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Morphology and properties of toughened poly(phenylene oxide)–polyamide blends

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High impact strength poly(phenylene oxide)–polyamide blends can be prepared by chemically coupling the two components and incorporating a rubbery impact modifier in the resin. The resulting materials exhibit a distinctive morphology in which the rubber is selectively incorporated in the dispersed poly(phenylene oxide) phase. In this paper both the structure and toughening mechanisms in these blends are examined. An analysis of their deformation behaviour is presented in a companion paper.

1. Introduction

Blends of incompatible glassy or semi-crystalline polymers often show a marked drop in impact strength and elongation near the midpoint of the composition range [1]. The deterioration in performance is attributed to the rapid initiation and growth of cracks in the weak interfacial region. Unmodified blends of poly(phenylene oxide) and Nylon 6,6 are typical of materials of this type. It has been demonstrated that substantial improvements in the properties of such blends can be achieved by incorporating a suitable copolymer in the resin. The copolymer may be independently synthesized or generated "*in situ*" by the addition of a suitable chemical coupling agent during compounding [2]. By reducing the size of the dispersed phase and increasing the interfacial adhesion, these modifications retard the development of flaws leading to catastrophic failure [3, 4]. Such methods have been used with some success to produce blends having advantages in cost, solvent resistance, etc., over those of their components. In most cases an impact modifier is required to achieve the required toughness. A brief description of the factors affecting the mechanical behaviour of several commercial blends of this type has recently appeared [5].

In the current study of poly(phenylene oxide)–polyamide blends, the effects of adding a rubbery impact modifier and changing the level of coupling between the glassy and semicrystalline homopolymers are examined in detail. Scanning and transmission electron microscopy are used to characterize the morphologies of the resulting materials. A number of important and unique correlations between microstructure and fracture behaviour are discussed.

2. Experimental details

2.1. Sample preparation and testing

The samples used in this study were prepared by compounding poly(2,6-dimethyl-1,4-phenylene oxide) and Nylon 6,6 with a styrene–butadiene–styrene (SBS) block copolymer impact modifier and proprietary coupling agent on a Werner–Pfleiderer twin screw extruder. The poly(phenylene oxide) resin was supplied by the PPO Technology Department of the General Electric Plastics Business Group and had an intrinsic viscosity of 0.45 dl g^{-1} in chloroform at 25° C. A commercial Nylon 6,6 moulding resin was obtained from Nilit, Incorporated. Unless otherwise noted, the poly(phenylene oxide)–Nylon 6,6 ratio in the starting material was fixed at 50:40 parts by weight. The rubber loading and coupling agent concentration were systematically varied. The fraction of material converted to copolymer during the extrusion was determined by selectively extracting the poly(phenylene oxide) and SBS rubber with chloroform and the Nylon 6,6 with formic acid and weighing the remaining insoluble resin. The resulting blends were injection moulded into ASTM Type D tensile dogbones and Izod impact specimens and double-bagged and stored with a dessicant to minimize water pickup.

Notched Izod impact testing was carried out on a Baldwin impact tester with appropriate corrections made for windage and friction. All samples were notched (0.25 mm notch radius) with a fly cutter immediately prior to testing. Samples fractured below room temperature were cooled for 2 h before insertion in the testing apparatus while those broken at elevated temperatures were held for 30 min to minimize thermal ageing effects. Transfer times were generally 10 sec or less. Other physical properties such as modulus, elongation, etc., were determined using an Instron 1350 servohydraulic testing machine. The tests were run at room temperature and a strain rate of 5×10^{-3} sec^{-1} unless otherwise noted.

