Strength Development at the Interface of Amorphous Polymers and Their Miscible Blends, below the Glass Transition Temperature

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Received July 15, 1996; Revised Manuscript Received August 12, 1997

ABSTRACT: Bonding amorphous polystyrene (PS) and poly(2,6-dimethyl 1,4-phenylene oxide) (PPO) has been carried out in a broad range of temperatures and contact times (*t*), but always below the glass transition temperature (T_g), in a lap−shear joint geometry. Strength at the symmetric and asymmetric polymer/polymer interfaces develops with $t^{1/4}$ and, hence, is diffusion controlled. The development of strength at the homopolymer/miscible blend interface below T_g can be simulated from data for homopolymer/homopolymer interfaces, taking into account the wetting (and "fast diffusion") and diffusion contributions to the development of strength.

Introduction

Macromolecular chain segments may cross a polymer/polymer interface and establish entanglements on the opposite side.[1] As a result of this interpenetration, there is optical disappearance of cracks during healing[2] and development of strong bonds between the two surfaces after welding.[3−8] The strength developing at an interface depends on the chemical structure of the polymers involved, their molecular weights and polydispersity, the geometry of the joint, and the method of testing; it is a function of temperature and pressure.[3−5,8,9]

Symmetric amorphous interfaces, where on both sides the polymers are the same, providing an equivalent flux into opposite directions, tend to develop a strong bonding between the two polymer surfaces. A well-known example is the polystyrene/polystyrene (PS) interface.[2,3,8,10,11] In contrast, the strength at the interface between immiscible amorphous polymers is rather low, being about 5−10% of their bulk values for poly(styrene-*co*-acrylonitrile)/poly(methyl methacrylate) (SAN/PMMA), PS/PMMA, and SAN/polycarbonate pairs.[9,12] The forces of contact at incompatible amorphous polymer interfaces can be improved with the addition of a block copolymer.[7,13−19]

An increase in time and temperature of interdiffusion results in an enhancement of the mechanical properties[3−8] (although, for immiscible amorphous polymers welded above the glass transition temperature (T_g) of both polymers, the strength at the interface was found to be independent of temperature for experiments done in a narrow temperature range[12]). Both healing and welding have mostly been followed at temperatures above T_g where the mobility of the molecular chains is rather high. The upper temperature limit for welding is determined by the need to keep the sample geometry constant (for mechanical characterization) and by the thermostability of the polymer.

A polymer/polymer interface can vanish at times greater than the so-called reptation time (T_r) in terms of the model developed by de Gennes[20] and by Doi and Edwards[21] for the dynamics of polymer melts. This is the time required by the chains to escape from their initial tubes in a curvilinear snakelike manner. Applying the reptation model to the interdiffusion at polymer/polymer interfaces, de Gennes,[22] Prager and Tirrell,[23] and Kim and Wool[24] have shown that the stress at fracture is a function of the contact time (*t*) to the fourth power. Earlier, the same scaling law for the development of an adhesive bond strength was derived by Vasenin.[25] The development of strength with $t^{1/4}$ (above T_g) has been confirmed in several experimental studies.[3−5,8,26]

The diffusion at the interface of amorphous polymers and their miscible blends has been studied by different techniques such as attenuated total reflectance infrared spectroscopy,[27] forward recoil spectrometry,[28,29] Rutherford backscattering spectrometry,[30] specular neutron reflection,[31,32] and spectroscopic ellipsometry.[31,32] However, only two examples of a mechanical characterization of the interface of miscible polymer blends can be found in the literature: poly(vinyl chloride)/PMMA[33,34] and poly(vinylidene fluoride)/PMMA interfaces[35] which have been welded in a temperature range well above T_g. Craze healing of atactic PS was carried out by Wool and O'Connor[2] above and below T_g. The optical disappearance of crazes at T_g − 28 °C points out to the possibility to heal completely an interface below T_g. However, craze healing is certainly easier to realize at low temperatures as compared to welding since the two parts of the interface are not completely separated. The lowest possible temperature for PS craze healing was considered to be 52 °C[2], i.e., T_g − 46 °C; to our knowledge, it has not yet been experimentally confirmed.

