

Compatibility of ABA Poly(styrene-*b*-isoprene)/ Poly(2,6-dimethylphenylene Oxide) Blends

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Synopsis

A variety of blends of ABA poly(styrene-*b*-isoprene) copolymers with poly(2,6-dimethylphenylene oxide) were prepared. Their compatibility was examined by measuring both the apparent modulus of rigidity and the loss tangent. Several blends showed a unique glass transition temperature between those of the individual components, which indicated compatibility. It was found that only those copolymers which phase separate are compatible with poly(2,6-dimethylphenylene oxide).

INTRODUCTION

One considers the use of blends whenever a material has to exhibit properties which cannot be imparted by one component alone. However, in the case of polymer blends, a demixtion may occur, which could cause drastic changes in processing, mechanical, and other properties. This is a result of the mutual incompatibility inherent in polymers, as their free energy of mixing is always positive.¹ Energy of mixing may be expressed as a function of the difference in the solubility parameters δ_A and δ_B , where A and B are components of the blend. When this difference tends toward zero, compatibility increases to some extent.² A few examples of polymer couples are known where, under well-defined conditions (composition, temperature), demixtion may not occur.

We are currently examining the adhesive properties of ABA poly(styrene-*b*-isoprene) copolymers (SIS).³ One of the problems encountered is their low heat resistance, as limited by the transition temperature T_g of the polystyrene blocks. We have tried to increase this temperature by about 20°–30°C, as required by the intended end use, by blending SIS copolymers with a higher- T_g polymer such as poly(2,6-dimethylphenylene oxide) (PPO) ($T_g = 220^\circ\text{C}$). This polymer has been shown to be compatible with homopolystyrene (PS), and one

TABLE I
Sample Codes and Characteristics of ABA Poly(styrene-*b*-Isoprene) Block Copolymers and
Polystyrene Homopolymers

Sample code	Molecular weight $\bar{M}_n \times 10^{-3}$			Total molecular weight $\bar{M}_n \times 10^{-3}$	% Polyisoprene
	PS block	PI block	PS block		
SIS 209	87	7	136	230	3
SIS 74	26	7	22	55	13
SIS 344	11	8	11	30	27
SIS 345	15	51	17	83	61
SIS 200	78	52	80	210	26
PS I	10	—	—	10	—
PS II	24	—	—	24	—

would expect it to be so with the polystyrene blocks of the SIS copolymers.⁴⁻⁷ If such a compatibility were reached, the resulting blend would exhibit only one transition at a higher temperature. Of course, the lower transition due to polyisoprene block undergoes no change.

This paper presents the results obtained in the study of SIS/PPO blends. The adhesive properties of such blends will appear in another paper.

EXPERIMENTAL

Materials

PPO. A commercially available material, Noryl 731, marketed by General Electric, was utilized. This is a standard PPO containing several charges and plasticized by polystyrene, Vicat temperature (method A) 148°C.

PS and SIS. PS and SIS were prepared in our laboratory by anionic (co)-polymerization. Synthesis procedure is well known³ and will not be detailed here. Compositions and molecular weights are listed in Table I.

Preparation of Blends

Given amounts (expressed in parts by weight) of Noryl and PS or SIS were dissolved in benzene, thoroughly mixed by agitation. The solution was then refrigerated to 0°C and the blend was obtained as a solid by lyophilization. Afterward, the material was completely dried under vacuum.

