

## Thermo-optical Analysis of Poly(2,6-dimethyl-1,4-phenylene Oxide)/Triblock Styrene-Butadiene-Styrene Copolymer Blends

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### Synopsis

Blending of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO resin) with a triblock butadiene-styrene-butadiene copolymer (Kraton 101) monotonically increases the softening temperature of the latter as measured by TOA. The TOA transition temperatures of the styrene/PPO resin phases closely approximate those of polystyrene/PPO resin blends having the same styrene/aromatic ether unit compositions. Uniform mixtures of the styrene blocks with the poly(2,6-dimethyl-1,4-phenylene oxide) molecules is inferred.

### INTRODUCTION

Kambour<sup>1</sup> found that the blending of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO resin, registered trademark of the General Electric Company) with a styrene-butadiene-styrene triblock thermoplastic elastomer (Kraton 101, registered trademark of the Shell Chemical Company) markedly elevated the elastomer's use temperature. The introduction of rather small amounts of PPO resin to the thermoplastic elastomer raised the yield temperature of its "network"-stabilizing styrene unit domains to technologically advantageous levels. The enhancement of mechanical properties actually exceeded that based solely on  $T_g$  elevation expectation. We have reported thermo-optical and differential scanning-calorimetric measurements on polystyrene/PPO resin blends.<sup>2</sup> The present study was initiated to determine the degree of correspondence between the thermo-optical transition temperatures  $T_{TOA}$  in the Kraton 101/PPO resin blends and the  $T_{TOA}$  of polystyrene/PPO resin blends having the same polystyrene/polyether composition ratios.

### EXPERIMENTAL

The thermoplastic elastomer Kraton 101 has been rather extensively analyzed for structure.<sup>3-5</sup> From the various data we conclude that it is satisfactorily approximated by  $M_n = 96,500$  and an average triblock copolymer structure  $S_{140}-B_{1250}-S_{140}$ , with S and B representing styrene and butadiene units, respectively. The terminal styrene blocks each have molar masses of 14,500, and the interior butadiene block has a molar mass of 67,500 on the average. The

TABLE I  
Blends of PPO Resin and Kraton 101 Thermoplastic Elastomer:  
Compositions and Thermo-optical Transitions  $T_{TOA}$

Sample	Wt. fraction PPO resin	Molding temp., °C	$T_{TOA}$ , °C			
			Annealed		Unannealed	
			Run 1	Run 2	Run 1	Run 2
A	0.05		123 <sup>a</sup>			
B	0.10		131 <sup>b</sup>			
C	0.20		148 <sup>c</sup>			
D	0.30		165 <sup>c</sup>			
E	0.40	180	170 <sup>d</sup>	163	176	163
F	0.50	190	179	171	189	173
G	0.60	200	193	187	198	181
H	0.70	220	193	190	208	201
I	0.80	230	200	193	214	217

<sup>a</sup> Annealed 5 min at 250°C.

<sup>b</sup> Drawn at 150°C.

<sup>c</sup> Annealed 3 min at 180°C, then 3 min at 230°C.

<sup>d</sup> Samples E–I annealed 3 min at 220°C.

molding-grade PPO resin has an intrinsic viscosity in chloroform of 0.51 d/g. Therefore, its  $M_n$  is approximately 20,000, and its  $M_w$  is approximately twice this value. Five-gram mixtures of Kraton 101 and PPO resin were dissolved in 45 ml chloroform with 0.025 g acetylphenylhydrazine (APH) and 0.025 g tricetyl borate (TCB). The solutions were precipitated into 250 ml methanol. The precipitates were filtered, slurried with 250 ml fresh methanol, refiltered, and dried in a 60°C vacuum oven for 16 hr. The dry blends were then compression molded into films for study. The blends, their weight fraction of PPO resin based on total polymer, and their molding temperatures are shown in Table I.

