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Healing of interfaces of amorphous and semi-crystalline poly(ethylene terephthalate) in the vicinity of the glass transition temperature

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Abstract

Healing of interfaces of amorphous and semi-crystalline poly(ethylene terephthalate) (PET) was carried out above and below the (bulk) glass transition temperature (T_g) of the samples (two amorphous and two semi-crystalline polymers of different molecular weights). The lap-shear strength of the amorphous/amorphous interface was found to develop without discontinuity in the vicinity of the T_g and, in addition, it develops at amorphous/amorphous and amorphous/crystalline interfaces to the one-fourth power of healing time indicating that it is, in both cases, a diffusion controlled process. Similar values of strength were found with these two interfaces whereas the strength at the crystalline/crystalline interface of PET was at least one order of magnitude lower after healing under the same conditions. However, the largest values of strength were obtained by a procedure where diffusion is followed by crystallisation.

These results were compared with those measured for an amorphous and incompatible PS/PET interface, below and above the T_gs of PS and PET, and it was found that the strength of the incompatible PS/PET interface is close to the strength of the compatible PET/PET interface. A comparison of the strength developed at symmetric amorphous interfaces of crystallisable PET and non-crystallisable atactic PS showed a more rapid growth in strength in the second case, even at temperatures below T_g.

Keywords: Interfaces; Healing; Strength

1. Introduction

Several recent experimental observations [1–9] as well as theoretical considerations [10–12] indicate that significant molecular motions exist at the polymer surfaces below T_g meaning that the surface is more mobile than expected in the glassy state. For example, in previous papers [5–7], adhesion at symmetric and asymmetric interfaces made of polydisperse polymers was mechanically detected at healing temperatures below T_g. In particular, partial healing of the polystyrene/poly(phenylene oxide) (PS/PPO) interface, which is a miscible polymer pair, has been shown to occur at temperatures as low as $T_g - 146$°C for PPO corresponding to $T_g - 33$°C for PS [6]. This behaviour is not due to the surface segregation of the low-molecular fraction of the samples since a similar level of strength was also observed at $T_g - 13$°C for monodisperse and polydisperse PS/PS interfaces [7]. Moreover, the interpenetration of segments was confirmed by the observation of extensive plastic deformation of the fractured interfaces previously healed below T_g [13,14]. It is finally important to note that, below T_g, strength was found to develop with contact time to the one-fourth power ($t^{1/4}$) in accordance with diffusion models [15,16] (as it does above T_g).

Atactic PS and PPO are amorphous polymers. If, instead, semi-crystalline polymers are considered, there is a possibility not only to achieve diffusion and adhesion but also to lock the chains diffused across the interface in the crystallites. It is the general goal of this study to investigate this possibility. For this purpose, poly(ethylene terephthalate) (PET) was chosen since PET is a crystallisable polymer but it can also be prepared in the amorphous state. More specifically, healing of three compatible interfaces of PET, i.e. amorphous/amorphous, amorphous/crystalline and crystalline/crystalline interfaces have been considered in this study. For comparison, the bonding process between immiscible polymer surfaces of PET and PS has also been investigated, at relatively low temperatures. In the literature, several immiscible polymer pairs have been studied at high temperatures, above T_g [17–19], but neither, to our

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knowledge, below T_g nor the PS/PET interface. In this paper, the development of strength was followed with time for experiments done in the lap-shear joint geometry.

2. Theory

The driving force for the interfacial mixing of two immiscible polymers is the increase in entropy of the chains located near the interface when crossing the interface. Thus, bonding occurs at such interfaces despite unfavourable repulsions between the immiscible chain segments of different chemical structures. However, this interdiffusion is limited and it stops when an equilibrium interpenetration depth d_∞ is attained. For polymers with infinite molecular weight, this depth may be calculated as [20,21]:

$$d_\infty = 2b/(6\chi)^{1/2} \tag{1}$$

where b is the statistical segment length and χ the Flory–Huggins interaction parameter.

According to the approach proposed by Foster and Wool [17], the interpenetration depth can also be related to an average repeat unit interpenetration distance $X(t)$ in the case of an incompletely healed symmetric (compatible) interface. The strength of this symmetric interface is given as [19]:

$$s(t) = s_0(t/T_r)^{1/4} \tag{2}$$

where $s(t)$ is the strength at time t and s_0 the maximum strength (for a fully healed interface) achieved at the reptation time T_r.