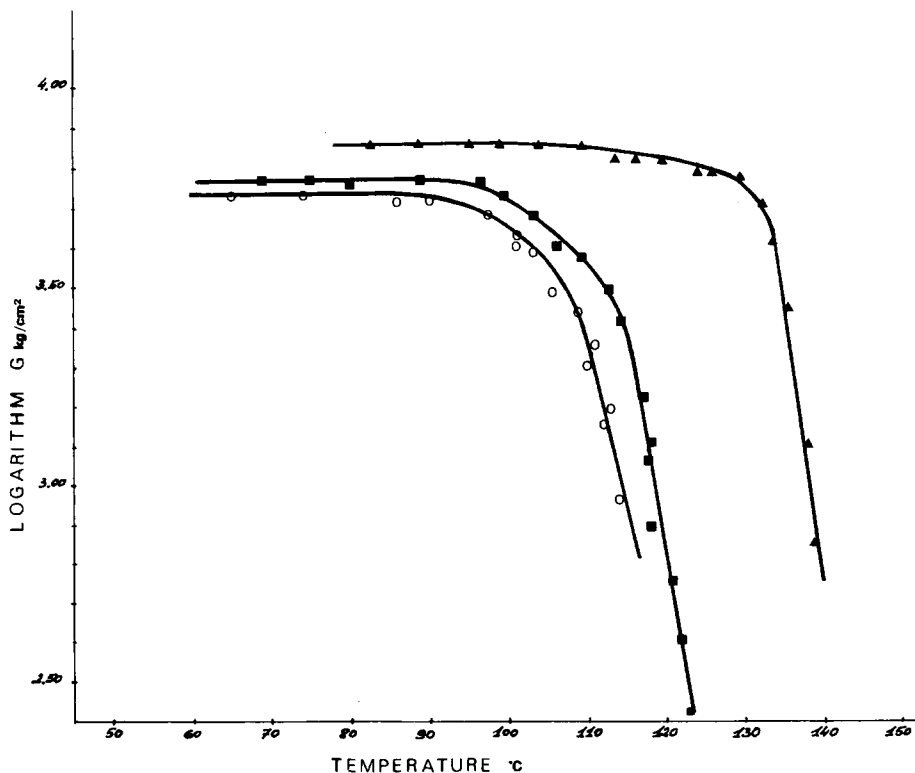


Fig. 1. Logarithm of apparent modulus of rigidity vs temperature for Noryl and Noryl/polystyrene blends: (▲) Noryl 731; (○) 75 Noryl/25 PS I; (■) 75 Noryl/25 PS II.

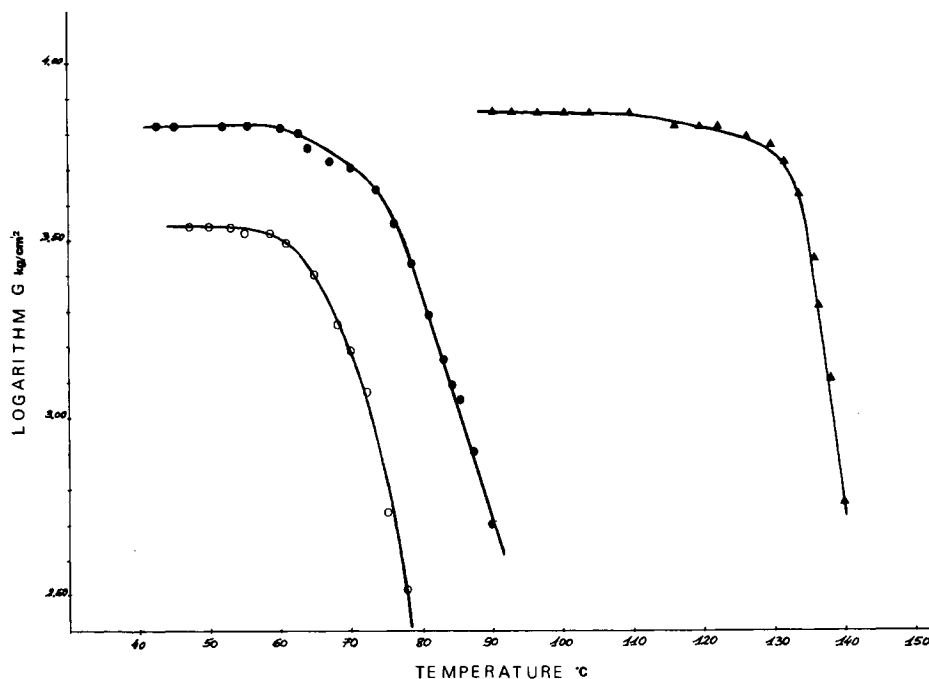


Fig. 2. Logarithm of apparent modulus of rigidity vs temperature for an incompatible Noryl/SIS blend: (▲) Noryl 731; (O) SIS 209; (●) 75 Noryl/25 SIS 209.

