# Mechanical Properties Developing at the Interface of Amorphous Miscible Polymers, Below the Glass Transition Temperature: Time-Temperature Superposition

#### YURI M. BOIKO,\* ROBERT E. PRUD'HOMME

Centre de recherche en sciences et ingénierie des macromolécules, Chemistry Department, Laval University, Sainte-Foy (Qué), Canada G1K 7P4

ABSTRACT: The bonding of amorphous polystyrene (PS) and poly(2,6-dimethyl-1,4phenylene oxide) (PPO) was conducted over a broad range of time and temperatures, but always below the (bulk) glass transition temperature ( $T_g$ ). Stress–strain properties developing at the symmetric (PS/PS and PPO/PPO) and asymmetric interfaces (PS/ PPO), in a lap–shear joint geometry, were measured at room temperature as a function of contact time and bonding temperature. Master curves of shear strength and modulus, obtained by time–temperature superposition, were constructed over several decades of time. Arrhenius apparent activation energies calculated for shear strength are 99, 81, and 144 kcal/mol for, respectively, PS/PS, PPO/PPO, and PS/PPO interfaces. A higher value of 191 kcal/mol was calculated for the shear modulus at the PS/PS interface, suggesting that the development of the strength and modulus is controlled by different molecular factors, that is, the modulus is controlled by the number of chains across the interface and the strength by the depth of penetration. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 825–830, 1999

**Key words:** interface; mechanical properties; time-temperature superposition; polystyrene; poly(phenylene oxide)

## INTRODUCTION

When two miscible polymer surfaces are brought into contact at a constant low pressure, adhesion occurs at the interface as a result of interdiffusion. This process has been investigated mainly above the glass transition temperatures  $(T_g)$  of the two polymers involved,<sup>1-5</sup> between their two  $T_g$ ,<sup>6-8</sup> and even below both of them,<sup>9,10</sup> since it has been shown that the effective  $T_g$  in the surface layer of a polymer film is lower than the bulk  $T_g$ ,<sup>11</sup> at a depth of about a radius of gyration.

The mechanical properties at polymer/polymer interfaces, like bulk properties, depend on the time and temperature of testing. In many instances, using the principle of time-temperature equivalence,<sup>12</sup> they can be described by a master curve<sup>13-16</sup> over a broad range of testing times or rates. In a welding experiment, they also depend on the contact time and bonding temperature. In this article, it is shown that such mechanical properties can be described by a master curve, keeping constant the temperature and the rate of testing, thus providing information about the chosen property as a function of technological variables. For example, Kline and Wool measured, above  $T_{\sigma}$ , the shear strength of a polystyrene/polystyrene (PS/PS) interface in a narrow temperature range.<sup>2</sup>

In this article, the principle of time-temperature superposition will be used to describe the

Correspondence to: R. E. Prud'homme (Robert. Prud'homme@chm.ulaval.ca).

<sup>\*</sup>*Present address*: Fracture Physics Dept., A.F. Ioffe Physico-Technical Institute, Politekhnicheskaya 26, St.-Petersburg 194 021, Russia.

Contract grant sponsors: Natural Sciences and Engineering Research Council of Canada; Fonds FCAR of the Province of Québec.

Journal of Applied Polymer Science, Vol. 74, 825-830 (1999)

<sup>© 1999</sup> John Wiley & Sons, Inc. CCC 0021-8995/99/040825-06



**Figure 1** (a) Shear strength as a function of the logarithm of the contact time for a PS/PS interface at several bonding temperatures (the lines through the data correspond to a least-square analysis); (b) master curve of the same data (the insert gives the horizontal shift factor used as a function of the reciprocal temperature). The reference temperature is 70°C.

shear strength and modulus of polymer/polymer interfaces above the effective  $T_g$  at the surface (but below the bulk  $T_g$ ) over many decades of contact time, using data recorded following welding at several temperatures. PS and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) were chosen because they are miscible polymers. In this study, we consider two symmetric (PS/PS and PPO/PPO) and one asymmetric interface (PS/PPO), which were bonded over the temperature ranges of 55–90, 113–156, and 70–100°C, respectively.

### **EXPERIMENTAL**

#### Materials

Atactic PS ( $M_w = 23 \times 10^4$ ,  $M_w/M_n = 2.84$ ,  $T_g = 103^{\circ}$ C) was obtained from Dow Chemicals (Midland, MI), and PPO ( $M_w = 44 \times 10^3$ ,  $M_w/M_n = 1.91$ ,  $T_g = 216^{\circ}$ C,) from General Electric (Schenectady, NY).

