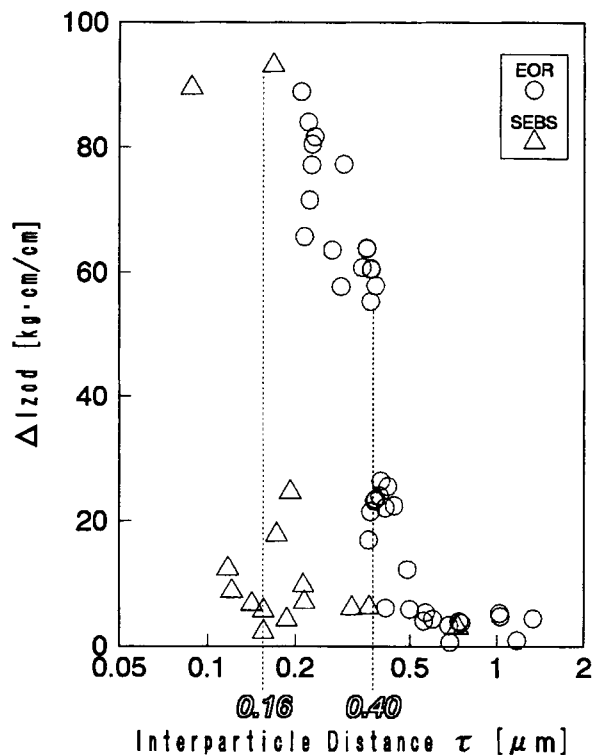


Figure 22 Notched Izod vs. interparticle distance for PBT with EOR and SEBS.

indicating that the rubber with the lower modulus had a significantly higher critical interparticle distance.

Polycarbonate/Poly(ethylene terephthalate) (PC/PET) Blends

It was of interest to examine semimiscible systems containing two polymer components, because the impact modifier might be found in one of two different phases. Hobbs et al. found that in a PC/PBT or PET blend containing a core shell acrylic modifier that the impact modifier resides in the PC phase. The dominant matrix phase at the concentration ranges studied was PET.¹² In our studies, the molecular weight of the PET and PC was varied to determine the effect on the impact strength. Increasing the molecular weight of the PET phase resulted in an increase in the impact, whereas a comparable change was not found when the PC phase molecular weight was increased (Figs. 23 and 24). Table III summarizes the data on the ratio of M_n/M_e ratios.

When another amorphous polymer (designated PA) was substituted for PC, it was found that the impact modifier resided predominately in the polyester phase. A similar trend was found with respect to the molecular weight of the polyester vs. impact (Fig. 23) in spite of the fact that the impact modifier resided in the amorphous vs. the crystalline phase (PC vs. PA). Impact modifier particle sizes were within the 0.3–0.5 micron particle size expected for core shell impact modifiers, but the degree of overall particle aggregation in the sample was not measured.

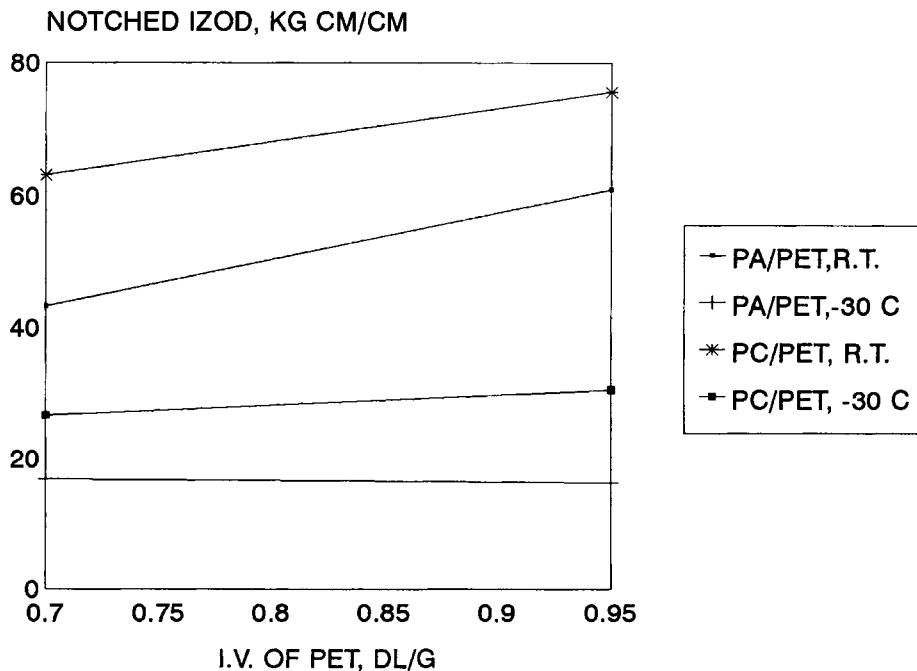


Figure 23 Notched Izod vs. I.V. of PET in a PET/PC or PA impact-modified blend.

