Bonding at Symmetric Polymer/Polymer Interfaces below the Glass Transition Temperature

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Introduction. When two compatible polymer surfaces are brought into contact at elevated temperatures, adhesion occurs at the interface and a mechanical load is required to separate the surfaces. A high strength can develop during welding above the glass transition temperature (T_g) of amorphous polymers where the molecular mobility is high. If strength at the interface develops to the fourth power of time (t), the process is diffusion controlled, which has already been shown both theoretically[1−4] and experimentally.[5,6] In contrast, welding below T_g is hindered by the rigidity of the chains and few studies have been reported under these conditions.[7]

Experiments on craze healing[8] in atactic polystyrene have shown the possibility to heal completely the interface at T_g − 28 °C despite its low molecular mobility. In this paper, this possibility will be explored but, for this purpose, we have chosen the lap-shear joint geometry that provides higher load-at-failure values[9] because the expected mechanical properties are low. More specifically, we have selected for this study two polymers: polystyrene (PS) and poly(2,6-dimethyl 1,4-phenylene oxide) (PPO). The welding of PS onto PS above T_g has already been studied[5] but not, to our knowledge, the PPO/PPO interface. The goal of this study is to follow the development of strength as a function of time at symmetric amorphous polymer/polymer interfaces below T_g.

Experimental Section. Atactic PS ($M_w = 230\,000$, $M_w/M_n = 2.84$, and $T_g = 103$ °C) and PPO ($M_w = 44\,000$, $M_w/M_n = 1.91$, and $T_g = 216$ °C) were obtained from Dow Chemical and General Electric, respectively. Polymer films of about 100 μm in thickness were obtained using a twin-screw laboratory extruder (Haakebuchler, Rheocord System 40) with smooth calendaring rolls. The temperature in the die was 225 and 286 °C for PS and PPO, respectively.

The samples were bonded in a lap-shear joint geometry with a contact area of 5 × 5 mm^2, using a Carver laboratory press, and submitted to tensile loading (see, for example, ASTM D3163). These samples were cut from 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. In this paper, the bonding temperature was, in all cases, 62 °C (T_g −41 °C) and 90 °C (T_g − 126 °C) for PS and PPO, respectively, except if indicated otherwise. The temperature of the heating plates was controlled at ± 2.5 deg. For these experiments, 10 samples were placed side by side between two stainless steel plates of 2 mm thickness and preheated for 1 min in the press, which had already been warmed up to the chosen temperature. An 0.8 MPa contact pressure was then applied to the samples. This is within the range of pressures, as shown in ref 10, where the force-displacement curves are pressure independent. To apply pressure to the 10 overlapped areas as uniformly as possible, the thickness of the joint areas, as measured with a micrometer, was kept constant at ±2 μm [in order to do that, the thickness of each film was measured individually and the samples were sorted out such that the thickness of each overlapped area was constant, at ±2 μm]. After bonding for a given time (from 2 min to 4 days), the samples were cooled to room temperature under pressure, by circulating water in the plates of the press.

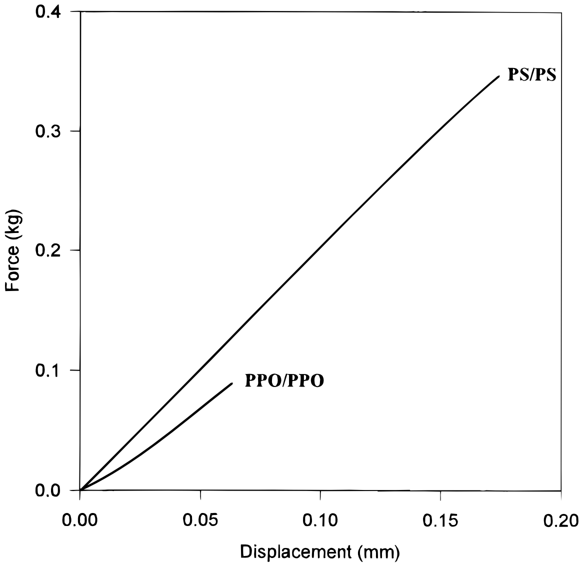

Figure 1. Load-displacement curves for PS/PS and PPO/PPO interfaces bonded for 24 h at T_g − 41 °C and T_g − 126 °C, respectively.

Mechanical testing was conducted not less than 24 h after bonding. Force-displacement curves were recorded on an Instron tensile tester, Model 1130, at room temperature and at a crosshead speed of 0.5 cm/min. From 16 to 25 joints were measured for each experimental data point. Shear strength was calculated as the measured force at break divided by the contact area, neglecting the fact that shear stresses are nonuniform and the highest at the overlap ends.[11] The distance between jaws was 5 cm, with the joint located in the middle. Fractured surfaces were analyzed using a JEOL JSM 840A scanning electron microscope.