2.2. Microscopy

Scanning electron microscopy was carried out on an ISI 40 SEM equipped with a GW Electronics backscattered electron detector. Microtomed cross sections of the blends were prepared for examination using a Reichert Ultracut E Ultramicrotome. The surfaces of the freshly cut samples were featureless and it was

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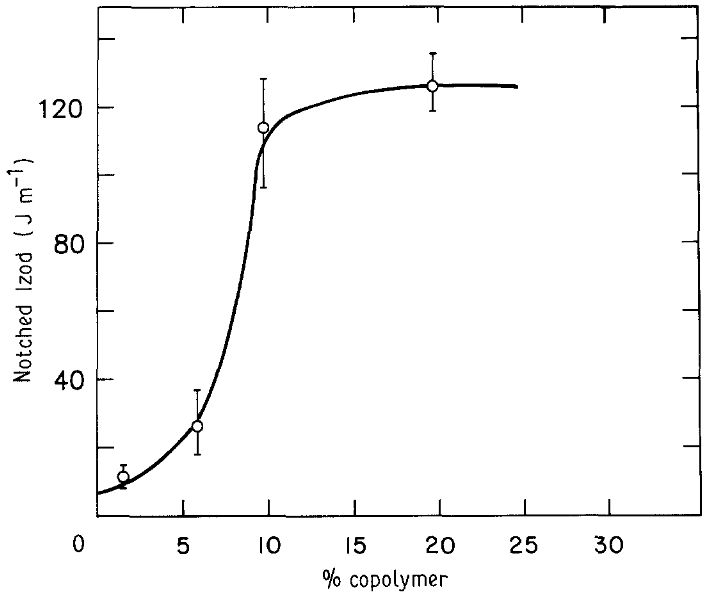

Figure 1 Variation in notched Izod impact strength with post-extrusion copolymer concentration for 50:40:10 poly(phenylene oxide)–Nylon 6,6–rubber blends.

necessary to enhance the contrast between the phases by plasma etching or selective staining. Satisfactory etching was obtained by exposing the samples to an oxygen plasma at a pressure of 100 μm for 10–15 min (SPI Plasma Prep II). The resulting samples were sputtered with an Au-Pd alloy and examined using standard secondary electron imaging. Staining was carried out under very mild conditions by immersing the samples in a 2% methanolic bromine solution for two minutes at room temperature. Earlier studies had shown that sufficient halogenation of the poly(phenylene oxide) occurred under such circumstances to produce sharp chemical contrast differences between it and other blend components in backscattered images [6]. Stained samples were coated with a thin layer of evaporated carbon prior to examination.

TEM observations were carried out on a Hitachi H-600 transmission electron microscope. Thin sections were cut from microtomed blocks which had been exposed to a 1% solution of osmium tetroxide in hexane for several hours. The sections were mounted on 200 mesh copper grids for examination.

3. Results

The variations in notched Izod impact strength with copolymer concentration are shown in Fig. 1 for several blends containing poly(phenylene oxide), Nylon 6,6 and rubber in the ratio of 50:40:10 by weight. A similar plot showing the change in impact strength with temperature for corresponding blends containing 45% copolymer but different loadings of rubber is presented in Fig. 2. As expected, the toughness of the blends improves steadily as the impact modifier and copolymer levels increase. Significantly, neither high rubber levels nor high copolymer concentrations alone are sufficient to produce high impact strength specimens. Increasing the copolymer concentration produces a rapid decrease in the size and anisotropy of the dispersed phase. These characteristics are shown in the SEM photomicrographs presented in Figs 3 to 5 and more quantitatively in the plots in Figs 6 and 7. It was possible to positively identify the dispersed phase as poly(phenylene oxide) from backscattered images of bromine-stained specimens such as the one shown in Fig. 8. In this photograph, the increased emission from the halogenated polymer differentiates it sharply from the nylon matrix. Contrast is further enhanced by preferential absorption of the stain at the poly(phenylene oxide)–Nylon 6,6 interface where it produces a well defined outline of the individual dispersed particles. By staining with osmium rather than bromine, it was possible to use a similar procedure to highlight only the rubber phase (see Fig. 9). From photomicrographs such as these and transmission electron micrographs of corresponding thin sections such as that shown in Fig. 10 it became evident that the SBS rubber was incorporated exclusively in the dispersed poly(phenylene oxide)