Evaluation of Compatibility

Apparent Modulus of Rigidity G . We measured the apparent modulus of rigidity G on a Clash and Berg torsion tester according to ASTM Standard D 1043-51 T. The above blends were compression molded and hole punched to test specimens of 60×6 mm in size. Thickness varied from 1 mm for the more elastomeric blends to 3 mm for the more brittle ones.

Loss Tangent $\tan \delta$. For several blends, we compared the results obtained by G modulus measurements with those obtained by measuring the loss tangent. Measurements were performed on a Zwick Torsiomat Mod 5202, frequency range 0.1–20 Hz. Test specimens consisted of extruded cylindrical rods 2 mm in diameter and of appropriate length.

RESULTS AND DISCUSSION

Figure 1 shows the log G curves as a function of temperature for Noryl 731 and for two blends of Noryl (75 parts by weight) with PS I and PS II, respectively. Noryl yields a T_g of 132°C in fair agreement with the Vicat temperature of 148°C . Both blends exhibit a unique transition temperature, thus corroborating compatibility found by other authors. The higher T_g of the blend with PS₂ (113°C vs 106°C) is due to the higher molecular weight of this PS.

Figure 2 shows the same kind of curves for a Noryl/SIS 209 blend. Mixing Noryl with SIS 209 increases modulus but not heat resistance, as the same T_g as for pure SIS 209 is found within experimental error. Therefore, no compatibility exists between Noryl and SIS 209. This is due to the extremely low isoprene content associated with the low molecular weight of the central block of