In this study, we have chosen PS and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) as a representative example of miscible polymers. Blends of these polymers are commercial[36] and are widely used in industry. Both polymers are amorphous, which facilitates the interpretation of the results. Since there is a significant difference in T_g between these two polymers, i.e., 105 °C for PS and 216 °C for PPO,[30] it is difficult with this system to keep the same isoviscous state for each polymer. Above the T_g of PPO, PS has a much lower

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S0024-9297(96)01036-4 CCC: $15.00

Table 1. Temperature Conditions of Extrusion (°C)

material	extrusion zones 1	2	3	4	die
PS	155	180	205	220	225
PPO	240	275	280	283	286
PS/PPO (wt. ratio 1:1)	240	275	285	288	292
PS/PPO (wt. ratio 3:1)	230	272	280	285	290

Table 2. Characterization of Extruded Samples

material	tensile strength[a] (MPa)	strain at break[a] (%)	Young's modulus[a] (Gpa)	T_g (°C)
PS	43.2	3.5	2.47	103
PPO	62.0	23.5	1.76	216
PS/PPO (wt. ratio 1:1)	58.8	5.0	2.04	149
PS/PPO (wt. ratio 1:1) (pressed after extrusion)	55.7	3.7	2.16	149
PS /PPO (wt. ratio 3:1)	55.7	4.1	2.05	121

[a] Measured at a strain rate of 0.0017 s^{-1} and at room temperature.

melt viscosity than PPO, and in addition, PPO is not thermostable in air. For these reasons, Composto and Kramer have studied a PS/PPO interface in a temperature range between the T_g values of the two polymers.[30] However, early in this study, we discovered that adhesion is possible even below the T_g of PS. In this context, the goal of this paper is (i) to characterize the mechanical behavior at symmetric and asymmetric amorphous polymer/polymer interfaces bonded below T_g and (ii) to consider the possibility to predict the fracture stress at a homopolymer/miscible blend interface on the basis of data for homopolymer/homopolymer interfaces.

Experimental Section

Materials. Pellets of atactic PS ($M_w = 230\,000$, $M_w/M_n = 2.84$, $T_g = 103$ °C) and a powder of PPO ($M_w = 44\,000$, $M_w/M_n = 1.91$, $T_g = 216$ °C) were obtained from Dow Chemical and General Electric, respectively.

Preparation of Samples. Films of PS and PPO were extruded using a twin-screw laboratory extruder (Haakebuchler, Rheocord System 40) with smooth calendaring rolls. Films of PS/PPO blends (weight ratios of 1:1 and 3:1) were prepared by milling the PS pellets, dry mixing with PPO powder, and extrusion. Temperature conditions of extrusion are given in Table 1. No deformation field was applied to the extrudates. To make the surface of the blend (weight ratio 1:1) as smooth as the surface of the other films, extruded films of this blend were pressed against an aluminum foil at $T_g + 15$ °C for 3 min, after a 3 min preheating period, followed by cooling to room temperature under pressure for ~4 min. Characterization of the samples is given in Table 2. As can be seen from these data, there is no significant change in mechanical properties of this blend after such a treatment. To detect a possible effect of the method of preparation of the blend on its thermal behavior, PS and PPO (wt. ratio 1:1) were dissolved in chloroform and mixed for 6 h at room temperature. A blend was obtained by casting the solution onto glass. After evaporation of solvent for 24 h at room temperature, a film of about 100 μm in thickness was floated off the glass onto the surface of water and dried under vacuum at 60 °C for 24 h and then at $T_g + 5$ °C for a week. All above-indicated films were about 100 μm in thickness. A limited number of PS films of 140 μm in thickness have also been used for bonding PS/PS interfaces at a temperature of 90 °C for long periods of time, i.e., 1 and 4 days.

Bonding Procedure. The samples were bonded in a lap-shear joint geometry and submitted to tension loading (see, for example, ASTM D3163) in order to achieve higher load-at-failure values in shear,[37] which is important here since the expected mechanical force at the interface is rather low. The experimental setup for joining the samples is shown in Figure 1.

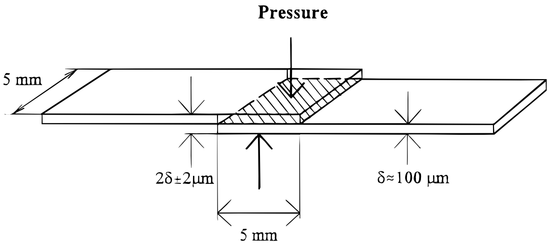

Figure 1. The lap-shear joint experiment. The contact area is shown by strips.