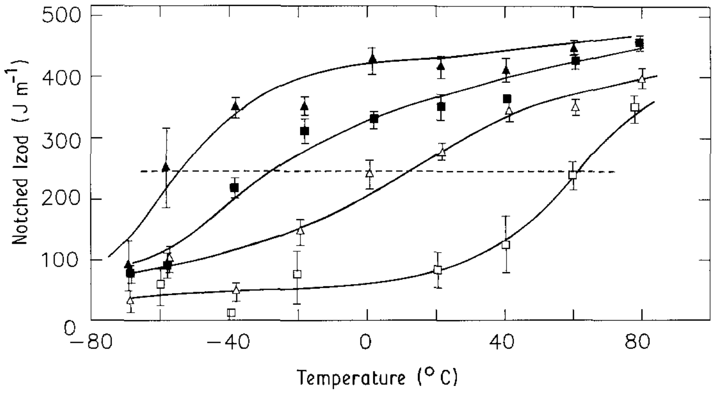

Figure 2 Variation in impact strength with temperature and rubber loading for 50:40 poly(phenylene oxide)–Nylon 6,6–rubber blends containing 45% copolymer after extrusion at rubber levels of 4 (□), 6 (△), 10 (■) and 15 (▲) %.

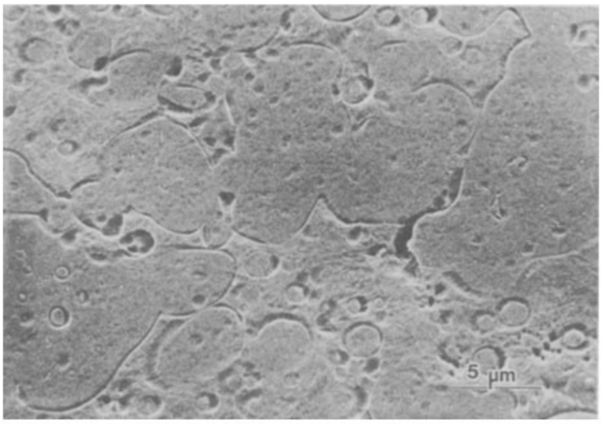

Figure 3 SEM photomicrograph of plasma-etched 50:40:10 poly(phenylene oxide)–Nylon 6,6–rubber blend containing no copolymer.

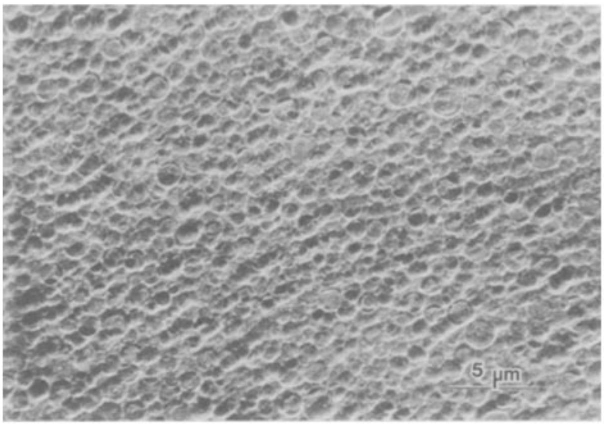

Figure 5 SEM photomicrograph of plasma-etched 50:40:10 poly(phenylene oxide)–Nylon 6,6–rubber blend containing 25% copolymer after extrusion.

particles. It will be shown later that this feature results in a unique mode of toughening for these resins.