According to de Gennes [22], the average repeat unit interpenetration distance at a symmetric interface $X(t)$ is given by:

$$X(t) = X_0(t/T_r)^{1/4} \tag{3}$$

where X_0 is the interpenetration distance achieved at the reptation time T_r, which can be expressed via the radius of gyration R_g as [23]:

$$X_0 = 0.81R_g \tag{4}$$

And, according to the reptation theory [15], the strength at the interface is a function of the penetration depth, i.e. $s(t) \sim X(t)$.

Let us now consider equilibrium situations at compatible and incompatible interfaces. According to Wool [17], s_0 and X_0 of the compatible interface can be related to the equivalent parameters s_i and d_∞ of the incompatible interface (those values are necessarily smaller than s_0 and X_0, respectively), such that, for the equilibrium state, we can write:

$$s_i/s_0 = d_\infty/X_0 \tag{5}$$

Substituting X_0 by R_g using Eq. (4), and taking into account that the full interface depth is given by $2X_0$, d_∞ is finally expressed as

$$d_\infty = 1.62R_g(s_i/s_0) \tag{6}$$

Relation (6) will be used to calculate d_∞ in the following sections.

3. Experimental section

3.1. Polymers

Pellets of PET (viscosity-average molecular weight, M_0, of 30 000) and of atactic PS ($M_w = 2\,30\,000$, $M_w/M_n = 2.84$) were obtained from Khimvolokno (Mogilev, Belarus') and Dow Chemicals (Midland, MI), respectively.

3.2. Preparation of samples

Amorphous films of PET with a thickness of 100 μm were obtained by melting the pellets at 280°C between thin Teflon sheets in air, followed by rapid quenching in ice-water. This step is accompanied by a decrease in M_0 to 15 000, probably due to the hydrolysis induced by the air humidity. Some samples of this amorphous PET were submitted to cold crystallisation at 180°C for 10 min to obtain semi-crystalline samples with a DSC crystallinity index of 0.27. Some of the initial amorphous films were submitted to solid-state polymerisation in high vacuum at 245°C for 20 h [24] in order to obtain a higher molecular weight polymer ($M_0 = 3\,00\,000$) with a crystallinity index of 0.4. This polymer was then melted at 285°C and quenched in ice-water to obtain a high molecular weight ($M_0 = 76\,000$) amorphous polymer. PS films ($M_n = 81\,000$, $M_w = 2\,30\,000$) of 100 μm in thickness were obtained by extrusion and thicker films (500 μm) were obtained by compression moulding by procedures that can be found elsewhere [5–7].

3.3. Healing procedure

The samples were bonded in the lap-shear joint geometry at a small pressure [6] and submitted to tensile loading [25]. The contact area was 5×5 mm^2. For these experiments, 10 joints were placed side by side in an aluminium assembly and set in a Carver press which had already been warmed up to the chosen healing (or bonding) temperature. In order to apply pressure to all joints as uniformly as possible, the thickness of the joint areas was kept constant at ±2 μm. After healing for a predetermined time, the assembly was cooled to room temperature by circulating water in the plates of the press.

3.4. Mechanical measurements

Force-displacement curves were recorded on an Instron tensile tester, Model 5565, at room temperature and at a cross-head speed of 0.5 cm/min. At least 10 joints were

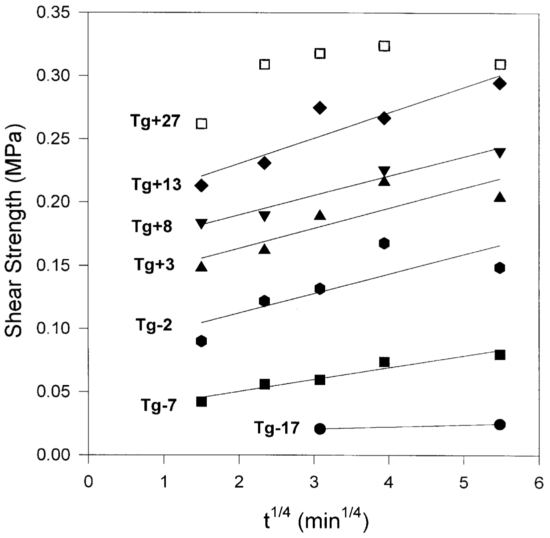

Fig. 1. Shear strength as a function of $t^{1/4}$ at amorphous/amorphous PET ($M_0 = 15\,000$) interfaces after healing between 64 ($T_g - 17°C$) and 108°C ($T_g + 27°C$). For clarity, errors bars are not shown, but they are of the same magnitude as those drawn in Figs. 2 and 3.

measured for each bonding condition. More details about bonding and testing procedures can be found elsewhere [5–7].