Samples for lap-shear testing were cut off in the central part of the extruded films, which had a width of 4 cm. This central portion (5 mm) had a uniform thickness and did not touch the rolls because it was thinner than the edges. To apply pressure to the overlapped area as uniformly as possible, the thickness of the joint areas, as measured with a micrometer, was kept constant, at ±2 μm. [To achieve that, the thickness of each film was measured individually and the samples sorted out such that the thickness of each overlapped area was constant, at ±2 μm]. The contact area was 5×5 mm^2. Increasing the contact area by a factor of 2 did not influence the average measured values of strength (for a given temperature and time), but it decreased their standard deviation. However, at higher temperatures of bonding, an increase in contact area led to the failure of the sample in its unwelded zones (in the tensile mode).

For these experiments, 10 joints were placed side by side between two stainless steel plates of a 2 mm thickness and preheated for 1 min in a Carver press which had already been warmed to the necessary temperature. Taking into account the thickness of the plates and of the polymer films, this time was sufficient to reach the chosen temperature of bonding at the interface. The temperature of the heating plates was controlled at ±2.5 °C. A contact pressure was applied to the joints after the 1 min preheating period, and the contact time varied from 2 min to 4 days. The assembly was then quickly cooled to room temperature (for 2−4 min, depending on temperature) under pressure by circulating water in the plates of the press. For asymmetric interfaces, the PS sample was placed on the top of the joint. To discover a possible influence of the sample preparation on the mechanical properties, measurements were made on PS/PS joints prepared from extruded and molded films; no difference was found.

Mechanical Measurements. Mechanical testing was conducted not less than 24 h after bonding. To obtain force−displacement curves, the bonded joints were tested at room temperature on an Instron tensile tester, Model 1130, at a crosshead speed of 0.5 cm/min. This speed was chosen because Kline and Wool[3] indicated, for lap-shear testing of PS/PS interfaces welded above T_g, an independence of the load−displacement characteristics in a crosshead speed range between 0.013 and 1.25 cm/min. The distance between jaws was 5 cm, with the joint located in the middle. From 16 to 25 joints were measured for each experimental data point. In the lap-shear joint loading, one of the assumptions is that shear stresses only are included into the measured value of force. Shear stress was calculated as the measured force divided by the contact area, neglecting the fact that the stresses induced in the overlap area (in tensile loading) are nonuniform and higher at the overlap ends.[38] Shear modulus could not be calculated with an acceptable accuracy.

DSC Measurements. T_g was measured using a Perkin-Elmer DSC-4 differential scanning calorimeter, at a heating rate of 20 °C/min; the transition temperature was read as the middle point on the curves. The two blends investigated showed a single glass transition, confirming their miscibility. The extruded films, the extruded and pressed films, and the films obtained from solution of the blend (wt. ratio 1:1) showed the same T_g of 149 °C.

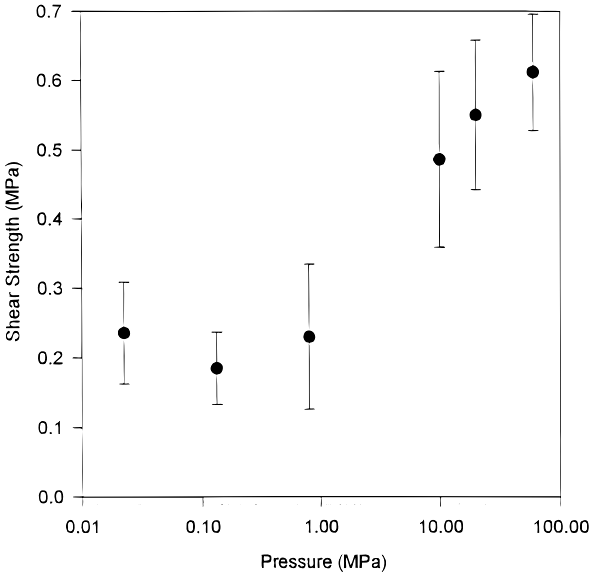

Figure 2. Shear strength of a PS/PS interface, bonded at $T_g - 23$ °C for 30 min, as a function of contact pressure. The error bars correspond to the standard deviation of the mean.