As might be expected, changes in fracture surface morphology correlated more strongly with the measured impact strengths than with independent variations in either copolymer level or rubber loading. The fracture surfaces of those samples failing with N.I. values of less than 40 J m^{-1} displayed comparable numbers of debonded poly(phenylene oxide) particles and matrix craters (see Fig. 11). Relatively little deformation of the dispersed particles was evident at low levels of copolymer or rubber. Likewise, there was little indication of cavitation around the particles which remained partially imbedded in the fracture surface. Remnants of plateau-like structures created by microscopic crack bifurcation during fast fracture could be seen in the nylon matrix. There was a marked increase in the amount of plastic deformation in the dispersed phase in samples having Izod values on the range of 60 to 140 J m^{-1} although interfacial failure was still observed (see Fig. 12). In these samples, as well as in the samples exhibiting impact strengths in excess of 170 J m^{-1}, extensive plastic deformation of the nylon matrix was noted and it became progressively more difficult to distinguish the dispersed and continuous phases.

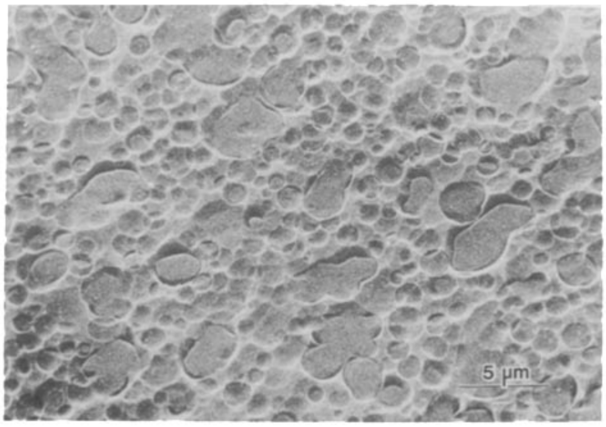

Figure 4 SEM photomicrograph of plasma-etched 50:40:10 poly(phenylene oxide)–Nylon 6,6–rubber blend containing 15% copolymer after extrusion.

4. Discussion

The toughening of resins through the introduction of a rubbery dispersed phase has been extensively addressed in the technical literature [7]. It is generally agreed that the increases in stress concentration which develop around these soft inclusions promote the initiation and growth of crazes and/or shear bands which are the primary means of energy dissipation in the system. By controlling and delocalizing these processes on a microscopic scale throughout the solid, the growth of supercritical flaws leading to catastrophic failure is restricted. The extent to which either of these processes occurs depends on a number of factors including the inherent ductility of the matrix resin, the geometry of the local stress field, the quality of interfacial bonding, and the amount of rubber which is added to the system. Recent studies have indicated

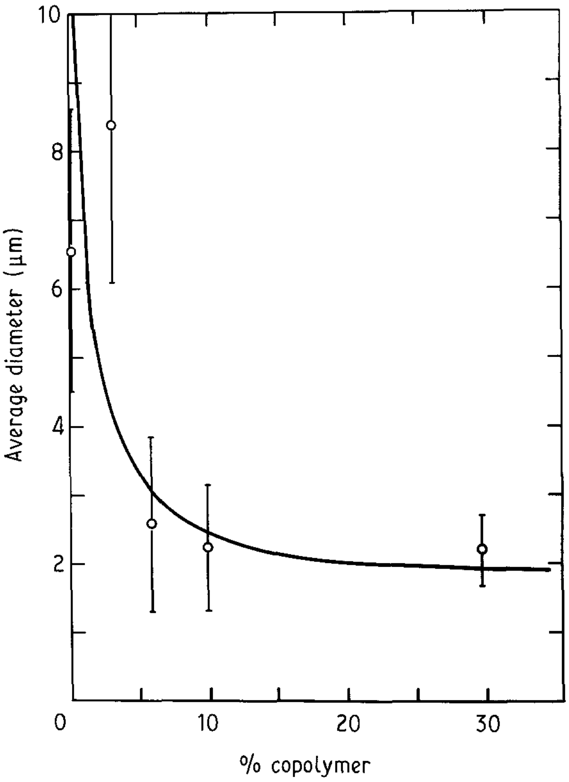

Figure 6 Variation in dispersed particle diameter with post-extrusion copolymer concentration.