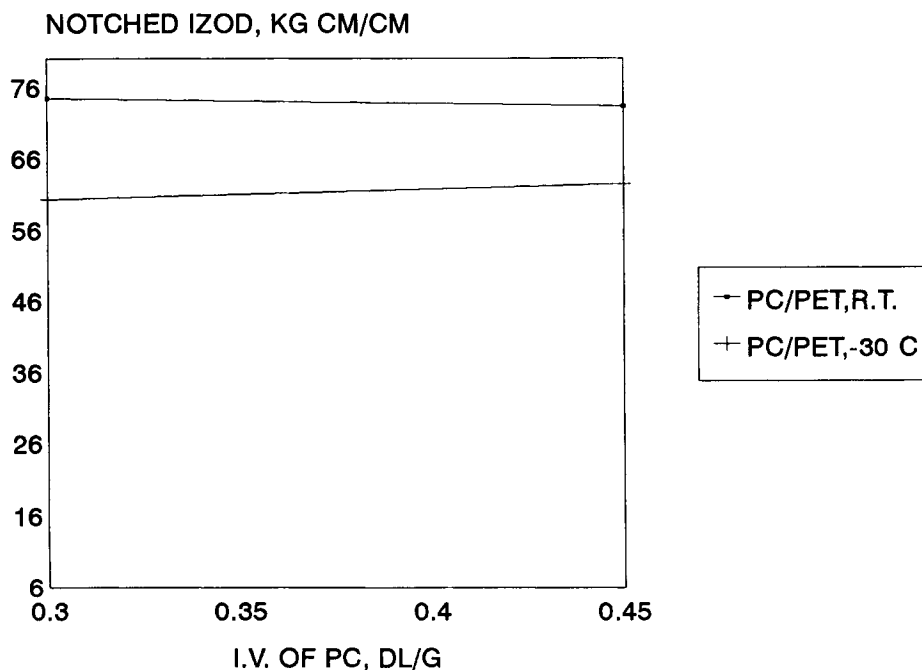


Figure 24 Notched Izod vs. I.V. of PC in a PET/PC impact-modified blend.

DISCUSSION

Poly(phenylene sulfide) (PPS)

The data obtained on the impact modified PPS systems (Fig. 7) was consistent with the Wu model. Trends such as the effects of the impact modifiers on critical interparticle distance are difficult to evaluate because of the fact that sample B is a graft copolymer, as well as being functionalized with a reactive group.

Although most of the data in Figure 7 falls within a fairly narrow band, the point representing a blend containing 15 wt % of modifier B in high molecular weight (W300) PPS falls well outside this band, almost on the abscissa. This blend differs from the rest in that it was compounded on a 40 mm twin-

screw extruder. This extruder subjected the sample to a longer residence time and higher melt temperatures than were seen by the other samples, which were compounded on a lab scale twin-screw extruder. It has not yet been determined whether this change in processing resulted in a different particle-size distribution for this sample from that obtained in the other blends. Such a change could result in a significant deviation from the general trend.

The data in Figure 8 indicated that change in the level of crystallinity can alter the critical interparticle distance. This suggests that there is a change in mechanism as the material goes from amorphous to crystalline. The nature of these differences is not fully explained by the current data and the Wu model. In subsequent studies described in this article, it is assumed that the crystallinity remains constant for a given matrix.

Table III Poly(ethylene terephthalate) (PET) and Polycarbonate (PC) Molecular Weight (M_n), Entanglement Molecular Weight (M_e), and Ratios (M_n/M_e)

| | PET | PET | PC | PC |
|---------------------------|------|------|------|------|
| Inherent viscosity (dL/g) | 0.7 | 0.95 | 0.3 | 0.45 |
| $M_n \times 10^{-3}$ | 8.8 | 12.7 | 5.1 | 8.3 |
| $M_e \times 10^{-3}$ | 1.63 | 1.63 | 1.79 | 1.79 |
| M_n/M_e | 3.4 | 7.8 | 2.8 | 4.6 |

Polyoxymethylene (POM)

No supertough behavior is observed with this system at room temperature, but supertough behavior was observed at elevated temperatures. The dispersion morphology obtained in the present samples meets the required interparticle distance above room temperature, but not at room temperature. To achieve supertough behavior, efforts would have to be made to lower the interparticle distance (<0.18 micron).

Presumably, a reduction in the modulus of the rubber would result in an increase of the critical interparticle distance within a given modulus range. More research is needed to define a suitable system. Based on our current studies, the following would be predicted:

| τ | Characteristic Fracture and Impact |
|---------------|---|
| > 1 | Brittle, no increase in impact |
| $< 1, > 0.18$ | Brittle, increase to 20 kg cm/cm independent of POM molecular weight |
| $= 0.18$ | Brittle-tough transition; increase depends on POM molecular weight (7-26 kg cm/cm for melt index range studied) |
| < 0.18 | Tough, sharp increase in impact (not observed) |

This scheme is summarized in Figure 18. The molecular weight dependence of the increment of impact increase at the critical interparticle distance has been related to the number-average molecular weight to the entanglement molecular weight ratio as in the previous discussion. At very high molecular weights, the impact increment dependence on molecular weight should disappear as the matrix resin possesses the necessary entanglement density. No data, however, are available to demonstrate this effect. The high molecular weight material would be very difficult to process.