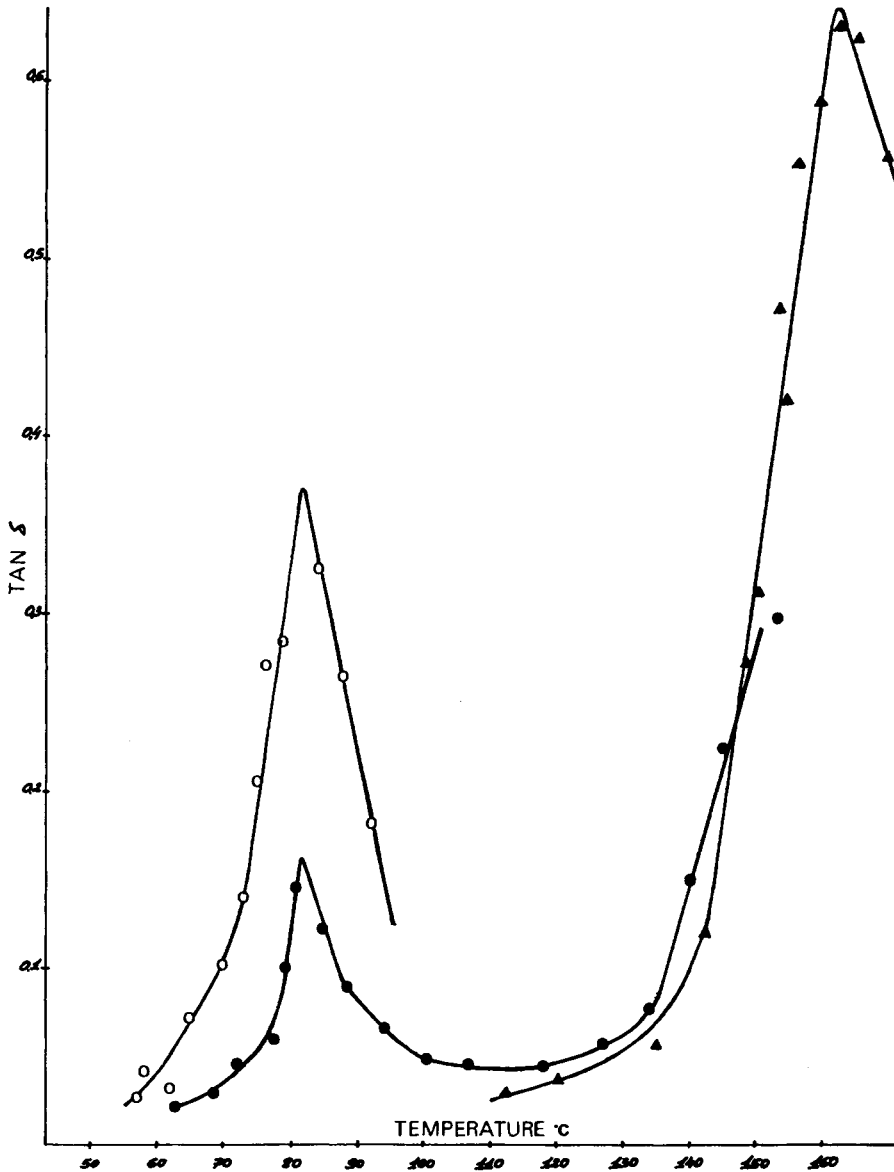


Fig. 3. Tan δ vs. temperature for an incompatible Noryl/SIS blend: (\blacktriangle) Noryl 731; (\circ) SIS 209; (\bullet) 75 Noryl/25 SIS 209.

this copolymer. It is well known that in that case, no phase separation will occur between polystyrene and polyisoprene blocks.⁸ The diene acts simply as a plasticizer with a repartition statistically identical over the whole material. Miscibility with Noryl is, therefore, excluded. These results are confirmed by the tan δ -vs.-temperature curves shown in Figure 3; both pure SIS and blend exhibit the same T_g (82°C).

Of course, the low isoprene content of SIS 209 may just be considered as an impurity unable to play any role in formation of a continuous phase between Noryl and the copolymer. Here, in our opinion, the fact intervenes that isoprene is chemically bound to the styrene blocks and behaves in a different way as would