3.5. Thermal characterisation

DSC scans of the samples were made on a DSC-7 Perkin-Elmer differential scanning calorimeter, at a heating rate of 20°C/min. The glass transition temperature was read as the middle point of the corresponding heat capacity jump. Values of T_g for the amorphous PETs with M_0 of 15 000 and 76 000 were found at 81 and 82°C, respectively. The crystallinity index of the samples was calculated from the measured heat of fusion divided by the heat of fusion of a PET crystal of 140 J/g [26].

4. Results

4.1. Strength development at a symmetric amorphous PET interface

Shear strength measured as a function of time for a symmetric interface made of the amorphous low molecular weight PET ($M_0 = 15\,000$), at seven healing temperatures taken above and below the bulk T_g, is shown in Fig. 1. In the corresponding stress–strain curves (for each of the data points reported), the force measured until fracture as a function of the shear strain is linear, for all the bonding conditions reported in Fig. 1 (these curves are not presented in this paper but their shape is similar to those reported before for PS/PS and PPO/PPO interfaces [5]). As seen in Fig. 1, adhesion occurs between the surfaces of amorphous PET not only above T_g but also at $T_g - 7°C$ and at $T_g - 17°C$. Hence, the phenomenon of self-bonding below T_g does occur in the case of PET as it does with PS and PPO. However, the lowest temperature where the auto-adhesion of PET could be measured is $T_g - 17°C$ as compared to $T_g - 48°C$ for PS and $T_g - 126°C$ for PPO [6].

It is also seen in Fig. 1 that the shear strength increases linearly with $t^{1/4}$ at the bonding temperatures investigated, except at $T_g + 27°C$ where we have verified that crystallisation occurs at 30 min and longer times, contrary to the other temperatures where X-ray diffraction indicated no traces of crystallinity. This observation indicates a diffusion mechanism of strength development [15,16]. It is noticed that the strength measured at the shortest contact time studied of 5 min is fairly high and it increases with temperature. The data in Fig. 1 finally indicate that there is no discontinuity in the strength behaviour when going from above to below the bulk T_g of PET, as was found for PS and PPO.

The onset of cold crystallisation in PET usually occurs at temperatures of the order of 110–120°C [27,28]. Nevertheless, if it is assumed that there is a depletion of the surface T_g, then crystallisation at the outermost surface layer cannot be excluded at the temperatures investigated. However, WAXS measurements revealed the presence of crystallinity at 108°C ($T_g + 27°C$) only, for 30 min and longer times of crystallisation, but the samples remained amorphous after healing for 15 h at temperatures up to 94°C ($T_g + 13°C$) both at and outside the contact zones and at 108°C at shorter times of healing.

4.2. Strength of amorphous and crystalline PET interfaces

In order to distinguish a possible contribution from transesterification to the strength development, healing of amorphous/amorphous and crystalline/crystalline interfaces of PET with the same molecular weight of 15 000 was carried out. The values of the shear strength measured after a 30 min healing time are plotted in Fig. 2 as a function of healing temperature. It is seen that the strength of the amorphous interface is one order of magnitude larger than that of the crystalline interface. Actually, the T_g of the semi-crystalline bulk sample, as measured by dynamic mechanical spectroscopy [29], was higher by 12°C than that of the amorphous sample (the T_g of the semi-crystalline sample was undetectable on the DSC curve despite the low crystallinity (27%) of the sample). In view of that, if the curve for the crystalline sample is shifted to lower temperatures by 12°C in order to compare the development of strength at the same healing temperature relative to T_g, values for the amorphous interface are still larger by a factor of 5–7.

In a crystalline polymer, chain ends are located in the disordered intercrystalline regions for the minimisation of the free energy of the crystal [30] and, in addition, the disordered regions are preferentially segregated to the surface [31]. Therefore, the chain end concentration at the surfaces of crystalline and amorphous samples of the same molecular weight should be roughly the same. Under these conditions, if interface healing is controlled