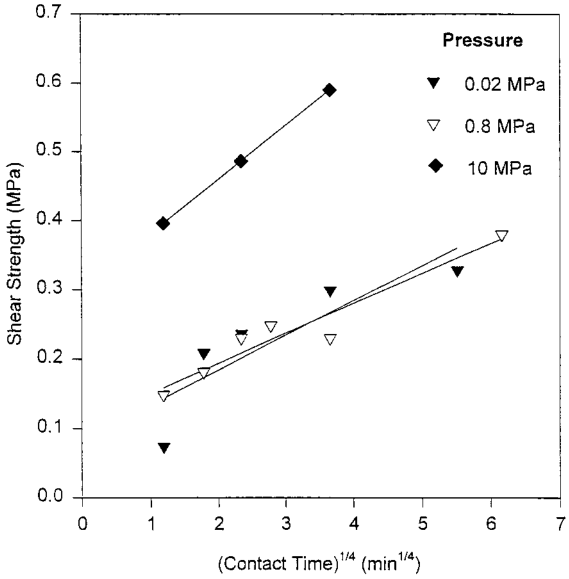

Figure 3. Shear strength of a PS/PS interface as a function of contact time for bonding at $T_g - 23$ °C, at several contact pressures. The lines through the data correspond to a least-squares analysis.

Results and Discussion

Effect of Pressure. First of all, the influence of pressure on the development of the mechanical properties (shear strength and shear modulus) at the interface was studied because it is known that a small pressure (0.07,[3] 0.1,[5] or 1 MPa[33]) is necessary to provide a satisfactory contact between two surfaces. If no pressure is applied, no bonding occurs even above T_g (for example, with PS/PS interfaces[8,39]). However, this pressure should not be too high because it will change the geometry of the joint and contribute to the diffusion process.

Here, bonding of PS/PS interfaces for 30 min at 80 °C ($T_g - 23$ °C) was chosen (the same time was used by McGarel and Wool[8,39] for welding a PS/PS interface above T_g). We have studied a range of pressures differing by more than 3 orders of magnitude (from 0.02 to 50 MPa), but even the largest pressure used did not modify the sample geometry. Fracture always occurred in the shear mode. Shear strength (σ_s) is shown in Figure 2 as a function of the logarithm of contact pressure. σ_s does not depend on pressure up to ~1 MPa, but increases afterward, as found in the literature for several polymer interfaces.[40,41] On the basis of the data of Figure 2, a pressure of 0.8 MPa seemed to be reasonable for the following tests since it permits a good contact between the two surfaces below T_g, keeping the shear strength independent of contact pressure. McGarel and Wool[8,39] have also found that the fracture energy of PS/PS interfaces, partially welded above T_g, does not depend on contact pressure between 0.3 and 2 MPa.

Values of shear strength are plotted in Figure 3 against $t^{1/4}$, for bondings carried out at 80 °C, at several contact pressures. It is seen that the pressure does not influence the development of strength with time at low pressures (0.02 and 0.8 MPa) since the slope of the two curves is almost the same. At a higher contact pressure (10 MPa), the slope is larger. The same behavior has been reported for rubber materials,[1] but at pressures up to 1 MPa and temperatures above T_g.

Considering that there is no influence of contact pressure on the development of shear strength with time in the range of pressure between 0.02 and 0.8 MPa (Figures 2 and 3), a contact pressure of 0.8 MPa was chosen for all the following experiments.

Mechanical Properties at Homopolymer/Homopolymer Interfaces. For symmetric (PS/PS and PPO/PPO) and asymmetric (PS/PPO) interfaces, force increases almost linearly with elongation (curves not shown) until fracture which always occurred at the interface, i.e., in the shear mode. There is no significant change in the slope of any of the curves. In samples containing PPO, values of elongation at rupture are very small because both bonding and mechanical measurements have been performed well below the T_g of PPO, i.e., bonding between $T_g - 70$ °C and $T_g - 126$ °C, and measurements at $T_g - 194$ °C.