Results and Discussion. In Figure 1, force-displacement curves are shown for two lap-shear joints bonded for a period of 24 h. Higher mechanical forces and elongations are observed for PS meaning that there is more interdiffusion than in the case of PPO. In both cases, the curve is linear until fracture. Moreover, the fracture always occurs in the adhesive mode. These observations suggest similar mechanisms responsible for the development of interface resistance below T_g.

The shear strength for PS/PS and PPO/PPO interfaces is plotted in Figure 2 against contact time to the fourth power. The error bars on the experimental data points are fairly large, but this is typical in the mechanical characterization of polymer/polymer interfaces. It is seen that, in both cases, the strength develops linearly with $t^{1/4}$, and therefore, we can conclude that it is

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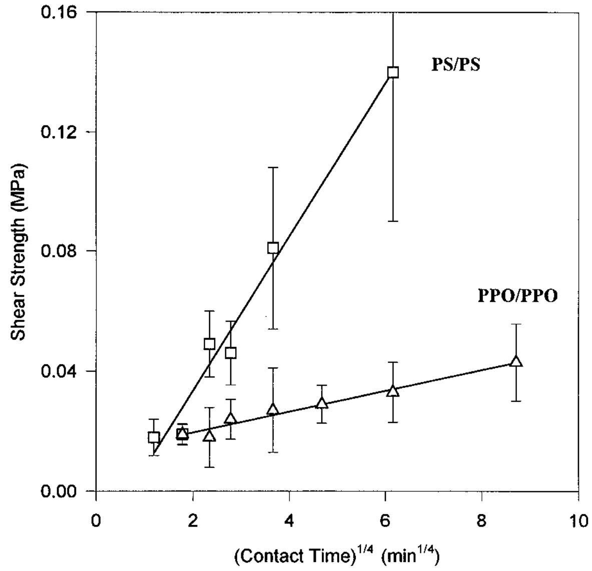

Figure 2. Shear strength as a function of contact time for PS/PS and PPO/PPO interfaces bonded at $T_g - 41$ °C and $T_g - 126$ °C, respectively. The error bars correspond to the standard deviation of the mean. Lines through the data correspond to a least-squares analysis.

diffusion controlled. This means that there is diffusion of segments of the macromolecular chains across the interface below T_g. A limited number of experiments, reported in ref 15, were also carried out with samples prepared by molding between Al foils. When examined by scanning electron microscopy, these films exhibited more surface roughness than those prepared by extrusion, but similar values of strength, indicating that the surface roughness is not the dominant factor in this process. More data, i.e. shear strength versus contact time, will be given in ref 10, at several temperatures. These data show, in general, that strength does not extrapolate to zero at time zero, which is attributed to the preheating period that is necessary to reach the desired temperature, before applying pressure, as described in the Experimental Section. It can also be due to the establishment of van der Waals forces, i.e. wetting, at very short times.

The strength at the PS/PS interface increases more rapidly than that of the PPO/PPO interface since the surfaces were bonded at a much higher temperature relative to T_g. However, T_g −41 °C for PS is one of the lowest possible temperatures for wetting and healing (T_g −46 °C is mentioned in ref 8). In other words, the contact of two PS surfaces at T_g −126 °C, or even T_g −60 °C, leads to no strength development, contrary to the case with PPO. The values of strength measured for both interfaces are low. For example, the strength developed here at the PS/PS interface at T_g −41 °C for 24 h is about 2% of that obtained for a PS/PS interface welded above T_g in the same lap-shear joint geometry (this PS has similar molecular characteristics,[5] i.e., M_w = 262 000, M_n = 142 000). It is even lower for PPO, but to our knowledge, no polymer besides PPO has demonstrated an ability for self-bonding at such a low temperature as T_g −126 °C. The strength measured is due to interdiffusion (and, possibly, wetting) only, and not to friction. Forces of friction between two surfaces do not contribute significantly here since loading two polymer surfaces in contact (for example, the lap-shear coupon after fracture or the lap-shear coupon without interdiffusion) gives a “zero” force.