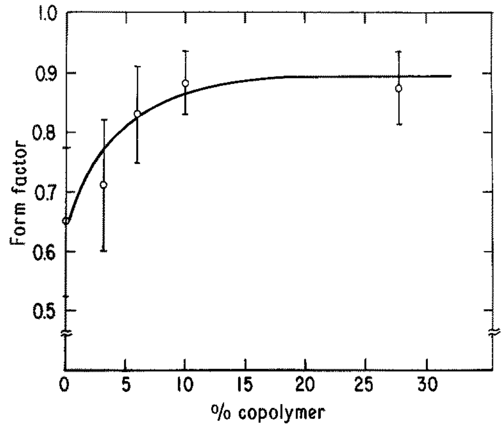

Figure 7 Variation in dispersed particle anisotropy with post-extrusion copolymer concentration (form factor $F = 4\pi A/p^2$ where A is the area are p the perimeter of the particle).

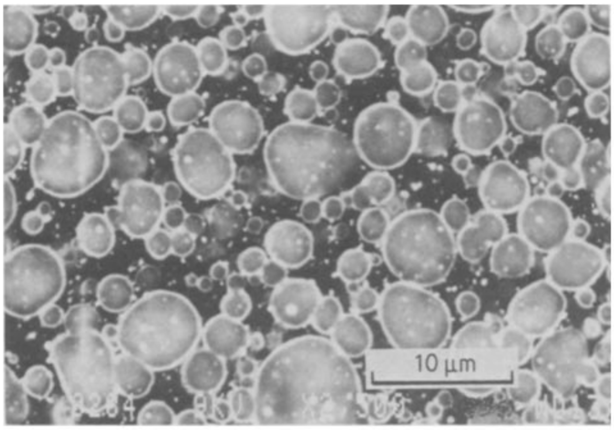

Figure 8 Backscattered electron SEM photomicrograph of bromine-stained 50:40:10 poly(phenylene oxide)–Nylon 6,6–rubber blend.

that the development of stress field overlap between neighbouring rubber particles with increasing concentration is a critical feature of the toughening process for more ductile resins [2, 8].

The system of current interest is unique in that the number of particles of the dispersed phase (poly(phenylene oxide)) does not increase substantially with the rubber loading. The base morphology of the system and the level of interfacial bonding are largely fixed by the amount of copolymer formed and the processing conditions. As a result, it appears that the primary effect of increasing the rubber level is to produce a gradual softening of the dispersed phase. It is worthwhile to consider whether the resulting variations in the local stress fields are sufficiently large to account for the observed improvements in toughness. For the purposes of the current discussion, only the principal equatorial tensile stress will be considered since it is this stress which largely determines the magnitude of the dilational and deviatoric stress fields. It has been shown that other stress components of interest such as the major principal shear stress are also maximized along the particle equator [9].

The stress concentration factors were calculated using Goodier's solutions for isolated, perfectly adhering spherical inclusions in a semi-infinite matrix [10]. Although this assumption is inappropriate for the concentrated system at hand, subsequent finite element analyses have demonstrated that the conclusions can be realistically extended to particle loadings approaching 40 to 50% [11]. Both the matrix and inclusions were assumed to have a Poisson's ratio of 0.4. Modulus values determined for the nylon homopolymer and several poly(phenylene oxide)–rubber blends from tests on macroscopic ASTM test specimens are listed in Table I. The calculated stress concentrations are plotted as a function of rubber level in the dispersed phase in Fig. 13. The stress concentration factor at the surface of an imbedded poly(phenylene oxide) particle increases from 1.15 to 1.27 on the addition of 20 wt % rubber.

It has been noted that the effective modulus of a dispersed particle having a hybrid composition may depend more strongly on its internal morphology than on its overall composition [12]. In the extreme case in which the rubber is isolated on the exterior surface of the particle, for instance, the surrounding stress field is comparable to that produced by a pure rubber particle of equivalent dimensions. In the opposite case, in which the soft component is located at the core of the particle, the stress field is like that around a hard inclusion. Fig. 10 shows that the blends in this study lie somewhere between these two extremes. It thus seemed likely that behaviour of the dispersed poly(phenylene oxide)–rubber particles might be substantially different than that of the macroscopic specimens.