Shear strength for PS/PS, PPO/PPO, and PS/PPO interfaces, at several temperatures, is plotted against $t^{1/4}$ in Figures 4–6. Fracture of PS/PS joints prepared from films of 100 μm in thickness, bonded at 90 °C for 24 and 96 h, occurred in some cases outside the contact zones (in the tensile mode), at the edge of the overlapped area. To prevent such type of fracture, films of 140 μm in thickness were also used for bonding under these conditions. Values of shear strength reported in Figure 4, at 90 °C for contact times of 24 and 96 h, were calculated from measurements of both 100 and 140 μm samples. In all cases, a linear variation of σ_s is seen with $t^{1/4}$, in the limit of the rather large scatter of the experimental data (the error bars are not shown here for clarity, but they are of the same order of magnitude as in Figure 2). For symmetric polymer/polymer interfaces (Figures 4 and 5), the slopes change with temperature, meaning that the development of strength is a thermally activated process. From Figure 6, it is noted that bonding at the PS/PPO interface can occur even at a temperature as low as T_g(PPO) − 146 °C (corresponding to T_g(PS) − 33 °C, in agreement with the lowest possible temperature for wetting and healing in PS mentioned in refs 2 and 42). The driving force for bonding is the miscibility between PS and PPO. One of the common features of the curves in Figures 4–6 is that their extrapolation to the origin gives a finite value

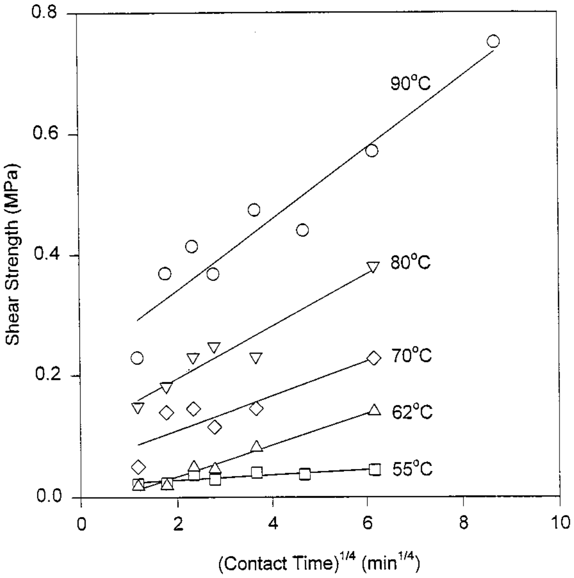

Figure 4. Shear strength of a PS/PS interface as a function of contact time for bonding at several temperatures below T_g. The lines through the data correspond to a least-squares analysis.

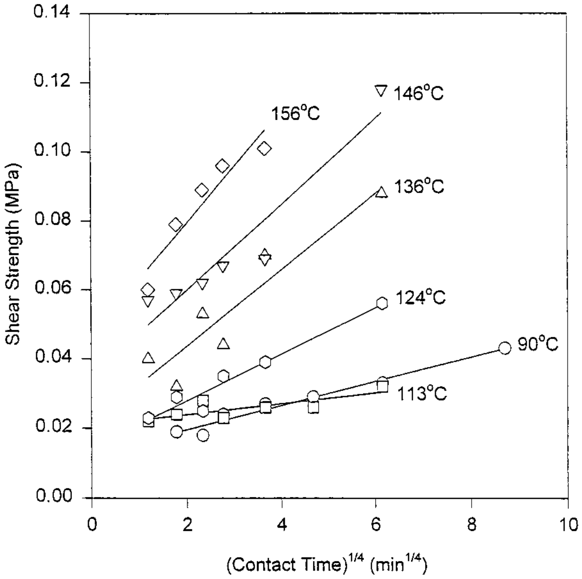

Figure 5. Shear strength of a PPO/PPO interface as a function of contact time for bonding at several temperatures below T_g. The lines through the data correspond to a least-squares analysis.

of strength, similar to that observed for some polymer/polymer interfaces welded above T_g;[4,43] we will comment this observation later.

The development of mechanical properties at amorphous polymer/polymer interfaces below T_g can be better understood with experiments carried out at very short contact times. We have then performed the following experiments: after a 1 min preheating period from room temperature to 90 °C at a contact pressure of 0.02 MPa, the PS/PS interface was submitted to a pressure of 0.8 MPa for 1 s ("zero" contact time), 10 s or 1 min, and then cooled to room temperature for 2−3 min before recording force−displacement curves. Values of σ_s, measured as described in the Experimental Section, are shown in Figure 7. There is a finite level of shear strength at "zero" time, which was developed during the preheating−cooling period. More precisely, at "zero" time, σ_s already has one-fourth the value it reaches after 2 min (Figure 7), which is the shortest time studied here.

