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The adhesion of amorphous polystyrene surfaces below T_g

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Abstract

The bonding of polystyrene (PS) surfaces below T_g was investigated by two different fracture tests: the lap-shear joint method and the cantilever beam method. Adhesion energy values obtained by the two methods are in agreement and develop with $(\text{time})^{1/2}$, at temperatures as low as $T_g - 16$ °C. Even if the double cantilever method is the most common test found in the literature for adhesions above T_g, for low adhesion values, below T_g, the lap-shear joint geometry is more appropriate. Moreover, when the glass transition temperature is used as a reference temperature, polydisperse and monodisperse PS adhesion energy curves are superposable, suggesting that the auto-adhesion is not significantly favored by the presence of numerous chain ends at the surface (due to the low molecular weight chains provided by the polydisperse PS).

Keywords: Polystyrene; Adhesion; Transition temperature

1. Introduction

The dynamics of a high molecular weight polymeric chain above T_g is well described by the reptation model [1–5]. de Gennes [6,7], Wool and O'Connor [8], and Adolf et al. [9] have shown that this model also explains the time dependence of the adhesion between two surfaces made of amorphous compatible polymers in their viscoelastic state since it describes satisfactorily the experimental results obtained by Jud and Kausch [10] who observed that, at constant temperature and pressure, the energy of adhesion, G_c, evolves as a function of the contact time, t, to the half-power:

$$G_c \propto G_0 + (bt)^{0.5} \tag{1}$$

where G_0 is the energy of adhesion at time $t = 0$, and b is a constant which depends on temperature [11]. Moreover, it has been observed that the temperature dependence of b, above T_g, can be described by an Arrhenius law [10,12], with an activation energy E_a similar to that obtained for the α transition, indicating, in a different way, that adhesion above T_g is diffusion-controlled:

$$b \propto D(T) = D_0 e^{(-E_a/RT)} \tag{2}$$

where $D(T)$ is the diffusion coefficient, T the welding temperature, and R the gas constant.

Boiko and Prud'homme [13–15] have investigated the adhesion between two amorphous polymeric surfaces below T_g, where the chain diffusion is, a priori, prohibited. Under these conditions, in a lap-shear joint geometry, they have shown that the adhesion between the polymers at the interface is a function of the contact time, and that the strength at the interface develops with $t^{1/4}$ and, thus, is diffusion-controlled. However, the most frequently used geometry for adhesion strength measurements above T_g is the double cantilever beam (DCB) method, because it gives directly the energy of adhesion while, in the lap-shear test, although it has been successfully used to study the adhesion between two polystyrene (PS) films above and below T_g [16], the energy of adhesion, calculated from strength results, could be highly distorted if different fracture modes were involved during the test.

To validate the lap-shear experiments done before [13–15], the bonding of polystyrene surfaces below T_g has been carried out using two different fracture tests: the lap-shear joint method, as before, and the DCB test. These

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two techniques will be compared in experiments made between 80 and 100 °C, with a polydisperse PS but, also, with a monodisperse PS, at 90 and 100 °C. Making the assumption that the lap-shear test involves only one fracture mode, the two methods lead to very similar conclusions. In addition, using the temperature dependence of the energy of adhesion of monodisperse and polydisperse PS, activation energies will be calculated and compared with those obtained above T_g.

2. Experimental methods

2.1. Materials

Polydisperse atactic polystyrene ($M_w = 225,000$, $M_w/M_n = 1.5$, and $T_g = 96$ °C) was obtained from Dow Chemicals, while monodisperse atactic polystyrene ($M_w = 200,000$, $M_w/M_n < 1.06$, and $T_g = 105$ °C) was purchased from Pressure Chemicals.

2.2. Fracture toughness

Blocks of polydisperse PS were obtained by extrusion. The thick blocks were sawed and polished to give sheets of dimensions 60 mm × 13 mm, with a 3 mm thickness. These sheets were then heated and pressed at $T_g + 10$ °C for 1 h to remove all stresses induced by the former manipulations. Monodisperse samples were prepared by coating, at $T_g + 20$ °C, during 20 min, a 100 μm thick film on a polydisperse block. The film thickness and the coating conditions were such that no polydisperse material can be found on the monodisperse side.

Mechanical tests were performed at room temperature by inserting a wedge, i.e. a single-edge razor blade, at the interface between films in contact, and pushing it in at a constant velocity of 100 μm/min (it has been shown by Schnell et al. [17] and by Creton et al. [18] that, between 60 and 9000 μm/min, the velocity of the razor blade does not influence the adhesion energy), using an appropriate set-up on an Instron tensile testing machine (model 5565), as shown in Fig. 1. In this figure, the camera is shown to be normal to the surface of contact of the two samples. This configuration permits to follow easily the propagation of the fracture, because there is a change of refractive index induced by the presence of air between the two polymer blocks where the fracture occurs.