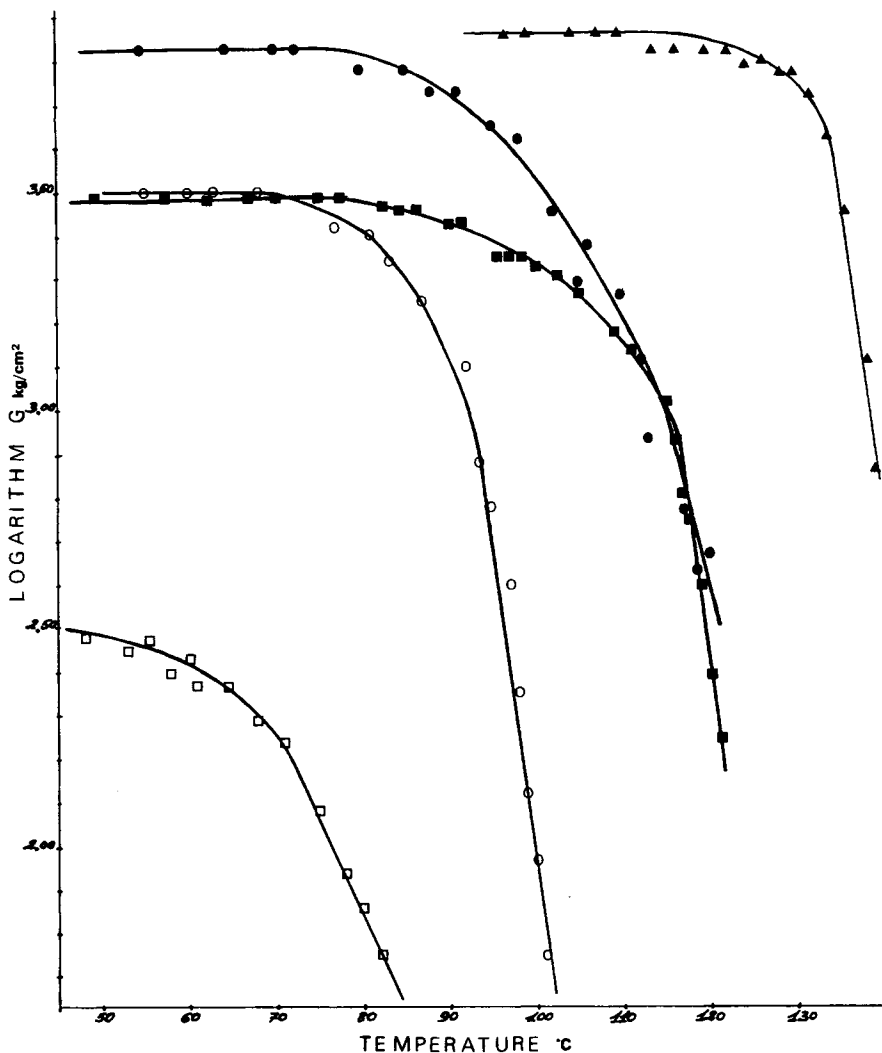


Fig. 4. Logarithm of apparent modulus of rigidity vs temperature for compatible Noryl/SIS blends: (▲) Noryl 731; (○) SIS 200; (□) SIS 345; (●) 75 Noryl/25 SIS 200; (■) 75 Noryl/25 SIS 345.

homopolyisoprene which could migrate and form a modulus of some size. There seems to be a "copolymer effect."

Table II shows two other examples of incompatibility of Noryl with copolymers SIS 74 and SIS 344. The low molecular weight of the diene block still does not allow phase formation and thus compatibility with Noryl. On the other hand, with copolymers SIS 345 and SIS 200, compatibility is obtained, as those copolymers phase separate without difficulty. The corresponding curves (Fig. 4) are translated toward higher temperatures, and a unique transition occurs, denoting a unique PS-Noryl phase. Compared to the pure SIS modulus, all the blends show increased modulus, as would be expected.

Measurements of $\tan \delta$ for blends with SIS 345 are shown in Figure 5. They confirm its compatibility with Noryl. As can also be seen, compatibility extends over the whole range of composition.