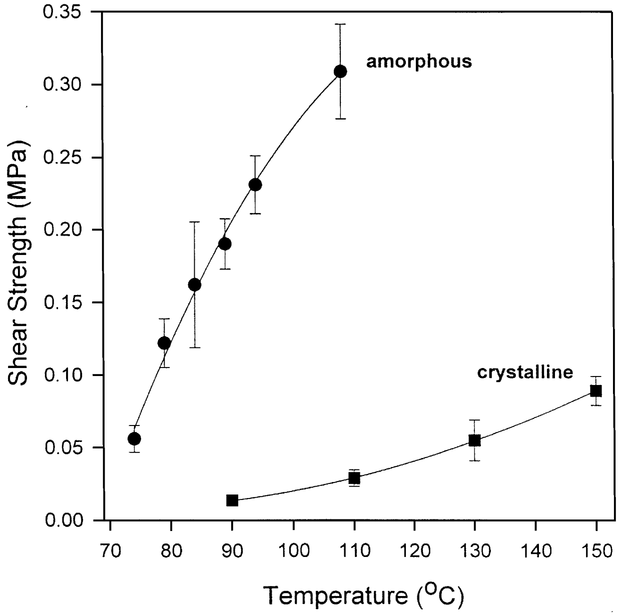

Fig. 2. Shear strength as a function of healing temperature at amorphous/amorphous and crystalline/crystalline PET ($M_0 = 15\,000$) interfaces. Healing time is 30 min.

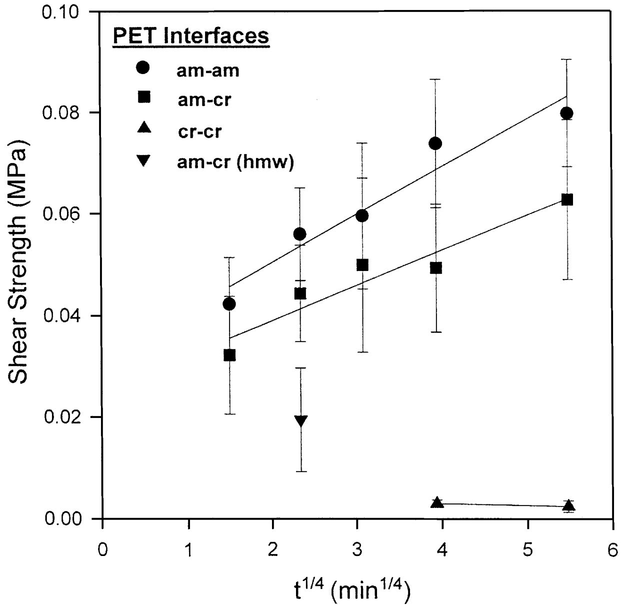

Fig. 3. Shear strength as a function of $t^{1/4}$ for several PET interfaces after healing at 74°C: (●) amorphous/amorphous, (■) amorphous/crystalline and (▲) crystalline/crystalline interfaces with $M_0 = 15\,000$; (▼) for an amorphous ($M_0 = 15\,000$)/crystalline ($M_0 = 3\,00\,000$) interface.

by transesterification, i.e. by a chemical reaction between a chain end belonging to the first surface and the central portion of a chain belonging to the second surface, amorphous/amorphous and crystalline/crystalline interfaces should lead to similar shear strengths upon healing. This behaviour is not observed in Fig. 2. On the contrary, if healing is controlled by diffusion, then the strength of an amorphous/amorphous interface should develop faster than that of a crystalline/crystalline interface following the wetting between the surfaces and the diffusion of the mobile chain ends across the interface [19]. For a semi-crystalline polymer, the diffusion of the chain ends is possible at the beginning only, the subsequent translational segmental motions being blocked fairly soon since the central portion of the chain is firmly fixed within the crystals. Thus, it is concluded from the data in Fig. 2 that the contribution of transesterification to the PET interface healing at 150°C and below, if any, is negligible.

4.3. *Strength development at amorphous and crystalline PET interfaces below T_g*

Let us now consider amorphous and semi-crystalline interfaces below the bulk T_g. In Fig. 3, values of shear strength for several interfaces of PET with $M_0 = 15\,000$ are plotted versus $t^{1/4}$. All these interfaces were healed at 74°C, i.e. at $T_g - 7$°C for the amorphous polymer. It is shown in Fig. 3 that the strength of the crystalline/crystalline interface is one order of magnitude smaller than that of the amorphous/amorphous interface (similar differences are shown in Fig. 2 at 90 and 110°C) and of the amorphous/crystalline interface. In the latter case, a linear increase of the strength with $t^{1/4}$ is also observed meaning that this process is diffusion controlled. It is assumed that the dominant contribution to the strength development of the amorphous/crystalline interface is provided by the penetration of segments of the amorphous polymer into disordered domains of the semi-crystalline PET. Hence, the disordered regions of the surface layer in a semi-crystalline polymer are easily penetrable by the mobile chain ends of the amorphous polymer leading to the formation of entanglements. However, an increase in crystallinity from 0.27 to 0.40, when using the higher molecular weight PET that has a concentration of chain ends more than one order of magnitude smaller than that of the low molecular weight sample, leads to a significant decrease of strength at the amorphous/crystalline interface (see Fig. 3).