The length of the crack ahead of the blade was measured by taking photographs with a 3-CCD camera (Hitachi HV-D27) at regular intervals; the ImagePro Plus software was used for data analysis. The first data points were disregarded until the crack propagation was stabilized. By this procedure, at least 30 values of fracture energy could be obtained for each specimen, and means and variances could be calculated for each sample.

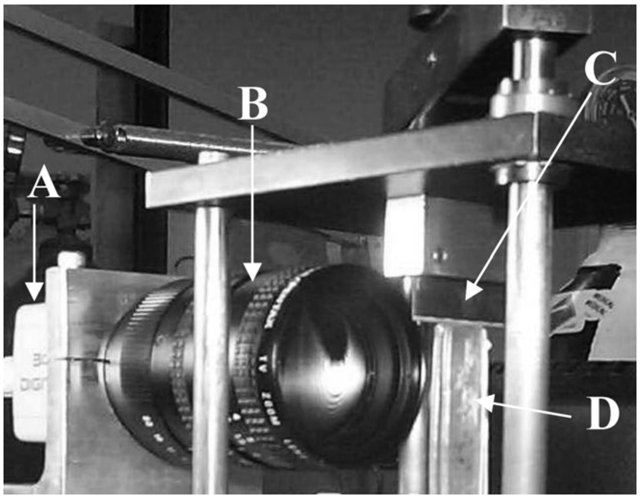

Fig. 1. Experimental set-up for the double cantilever beam test. (A) 3-CCD camera; (B) magnifying system; (C) razor blade used to cleave the sample (D).

The chosen test geometry was a symmetric double cantilever beam (DCB) (Fig. 2(a)). The elastic modulus of polydisperse PS was always used in the calculation of the adhesion energy since polydisperse PS was in all cases the substrate for monodisperse PS. It was calculated in a three-point bending test under the same conditions as in the DCB test. Under these conditions, the elastic modulus of PS is 3.7 GPa.

The critical energy release rate, G_c, or fracture toughness, of the interfacial crack was obtained from the model derived by Kanninen [19] in which the beam is supported by an elastic foundation ahead of the crack tip.

$$G_c = \frac{3\Delta^2 E h^3}{16 a^4 \alpha^2} \tag{3}$$

with

$$\alpha = \frac{\left[1 + \frac{1.92h}{a} + 1.22\left(\frac{h}{a}\right)^2 + 0.39\left(\frac{h}{a}\right)^3\right]}{\left(1 + \frac{0.64h}{a}\right)} \tag{4}$$

where E is the elastic modulus, a the crack length, h the thickness of the sample, and Δ the thickness of the razor blade. A study of the adhesion energy as a function of contact pressure has shown that from 0.8 to 5 MPa, the pressure has no influence on the results. To insure a good contact between the two surfaces, which are very large in the DCB test (60 mm × 13 mm), a pressure of 1.5 MPa was applied on the samples.

2.3. Lap-shear test

Films of monodisperse and polydisperse PS were prepared by casting a 4% chloroform solution on a glass plate. Films were air-dried at room temperature for 2 days, gradually heated under vacuum up to $T_g + 20$ °C, maintained at that temperature for at least 48 h to remove the last