To test this hypothesis, modulus measurements were carried out on a series of blends in which the poly(phenylene oxide)–rubber ratio in the dispersed

TABLE I Tensile moduli of blend components ($\dot{\varepsilon} = 5 \times 10^{-3}\,\mathrm{sec}^{-1}$)

Component	Modulus (MPa)
Nylon 6,6	3270
Poly(phenylene oxide)	2480
Poly(phenylene oxide)/rubber	
98/2	2380
95/5	2330
90/10	2240
80/20	1950

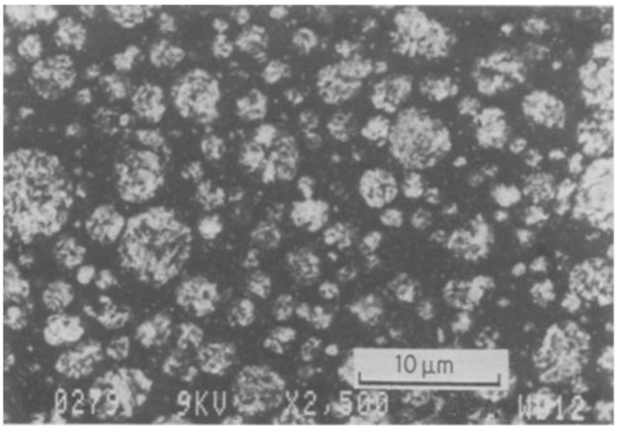

Figure 9 Backscattered electron SEM photomicrograph of blend in Fig. 8 stained with osmium tetroxide.

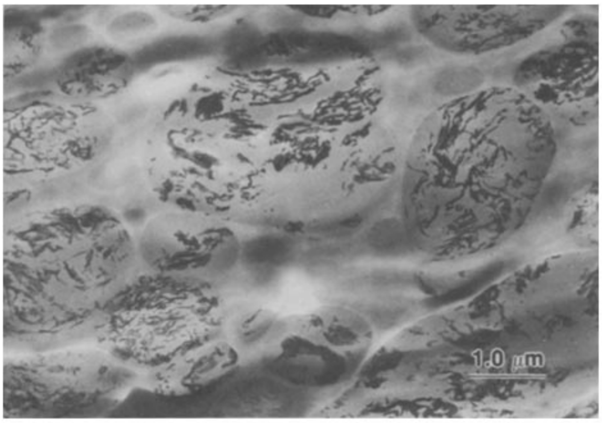

Figure 10 Transmission electron micrograph of microtomed thin section from Sample 9.

phase was held constant at 80 : 20 but the overall blend composition was varied by adding additional Nylon 6,6. There was no significant change in the size or internal morphology of the dispersed particles in these specimens. The results are shown in Fig. 14. Also plotted are curves showing the predicted moduli for these blends based on independent modulus measurements carried out on macroscopic samples of the blend components (see Table I). The values were calculated using upper (parallel) and lower (series) bound models according to Equations 1 and 2

$$E = \Phi_m E_m + \Phi_D E_D \tag{1}$$

$$\frac{1}{E} = \frac{\Phi_m}{E_m} + \frac{\Phi_D}{E_D} \tag{2}$$

In these equations, E_m is the Young's modulus of the nylon matrix, E_D is the Young's modulus of an 80 : 20 poly(phenylene oxide)–rubber blend and Φ_D and Φ_m are the volume fractions of the dispersed and continuous phases, respectively. Other approximations lie somewhere between these two extremes [13, 14]. What is significant is that, in both cases, the calculated moduli exceed the measured values by a significant amount indicating that the dispersed phase in the blends of interest is significantly softer than suggested by its macroscopic composition. The broken line in Fig. 13 shows the change in equatorial stress concentration with rubber loading predicted from these results. In this more realistic case, the stress concentration factor at the surface of an imbedded poly(phenylene oxide) particle increases from 1.15 to almost 1.6 on the addition of 20 wt % rubber.