## **Preparation of Samples**

Films of PS and PPO of about 100  $\mu$ m in thickness were prepared using a twin-screw laboratory

extruder (Haake–Buchler, Rheocord System 40) with smooth calendering rolls. The temperature in the die was 225°C for PS and 286°C for PPO. No deformation field was applied to the extrudates (see ref. 10 for more details).

### Welding Step

Previously uncontacted samples were bonded in a lap-shear joint geometry with a contact area of  $5 \times 5$  mm<sup>2</sup>, using a Carver laboratory press, and submitted to tensile loading (see, e.g., ASTM D3163) in order to achieve high load-at-failure values in shear,<sup>17</sup> which is important here since the expected values of mechanical force at the interface are low. The contact pressure was 0.8 MPa, and the contact time varied from 2 min to 96 h. PS/PS, PPO/PPO, and PS/PPO interfaces were bonded in temperatures ranges of 55-90, 113-156, and 70-100°C, respectively. For the asymmetric PS/PPO interface, the PS sample was placed on the top of the joint. A limited number of PS films of 140  $\mu$ m in thickness were also used for bonding the PS/PS interface at 90°C for 24 and 96 h.



**Figure 2** (a) Shear modulus (normalized by the value at 90°C and 96 h) as a function of the logarithm of the contact time for a PS/PS interface at several bonding temperatures (the lines through the data correspond to a least-square analysis); (b) master curve of the same data (the insert gives the horizontal shift factor used as a function of the reciprocal temperature). The reference temperature is 70°C.

#### **Mechanical Measurements**

Mechanical testing was conducted not less than 24 h after bonding. To obtain the force-displacement curves, the bonded joints were fractured at room temperature on an Instron tensile tester, Model 1130, at a crosshead speed of 0.5 cm/min. The distance between jaws was 5 cm, with the joint located in the middle. To obtain accurate results, from 16 to 25 joints were measured for each experimental data point. Shear stress was calculated as the measured force divided by the contact area, neglecting the fact that stresses induced in the overlapped area (in tensile loading) are not uniform and are higher at the overlap ends.<sup>18</sup>

In the lap-shear joint test, it is difficult to calculate an absolute value of the shear modulus since deformation occurs both in the overlapped area (shear mode) and outside the contact zone (tensile mode). However, an apparent modulus (E) can be calculated, making the assumption that deformation occurs in the overlapped area only. The contribution of un-contacted zones to the slope of the force-displacement curves is the same for each interface, at a given testing temperature and strain rate. Thus, normalization

values of *E* by any chosen  $E^*$  value (e.g., the highest value measured)  $(E/E^*)$  excludes the contribution of the tensile mode; this ratio is used here for analysis. Details about the experimental procedures of bonding and mechanical measurements can be found elsewhere.<sup>10</sup>

The temperature-shift factor, which is necessary in the time-temperature analysis, can be either measured or calculated.<sup>12</sup> The calculation proposed by Williams et al.<sup>19</sup> works generally well, but, unfortunately, the surface  $T_g$ , which is required in this calculation, is unknown. Therefore, in this article, shift factors were obtained experimentally by horizontally shifting the strength and modulus isotherms along the contact time axis.

## RESULTS

Shear strength ( $\sigma_s$ ) for a PS/PS interface bonded at 55, 62, 70, 80, and 90°C is shown in Figure 1(a) as a function of the logarithm of the contact time. Each experimental data point represents the average of 16–25 measurements. Within experimental error,



**Figure 3** (a) Shear strength as a function of the logarithm of the contact time for a PPO/PPO interface at several bonding temperatures (the lines through the data corresponds to a least-square analysis); (b) master curve of the same data (the insert gives the horizontal shift factor used as a function of the reciprocal temperature). The reference temperature is 136°C.

it is seen that  $\sigma_s$  increases linearly with log(time) at each bonding temperature, but the rate of this increase is more rapid at higher temperatures. For time-temperature superposition analysis, the curves were horizontally shifted against the chosen reference curve of 70°C. The master curve resulting from this operation is shown in Figure 1(b); it gives the strength developed at 70°C at the PS/PS interface over ten decades of time. The logarithm of the shift factor  $a_T$  thus obtained is plotted in the insert of Figure 1(b) against the inverse of the bonding temperature. This plot is linear and the apparent activation energy ( $\Delta H$ ) can be calculated by the Arrhenius equation:

$$\Delta H = R \ln a_T / (T^{-1} - T_0^{-1}) \tag{1}$$

where R is the gas constant; T, the current temperature, and  $T_0$ , the reference temperature. According to this calculation,  $\Delta H$  equals 99 kcal/mol.