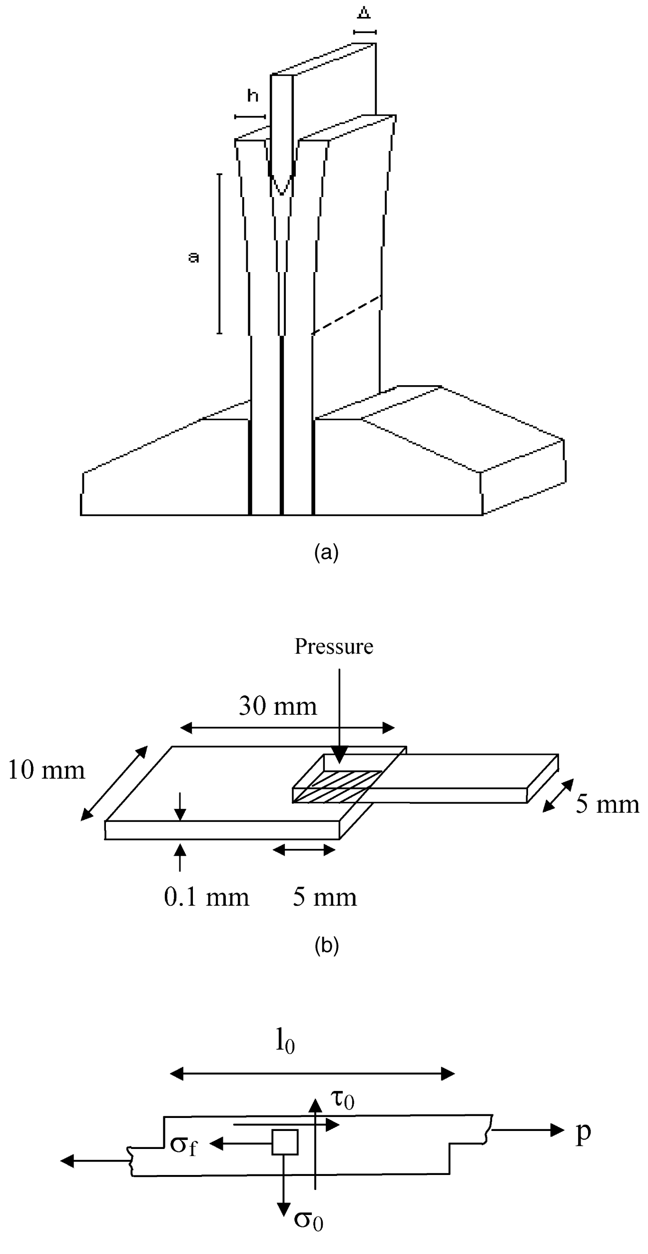

Fig. 2. (a) Geometry of the DCB method and parameters used in the calculation of the adhesion energy; (b) geometry of the lap-shear joint test; (c) stress distribution along the shear plane (see the text for details).

traces of solvent and residual stresses, and quenched to room temperature. All the films were about 100 μm thick. The solvent cast films had a flat surface (their root mean square roughness, R_q, calculated using an AFM Nanoscope III Multimode of Digital Instruments, being typically equal to 0.7 nm), and the variation of the thickness of these films, in the contact area, was less than 1 μm.

The samples were bonded in a lap-shear joint geometry under a slight pressure of 0.03 MPa for the chosen time of healing, then the pressure was removed, and the samples were submitted to tension (ASTM D3163). The bonded joints were fractured on an Instron tensile machine (Model 5565) at room temperature. The contact area was 5 mm × 5 mm (Fig. 2(b)). The distance between the jaws was 3 cm, with the joint located in the middle (no change could be observed if the location of the joint between the two jaws was slightly shifted upward). At least 20 samples were measured for each experimental data point. Shear strength was calculated by dividing the measured force at break by the contact area.

Monodisperse PS films healed at 90 °C for 8 h were stretched at rates of 0.1 and 5 mm/min and since the adhesion energies obtained in both cases were in good agreement, a crosshead speed of 5 mm/min has been used afterwards. Kline and Wool [16] have reached a similar conclusion by finding that, in the lap-shear test, the adhesion energy does not depend on the crosshead speed in a range between 0.13 and 12.5 mm/min.

3. Results and discussion

3.1. Lap-shear test

The stress distribution along a lap-shear joint (submitted to tension) was approximated by Goland and Reissner [20] considering the case where the thickness of the adherent is so small that it can be ignored. In the following paragraphs, we will describe their main observations and apply their development to the test configuration used in the present study.

Goland and Reissner [20] have shown that three stresses, σ_f, σ_0 and τ_0 are acting on the contact area shown on Fig. 2(c): the normal stress, σ_0, acting in a direction perpendicular to the plane of the joint, reaches its maximum value at the joint edges, and drops to values close to zero within a distance along the shear plane of about $2d$, where d is the thickness of the film. The shear stress, τ_0, has a zero value at the joint edges, increases to a peak value, and quickly decreases to zero within the same distance than σ_0. The longitudinal tensile stress, σ_f, behaves like the normal stress but reaches a constant value, which is equal to half the value of the tensile stress, p, applied on the film 'in the unjointed sheet' as defined by Goland and Reissner [20].

Considering that $l_0/(2d) = 25$, where l_0 is the initial contact length, it can be easily shown [20] that σ_0 and τ_0 are negligible, and that σ_f is close to $0.55p$, such that the shear strength, σ, can be written:

$$\sigma = \sigma_\mathrm{f} d/l_0 = 0.55pd/l_0 \qquad (5)$$

The modulus E_s, representing the shear at the interface between the two samples, is related to the Young modulus, E, and d as follows:

$$E_\mathrm{s} = \sigma/\varepsilon = 0.55pd/(l_0\varepsilon) = 0.55(Ed)/l_0 \qquad (6)$$

where ε is the strain in percent, which is assumed to be the same in the overlap region and in the rest of the film. This assumption was verified by comparing the Young modulus deduced from the force–displacement curves shown in Fig. 3 with the Young modulus obtained by a three-point bending test. It has to be noticed that E_s does not correspond to the shear modulus of bulk polystyrene. Actually, calculation of E_s and E gives, respectively, 42 MPa and 3.8 GPa; since the latter value is close to the modulus obtained with the three-point bending test (3.7 GPa), we can conclude that ε is effectively uniform in the film. Consequently, it can be written:

$$\varepsilon = (L - L_0)/L_0 = (l - l_0)/l_0 \tag{7}$$

where L_0 is the initial length of the sample, L, the length under stress, and l, the overlap length under stress.