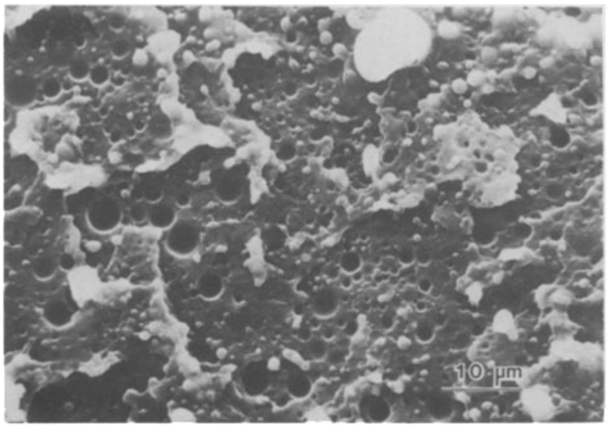

Figure 11 Fracture surface of 55 : 45 : 10 poly(phenylene oxide)–Nylon 6,6–rubber blend containing 7% copolymer after extrusion.

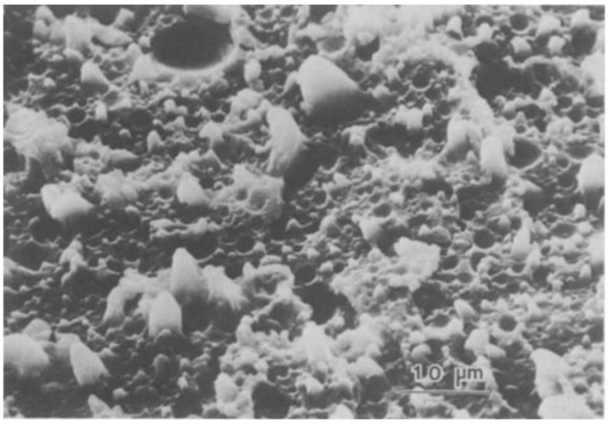

Figure 12 Fracture surface of 50 : 40 : 10 poly(phenylene oxide)–Nylon 6,6–rubber blend containing 20% copolymer after extrusion.

The preceding analysis indicates that incorporation of rubber in the poly(phenylene oxide)–nylon blends is capable of markedly reducing the modulus of the dispersed phase and enhancing the surrounding stress field. Since both the dilational and deviatoric stresses rise, crazing and shear banding are expected to be enhanced. Impact test results demonstrate, however, that in order for these processes to become effective in increasing toughness, a significant level of interfacial coupling must be simultaneously achieved. Nylon itself, although highly ductile, is extremely notch sensitive suggesting that the craze strength is relatively low (i.e., once initiation occurs, craze breakdown occurs readily with little energy dissipation).

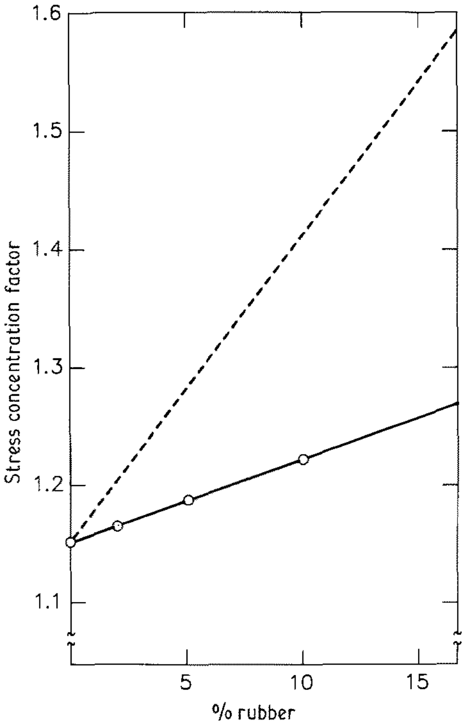

Figure 13 Calculated stress concentration factor vs. rubber level in dispersed phase. (—— prediced from tests on large poly(phenylene oxide)/rubber specimens, - - - calculated from measured blend moduli).

