

# 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<sup>®</sup> 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<sup>®</sup> 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 polymers which had exceptional mechanical properties<sup>1</sup>, but were either intractable (e.g. unsubstituted polyparaphenylene or aromatic polypyromellitimides)<sup>2</sup> or soluble only in strong acid solvents (e.g. polybenzazoles and polyquinolines)<sup>3</sup>. Parmax<sup>®</sup> SRP polymers have been designed to overcome the processing deficiencies of earlier rigid-rod polymers *via* the use of carefully chosen pendant sidechains to impart solubility and thermal processability to the normally intractable rigid-rod polyparaphenylene backbone.

The resulting materials possess outstanding mechanical properties, as enumerated in Table A., but are predominantly amorphous (with a low ~ 5 wt. % level of

nematic order at room temperature),<sup>4,5</sup> exhibit thermoplastic behavior, and have a number of other worthwhile properties.<sup>6</sup> In addition to outstanding thermal and thermooxidative stability<sup>7</sup>, 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<sup>®</sup> SRP materials are soluble in a select few organic solvents (N-methylpyrrolidinone, CH<sub>2</sub>Cl<sub>2</sub>); but not in common solvents such as toluene, alcohols, gasoline, acetone, esters, or ethers. They can be thermally processed in the conventional manner (compression molded, extruded, injection molded, etc.).

Parmax<sup>®</sup> 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<sup>8</sup>, PEEK ~54 J/m<sup>9</sup>). This presented an impetus to examine the fracture characteristics of Parmax<sup>®</sup> SRPs in more detail and the results are the focus of this paper.

## Experimental

The Parmax<sup>®</sup> SRP used in this study was Parmax<sup>®</sup> 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 °C 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<sup>10</sup>. The notches were made using a CEAST Notchvis with a 250 μm radius blade. An Instron Model 1125 test frame with MTS ReNew<sup>®</sup> 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 (80/20). Samples intended for transmission electron microscopy (TEM) were microtomed using a diamond knife fitted to a Leica Ultracut UCT at room temperature. An Hitachi H600 was used for the TEM at an operating voltage of 100kV.

## Results and Discussion

Typical Parmax<sup>®</sup> 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<sup>®</sup> 1200 is shown in the transmission electron photomicrograph of Figure 5. The craze is relatively short (~ 1  $\mu\text{m}$ ) 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<sup>®</sup> 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<sup>®</sup> 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).<sup>11</sup>

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.<sup>9,12</sup> Evidently, the energy associated with the localized yield, surface generation, and ligament bending (i.e., bending of matrix polymer between craze/cracks<sup>13</sup>) 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.

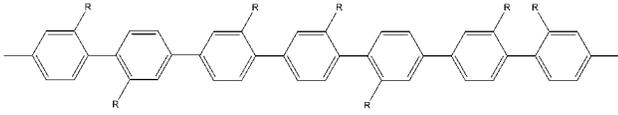
## Conclusions

The fundamental mechanistic aspects of fracture initiation and propagation in Parmax<sup>®</sup> 1200, a rigid-rod polyarylene, were investigated. Considering the very high modulus of the material, Parmax<sup>®</sup> 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<sup>®</sup> 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<sup>®</sup> 1200 and, thereby, further enhance its toughness.

## References

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- <sup>7</sup>Trimmer M., Isomaki M. and Ulman M. “Self-Reinforced Polyphenylenes: New High Performance Fire Resistant Materials”, *SAMPE* 42, 1997.
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- <sup>12</sup> Lawn, B.R. and Wilshaw, T.R., *Fracture of Brittle Solids*, Cambridge University Press, Cambridge, UK (1975) pg. 123.
- <sup>13</sup> Wu, S. *J. Appl. Polym. Sci.* **35**, 549 (1988).

## Figures and Table

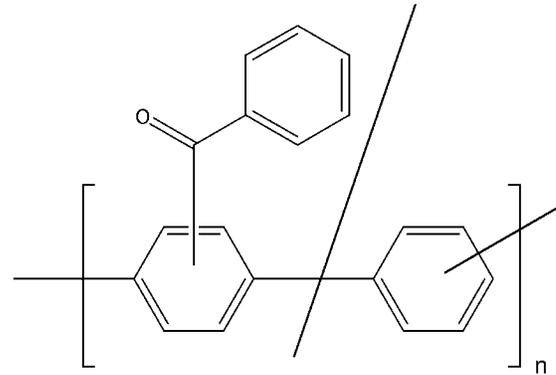


**Figure 1.** Generic structure of Parmax<sup>®</sup> SRPs

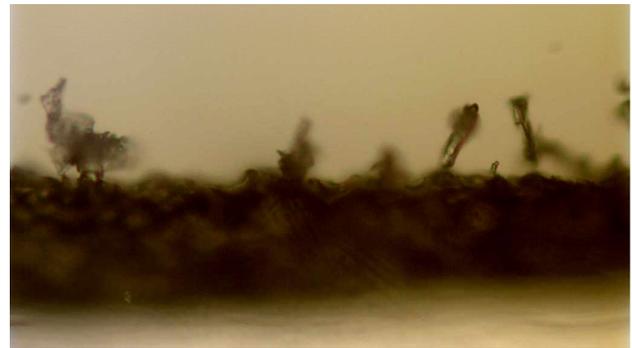
### Properties of Parmax<sup>®</sup>-1200

Density, g/cm <sup>3</sup>	1.21
Glass Transition Temp., C	155
Tensile Strength, MPa	207
Tensile Modulus, GPa	8.3
Flexural Strength, MPa	310
Flexural Modulus, GPa	7.7
Flexural Elongation	>5%
Notched Izod (1/8 inch), J/cm	0.64
Compressive Strength, MPa	655
Hardness, Rockwell (B Scale)	B80