In Fig. 3, force–displacement curves are shown for lap-shear experiments made with monodisperse PS bonded at 90 °C for 1, 12, 19 and 48 h. It can be observed that the four curves are superposable but that the force of adhesion increases with time of healing. In other words, whatever the force of adhesion between the two films, the slopes are similar and give a value of 42 MPa close to the value of E_s, calculated in the previous paragraph. The linear part of the force-elongation curve corresponds to the stretching of the whole sample, while its first part (which is disregarded) corresponds to the removal of slack.

Since the force–displacement curves shown in Fig. 3 give the strain of the whole sample $(L - L_0)$ and not that in the overlap region $(l - l_0)$, the adhesion energy, G_c, can be calculated from the lap-shear test as follows:

$$G_c = [F_c(l - l_0)]/(2A) \tag{8}$$

where F_c is the load at break and A, the overlap area. This leads to:

$$G_c = [F_c(L - L_0)]/(2A)(l_0/L_0) \tag{9}$$

and this adhesion energy can be compared with that obtained with the double cantilever beam test.

3.2. Comparison between lap-shear and double cantilever beam tests

Adhesion between two polymer surfaces above T_g is due to the diffusion of macromolecular chains through the interface. Using the reptation model [1], different groups have found theoretically [6,9] and experimentally [10,16, 21–24] that the adhesion energy of such a welding is a function of the square-root of contact time (Eqs. (1) and (2)).

Values of adhesion energy of polydisperse PS are plotted in Fig. 4 against $t^{1/2}$, for weldings carried out at 80 °C by two different methods. In the two cases, the adhesion energy increases linearly as a function of $t^{1/2}$. The DCB test gives slightly weaker values but, in general terms, the two series of adhesion energy are in agreement. The weaker adhesion results obtained by the DCB test are due to the large difference of contact areas between the two methods: in the DCB test the contact area is about 30 times larger than that in the lap-shear test; consequently, the contact between the two surfaces is less uniform, which leads to a slight decrease in the adhesion values.

In Fig. 5, adhesion energies of polydisperse PS, obtained with the DCB method, are drawn as a function of $t^{1/2}$, at 80, 90 and 100 °C. As comparatively to the adhesion energy of a

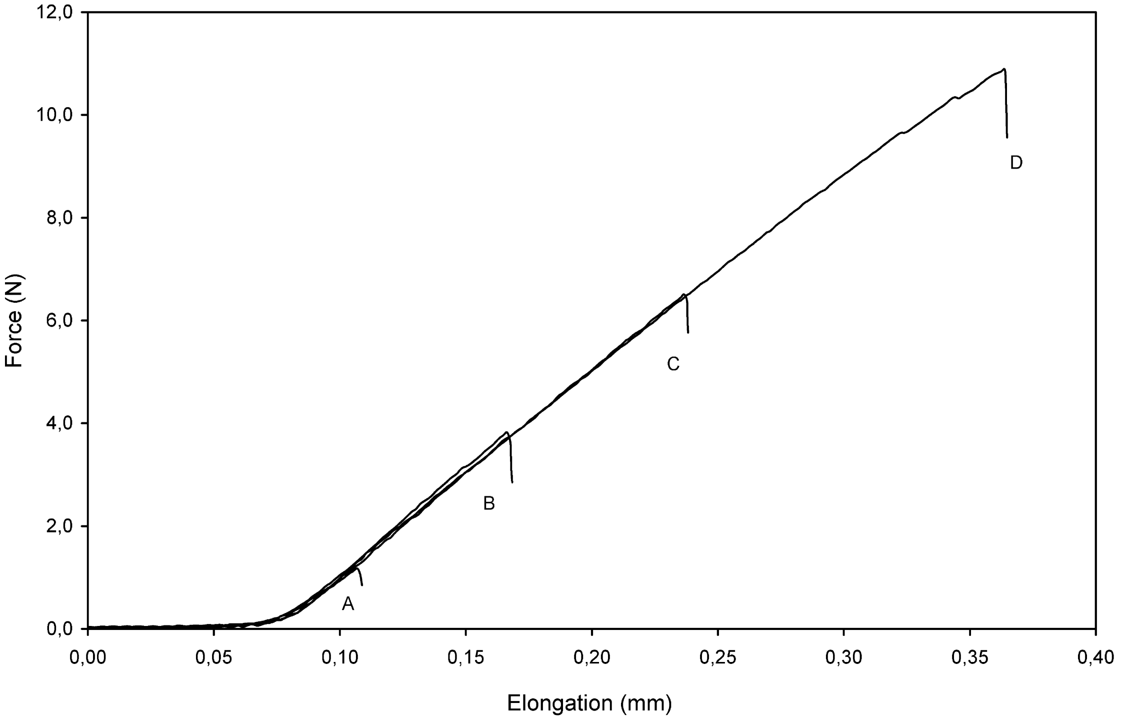

Fig. 3. Stress–strain curves of monodisperse PS/PS interfaces healed at 90 °C. (A) 1 h; (B) 12 h; (C) 19 h and (D) 48 h.