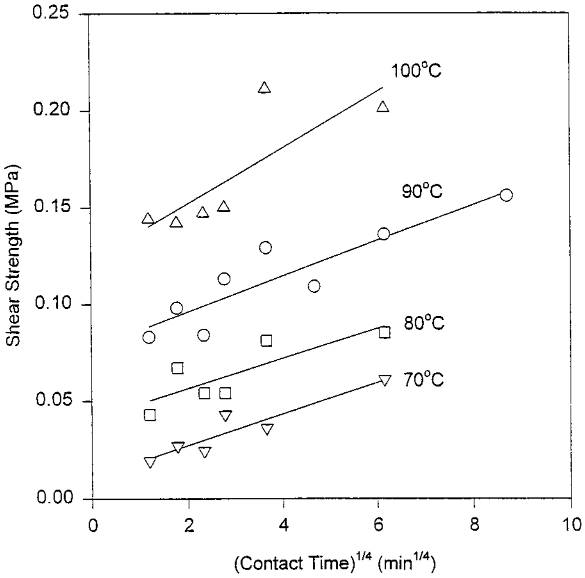

Figure 6. Shear strength of a PS/PPO interface as a function of contact time for bonding at several temperatures below the T_g of both polymers. The lines through the data correspond to a least-squares analysis.

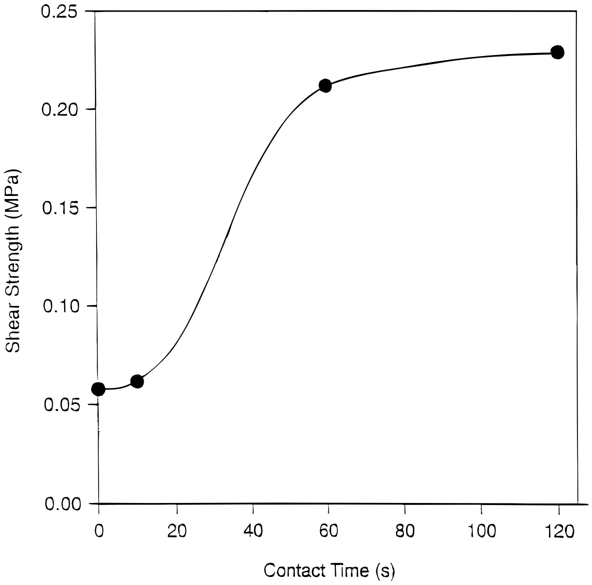

Figure 7. Shear strength of a PS/PS interface bonded at $T_g - 13$ °C, for short contact times. The line through the data is provided as a guide to the eye.

Homopolymer/Polymer Blend Interface. From the previous experiments, a possible mechanism of bonding is illustrated in Figure 8. At room temperature, the chain ends of the two slabs are located on opposite sides of the interface (Figure 8, top). When the temperature is increased, during the 1 min preheating period, with a small applied pressure, some of the chain ends can start crossing the interface, resulting in a certain level of mechanical strength (Figure 7) but, presumably, with a small depth of penetration (Figure 8, middle) since the values of shear strength for symmetric interfaces (Figures 4 and 5) remain low. A further increase in contact time leads to an increase in the depth of penetration (Figure 8, bottom), corresponding to a significant increase in shear strength (Figures

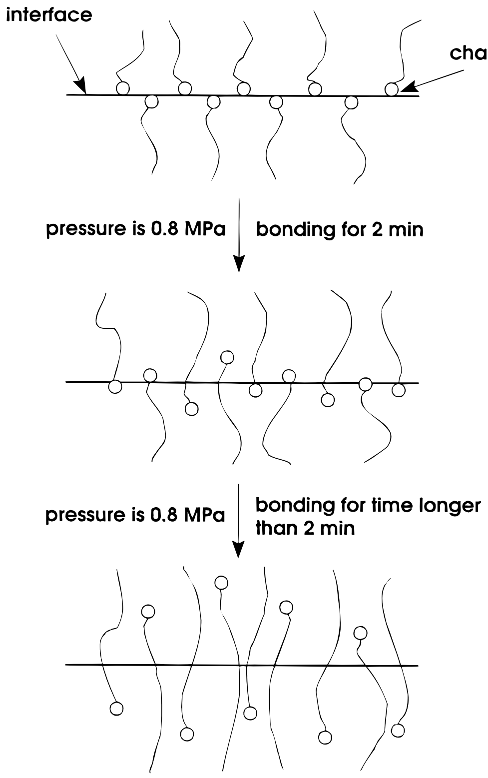

Figure 8. Schematic representation of the molecular mechanism of bonding of amorphous polymer/polymer interfaces below T_g.