The thermo-optical analysis procedure has been previously described.<sup>2</sup> Birefringence is introduced into the blend samples by scratching them at room temperature with a steel stylus. They are then placed in a programmed hot stage of a polarizing microscope between a crossed (90°) polarizer/analyzer combination. Transmitted light intensity is monitored by a photocell with readout on a stripchart driven at 1 in./3 min. A heating rate of 10°/min from 60°C (or 90°C) to 250°C is used yielding a 30°/in. scale on the time axis of the chart. The thermo-optical transition temperature  $T_{TOA}$  is the temperature at which the birefringence of the scratches disappears as indicated by a near zero intensity of light transmitted through the polarizing microscope.

## RESULTS AND DISCUSSION

Table I lists the blends, their compositions, molding temperatures, and their observed thermo-optical transition temperatures  $T_{TOA}$ . Figure 1 illustrates the light intensity (arbitrary scale and vertical displacement)-versus-temperature curves for the first runs on the annealed samples. The  $T_{TOA}$  are the intersections of the limiting tangents with the tangents through the curve inflections. Figure 2 displays the  $T_{TOA}$  observed in the first and second runs on the annealed and unannealed samples. The composition variable is the weight

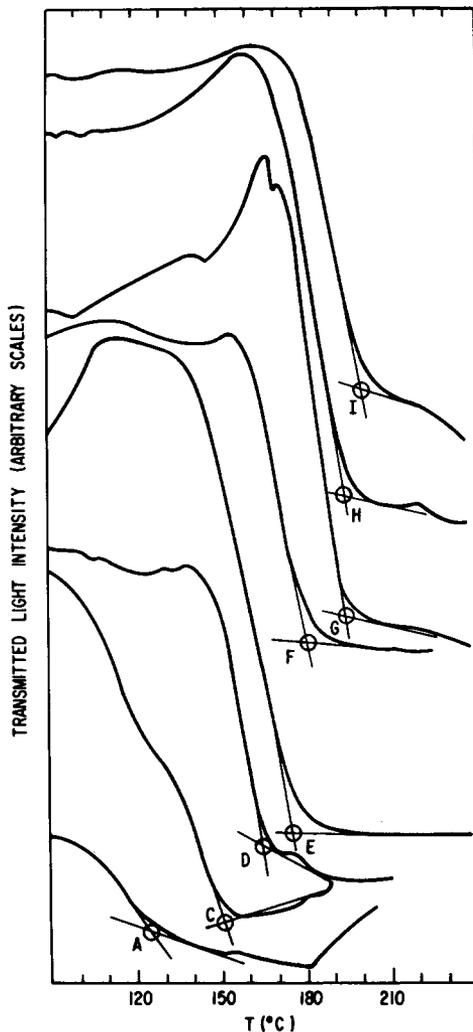


Fig. 1. Thermo-optical analysis curves of light transmission vs temperature for annealed blends. Blend compositions are given in Table I;  $10^{\circ}/\text{min}$  heating rate.

fraction PPO resin based upon the sum of the PPO resin and polystyrene segment weights. Thus, on the basis of the simplest two-phase model of the triblock copolymer, it is the weight fraction of PPO resin in the styrene + PPO resin domains.

The data in Table I and their representation in Figure 2 show that the addition of PPO resin increases the temperature of birefringence loss in the scratched Kraton K-101 in a smooth, systematic fashion. The  $T_{\text{TOA}}$  of pure Kraton 101 was not obtained because scratching did not produce sufficient birefringence for satisfactory transmitted light intensity measurements. The data indicate that its  $T_{\text{TOA}}$  should be approximately  $110^{\circ}\text{C}$ . The  $T_{\text{TOA}}$  of pure PPO resin is  $222^{\circ}\text{C}$ . The upper broken line curve shown in Figure 2 is the  $T_{\text{TOA}}$ -versus-weight fraction PPO resin relation determined for polystyrene-PPO resin blends in which the polystyrene had  $M = 97,200$ . The lower broken line curve is drawn to represent the expected  $T_{\text{TOA}}$ -versus- $w_{\text{PPO}}$  relation for blends in which the

