

# Adhesion of Block Copolymers to Glass: Lap Shear Strengths as a Function of Bonding Conditions

J. M. WIDMAIER and G. C. MEYER, *Ecole d'Application des Hauts Polymères, Université Louis Pasteur, F-67000 Strasbourg, France*

## Synopsis

ABA poly(styrene-*b*-isoprene) block copolymers with various molecular weights and composition were used as heat activated films in simple overlap glass joints. The influence of bonding temperature on their shear strength at break was investigated. On increase of temperature, the joint resistance for most of the copolymers passed through a maximum, which temperature was dependent on the molecular characteristics of the copolymers. The decrease in melt viscosity or chemical degradation could not explain the data. A morphological interpretation which fits well the present and previous observations is proposed and verified for one copolymer used in this work.

## INTRODUCTION

In recent years, great interest has been caused by a new class of thermoplastic elastomers which consists of block copolymers produced by anionic polymerization.<sup>1</sup> These materials, especially triblock copolymers of the ABA poly(styrene-*b*-diene) type, exhibit good elastic and strength properties generally attributed to their characteristic morphology:<sup>2</sup> it is well established that block copolymers undergo microphase separation, resulting in the formation of domains consisting of pure A- or B-block chains which are periodically arranged in space.<sup>1</sup> Consequently, these triblock copolymers behave like vulcanized elastomers at room temperature, but they may be processed like any other plastic material at temperatures above the glass transition of the polystyrene blocks. The commercially available ABA block copolymers are about 100,000 in molecular weight, with high (over 60%) diene content. Butadiene mostly constitutes the center block, although sometimes isoprene is used.

The copolymers in question have been widely used in various engineering applications, among others for the fabrication of adhesives.<sup>3</sup> Additional ingredients such as oil, resins, mineral fillers, etc., are generally added according to end use. In spite of considerable published information on the physico-mechanical properties of adhesive formulations with thermoplastic elastomers, there is an evident lack of data on the adhesive properties of pure triblock copolymers.

In previous publications,<sup>4,5</sup> we have reported on the adhesive properties of noncompounded ABA poly(styrene-*b*-isoprene) block copolymers (SIS). Solvent-cast or compression-molded SIS give transparent and colorless films suitable for glass-to-glass joints. Heat was used to replace solvent to allow adequate wetting of such non-porous substrate. The tensile resistance<sup>6</sup> and the shear strength<sup>4</sup> at break of simple overlap joints were studied as a function of the molecular characteristics of the SIS copolymers. The results for over 50 SIS

indicated a strong dependence of the adhesive performances on the test mode and on the composition of the copolymers. Also, total molecular weight is an important parameter. Especially, whereas for most SIS investigated, a rather weak lap shear strength close to 3 MPa was found, a cluster with high shear resistance (over 10 MPa) appeared with a total molecular weight of around 30,000 g/mol and 30% polyisoprene content. We have ascribed this behavior to a particular morphology of these copolymers.<sup>7</sup>

For industrial purposes, it would be interesting to extend this zone over a broader range of SIS (or SBS). Usually, formulators add suitable fillers to impart better properties to a given adhesive. We in turn tried to enhance the performances by fitting activation temperature to the actual chain characteristics of the copolymers. We previously activated the SIS film by increasing the temperature up to 135°C, a temperature which is about 40°C above the glass transition temperature of the polystyrene phase, but was set arbitrarily to be the same for all SIS copolymers. Higher activation temperatures could lead to an increased adhesion as the viscosity of the film, which is governed in fact by the viscosity of the polystyrene block, will decrease, thus providing better interfacial contact with the substrate. The viscosity of the glassy phase in turn depends on its molecular weight.

In the present paper, we examine the relationship between activation temperature and the lap shear strength at room temperature of glass joints bonded with SIS block copolymers having various molecular characteristics.