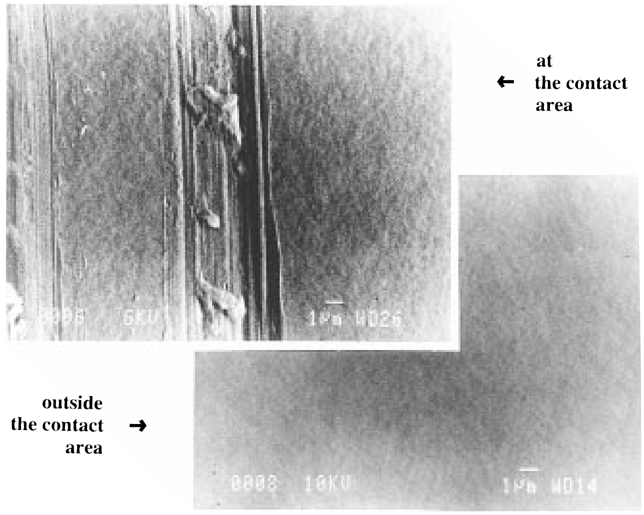

Figure 3. Scanning electron micrographs of the PPO surface after bonding 24 h at $T_g - 126$ °C: (bottom) outside the contact zone; (top) after fracture of the PPO/PPO interface at the contact area. The magnification is 5000. Directions of extrusion and loading are horizontal. (Figure reproduced at 37% for publication.)

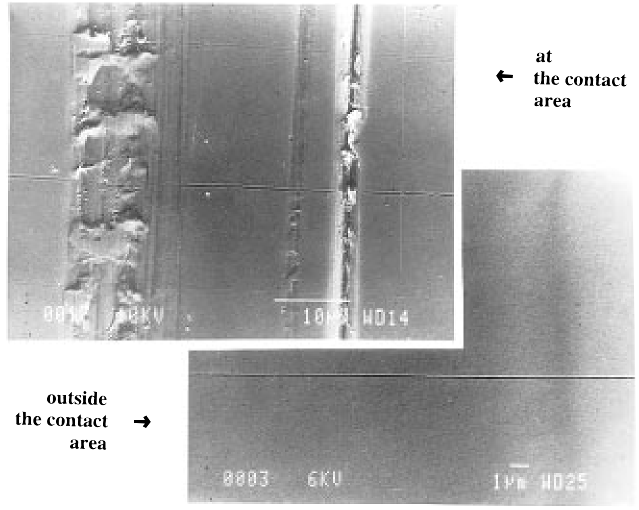

Figure 4. Scanning electron micrographs of the PS surface after bonding 24 h at $T_g - 41$ °C: (bottom) outside the contact zone (a trace of the die is seen on the surface); the magnification is 5000; (top) after fracture of the PS/PS interface at the contact area; the magnification is 2000. Directions of extrusion and loading are horizontal. (Figure reproduced at 37% for publication.)

Scanning electron microscopy was used to observe the surface morphology of PS and PPO after fracture of the bonded joints. Figures 3 and 4 compare the surfaces outside and inside the contact areas for interfaces healed 24 h and fractured in the Instron tester. It is seen that the noncontacted areas (Figures 3 and 4, bottom) are smooth whereas the fractured surfaces show a specific morphology (Figures 3 and 4, top). This morphology (and rugosity) indicates that there is some molecular mobility at the PS/PS and PPO/PPO interfaces below T_g and is, to the best of our knowledge, the first experimental observation of this kind at such low temperatures (at $T_g - 126$ °C for PPO). A fraction only of the contact area exhibits this roughness, which proves the occurrence of interdiffusion in those zones, but it does not necessarily indicate that interdiffusion is limited to those zones because bonding is mechanically detected for surfaces treated at lower temperatures and shorter times without the observation of any roughness in the photomicrographs. It is then presumed that interdiffusion takes place at both the smooth and relief surfaces analyzed.

It has recently been proposed that the polymer surface layer is more mobile than the chains in the bulk since very significant decreases of T_g have been observed in that layer.[12, 13] Atomic force microscopy investigations also suggest that the PS surface is closer to the rubbery state than to the glassy state at room temperature.[14] These studies indicate that the conformational structure and molecular mobility at the polymer surfaces differ from those in the bulk: molecules and especially chain ends are less entangled and more mobile. Therefore, there is the possibility for chain ends to penetrate the opposite side of the interface in the surface layer, leading to an interdiffusion at the surfaces of glassy polymers below T_g, as observed in this paper. This phenomenon of bonding between amorphous polymer surfaces cannot be assigned to the polydispersity of the polymers since we observe similar values of strength, developed below T_g, at the symmetric interfaces of polydisperse and monodisperse PS having similar M_w values.[15]

Conclusions. The possibility of self-bonding, below T_g, two amorphous polymers such as PS and PPO has been demonstrated, even at such a low temperature as $T_g - 126$ °C for PPO. The strength at the interface, after contact below T_g, develops with $t^{1/4}$, like most polymers do above T_g, indicating that the process is diffusion controlled. Surface rearrangement at the amorphous polymer/polymer interfaces indicates that there is some molecular mobility below T_g.

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