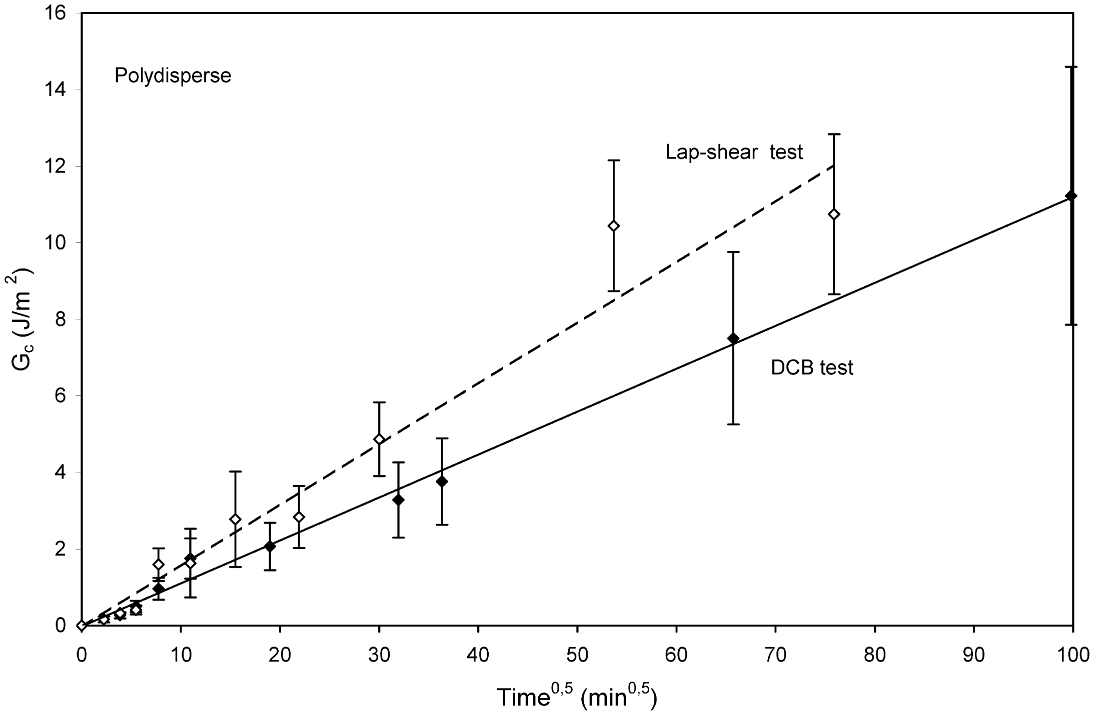

Fig. 4. Adhesion energy as a function of $t^{1/2}$ for polydisperse PS/PS interfaces welded at 80 °C ($T_g - 16$ °C): DCB method (◆); lap-shear joint method (◇).

fully healed interface, which is close to 1000 J/m^2, it can be seen that, even slightly above T_g (at 100 °C), the adhesion obtained after 68 h of contact is low, since it is around 60 J/m^2, i.e., 6% of the fully healed adhesion energy. However, adhesion energy observed still develops clearly linearly with $t^{1/2}$, whatever the healing temperature. Therefore, the temperature, chosen above or below the glass transition, does not influence the time dependence of the adhesion since 80 °C is below the T_g range whereas 100 °C is located at the end of the glass transition range (the T_g of the polydisperse PS is 96 °C). However, it can be argued that the presence of short polymer chains at the surface of the