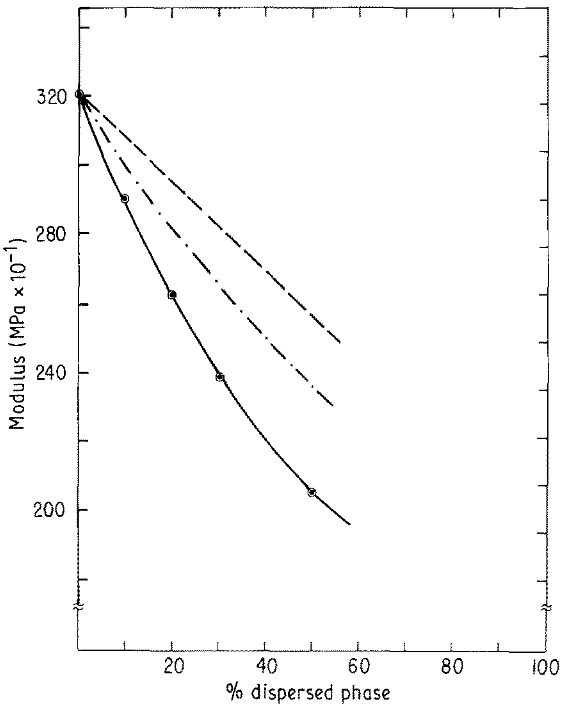

Figure 14 Variation in blend modulus with dispersed phase concentration (dispersed phase composition fixed at 80 : 20 poly(phenylene oxide)–rubber).– – – "upper bound" parallel model*, –·–·–·– "lower bound" series model*, —○—○— measured. *Assumed dispersed phase modulus = 270 k.s.i.

Such behaviour is consistent with the relatively short chain length of this condensation resin. The same process appears to occur in the blends. When the dispersed particles are large and/or poorly bonded to the matrix, large defects are introduced during the initial stages of crazing, craze stabilization is poor, and rapidly growing cracks develop before the craze envelope becomes sufficiently large to absorb significant energy. A process of this type has been discussed previously [2]. In the current work it is supported by photomicrographs such as Fig. 11 which show a large number of undeformed, debonded particles in broken specimens containing high levels of rubber but low concentrations of coupling agent. When interfacial bonding is improved and the dispersed phase size is reduced by the "*in situ*" copolymer formation, however, sufficient time is made available for plastic flow to play a major role in dissipating energy (see Fig. 12). It is the combination of effects which is responsible for the improvements in toughness exhibited by the materials described herein. A more detailed analysis of the deformation behaviour of blends of this type is presented in a companion paper [15].

5. Conclusions

1. The morphology of toughened poly(phenylene oxide)–Nylon 6,6 blends has been characterized by scanning and transmission electron microscopy. In all of the materials examined, Nylon 6,6 forms the continuous phase and the rubbery impact modifier is contained within the dispersed poly(phenylene oxide) domains. The size and anisotropy of the dispersed phase decreases with increasing copolymer concentrations.

2. High notched Izod impact strengths are obtained at room temperature only in those blends which are strongly coupled and have rubber loadings of 10% or greater. When the copolymer concentration is fixed, the ductile–brittle transitions shift to lower temperatures with increasing rubber concentration.

3. Increases in toughness in the blends of current interest appear to arise primarily as the result of progressive softening of the dispersed phase through addition of rubber. The effective modulus of the poly(phenylene oxide)–rubber component has been found to drop much more rapidly than expected using test data on macroscopic poly(phenylene oxide)–rubber blends.

4. In order for the addition of rubber to be effective in improving the impact strength of poly(phenylene oxide)–Nylon 6,6 blends an appreciable level of copolymer must be present. The copolymer reduces the size of the dispersed phase, increases interfacial adhesion, and retards craze breakdown until extensive shear flow can take place.

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