4.4. *Effect of molecular weight on the strength development in amorphous PET*

The strength of two symmetric amorphous PET interfaces with $M_0 = 15\,000$ and 76 000 is plotted in Fig. 4 as a function of healing time to the one-fourth power at three healing temperatures relative to T_g. A linear relationship is seen for the two interfaces at the three temperatures meaning that this process is diffusion controlled in the two cases. At each temperature, the strength developed at the low molecular weight polymer interface is always higher due to the faster diffusion of the shorter chains and the higher concentration of the more mobile chain ends in the low molecular weight polymer.

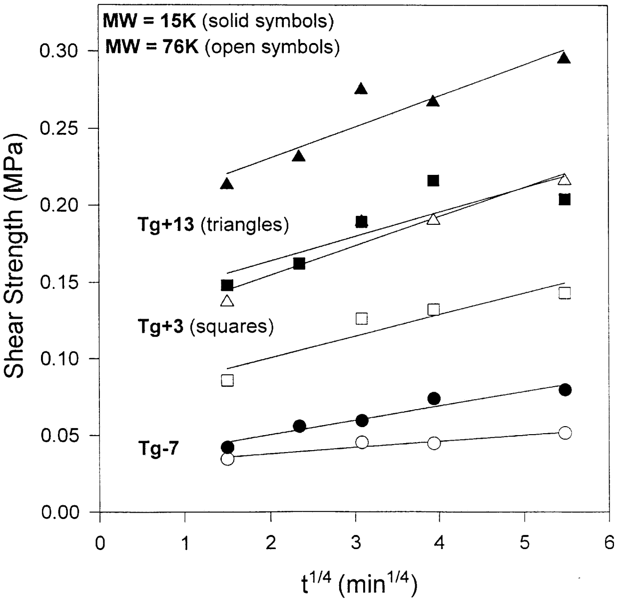

Fig. 4. Shear strength as a function of $t^{1/4}$ for symmetric amorphous PET ($M_0 = 15\,000$ (solid symbols) and $M_0 = 76\,000$ (open symbols)) interfaces at three healing temperatures relative to T_g.

4.5. Enhancement of the PET interface strength via crystallisation

It has been demonstrated above that the strength developed at the interface of a semi-crystalline PET is smaller than that at the interface of an amorphous PET due to hindered diffusion (see Figs. 2 and 3). In an attempt to dissociate the contributions from diffusion and from crystallisation to healing, we have performed two series of experiments. In the first series, amorphous PET interfaces were brought from room temperature to a healing temperature of 150°C and kept in the press between 5 min and 15 h where there is simultaneous diffusion and crystallisation. In the second series, amorphous PET interfaces were, first, healed at T_g + 13°C (94°C) between 5 min and 15 h where there is diffusion but no crystallisation and, then, after cooling the assembly to room temperature in the press, it was again set in the press to 150°C for 5 min.

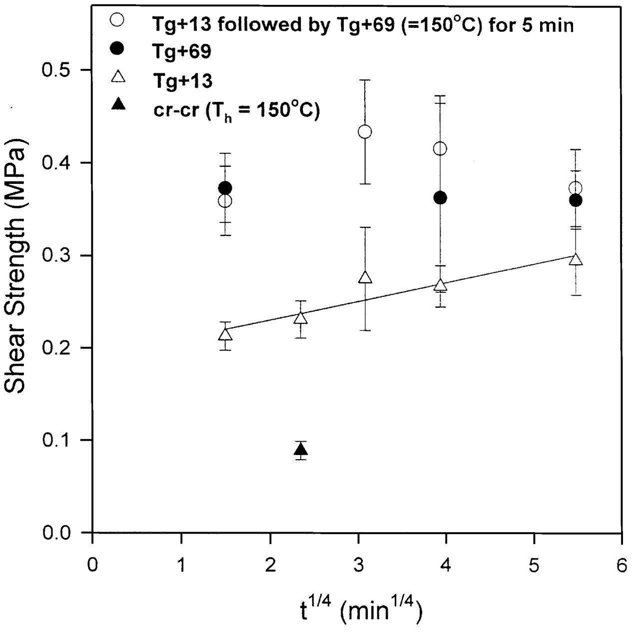

Fig. 5. Shear strength as a function of $t^{1/4}$ for several PET ($M_0 = 15\,000$) interfaces. Crystalline/crystalline ((▲) 150°C), and amorphous/amorphous interfaces: (△) healing at 94°C (T_g + 13°C); (○) healing at 94°C (T_g + 13°C) followed by healing and crystallisation at 150°C for 5 min; (●) healing and crystallisation at 150°C.