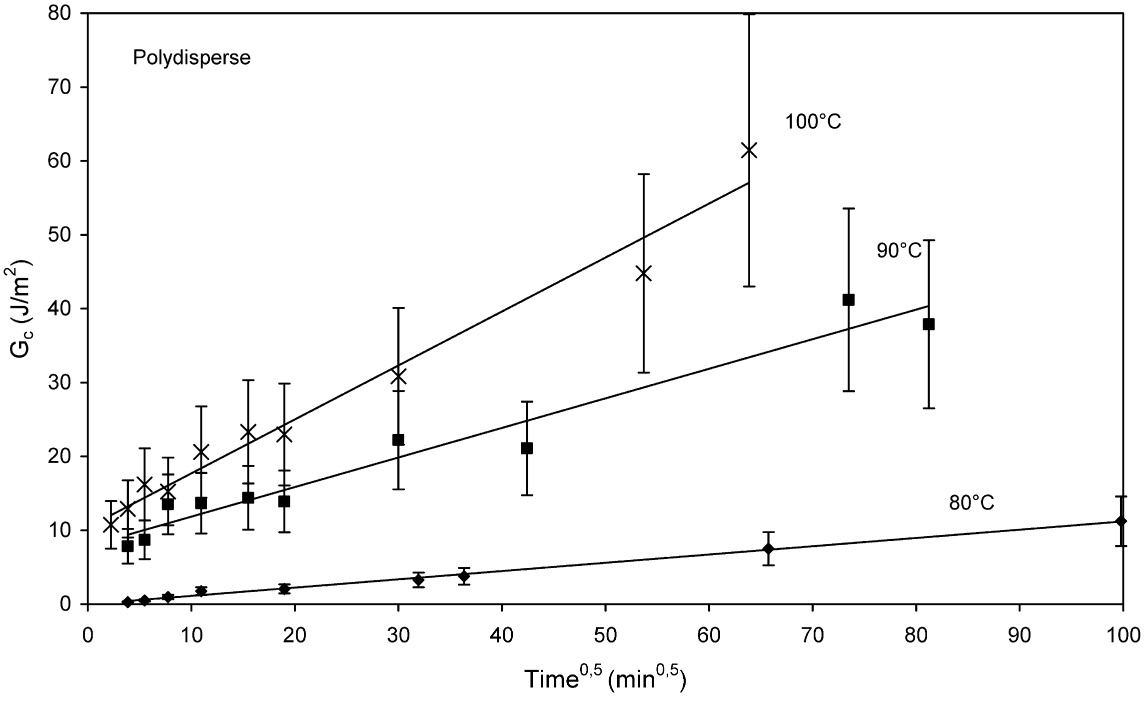

Fig. 5. Adhesion energy obtained by the DCB method as a function of $t^{1/2}$ for polydisperse PS/PS interfaces welded at 80 ($T_g - 16$ °C) (◆), 90 ($T_g - 6$ °C) (■), and 100 °C ($T_g + 4$ °C) (×).

polydisperse sample could enhance the adhesion strength between the two surfaces by diminishing the glass transition temperature at the surface.

In Fig. 6, the adhesion energy obtained with the DCB test, at temperatures of $T_g - 6$ and $T_g - 16$ °C, is plotted as a function of $t^{1/2}$ for monodisperse and polydisperse PS. At each relative temperature, whatever the PS polydispersity, the adhesion energy increases linearly with $t^{1/2}$, as observed in Figs. 4 and 5. The adhesion energy also increases with the welding temperature. Moreover, adhesion energy of polydisperse and monodisperse PS obtained at the same reference temperature, i.e., $T_g - 6$ and $T_g - 16$ °C, are in good agreement, despite the presence of short chains in the polydisperse PS.

This result suggests that short chains have no significant influence upon the adhesion strength of PS below T_g, although the short chains tend to increase the concentration of chain ends at the surface [11]. A simple approximation of the chain end concentration in the polydisperse PS can be done by evaluating, first, the molecular weight of a monodisperse PS having the same T_g as the polydisperse polystyrene used, considering the empirical relation between T_g and the polymer chain molecular weight found by Fox et al. [25,26]:

$$T_g(M_n) = T_{g\infty} - K/M_n \tag{10}$$

where T_g (M_n) is the T_g of a monodisperse PS having a number-average molecular weight, M_n, $T_{g\infty} = 106$ °C, the T_g of an infinite molecular weight PS, and $K = 120$ °C kg/mol, a constant [26]. In this case, it can be found that the 200 kg/mol polydisperse PS used in this study is equivalent to a 12 kg/mol monodisperse PS. The chain end concentration $\phi = 2/N$—where N is the statistical length segment—is, therefore, $\phi = 1.0 \times 10^{-3}$ for the 200 kg/mol monodisperse PS and 17×10^{-3} for the 12 kg/mol equivalent monodisperse PS which means that the concentration of chain ends is approximately 17 times higher in the polydisperse than in the monodisperse PS.

In Fig. 7, the adhesion energy obtained with the lap-shear and DCB tests is plotted as a function of $t^{1/2}$ for a monodisperse PS healed at 90 and 100 °C. Due to the large difference between the adhesion energy values obtained at these two temperatures, two different ordinate scales are used. For the monodisperse PS/PS interface healed at 100 °C, the two methods give close values. However, at 90 °C, the adhesion energies obtained by cleavage fall below the lap-shear values although the difference is small. As discussed above, this difference is probably due to the difficulty of having an intimate contact between the two polymer blocks when they are welded below T_g, particularly in the DCB test. However, at 100 °C, i.e. above the T_g of the polydisperse PS, the blocks of polydisperse PS are smoother and the contact between the two monodisperse films is probably of higher quality, leading to a better agreement between the two methods than at 90 °C.