## EXPERIMENTAL

### Synthesis of SIS Copolymers

The polystyrene-polyisoprene-polystyrene block copolymers used in this study were prepared by the classical three-step anionic polymerization previously described.<sup>8</sup> The solvent was benzene, and the initiator was *n*-butyllithium. Reactions were performed at 50°C. After completion of each step, a sample was taken for analysis. The final product was isolated by precipitation in methanol or by freeze-drying, and dried under vacuum. All samples were stabilized by addition of 0.1–0.2% 2,6-di-*tert*-butyl-*p*-cresol. Molecular characteristics were determined by gel permeation chromatography (GPC) in THF, and by ultraviolet spectrometry in chloroform. They appear in Table I. The GPC analysis indicated that all triblock copolymers were of a narrow molecular weight distribution type, and free of homo or diblock polymer. Copolymer films were obtained by compression molding for 2 min at 180°C, to 0.1 mm thickness.

### Joint Formation

Glass plates (dimensions: 50 × 25 × 6 mm) were degreased with ethanol and air-dried before use. A simple lap joint (overlap area 6.25 cm<sup>2</sup>) was formed by inserting the SIS film, cut to size, between two glass plates. A special device allowed exact positioning of the different parts of the joints. The test samples were prepared by heating the whole assembly for 2 h. Then, the temperature was decreased slowly to room temperature.

TABLE I  
Lap Shear Strength at Break  $\bar{\tau}$  vs. Activation Temperature for SIS Copolymers of Various Molecular Characteristics

Polyisoprene content (%)	30	30	30	40	40	50	50	65
$M_{\text{tot}}/10^3 \text{ g}\cdot\text{mol}^{-1}$	31	45.5	89	31.5	45	32.5	49.5	52
SIS sample	346	514	558	583	320	564	222	342
115 <sup>a</sup>	55.7	41.0	11.4	42.0	29.6	46.3	23.2	15.2
135	111.9	71.8	31.7	80.9	36.5	57.6	26.4	23.3
155	122.3	97.7	45.1	81.3	49.8	60.4	66.5	60.4
175	117.8		52.7	90.6	64.3	63.8	80.0	56.9
185		113.5	79.2		69.7	62.7		
195	128.3	124.0	96.8	86.5	71.9	53.3	62.9	46.4
205		120.6	100.9		66.7			
215	114.5	126.8	108.6	75.3	52.1	40.2	39.4	
225		123.2	112.7					
235	114.6	116.7	119.2		31.0			
	$\bar{\tau}/10^5 \text{ Pa}$							

<sup>a</sup> Activation temperature (°C)

### Breaking the Joint

The shear strength of all joints was measured 1 week after joint formation on a Zwick test machine, Model Z 13 with a crosshead separation speed of 2 mm/min. A minimum of five joints were tested for each copolymer.  $\bar{\tau}$  is the average value of the lap shear strength at break (Pa). The scattering of the data is indicated in the figures.

### Optical and Electron Microscopy

The copolymer films were examined between crossed polars in a Ortholux Leitz polarizing microscope. Their morphology was investigated using transmission electron microscopy. Thin sections were cut at room temperature with a diamond knife fitted to a Porter-Blum ultramicrotome. The sections were subsequently stained with osmium tetroxide vapor<sup>9</sup> for 2 h to provide contrast between the polystyrene and polyisoprene phases. Micrographs were taken on an Elmiskop Model 102 apparatus.

## RESULTS

At first, it seemed important to verify that the higher activation temperature ( $T_a$ ) used in the present work did not have an adverse effect on the polymer films, as some thermal degradation, mainly because of the presence of oxygen, could occur. We have heated therefore several joints well over 200°C for 2 h. All the films, once inserted between the glass plates, remained transparent and colorless. Moreover, films were removed afterwards from the substrates and their molecular weight distribution checked by gel permeation chromatography. No change could be noted, and thus it was concluded that films are not altered by the above heating process.

