MECHANICAL AND FRACTURE BEHAVIOR OF RIGID-ROD SELF REINFORCED POLYMERS

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Abstract

Recently, a novel family of processable rigid-rod polyphenylenes with outstanding mechanical properties was introduced (Parmax® SRPs). These materials possess strength and stiffness superior to other thermoplastics while retaining reasonable notched Izod values (65 J/m). To understand this better, the mechanical behavior of these materials, focusing on fundamental fracture mechanisms, was investigated. The materials appear to generate weak crazes at crack tips combined with a multi-planar step-deflection mechanism for crazing/cracking behavior during the crack propagation stage.

Background

Melt-processable rigid-rod self-reinforced polymers (SRPs) can be achieved by the utilization of carefully chosen sidechain substituents (thereby yielding what is sometimes referred to as “hairy-rod” polymers), and/or by utilizing a carefully controlled number of “kinked” comonomer units. These kinds of polymers can be very versatile materials; depending on the exact structure (e.g. size and identity of sidechains, type and length of rigid-rod backbone segments, and identity and number of kinks), a great diversity in properties of the resulting polymers can be obtained.

A family of SRPs based on rigid-rod polyarylenes, under a trade name of Parmax® SRPs has recently become commercially available (Figure 1). These materials possess a unique combination of high performance mechanical properties along with good processability. These materials differ from the earlier rigid-rod systems, Parmax® SRP materials are soluble in a select few organic solvents (N-methylpyrroloidinone, CH₂Cl₂); but not in common solvents such as toluene, alcohols, gasoline, acetone, esters, or others. They can be thermally processed in the conventional manner (compression molded, extruded, injection molded, etc.).

Parmax® SRP mechanical properties are well above those for any other thermoplastic currently available, as shown in Figure 2. Despite having moduli at least twice that of the next stiffest thermoplastic, it is interesting to note that their notched Izod values (~65 J/m - Table A) are as high (or higher) than a number of other thermoplastics in this group (for comparison PEI ~38 J/m, PEEK ~54 J/m). This presented an impetus to examine the fracture characteristics of Parmax® SRPs in more detail and the results are the focus of this paper.

Experimental

The Parmax® SRP used in this study was Parmax® 1200, supplied by Mississippi Polymer Technologies Inc. (MPT). This material is a copolymer of para-linked benzophenone and meta-linked unsubstituted phenylene units (Figure 3.)

Samples were fabricated by compression molding using a Carver AutoFour/30 press at 315 ºC and 2000 psi., and notched flexure samples were machined from the compression molded plaques. The fracture specimen geometry was double notched – 4 point bend (DN – 4PB) bar. The notches were made using a CEAST Notchvis with a 250 µm radius blade. An Instron Model 1125 test frame with MTS ReNew® Upgrade Package was used to either: (1) fracture the specimens, or (2) to generate an arrested crack for further examination.

Fracture surfaces were examined using an AMRAY Model 1820 Scanning Electron Microscope (SEM) at an operating voltage of 5kV. The fracture surfaces were prepared for SEM examination by first carbon coating followed by sputtering with a 10 to 20 nm layer of Au/Pd bar. The notches were made using a CEAST Notchvis with a 250 µm radius blade. An Instron Model 1125 test frame with MTS ReNew® Upgrade Package was used to either: (1) fracture the specimens, or (2) to generate an arrested crack for further examination.

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nematic order at room temperature), exhibit thermoplastic behavior, and have a number of other worthwhile properties. In addition to outstanding thermal and thermooxidative stability, films and molded samples possess isotropic tensile and flexural modulus in the range of 8-10 GPa (1,250,000 – 1,500,000 psi) with strengths of 250-350 MPa (36,000 – 52,000 psi). Differing from the earlier rigid-rod systems, Parmax® SRP materials are soluble in a select few organic solvents (N-methylpyrroloidinone, CH₂Cl₂); but not in common solvents such as toluene, alcohols, gasoline, acetone, esters, or others. They can be thermally processed in the conventional manner (compression molded, extruded, injection molded, etc.).