Moreover, the square-root time dependence of the adhesion energy shown in Fig. 7 confirms that, even below T_g and for a monodisperse PS/PS interface, a reptation-like process can happen. Therefore, using Eqs. (1) and (2), and the slope of the curves at 90 and 100 °C for the two mechanical tests, the average activation energy, E_a, for the welding of the monodisperse films, below T_g, can be

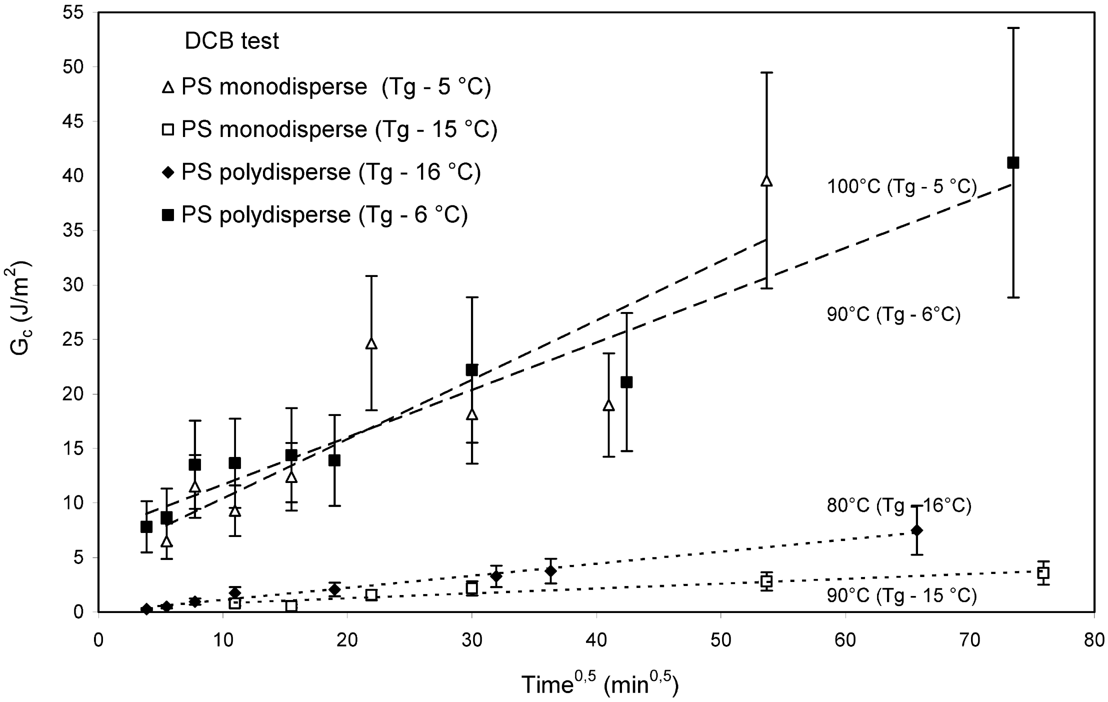

Fig. 6. Adhesion energy obtained by the DCB method as a function of $t^{1/2}$, for monodisperse PS/PS interfaces welded at 90 ($T_g - 15$ °C) (□) and 100 °C ($T_g - 5$ °C) (△), and for polydisperse interfaces welded at 80 ($T_g - 16$ °C) (◆) and 90 °C ($T_g - 6$ °C) (■).