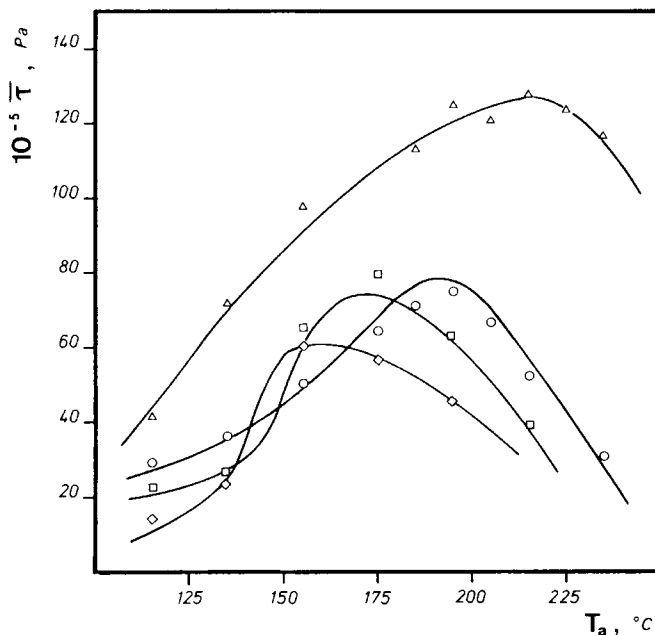


Fig. 1. Lap shear bond strength  $\bar{\tau}$  as a function of activation temperature  $T_a$  for SIS copolymers at constant molecular weight (50,000 g/mol). Polyisoprene content: ( $\Delta$ ) 30%; ( $\circ$ ) 40%; ( $\square$ ) 50%; ( $\diamond$ ) 65%.

The molecular characteristics of the SIS copolymers, namely their total molecular weight  $M_{\text{tot}}$  and their polyisoprene content by weight % I, are listed in Table I. In the same table, the average shear strength at break  $\bar{\tau}$ , is given as a function of the activation temperature  $T_a$ .

In Figure 1,  $\bar{\tau}$  is plotted vs.  $T_a$  for SIS with various % I and a constant  $M_{\text{tot}}$  of 50,000. All curves show a more or less pronounced maximum which is shifted towards higher temperatures when % I decreases, or, alternatively, the hard phase content increases. Break resistance values also move in the same direction and are roughly doubled when  $T_a$  goes from 115°C to the temperature of the maximum.

Figures 2-4 show the influence of the molecular weight on the variation of  $\bar{\tau}$  with  $T_a$  at three different compositions. It may be noted (Fig. 2) that for a high molecular weight ( $M_{\text{tot}} = 89,000$ ),  $\bar{\tau}$  increases continuously and its value increases four times within the temperature range considered. The maximum, if there is one, would be located at still higher temperatures. On the other hand, copolymers with low molecular weight, around 30,000 g/mol, exhibit only a slight variation of  $\bar{\tau}$  between 135°C and 200°C whatever the composition.

## DISCUSSION

The unexpected maximum cannot be explained by a decrease in viscosity when temperature is raised, as had been assumed first. Such a variation would be monotonic. Nevertheless, Aharoni and Prevorsek<sup>10</sup> have shown that the shear resistance of joints bonded with polyester-type hot melts is zero when  $T_a$  equals the melting point; when temperature is further raised, it increases to a maximum

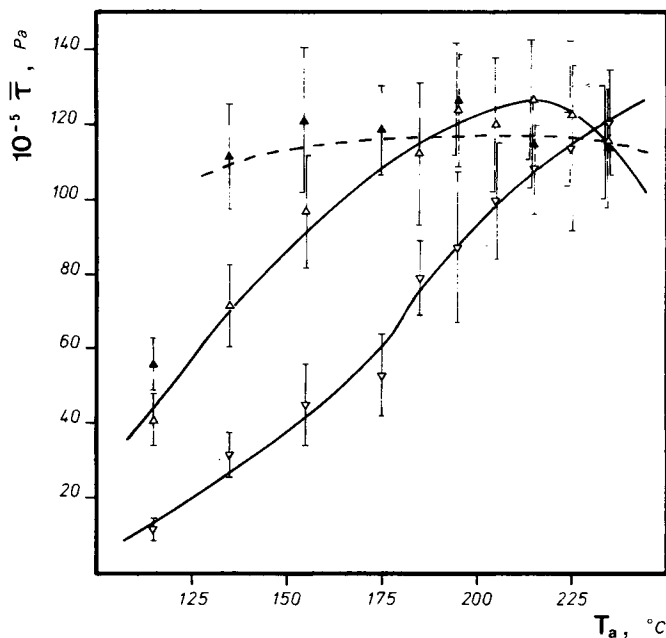


Fig. 2. Lap shear bond strength  $\bar{\tau}$  as a function of activation temperature  $T_a$  for SIS copolymers with 30% polyisoprene. Total molecular weight  $M_{\text{tot}}$ : ( $\blacktriangle$ ) 31,000; ( $\triangle$ ) 45,500; ( $\nabla$ ) 89,000.