Strength values for interfaces healed by these two different methods are given in Fig. 5 along with the results for a simple healing at T_g + 13°C. As seen in Fig. 5, when the amorphous interface is brought rapidly to a crystallisation temperature of 150°C, the strength developed after 5 min is larger than that achieved by a simple healing at T_g + 13°C; it is even higher than the value reached by healing at T_g + 27°C (Fig. 1). However, increasing the crystallisation time at 150°C from 5 min to 15 h does not improve the strength (and the crystallinity of all these samples, as measured by DSC at the end of the procedure, remains constant at 0.33). The second procedure involving a preliminary healing at 94°C before reaching 150°C gives the same result as the first procedure after 5 min of treatment. The small improvement seen at healing times of 1.5 and 4 h is not convincing in view of the overlapping error bars and requires additional measurements.

From these observations, it can be concluded that (i) the development of strength predominantly occurs when the temperature increases from room temperature to 150°C (for ca. 1 min) and during the very first minute at that temperature, and (ii) at 5 min, the diffused chains are already locked by the crystallites and little or no diffusion occurs afterwards (at the same temperature). However, the development of strength at this temperature is still possible if crystallisation precedes healing: samples crystallised at 180°C and brought into contact at 150°C exhibit a certain level of strength (Fig. 5), which demonstrates that some limited diffusion of the segments across the interface from the disordered regions of the semi-crystalline surfaces is possible. Nevertheless, the strength developed at the crystalline/crystalline interface at 150°C is smaller by a factor of four in comparison with the strength attainable at the amorphous/amorphous interface at the same temperature. Therefore, a higher strength can be achieved at the interface of a crystallisable polymer if it is initially amorphous, i.e. if healing precedes crystallisation.

4.6. Healing of an incompatible PET/PS interface below and above T_g

Incompatible interfaces of amorphous PS and PET were bonded at 74 and 108°C, i.e. below and above the T_gs of the two polymers involved. In Fig. 6, the strength developed at

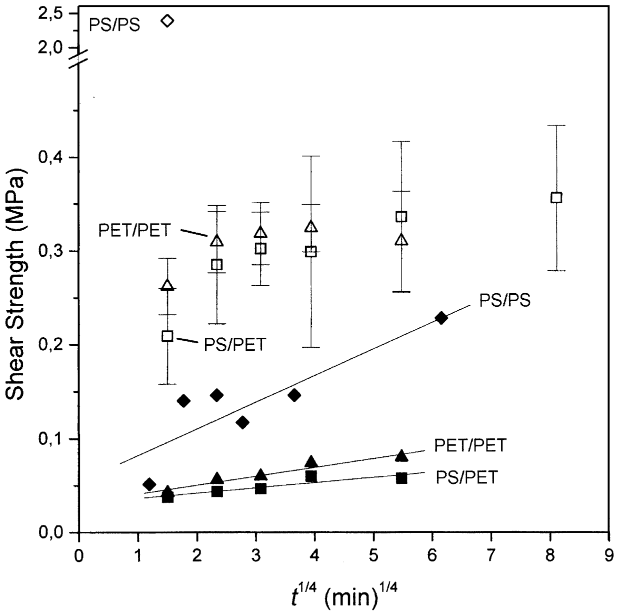

Fig. 6. Shear strength as a function of $t^{1/4}$ for PS/PET (■ and □), PET/PET (▲ and △) and PS/PS interfaces (◆ and ◇) healed above (at 108°C in the three cases) (open symbols) and below the bulk T_g of the two polymers (at 74°C for PET/PET and PS/PET interfaces, and at 70°C for the PS/PS interface) (solid symbols).

this interface as a function of time is compared with those of the corresponding symmetric (compatible) interfaces. It is shown that, below T_g, the strength of the symmetric PS/PS (healed at 70°C, i.e. at $T_g - 33$°C) and PET/PET interfaces (at 74°C) is larger than that of the asymmetric PS/PET interface but the difference between PET/PET and PET/PS interfaces is of 20–25% only. The healing temperature of 74°C corresponds to $T_g - 7$°C for PET whereas it corresponds to a lower temperature of $T_g - 29$°C for PS. Nevertheless, the surface mobility in PS is intensive enough to overcome the energy of repulsion of the segments of PET, which is unfavourable for healing, leading to the development of strength values comparable with those of the compatible PET/PET interface.