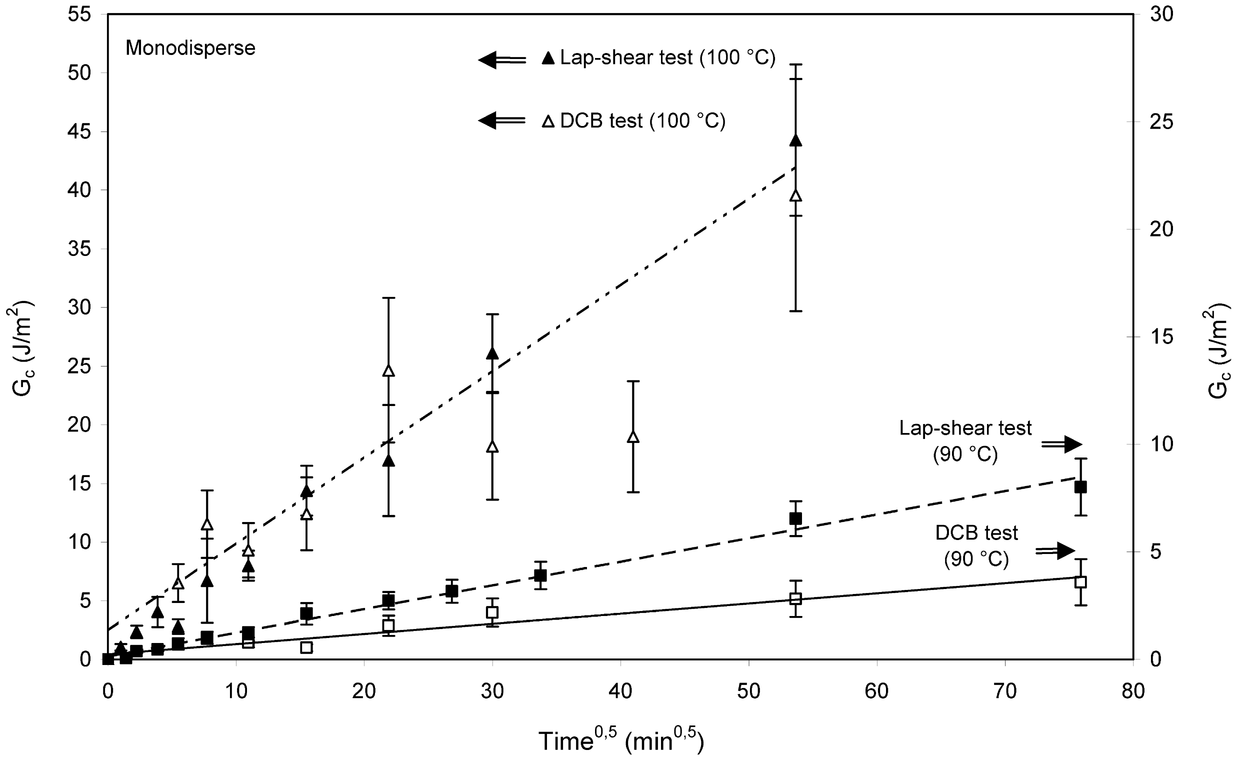

Fig. 7. Adhesion energy as a function of $t^{1/2}$ for monodisperse PS/PS interfaces welded at 90 °C ($T_g - 15$ °C) and 100 °C: DCB method (□ and △); lap-shear method (■ and ▲). Please note that two different ordinate scales are used to draw the series of data obtained at 100 °C (left scale) and 90 °C (right scale).

calculated. This gives $E_a = 520 \pm 130$ kJ/mol, which is a value as large as that obtained above T_g [16,27] for high molecular weight PS. From Fig. 5, an activation energy can also be calculated for the polydisperse PS films, which value is 210 ± 70 kJ/mol.

Adhesion below T_g has been explained in the past by the existence of the surface glass transition [13,15], i.e. by a higher mobility of the chains at the surface of the film. Assuming that there is a surface glass transition temperature, Kajiyama et al. [28] have suggested an activation energy of 230 kJ/mol for the diffusion of monodisperse PS chains located at the surface of the film, which is much lower than the value of 440 kJ/mol found for the bulk material. The value for monodisperse PS (520 kJ/mol) found above is in the range proposed by Kajiyama et al. [28] for the bulk material but it is obviously too high to be associated to an increase of the chain mobility at the surface of the film. We also believe that the lower activation energy obtained for the polydisperse PS (210 kJ/mol) cannot be explained by the enhancement of the mobility of the polymer chains at the surface since this explanation should hold for both the monodisperse and polydisperse PS. Actually, the low value of the activation energy of the polydisperse PS in comparison with that obtained for the monodisperse PS can be explained by the presence of numerous chain ends in the polydisperse sample, which diminish its glass transition temperature (96 °C instead of 105 °C) and should increase its overall mobility.

Finally, if there is a surface T_g lower than the bulk T_g, when the two films are placed in contact, the diffusion observed 'below T_g' should rapidly (relative to the time frame of days used for the experiments) slow down, and stop, because the two surfaces are not any more in contact with air since they become in contact with a mass of PS chains [29]. However, in this article, we have seen that the adhesion energy still increases after 4 days of contact, which constitutes another argument against the presence of a surface T_g, as we will more fully develop in upcoming papers [29,30].

4. Conclusions

We have studied, by two different methods, the adhesion between two PS surfaces below T_g. It has been shown that the lap-shear and DCB tests give similar results. However, the DCB test led to less accurate results due to the large contact area needed to make the experiment, and to the difficulty of applying a uniform contact between the two blocks. Nonetheless, the two methods are in agreement and have shown that the motion of the polymer chains below T_g is a reptation-like process. Using the glass transition temperature as a reference temperature, it has been observed that the adhesion energies obtained are not influenced by the polydispersity of the polymer. Moreover, from the activation energy values obtained for polydisperse and monodisperse samples, there is no need to invoke a higher mobility of the polymer chains at the surface as compared to the bulk to explain the results.

Acknowledgements

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