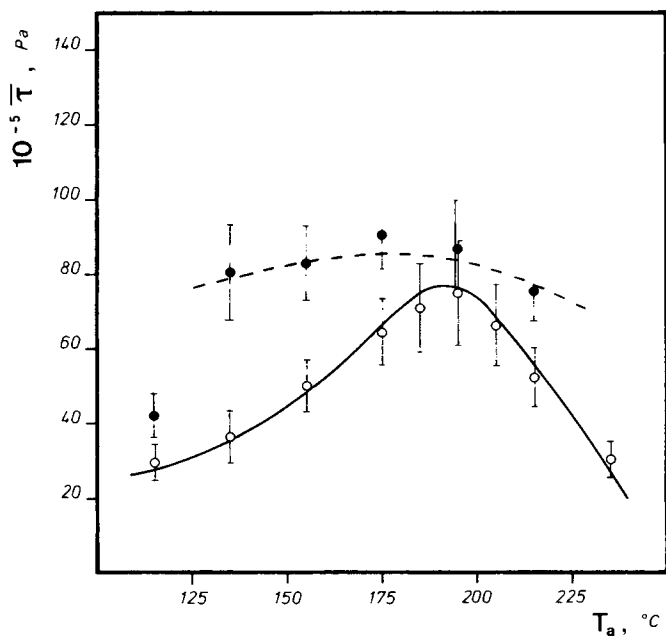


Fig. 3. Lap shear bond strength  $\bar{\tau}$  as a function of activation temperature  $T_a$  for SIS copolymers with 40% polyisoprene. Total molecular weight  $M_{\text{tot}}$ : ( $\bullet$ ) 31,500; ( $\circ$ ) 45,000.

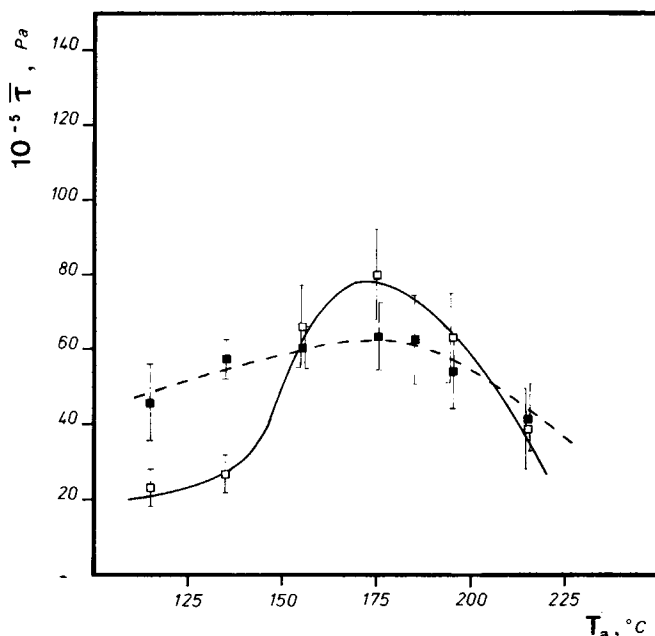


Fig. 4. Lap shear bond strength  $\bar{T}$  as a function of activation temperature  $T_a$  for SIS copolymers with 50% polyisoprene. Total molecular weight  $M_{tot}$ : (■) 32,500; (□) 49,500.

value before dropping again to a negligible level. They explain their observations by a too high fluidity of the melt which is consequently squeezed out by the pressure applied on the substrates. In our experiments, the viscosity of the films was not that low and the material remained mostly between the glass plates. We have furthermore checked that the final film thickness does not play a major role.