Contrary to the sharp development of the shear strength seen in Figure 1(a), the shear modulus increases slowly with time [Fig. 2(a)]: the difference between the lowest and highest values of Figure 2(a) is of the order of two, whereas the same difference for shear strength (Fig. 1) is 40. The shear modulus develops more rapidly with log(time) at intermediate temperatures, between 62 and 80°C and very little at the lowest and highest bonding temperatures studied. The isotherms of Figure 2(a) were horizontally shifted at the 70°C reference temperature. The master curve for *E* and the corresponding Arrhenius plot are given in Figure 2(b). This leads to a  $\Delta H$  of 191 kcal/mol, which is roughly twice the value of  $\Delta H$  calculated for the shear strength.

The shear strength developed at the PPO/PPO interface as a function of log(time), at bonding temperatures of 113, 124, 136, 146, and 156°C, is shown in Figure 3(a). Interdiffusion at the PPO/PPO interface occurs at much lower temperatures ( $\sim T_g$  –90°C) as compared to PS ( $\sim T_g$  –40°C) if the bulk  $T_g$  is taken as the reference. However, a comparison between Figures 1(a) and 3(a) indicates that shear-strength values are much smaller for PPO than for PS films. The shear strength increases almost linearly with log(time) at any given temperature. The slope of the curves increases sharply between 113 and 136°C but is almost the same above 136°C. The data in Figure 3(a) show that  $\sigma_s$  is a function of both



**Figure 4** (a) Shear strength as a function of the logarithm of the contact time for a PS/PPO interface at several bonding temperatures (the lines through the data correspond to a least-square analysis); (b) master curve of the same data (the insert gives the horizontal shift factor used as a function of the reciprocal temperature). The reference temperature is 70°C.

contact time and bonding temperature. The shifting of these curves, taking a reference temperature at 136°C, gives a master curve for  $\sigma_s$  [Fig. 3(b)] from which a  $\Delta H$  value of 81 kcal/mol is calculated [insert of Fig. 3(b)]. The analysis of the modulus of the PPO/PPO interface between 113 and 156°C reveals the absence of any tendency with either time or temperature.

The miscibility of two polymers with different chemical structures can serve as a driving force for their interdiffusion at the interface. It is well known that PS and PPO are miscible over the full range of compositions because specific interactions occur between them.<sup>20,21</sup> The shear strength for a PS/PPO interface is plotted against the logarithm of the contact time in Figure 4(a) for bondings at 70, 80, 90, and 100°C.  $\sigma_s$  increases with log t at all temperatures, as in the case of symmetric PS/PS and PPO/PPO interfaces (Figs. 1 and 3).

A master curve was constructed from the data in Figure 4(a), selecting a reference temperature of 70°C [Fig. 4(b)] and the corresponding Arrhenius plot is given in the insert of Figure 4(b). The apparent activation energy then calculated, using the Arrhenius equation, gives 144 kcal/mol. This value is higher than the values of  $\Delta H$  calculated for symmetric interfaces.

## DISCUSSION

The  $\Delta H$  value calculated here for the shear strength at a PS/PS interface at temperatures between 55 and 90°C, that is, 99 kcal/mol, is similar to that obtained by Kline and Wool<sup>2</sup> at bonding temperatures between 109 and 118°C, that is, 96.1 kcal/mol. These two values were obtained for PS with similar molecular weights, in the same lap-shear joint geometry and with the same overlapped length of 5 mm. This similarity suggests that the development of fracture stress at a PS/PS interface is controlled by diffusion with the same activation energy at temperatures between 55 and 118°C. It also suggests that there is no discontinuity in the diffusion behavior when going through the bulk  $T_g$ , as was recently shown for a PS/PPO interface in the vicinity of the (bulk) glass transition of PS.<sup>22</sup>

A higher  $\Delta H$  value of 144 kcal/mol is calculated for the shear strength of the asymmetric PS/PPO interface, where the temperature range of bonding is close to that of the PS/PS assembly. This difference is due, in part, to the low values of shear strength obtained at the PPO/PPO interface (Fig. 3) as compared to those at the PS/PS interface (Fig. 1). These values indicate that the molecular mobility at the PPO surface is significantly lower than that at the PS surface, at the same reference temperature. Therefore, the diffusion of PS chains into a less mobile surface of PPO requires more energy than does the diffusion of PS chains into a more mobile PS surface. Thus,  $\Delta H$  at the PS/PPO interface is reasonably higher than at the PS/PS interface.