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Results and Discussion

Typical Parmax® 1200 fracture surfaces appear macroscopically flat. Optical microscopy at low magnifications (50-200X), however, indicated microscopically rough surfaces, with material apparently pulled away from the bulk surfaces (Figure 4). There was no evidence of shear yielding. Further examination also suggested that there was more than one fracture initiation point, in addition to the “main” fracture, suggesting that crack propagation energy was high enough to allow formation of additional fracture initiation points. These results prompted further examination via SEM and TEM in an attempt to elucidate the exact mechanisms of crack initiation and propagation.

A craze at the tip of an arrested crack in Parmax® 1200 is shown in the transmission electron photomicrograph of Figure 5. The craze is relatively short (~1 µm) and has already undergone craze fibril fracture at the craze/matrix interface of the polymer. This type of crazing was found to be typical for Parmax® 1200. The observation indicates that amorphous polyphenylenes do have the ability for crazing, but that the crazes are relatively short, weak, and unstable and thus likely not dissipating enough energy to completely explain the relatively high notched Izod values.

Following the TEM observations above, the focus shifted to SEM examination of fracture surfaces. The SEM photomicrographs in Figure 6 and 7 depict what is typical for fracture surfaces in Parmax® 1200. Shown in Figure 6 is the area near a notch with relatively slow craze/crack growth concave feature under plane strain conditions. Shown in Figure 7 is the interior fracture surface generated under very rapid crack growth rates. General fracture surface features such as those observed here have been reported for other semi-brittle glassy polymers by Andrews (among others). 11

The fracture surface is markedly rougher in Figure 7, which illustrates extensive multi-planar fracture. These observations suggest that the relatively weak crazing quickly leads to extensive localized cracking governed by a step-deflection mechanism similar to what is observed in semi-brittle solids and polymers.9,12 Evidently, the energy associated with the localized yield, surface generation, and ligament bending (i.e., bending of matrix polymer between craze/cracks13) within the observed step-deflection mechanism in such a stiff polymer (~8.3 GPa modulus) results in fracture energy sufficient to produce 55+ J/m (1 ft-lb/in) notched Izod impact values.

Conclusions

The fundamental mechanistic aspects of fracture initiation and propagation in Parmax® 1200, a rigid-rod polyarylene, were investigated. Considering the very high modulus of the material, Parmax® 1200 has relatively good notched Izod values (~65 J/m) and the reasons for this behavior are suggested in this paper. The techniques utilized were optical, scanning electron and transmission electron microscopy. It was found that fracture in the Parmax® 1200 system initiates with weak crazing which rapidly evolves into extensive multi-plane fracture in the crack propagation stage. It is thought that the energy necessary to propagate the crack through this mechanism is high enough to explain the relatively high notched Izod values. Future work in this area will concentrate on the introduction of particulate second phases to alter the modes of deformation in Parmax® 1200 and, thereby, further enhance its toughness.

References

5 Unpublished data: Bubeck, R. Li, X., and Malkovich, N.
6 Connolly, M., Karasz, F. and Trimmer M., Macromolecules 1995, 28, 6, 1872-1881
8 GE Product Literature – Ultem 1010
9 Boedeker Product Literature – PEEK Unfilled
**Figures and Table**

**Figure 1.** Generic structure of Parmax® SRPs

**Properties of Parmax®-1200**

<table>
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<tr>
<th>Property</th>
<th>Value</th>
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<td>Hardness, Rockwell (B Scale)</td>
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**Table A.** Mechanical Properties of Parmax® 1200.

**Figure 2.** Tensile Property Comparison between Parmax® 1200 and other advanced thermoplastics

**Figure 3.** Parmax® 1200 structure

**Figure 4.** Optical micrograph of a fracture (3-point bend) surface of Parmax® 1200 (200X) showing material pulled away from the fracture surface.

**Figure 5.** Area at a crack tip in Parmax 1200 with a craze roughly 1 µm long that has fractured at the craze/matrix interface. Scale marker = 0.5 µm.
Figure 6. Position of fracture initiation at a surface notch. Scale marker = 200µm.

Figure 7. Detail of fracture surface in rapid crack growth region. Scale marker = 10 µm.