Poly(butylene terephthalate) (PBT)

The data indicated that PBT also followed the Wu model with respect to impact strength and interparticle distance. In contrast to POM, a critical interparticle distance at room temperature was found at which PBT-modified samples exhibited ductile behavior. It also was shown that the modulus of the impact modifier had a major effect on the critical interparticle distance. When rubber cavitation plays a major role in toughening, lower modulus rubbers are expected to be more efficient tougheners.⁸ On the other hand, if the rubber acts as a stress concentrator, the modulus of the rubber should have no effect on the toughness, as long as it is less than about $\frac{1}{10}$ that of the matrix.⁸ The moduli of each of the modifiers in this study are less than one-tenth that of the matrix. Functionalization of the modifier did not alter the basic impact vs. interparticle dis-

tance relationship. It would follow that adhesion of the impact modifier would be less important to impact properties than would the matrix particle morphology, which is moderated by the functionalization. The work of Oshima and Sasaki contrasts with this in that an epoxy-modified core shell impact modifier improved the impact of the blend vs. a nonmodified control. The particle sizes were similar in these blends since core shell modifiers have defined morphologies. This result was verified by direct microscopic examination. It is possible that use of a more reactive functionality (vs. anhydride) would produce an improvement in impact levels.

Polycarbonate/Poly(ethylene terephthalate) (PC/PET)

The effect of polymer molecular weight on impact follows Wu's analysis. Table III presents the molecular weight (M_n), the entanglement molecular weight (M_e), and the ratio of the two. It can be seen that the ratios are within the sensitive ratio levels for molecular weight effects on supertough behavior of amorphous and semicrystalline materials (approximately seven times; also see discussion in Polyoxymethylene section).

This system is considerably more complex than the systems examined with polymer and impact modifier alone. Additional factors to be considered include

- Partitioning and compatibility of the impact modifier in PET vs. the PC phase.
- Transesterification of PET and PC and miscibility effects.
- Changes in crystallization behavior due to transesterification.
- Polymer mixing and morphology.

Many of these are process-dependent parameters, which can lead to inherent variability in impact behavior. These factors will be considered in another article.

CONCLUSIONS

For the blend systems studied here (PPS, POM, PBT), elastomer interparticle distance provides a better correlation to brittle-tough transition temperature than does particle size, as predicted by the Wu model. The critical interparticle distance has been shown to depend on the degree of crystallinity

(PPS) and the modulus of the impact modifier relative to the matrix (PBT). Actual adhesion of the polymer to the matrix (variation of functionality levels) was not found to have a strong influence (PBT). An alternate functional modifier that was more reactive with the PBT could illuminate this conclusion.

In POM, the critical interparticle distance for room-temperature toughening was not achieved. In PET/PC blends, the molecular weight of the primary matrix resin (PET) was the determiner of impact properties within the molecular weight of the resin studied.

FUTURE WORK

Future work on these systems should focus on the role of processing conditions on particle-size distribution and blend toughness. In addition, study of the grafting reaction between matrix and elastomer would help to elucidate the role of adhesion in toughening PPS. For example, measurements of lap shear strength for different matrix-elastomer blends would allow a ranking of toughness vs. interfacial adhesion.

NOTATIONS

- M_n number-average molecular weight
 M_e entanglement molecular weight
 d particle diameter
 τ surface-to-surface interparticle distance
 ϕ volume fraction of the dispersed phase

List of Acronyms

- PC polycarbonate of bisphenol A
 PBT poly (butylene terephthalate)
 PET poly (ethylene terephthalate)
 POM polyoxymethylene, polyacetal
 PPS poly (phenylene sulfide)

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REFERENCES

1. C. B. Bucknall, *Toughened Plastics*, Applied Science, London, 1977.
2. E. J. Kramer, in *Polymer Compatibility and Incompatibility*, MMI Press, New York, 1982.
3. A. F. Yee, *Polym. Eng. Sci.*, **21**, 205 (1981).
4. S. Kunz-Douglass, P. W. R. Beaumont, and M. F. Ashby, *J. Mater. Sci.*, **15**, 1109 (1980).
5. S. Wu, *Polym. Eng. Sci.*, **30**, 75 (1990).
6. S. T. Wellinghoff and E. Baer, *J. Appl. Polym. Sci.*, **22**, 2025 (1978).
7. S. Wu, *Polymer*, **26**, 1855 (1985).
8. S. Wu, *Polym. Int.*, **29**, 229 (1992).
9. J. Oshima and I. Sasaki, *Polym. News*, **16**, 198 (1991).
10. S. Wu, *J. Appl. Polym. Sci.*, **35**, 549 (1988).
11. L. Wadhwa, T. Dolce, and H. L. LaNieve, *SPE RE-TEC*, **38** (1985).
12. S. Hobbs, M. Dekkers, and V. Watkins, *J. Mater. Sci.*, **23**, 1219 (1988).

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