Different molecular factors are responsible for the development of viscoelastic polymer properties like E and  $\sigma_s$  at an interface. Above  $T_g$ , at the interface of amorphous miscible polymers,  $\sigma_s$  is controlled by the depth of penetration, and  $E_s$ , by the number of chains across the interface.<sup>15</sup> This interpretation is consistent with the significantly different values of the apparent activation energy for Eand  $\sigma_{\rm s}$  calculated here. The  $\Delta H$  of 191 kcal/mol for the E at the PS/PS interface is roughly twice the value found for  $\sigma_s$ . Furthermore, a higher value of  $\Delta H$  for E indicates that a higher energy barrier should be overcome for the development of E as compared to the development of  $\sigma_s$ . Indeed, an increase in the number of chains across the interface is a less energetically favorable process than is the penetration of chain ends into a polymer matrix in which they are already present. Chain ends at the surface layer, crossing the interface at early stages of bonding, hinder the penetration of chain ends located deeper in the film: higher energies are needed to increase the number of chains across the interface. However, any further penetration of the chains, after they have crossed the surface layer, can continue more easily. Thus, the method of reduced variables supports the mechanism of bonding proposed earlier.<sup>15</sup>

## CONCLUSIONS

It has been shown, in this article, that the shear strength and shear modulus developing at symmetric and asymmetric polymer/polymer interfaces, at relatively low temperatures (below the bulk  $T_g$  of the polymers involved), can be described by master curves constructed using the classical principle of time-temperature superposition. The difference by a factor of two between  $\Delta H$  values calculated for the shear modulus and shear strength at the PS/PS interface indicates that these properties are controlled by different molecular factors, that is, shear modulus is a function of the number of chains across the interface whereas shear strength is a function of the depth of penetration, in accordance with the general mechanism of bonding proposed in the literature.  $^{15}$ 

The authors thank the Natural Sciences and Engineering Research Council of Canada and the Fonds FCAR of the Province of Québec for financial support, including a NATO Science Fellowship granted to Y. M. B.

## REFERENCES

- Jud, K.; Kausch, H. H.; Williams J. G. J Mater Sci 1981, 16, 204.
- 2. Kline, D.B.; Wool, R. P. Polym Eng Sci 1988, 28, 52.
- Vorenkamp, E.J.; van Ruiten, J.; Kroesen, F.A.; Meyer, J. G.; Hoeksta, J.; Challa, G. Polym Commun 1989, 30, 116.
- Siqueira, D. F.; Galembeck, F.; Nunes, S. P. Polymer 1991, 32, 990.
- 5. Cho, B.-R.; Kardos, J. L. J Appl Polym Sci 1995, 56, 1435
- Jabbari, E.; Peppas, N. A. Macromolecules 1993, 26, 2175; 1995, 28, 6229.
- Composto, R. J.; Kramer, E. J. J Mater Sci 1991, 26, 2815.
- Sauer, B. B.; Walsh, D. J. Macromolecules 1991, 24, 5948.
- Boiko, Yu. M.; Prud'homme, R. E. Macromolecules 1997, 30, 3708.
- Boiko, Yu. M.; Prud'homme, R. E. Macromolecules 1998, 31, 6620.
- Kajiyama, T.; Tanaka, K.; Takahara, A. Macromolecules 1995, 28, 3482; 1998, 39, 4665.
- Ferry, J. D. Viscoelastic Properties of Polymers, 3rd ed.; Wiley: New York, 1980.
- Hamed, G. R.; Shieh, C.-H. J Polym Sci Polym Phys Ed 1983, 21, 1415.
- Chang, R. J.; Gent, A. N. J Polym Sci Polym Phys Ed 1981, 19, 1619.
- 15. Wool, R. P. Polymer Interfaces: Structure and Strength; Hanser: New York, 1995; Chapter 11.
- Gent, A. N.; Lai, S.-M. J Polym Sci Polym Phys Ed 1994, 32, 1543.
- Encyclopedia of Polymer Science and Engineering, 2nd ed.; Kroschwitz, J. I., Ed.; Wiley-Interscience: New York, 1985; Vol. 1, p 541.
- Wu, S. Polymer Interface and Adhesion; Marcel Dekker: New York, 1982; Chapter 14, pp 510-513.
- Williams, M. L.; Landel, R. F.; Ferry, J. D. J Am Chem Soc 1955, 77, 3701.
- Stejskal, E. O.; Schaefer, J.; Sefcik, N. D.; McKay, R. A. Macromolecules 1981, 14, 276.
- Feng, H.; Feng, Z.; Ruan, H.; Shen, L. Macromolecules 1992, 25, 5981.
- Boiko, Yu. M.; Prud'homme, R. E. J Polym Sci Polym Phys Ed 1998, 36, 567.