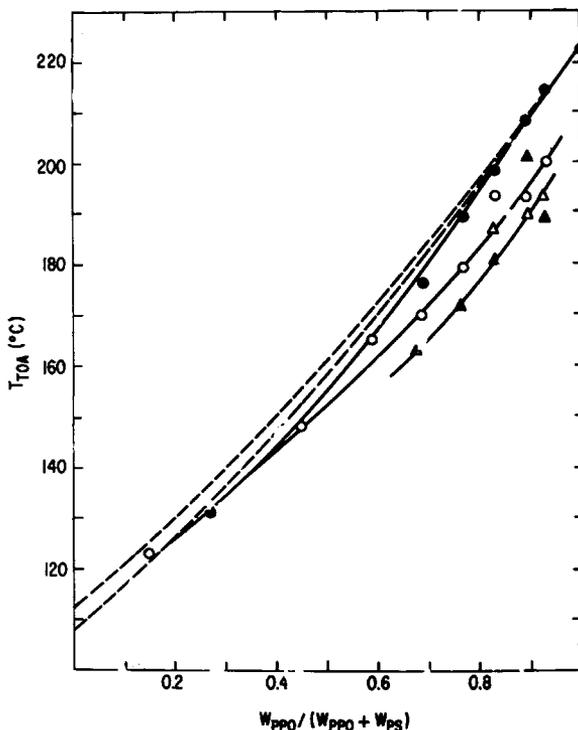


Fig. 2. Thermo-optical transition temperatures vs weight fraction of PPO resin in PPO + PS domains. Unannealed blends: (●) first run; (▲) second run. Annealed blends: (○) first run; (△) second run.

polystyrene has  $M = 14,500$  for which the glass transition is  $5^\circ$  lower than for polystyrene of  $M = 97,200$ . In the present Kraton 101/PPO resin blend system, the PPO resin molecular weights lie principally (on a weight fraction basis) in the  $M = 15,000$ – $60,000$  range. This makes the chain lengths of the PPO resin comparable to, but somewhat longer than, those of the styrene blocks. Their uniform incorporation into the styrene domains of the triblock polymer appears to be quite feasible. The  $T_{TOA}$ -versus- $w_{PPO}/(w_{PPO} + w_{PS})$  relation for the unannealed, high PPO resin content blends (cf. Fig. 2) lie quite close to the curve for polystyrene/PPO resin blends. The  $T_{TOA}$  data for the annealed Kraton 101/PPO resin blends show birefringence loss at temperatures somewhat below (at most  $14^\circ$ ) those for polystyrene/PPO resin blends of the same  $w_{PPO}/(w_{PPO} + w_{PS})$  compositions. However, up to  $w_{PPO}/(w_{PPO} + w_{PS}) = 0.6$ , they correspond quite closely. Second runs on the annealed and unannealed samples indicate a further lowering of the  $T_{TOA}$  suggesting that some thermal degradation with production of plasticizing low molecular weight species may be occurring during pressing, annealing, and scanned temperature runs.

The blending of PPO resin to Kraton 101  $S_{140}$ – $B_{1250}$ – $S_{140}$  thermoplastic rubber appears to yield complete incorporation of the PPO resin into the styrene domain regions. The styrene chain/PPO resin domains exhibit birefringence loss at temperatures nearly equal to those observed in polystyrene homopolymer/PPO resin blends of the same weight fraction composition. Enhancement of elevated temperature tensile modulus retention and creep resistance under

load above and beyond that expected from glass transition elevation as paralleled by  $T_{TOA}$  is quite likely due to two effects. First, the longer-chain, less flexible PPO resin molecules provide much improved chain entanglement and resistance to slippage in the styrene chain domains. Second, there exists the increased glassy filler effect of the added resin. Of the two effects, the domain stabilization should be overriding in importance.

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