Healing the three interfaces above T_g of the two polymers involved, at 108°C (= $T_g + 5$°C for PS and $T_g + 24$°C for PET), demonstrates better the effect of the high molecular mobility on the PS surface (as compared to that of PET). The strength of the PS/PS interface of 2.4 MPa at the shortest contact time of 5 min reported in Fig. 6 is one order of magnitude higher than the corresponding values at the PET/PET and PS/PET interfaces (even if it was obtained in tensile mode meaning that the expected strength of this interface is larger than 2.4 MPa).

5. Discussion

5.1. The compatible PET/PET interface

First of all, let us consider the healing process of PET above (bulk) T_g, i.e. when translational motions of segments across the interface of amorphous polymers certainly exist. When two amorphous PET surfaces are brought into contact at a small contact pressure (0.4 MPa), wetting between them rapidly occurs due to the elastic state of the surfaces. Since this pressure is higher than the stress required for high-elastic deformations above T_g, which is of the order of 0.07–0.08 MPa as calculated from the rubbery plateau modulus of PET [29], most of the interfacial gaps (even at the nanometer level) are expected to vanish quickly owing to large local elastic deformations at the points of contact, finally leading to full wetting between the surfaces over all the contact area.

As soon as physical links across the interface are established (wetting), interdiffusion of segments with a length less than the entanglement molecular weight 'M_e' (Rouse relaxation) follows [19]. This leads to a fairly rapid (order of minutes) intermixing [32]. In addition, if we assume that the M_e value of the polymer near the interface is three times the bulk M_e value, as suggested in the literature [42], longer segments can undergo rapid Rouse relaxation resulting in a deeper penetration. Hence, both wetting and 'fast' diffusion may contribute to a certain level of strength at PET/PET interfaces after a few minutes only of healing. Then, a curvilinear diffusion (reptation) of chain ends usually follows. The slow increase of strength at $t > 5$ min and the low values of strength at the amorphous PET/PET interface indicate that this diffusion process is rather slow, which might be explained by the strong dipole–dipole interactions between PET segments [33,34], by its relatively high density (1.34 g/cm^3 as compared to 1.05 g/cm^3 for PS), and by its larger energy of intermolecular cohesion (62 kJ/mol) as compared to that of PS (35 kJ/mol) [33]. All these factors indicate a more restricted segmental motion in PET than in PS.

Below or near (bulk) T_g, the development of the PET interface strength may be simultaneously accompanied by enthalpic (or volume) relaxation [35], including short-range ordering (coplanar coupling of benzene rings of the neighbouring segments) [36]. How significantly this process suppresses the strength development can be illustrated by the fact that ageing of amorphous samples at 74°C ($T_g - 7$°C) for 15 h prior to healing at this temperature resulted in a decrease in strength by a factor of two in comparison with the strength achieved without preliminary ageing.

The results on PET healing at 74°C (Fig. 3) have shown that the strength of the crystalline/crystalline interface is one order of magnitude smaller than the strength of amorphous/amorphous and amorphous/crystalline interfaces. When there is crystallinity, the polymer segments, in particular the chain ends, located in the interlamellar regions, are not free to move across the interface since the central portions of chains are firmly fixed within crystallites. Therefore, the main contribution to the strength development at an amorphous/crystalline interface is due to the amorphous side of the sandwich since the strengths developed at amorphous/amorphous and amorphous/crystalline interfaces are close.

In general, the values of strength measured at PET/PET interfaces are fairly small. For comparison, the strength of PS/PS interfaces after healing at $T_g - 13°C$ is twice higher [6] than the largest strength of the amorphous PET/PET interface measured in this work between $T_g - 17°C$ and $T_g + 27°C$. At the same time, the highest values of shear strength reported in Fig. 1, of the order of 0.32 MPa, are comparable with the values of shear strength of 0.5–0.9 MPa obtained by Fakirov [37] for a semi-crystalline PET interface healed at a much higher temperature of 240°C for 10–100 h meaning that, in both cases, a full healing of the interface, i.e. a fully interpenetrated structure has not been reached (for comparison, full healing of a PS/PS interface gives a value of the lap-shear strength of 7.2 MPa [38]). However, at 240°C, healing of the interface occurs mainly via chemical reactions of post-polymerisation and transesterification and the high crystallinity (60%) of the samples [37] considerably suppresses the diffusion. Nevertheless, our results indicate that the interface healing in crystallisable PET is significantly less efficient than in amorphous non-crystallisable polymers such as atactic PS and PPO.