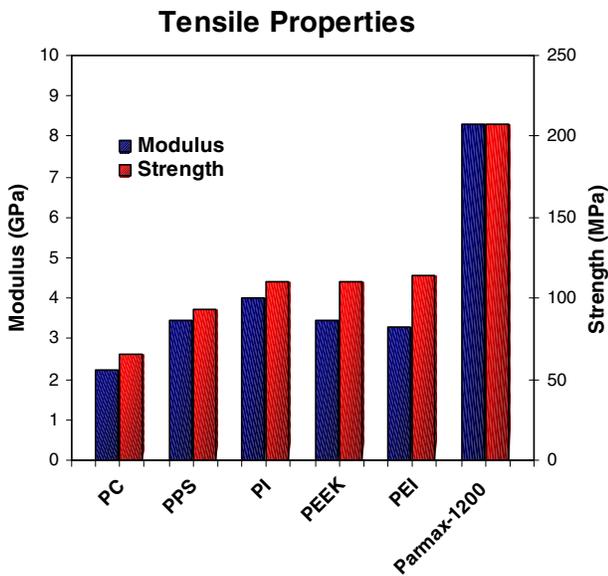
**Table A.** Mechanical Properties of Parmax<sup>®</sup> 1200.



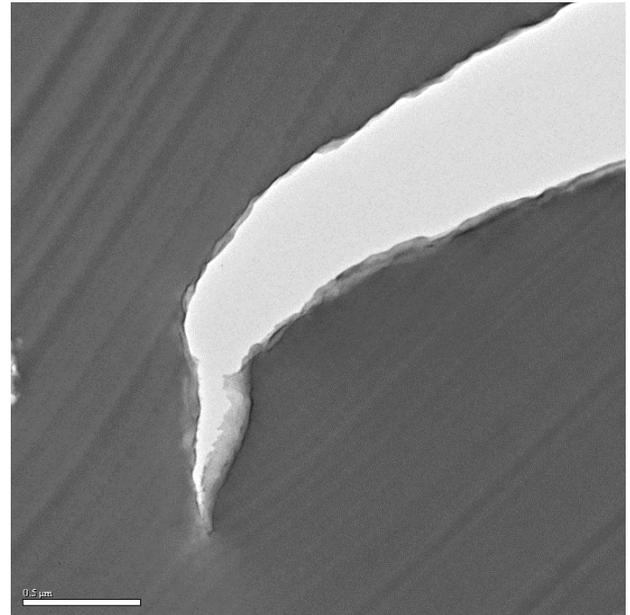
**Figure 3.** Parmax<sup>®</sup> 1200 structure



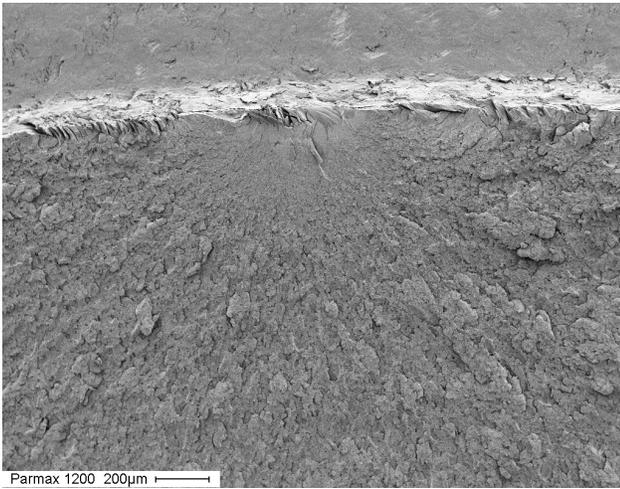
**Figure 4.** Optical micrograph of a fracture (3-point bend) surface of Parmax<sup>®</sup> 1200 (200X) showing material pulled away from the fracture surface.



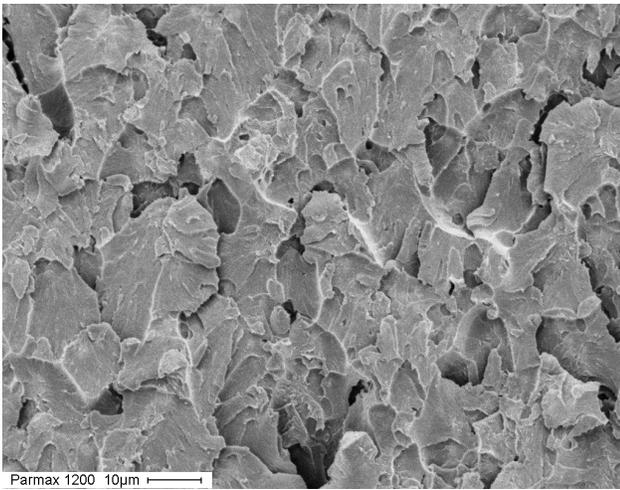
**Figure 2.** Tensile Property Comparison between Parmax<sup>®</sup> 1200 and other advanced thermoplastics



**Figure 5.** Area at a crack tip in Parmax 1200 with a craze roughly 1  $\mu\text{m}$  long that has fractured at the craze/matrix interface. Scale marker = 0.5  $\mu\text{m}$ .



**Figure 6.** Position of fracture initiation at a surface notch. Scale marker = 200 $\mu$ m.



**Figure 7.** Detail of fracture surface in rapid crack growth region. Scale marker = 10  $\mu$ m.