4−6). Thus, molecular factors responsible for the development of strength are the depth of penetration and the number of chains across the interface.

It is difficult, here, to evaluate the depth of penetration achieved except to mention that the level of strength developing at the PS/PS interface below T_g (Figure 4) is less than 10% of the value determined in lap-shear experiments for a completely healed PS/PS interface with similar molecular weights ($M_w = 26\,200$ and $M_n = 142\,000$).[3] That maximum strength is due to the displacement of the center-of-mass over a distance of about the radius of gyration[3] (R_g). Here the expected interpenetrated distance is certainly much less than $^1/_2$ R_g. The average repeat unit interpenetration distance (δ), in other words the interface thickness, depends on time and molecular weight (above T_g) as $\delta \sim t^{1/4}M^{-1/4}$ at times shorter than the reptation time.[24] Assuming that δ is responsible for the development of strength,[24] the same scaling law holds: $\sigma \sim t^{1/4}M^{-1/4}$. This relationship is valid if the chain pullout mechanism dominates during mechanical loading the interface;[44] in case of bond rupture, strength behaves as $\sigma \sim t^{1/4}M^{-3/4}$. In both cases, however, the strength at the interface (above T_g) develops with $t^{1/4}$ at $t < T_r$.

It has been mentioned before that the shear strengths observed in Figures 4−6 do not extrapolate to zero at the origin. This behavior indicates that both wetting and fast diffusion occur at short times. The wetting contribution is mainly due to van der Waals forces at all sites of contact between the two surfaces. Therefore, strength developing at amorphous interfaces below T_g consists of two contributions: (i) wetting and fast diffusion, hereafter called wetting for simplicity, and (ii) diffusion. For a PS/PS interface, the strength at a given temperature can be written

$$\sigma_{PS/PS}(t) = \sigma^{w}{}_{PS/PS} + \sigma^{d}{}_{PS/PS} \tag{1}$$

where the indexes "w" and "d" correspond to wetting and diffusion processes, respectively. Since $\sigma^{d}{}_{PS/PS} = \alpha_{PS/PS}\, t^{1/4}$ where $\alpha_{PS/PS}$ is a rate constant for the diffusion process, eq 1 can be written as

$$\sigma_{PS/PS}(t) = \sigma^{w}{}_{PS/PS} + \alpha_{PS/PS}t^{1/4} \tag{2}$$

Similarly, for a PS/PPO interface

$$\sigma_{PS/PPO}(t) = \sigma^{w}{}_{PS/PPO} + \alpha_{PS/PPO}t^{1/4} \tag{3}$$

To develop a similar relationship for PS/blend interfaces, two assumptions are made: (1) the wetting (and fast diffusion) contribution is proportional to the surface composition; (2) the diffusion contribution is proportional to the bulk composition. For the PS/blend(PS/PPO) interface, using eqs 2 and 3, we can then write

$$\sigma(t)_{PS/Blend(PS/PPO)} = \phi_s\sigma^{w}{}_{PS/PS} + (1 - \phi_s)\sigma^{w}{}_{PS/PPO} + \phi_b\alpha_{PS/PS}t^{1/4} + (1 - \phi_b)\alpha_{PS/PPO}t^{1/4} \tag{4}$$

where ϕ_s and ϕ_b are the PS surface and bulk compositions, respectively.

From a thermodynamic point of view, the surface of a miscible polymer blend is expected to be enriched with its low surface energy component[45−50] in order to decrease the overall free energy of the system. According to Jones and Kramer,[49] the surface of a blend can be almost completely covered with the low surface energy polymer even if the difference in the surface tension between the two polymers is about 1 mJ/m^2. For PS/PVME miscible blends (PVME = poly(vinyl methyl ether)), the surface composition (at the level of a few angstroms) was shown to be 94 wt % in PVME in a sample containing 50% of PVME in the bulk, and 65 wt % in a sample containing 25% of PVME in the bulk.[45] For the PS/PPO blend, such data are not available in the literature. Let us calculate the surface tension of PS, PPO, and PVME using the Parachor,[51] which takes into account the atomic and structure contributions of the repeat unit of the polymer to its surface tension. Such a calculation gives 43 mJ/m^2 for PS, 29.6 mJ/m^2 for PPO, and 32 mJ/m for PVME. On that basis, the expected surface enrichment in PPO in PS/PPO blends in the surface layer is about the same as that of PVME in PS/PVME blends. The wetting contribution to the strength at a PS/PS interface can be obtained by extrapolation of the corresponding curve in Figure 9 to zero time, i.e., 0.219 MPa; the slope of the same curve, which characterizes the diffusion process of PS into PS, is 0.0591 MPa/min.$^{1/4}$