A molecular interpretation, however, can be used to explain the experimental findings. Recent theories<sup>11,12</sup> based on thermodynamic statistics indicate that in polystyrene-polydiene block copolymers there is not a sharp boundary between the two thermodynamically incompatible phases, but that partial mixing occurs in the interfacial region. The thickness of the microdomain interfaces may be calculated<sup>13</sup>: for given molecular characteristics, it is temperature-dependent. With increasing temperature, the region in which the unlike segments intermix tends to increase at the expense of the pure phases. As a result, the classical organized structure (i.e., spheres, cylinders, or lamellas) is altered but the copolymers remain phase-segregated. Above a critical temperature<sup>14</sup>  $T_c$ , where the entropy of mixing equals the enthalpy of the system, the microdomains have finally disappeared and complete mixing of both components has taken place: the system may be regarded as thermodynamically homogeneous. The temperature-dependent behavior of the morphology has been corroborated by several authors.<sup>15,16</sup>

In previous publications,<sup>4,6</sup> we have shown that only SIS copolymers with a segregated structure but without latticelike arrangement, i.e., neither long-range organization nor complete phase mixing, exhibit notable adhesive strengths in shear. That particular morphology may be found at temperatures just below  $T_c$  and could explain the results obtained in the present work. Hence various behaviors, depending on the molecular weights of the copolymers, are expected. For SIS 558, the transition temperature from a heterogeneous state to a homo-

geneous one is high due to the high molecular weight of this copolymer and the increase of  $\bar{\tau}$  with temperature is hence continuous in the considered temperature range. Copolymers with  $M_{\text{tot}} \sim 50,000$  are on the verge of the microphase organization and  $T_c$  becomes accessible. As  $T_a$  increases, the microdomain organization is progressively destroyed and replaced by a randomly segregated system, before complete mixing occurs at  $T_c$ . Such a morphological evolution explains the increase followed by a decrease of  $\bar{\tau}$  found for these copolymers. Finally, phases in copolymers with still lower  $M_{\text{tot}}$  (about 30,000) never present any latticelike arrangement: the soft blocks are randomly dispersed in the hard matrix.<sup>6</sup> As already emphasized,  $\bar{\tau}$  is nearly independent of activation temperature, and rather high even for low  $T_a$  (see Figs. 2–4, solid symbols).

An *a priori* confirmation of this interpretation is given below. The structure of an SIS copolymer at a given temperature is likely to be maintained by quenching. Therefore, if the above explanation of the experimental results is correct, an SIS copolymer with suitable molecular characteristics would yield different adhesive behaviors, i.e.,  $\bar{\tau}$  values, according to its respective morphologies.

Copolymer SIS 320 was chosen for this purpose. Due to its molecular characteristics (Table I), it has a lamellar structure but the latter is easily destroyed.<sup>17</sup> A film of that copolymer was heated at 200°C for 2 h in an oxygen-free atmosphere and then quenched in liquid nitrogen. The treated film appeared isotropic under polarized light, contrary to the unquenched one. The electron micrographs revealed the absence of organization of the high-temperature structure (Fig. 5). Afterwards, we have established that after the 2 h heating required for joint formation, no further structural evolution has occurred.

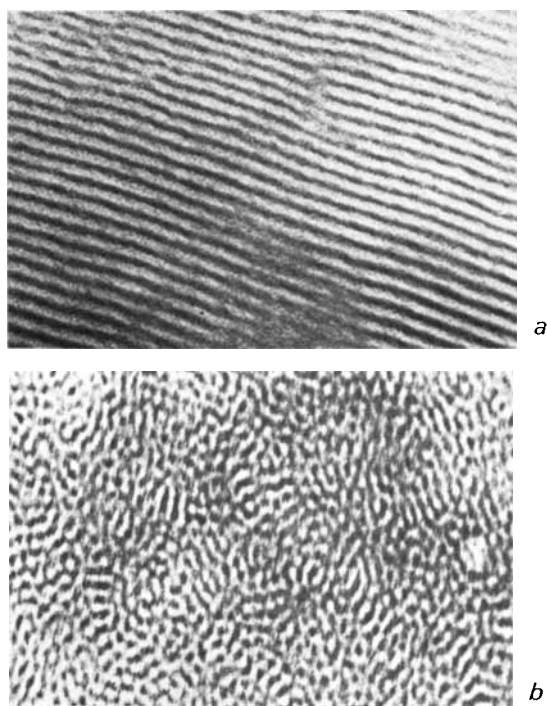


Fig. 5. Transmission electron micrographs of copolymer SIS 320: (a) annealed film; (b) after heating at 200°C and quenching. Magnification: 100,000  $\times$ .