5.2. The incompatible PS/PET interface

In order to calculate the equilibrium interpenetration depth of the PS/PET interface using Eq. (1), Flory–Huggins interaction parameter must be known. According to Hilderbrand:

$$\chi = \frac{V_r}{RT}(\delta_1 - \delta_2)^2 \tag{7}$$

where δ is the solubility parameter, V_r is the molar volume of the polymer repeat unit, and R is the gas constant. We have $\delta = 10.7$ for PET and 9.3 $(\mathrm{cal/cm^3})^{1/2}$ for PS. Since $V_r = M_{ru}/\rho$, where M_{ru} and ρ are the repeat unit molecular weight and density, respectively, the values of V_r are 99 and 143.8 cm^3/mol for PS (using $\rho = 1.05$ g/cm^3) and PET (using $\rho = 1.34$ g/cm^3). At a temperature of 108°C, Eq. (7) gives $\chi = 0.089$ employing the V_r of PET or 0.061 employing the V_r of PS. Finally, using the statistical segment length of 6.5 Å for PS or PET [18] and $\chi = 0.061$, the (maximal) equilibrium interpenetration depth d_∞ is calculated from Eq. (1) as 22 Å.

Let us also calculate d_∞ by a second approach using Eq. (6). At $T = 108°C$, the strength of the PS/PET interface remains fairly constant at $t^{1/4} > 5$ min$^{1/4}$ ($t > 15$ h) (see Fig. 6) suggesting that the equilibrium depth d_∞ could be achieved. Under these conditions, Kline and Wool [38] observed complete healing (welding) of the PS/PS interface at $T_g + 9°C$ and $t^{1/4} = 8$ min$^{1/4}$ ($t = 96$ h). Since a strength of 2.4 MPa achieved at $T_g + 5°C$ for 5 min, as reported in Fig. 6, is larger than that of 1 MPa achieved at $T_g + 9°C$ reported in Ref. [38] (which can be explained by the higher diffusivity of the shorter chains of PS with $M_n = 81\,000$ used here as compared to the PS of $M_n = 1\,43\,000$ used in Ref. [38]), we may expect full healing of the PS/PS interface at $T_g + 5°C$ and $t^{1/4} = 8$ min$^{1/4}$. Assuming also (for a PS/PS interface) the same shear strength of 7.2 MPa for the fully healed PS/PS interface as obtained in Ref. [38], using $R_g = 87$ Å for PS with $M_n = 83\,000$ [39] and the highest strength at the PS/PET interface from Fig. 6 of $s_i = 0.36$ MPa, Eq. (6) gives $d_\infty = 7$ Å. This value is low in comparison with the value of 22 Å calculated from the first approach, which means that the equilibrium state at the PS/PET interface has not been reached yet after healing at 108°C for 15 h. In part, it may be explained by the crystallisation of PET at 108°C at long times.

The depth of penetration of the fully healed symmetric PET/PET interface $2X_0$ can be calculated from Eq. (4) provided that the radius of gyration R_g is known. From Ref. [40], $R_g = 47$ Å for a $M_w = 15\,000$, which gives $2X_0 = 75$ Å. This value is larger, as it should be, than the value of $d_\infty = 22$ Å for the PS/PET interface. Qualitatively, the low depth of interpenetration at compatible and incompatible PET interfaces is in agreement with the low values of interfacial strength.

In conclusion, amorphous PET demonstrates very limited ability for interfacial healing in contrast to amorphous non-crystallisable polymers like PS and PPO. In particular, after healing at $T_g + 13°C$ for 15 h, only partial healing of the PET/PET interface is possible whereas full healing of the PS/PS [38] and PMMA/PMMA interfaces was observed under the same conditions [41]. For a better understanding of such behaviour, it would be interesting to study the healing of other polymers which can be obtained both in amorphous and crystalline states.

Finally, in spite of the low values of interfacial strength measured for PET, no discontinuity in strength development is seen in the vicinity of the T_g of the amorphous PET. In addition, we observed a linear increase of strength with $t^{1/4}$ at $T_g - 7°C$, a possibility of self-bonding of PET at $T_g - 17°C$, and a partial healing of incompatible PS/PET interfaces below the bulk T_gs of the two polymers. All these facts are consistent with a possible increased chain mobility at the PET surface (as compared to the bulk of the sample), i.e. a depletion in the surface T_g, as it has been suggested for PS and PPO [5–7,13,14].

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