

## Blends of semi-rigid substituted poly(p-phenylene) with BPA-polycarbonate

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### Introduction

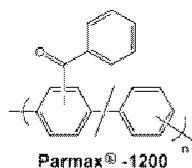
Poly(p-phenylene) is well known for its high temperature stability, but unfortunately it is a highly crystalline polymer that is insoluble and infusible, and therefore cannot be processed by means of conventional processing techniques.

Marrocco et al. [1] have reported large-scale synthesis of processable high-molecular-weight substituted polyphenylenes. Now several types of these processable semi-rigid polymers have been introduced under the trade name Parmax<sup>®</sup>. For an amorphous polymeric material, Parmax<sup>®</sup> has an unusually high Young's modulus of about 10 GPa and can be processed like a thermoplastic polymer. It is soluble in a few select organic solvents (e.g. methylene chloride, N-methyl pyrrolidinone, dimethyl acetamide), but not in common solvents such as toluene, alcohols, acetone, etc. A remarkable compatibility with several linear flexible polymers makes Parmax<sup>®</sup> a promising modifier and blend partner. Polyarylene can also be used as high-temperature, moisture-insensitive matrix resins in advanced composite materials [2] and self-reinforced foams [3].

In this contribution, we report on the worm-like morphology of Parmax 1200<sup>®</sup> and its blends with bisphenol-A polycarbonate and the influence of this morphology on the rheological properties.

### Experimental

The Parmax<sup>®</sup> 1200 sample was supplied by Mississippi Polymer Technologies, Inc. (MPT). Parmax<sup>®</sup> are polymers and copolymers based on poly(para-phenylene) structures that have substituents "R" derived from a variety of organic groups. In this paper we investigated Parmax<sup>®</sup> 1200 – a copolymer based on benzoyl phenylene backbone modified with occasional non-para linkages (kinks) (see Figure 1).



**Figure 1.** Chemical structure of Parmax 1200, a poly(paraphenylene) modified with occasional m-phenylene linkages (kinks)

The oscillatory shear measurements were performed using parallel plate geometry on a Rheometrics ARES rheometer. Plates with a diameter of 7 and 25 mm were used and the temperature range was between 180 and 300 °C with frequency sweeps from 0.01 to 10 Hz. The creep experiments were performed on a Paar-Physica UDS 200 rheometer at 300 °C.

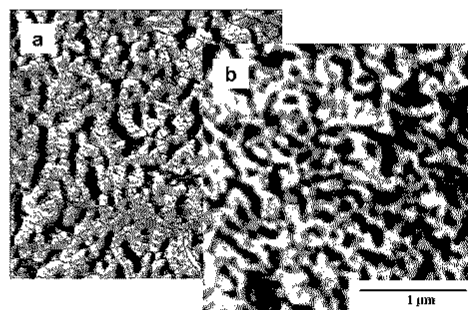
The Atomic Force Microscopy (AFM) measurements were performed with the aid of a commercial scanning force microscope (Digital Instruments D3000). The measurements were made in tapping mode with Si-tips (coated with a water absorption film) attached to 225 µm cantilevers, at resonance frequencies of about 60 kHz.

The X ray diffraction (XRD) measurements were performed on a commercial system (Bruker GADDS = General Area Detector Diffraction System).

The Transmission Electron Microscopy (TEM) measurements were done on a Philips EM420 at 80 kV. The sample was microtomed at RT to a thickness of less than 0.1 µm and was stained with ruthenium tetroxide.

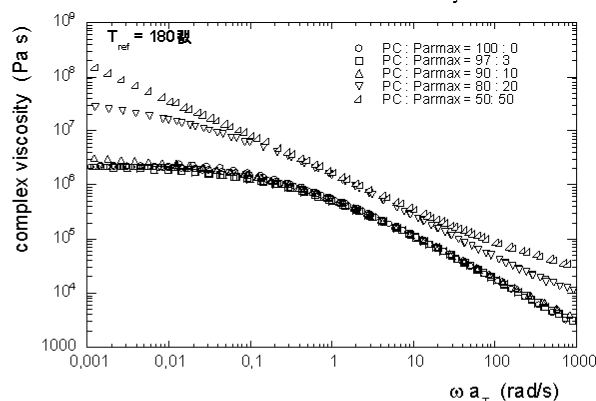
### Results and discussion

Surprisingly, the AFM micrograph of the substituted polyphenylene sample (Figure 2a) shows molecular aggregates. To make sure that this picture of the morphology isn't an artifact, the structure is reproduced in transmission electron microscopy (TEM), as can be seen in Figure 2b. Both in AFM and TEM the pure Parmax 1200 sample shows worm-like structures with a lateral dimension of about 0.1 µm, i.e. the diameter of such a worm like unit is about 220 times the diameter of one single polyphenylene molecule.



**Figure 2.** Micrographs of a microtomed cross section of compression-molded samples: (a) AFM image of Parmax 1200 and (b) TEM image of Parmax 1200

Figure 3 shows the viscosity of Parmax 1200 / Makrolon M2800 blends as measured in oscillatory rheometry. These blends were prepared from NMP solution. The blends with up to 10 % Parmax in M2800 do not show any significant increase in viscosity. The blends with 20 and 50 % Parmax show an increased viscosity.



**Figure 3.** Viscosity of Parmax 1200 / Polycarbonate blends measured in oscillatory shear as a function of the angular frequency ( $T_{ref} = 180$  °C)

### Conclusions

The rheological properties of Parmax 1200, a semi-flexible substituted polyphenylene, were investigated. The reported high stiffness of the material was confirmed. The rheological measurements proved that, despite the very high stiffness of the molecules, Parmax showed shear thinning and that, although the viscosity is very high and the melt is highly elastic, the polymer can be extruded in the melt.

A worm-like morphology was detected in AFM and TEM. This morphology could explain the reported mechanical and rheological behavior. The compatibility with flexible chain polymers (e.g. polycarbonate) could also be explained by the worm-like morphology.

### References

- [1] Marrocco M. L.; Gagné R. R.; Trimmer M. S., U.S. Pat 5.227.457
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- [3] Motamedi F.; Trimmer M. S.; Walter P.; Silva E.; Yen A. 44<sup>th</sup> International SAMPE Symp. May 23-27, 1999, pp. 1375