TABLE II  
Lap Shear Strength at Break  $\bar{\tau}$  as a Function of Film Morphology for SIS 320

Optical properties of film	Anisotropic	Anisotropic	Isotropic
Bonding conditions	2 h/135°C	2 h/195°C	2 h/135°C
Optical properties of joint	Anisotropic	Isotropic	Isotropic
Tensile shear resistance at break $\bar{\tau}/10^5$ Pa	36.5	71.9	51.5

Table II shows the effect of the morphology on the shear resistance at break. A joint formed at 135°C has a low strength (3.6 MPa); an activation temperature of 195°C increases markedly the value of  $\bar{\tau}$  (7.2 MPa) as observed for the other copolymers of same molecular weight. The film was isotropic as well, confirming the absence of any organization. When a previously quenched film is used, an activation temperature of 135°C is enough to impart a 40% increase in  $\bar{\tau}$  (5.2 MPa) to the joint. Partial reorganization may occur during the bonding procedure.

These various experiments on quenched and unquenched films prove the importance of the history of the sample on its adhesive behavior; they confirm the proposed relationship between the morphology of the SIS block copolymers and the shear strength of joints bonded with them.

## CONCLUSION

The tensile shear resistance at break of joints bonded with SIS films, as a function of activation temperature, goes through a maximum. The latter depends on the morphology of the copolymer and corresponds to a structural state where phases are merely segregated but still individualized with respect to their properties. We have confirmed this interpretation by showing that an SIS copolymer which may present different successive structures gives also joints with different and predictable shear resistances. In connection with these results, our work allows the use of a broader group of SIS for adhesive purposes than the one we had previously investigated.

## References

1. B. R. M. Gallot, *Adv. Polym. Sci.*, **29**, 87 (1978).
2. J. F. Beecher, L. Marker, R. D. Bradford, and S. L. Aggarwal, *J. Polym. Sci. Part C*, **26**, 117 (1969).
3. G. Kraus, F. B. Jones, O. L. Marrs, and K. W. Rollmann, *J. Adhesion*, **8**, 235 (1977).
4. J. M. Widmaier and G. C. Meyer, *Polymer*, **18**, 587 (1977).
5. G. C. Meyer and J. M. Widmaier, *Polym. Eng. Sci.*, **17**, 803 (1977).
6. G. C. Meyer and J. M. Widmaier, *Polymer*, **22**, 995 (1981).
7. J. M. Widmaier and G. C. Meyer, *Polymer*, **19**, 398 (1978).
8. C. Goett and J. Journé, *Rev. Gén. Caoutch. Plast.*, **558**, 47 (1976).
9. K. Kato, *Polym. Eng. Sci.*, **7**, 38 (1967).
10. S. M. Aharoni and D. C. Prevorsek, *Int. J. Polym. Mater.*, **6**, 39 (1977).
11. D. J. Meier, *J. Polym. Sci. Part C*, **26**, 81 (1969).
12. D. F. Leary and M. C. Williams, *J. Polym. Sci., Polym. Phys. Ed.*, **11**, 345 (1973).



13. E. Helfand and Z. R. Wasserman, *Polym. Eng. Sci.*, **17**, 582 (1977).
14. D. F. Leary and M. C. Williams, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 265 (1974).
15. C. I. Chung, H. L. Griesbach, and L. Young, *J. Polym. Sci. Polym. Phys. Ed.*, **18**, 1237 (1980).
16. M. Fujimura, H. Hashimoto, K. Kurahashi, T. Hashimoto, and H. Kawai, *Macromolecules*, **14**, 1196 (1981).
17. J. M. Widmaier and G. C. Meyer, *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 2217 (1980).

Received September 17, 1982

Accepted November 18, 1982