Similarly, for the PS/PPO interface, Figure 9 gives $\sigma^w = 0.0773$ MPa. $\alpha_{PS/PPO}$ is 0.00925 MPa/min$^{1/4}$. Using these values, and assuming that (i) $\phi_s = 0.06$ at $\phi_b = 0.5$ and (ii) $\phi_s = 0.35$ at $\phi_b = 0.75$, values of shear strength for PS/blend interfaces can be calculated using eq 4 and are shown in Figure 9 with the dashed lines. They are in a good agreement with the experimental data for the two PS/blend interfaces with different polymer compositions.

Finally, we have verified that the bonding of amorphous polymer/polymer interfaces below T_g, as shown in this paper, is not due to the polydispersity of the polymers used because a similar level of strength develops below T_g when using monodisperse PS samples.[52]

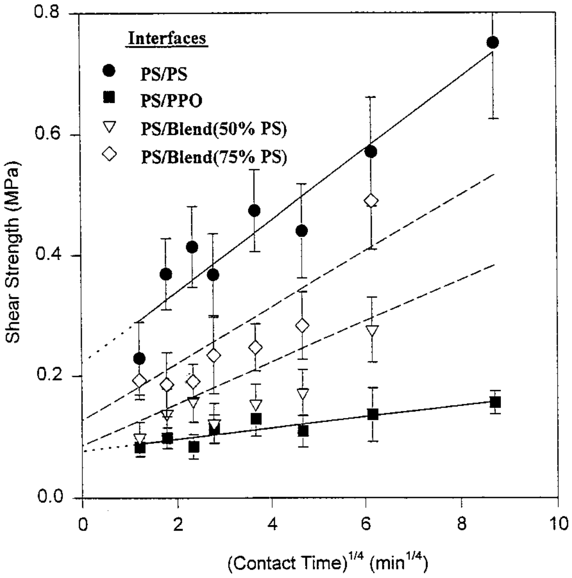

Figure 9. Shear strength of several PS-containing polymer/polymer interfaces as a function of contact time (the error bars correspond to the standard deviation of the mean). The dashed lines were calculated from eq 4 whereas the solid lines correspond to a least-squares analysis.

Conclusions

The following points have been demonstrated in this article. (i) The adhesion at symmetric and asymmetric amorphous polymer/polymer interfaces can occur well below T_g. For example, the adhesion at the interface of two miscible polymers, PS and PPO, occurs at such a low temperature as $T_g - 146$ °C for PPO, corresponding to $T_g - 33$ °C for PS. To the best of our knowledge, this is the first observation of this nature. (ii) The lap-shear strength at amorphous polymer/polymer interfaces bonded below T_g develops with time to the fourth power and, hence, is diffusion controlled. The fact that adhesion at polymer/polymer interfaces occurs at low temperatures relative to T_g indicates that the molecular chains, particularly the chain ends, have more degrees of freedom and a higher mobility than those in the bulk since the entanglement density near the surface is less than in the bulk.[53] Several groups[54-56] have recently shown that there is some molecular mobility at the polymer surface below T_g. In particular, Kajiyama et al.[55] used X-ray photoelectron spectroscopy to measure T_g at the surface of a symmetric poly(styrene-*b*-methyl methacrylate) copolymer and found a decrease of 41 °C and more, as compared to the bulk T_g, at depths up to 7.4 nm. Therefore, diffusion of polymer chains is possible below (bulk) T_g in a layer of the order of the radius of gyration of the PS used (here, 7.8 nm when calculated with $M_n = 81\,000$) but, in fact, in a layer thinner than that because the macromolecular coils are compressed at the film surface in a direction normal to the interface plane.[57]

Acknowledgment. The authors thank the Natural Sciences and Engineering 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.

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MA9610368