In Table II are listed the T_g 's of the copolymers and of some of their blends

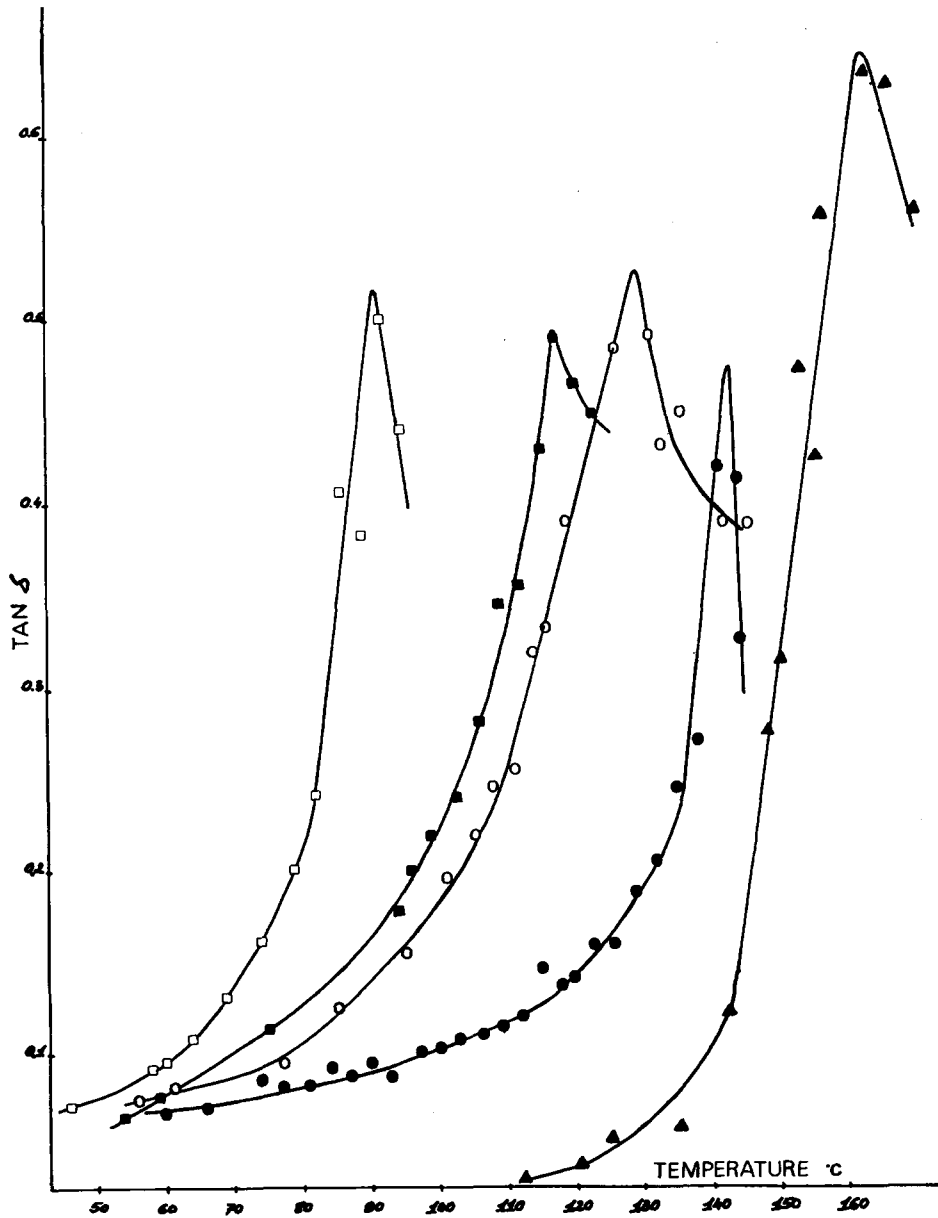


Fig. 5. $\tan \delta$ vs temperature for compatible Noryl/SIS 345 blends of various compositions: (\blacktriangle) Noryl 731; (\square) SIS 345; (\blacksquare) 25 Noryl/75 SIS 209; (\circ) 50 Noryl/50 SIS 209; (\bullet) 75 Noryl/25 SIS 209.

with Noryl. For a compatible blend, the T_g increases as expected with increasing Noryl content. As Noryl is itself a blend, there is no simple variation of T_g .

The experimental T_g values obtained by the two methods we utilized differ to an appreciable extent, confirmed by systematic duplicate runs. Such differences have also been noted by other authors [see, for example, Table I in reference 5 and Figure 7 in reference (6)]. They may be attributed to the fact that transition temperatures of a polymer depend largely on the type of the defor-

TABLE II
Glass Transition Temperature of Noryl 731, SIS Block Copolymers, and Some Noryl 731-SIS Blends

Composition, parts by weight	Copolymer	T_g , °C (G modulus)	T_g , °C ($\tan \delta$)	Observations
100 SIS	SIS 209	70	82	
	SIS 345	65	91	—
	SIS 200	89	—	—
75 SIS-25 Noryl 731	SIS 345	73	117	compatible
50 SIS-50 Noryl 731	SIS 344	74	—	incompatible
	SIS 345	81	129	compatible
25 SIS-75 Noryl 731	SIS 209	72	82	incompatible
	SIS 344	73	—	incompatible
	SIS 74	82	—	incompatible
	SIS 345	113	143	compatible
	SIS 200	105	—	compatible
100 Noryl 731	—	132	163	—

mation applied and also on the arbitrarily chosen time parameter. Nevertheless, these facts do not affect our findings about compatibility of SIS/Noryl blends.

We further note that transition temperature of SIS 200 is higher than that of SIS 345, contrary to their respective blends. This discrepancy is only apparent as, for a given Noryl content, T_g depends on the ratio PPO/total PS, where total PS = PS in SIS + PS in Noryl. This ratio increases when the percentage of PS in SIS decreases.

CONCLUSIONS

Our study has shown that not only homopolystyrene but also polystyrene engaged in a block copolymer is compatible with PPO under given conditions. This requires copolymer to be able to phase separate, i.e., to yield polystyrene domains able to undergo mixing with PPO as would homopolystyrene. Blends meeting this condition exhibit a unique T_g higher than that of the pure SIS, thus providing materials with increased heat-resistance properties.

In a forthcoming paper, we shall present some results concerning heat resistance of glass to glass joints assembled with compatible as well as with incompatible SIS/PPO blends.

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