Self adhesion of semi-crystalline polymers below their melting point

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Introduction

Adhesion between polymers is mainly due to the combination of three effects : the mutual interdiffusion of the chains across the interface creating entanglements, co-crystallization in a single lamella of chains from both sides of the interface and one or more chemical reactions. In this study we focus on the influence of crystallinity on the energy of adhesion. We used a series of copolymers of polybutylene(terephtalate-co-isophtalate), which can be prepared with different degrees of crystallinity, depending on thermal history and composition and measured self-adhesion resulting from contacts made at different temperatures between the glass transition temperature T_g and the melting point T_m. A characterization of these copolymers was carried out by differential scanning calorimetry (DSC) and by NMR. The copolymers used are composed of nearly random short sequences of a few isophthalate or terephthalate. The energy of adhesion was determined by a fracture test : the double cantilever beam test (DCB).

Experimental

Synthesis and characterization of the copolymers. The copolymers were synthesized by double condensation starting from dimethyl terephthalate (DMT) and dimethyl isophthalate (DMI) according to Bandiera, Munari et al. [1]. Three copolymers of mass composition in PBI of 15,35 and 45% were obtained (named 15PB, 35PB and 45PB). Pure PBT was synthesized industrially by DSM. The average molecular weight M_n was determined by end group analysis. T_g and T_m were determined by DSC (DSC TA instrument) with a 5°C/min ramp. The approximate degree of crystallinity was calculated from equation (1).

The heat of fusion of a pure crystal of PBT is of [2] :
$\Delta H_0 = 140$ J.g^{-1}.

$$\chi_c = \frac{\Delta H}{\Delta H_0} \qquad (1)$$

Measurements. The first step is the molding of plates from pellets, followed by the making of the assembly. The molding temperature was selected such as $T_{mold}>T_m+20°C$. We applied a cooling rate of 2.5°C/min to bring the plates to room temperature after molding. The adhesive assembly (the DCB sample) was made from two molded plates of the same copolymer, preheated at the temperature of contact T_c then put in contact during the time of contact t_c. The same cooling rate was then applied for all the assemblies. For PBT, 15PB and 35PB, the two plates were joined under inert atmosphere in order to avoid oxidation at high temperature.

The adhesion test we used was the so called DCB test which uses a mechanical model to calculate the fracture toughness G_c, from a measurement of crack length *a* only. The length of the crack was measured with a video camera, showing the side of the assembly. The DCB test was carried out at fixed crack opening of 0.32 mm and at a constant crack velocity of 0.5 mm/min at room temperature :

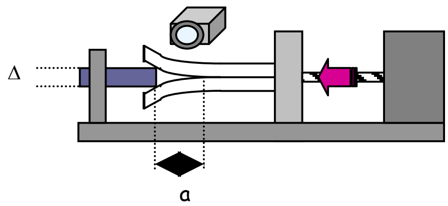

Figure 1. DCB test. *Δ* : opening displacement, *a* : length of crack

Kanninen's model [4] has been used to calculate G_c from the dimensions of the assembly and the elastic modulus of the polymers on both sides of the interface i.e. a, Δ, E_1, E_2, h_1, h_2, α_1 and α_2 respectively, the length of the crack, the opening displacement, the Young's modulus, the thickness of each arm, and the correction factors of the model. More details can be found in reference [3].

$$Gc = \frac{3\Delta^2}{8a^4}\frac{E_1h_1^3E_2h_2^3}{E_1h_1^3\alpha_1^2 + E_2h_2^3\alpha_2^2} \qquad (2)$$

We measured the Young's modulus with three points bending tests on samples molded according to the same experimental procedure used to make the assemblies. 45PB has a Young's modulus a bit too low to be used as an arm for the DCB test. For those samples we used a sandwich geometry where the 45PB has been reinforced with 15PB as follows : a 0.5 mm thick sheet of 45PB is overmolded on a 1.5 mm thick plate of 15PB and the two bilayers are then assembled following the standard procedures.

Table 1. PBT and PBTPBI copolymers characterization

Sample Description	M_n kg/mol	T_g (°C)	T_m (°C)	χ_c (%)	E (GPa)
PBT	20	40	225	32	2.8
15PB	21	33	201	22	2.9
35PB	24	29	163	14	1.6
45PB	25	28	141	14	0.6

Thermal characterization. DSC scans of the copolymers were made on a TA Instrument "2820 Modulated DSC" calorimeter. For each copolymer, a pellet was heated at a temperature 20°C higher than its melting temperature. The samples were then cooled until 0°C at 2.5°C/min in order to simulate the molding process. The DSC curve was recorded during heating with a modulated signal (Modulation +/- 0.796 °C every 60 seconds : "heat only"). The temperature ramp was 5°C/min.

Microscopy. Optical observations under polarized light of 15PB assemblies have been done from 3µm thick slices cut with a glass knife on a microtome. For TEM images, a small part of the assembly containing the interface was stained in ruthenium tetroxide, then cut with a diamond knife on a ultramicrotome in order to obtain 100 nm thick slices.

Results and Discussion

In the case of strong adhesion, the assembly could not be tested by the DCB test, since the crack could not be made to propagate at the interface. According to **figure 2**, by going from low to high proportion of PBI, we noticed that a significant polymer-polymer adhesion was observed for joining temperatures well below T_m. When the total degree of crystallinity increases, proximity to T_m becomes an important factor for adhesion. Nevertheless, when the temperature is lower than T_m - 40°C, the fracture toughness of all assemblies is low even for the copolymers with high PBI content. Therefore, although we are still well above the glass transition of the polymer, the presence of crystallites seems to prevent chain mobility.

From the DSC curves in **figure 3**, we can observe a broadening of the melting peaks when going from pure PBT to 45PB. It appears that adhesion becomes measurable for contact temperatures roughly above this temperature of initial melting T_i.

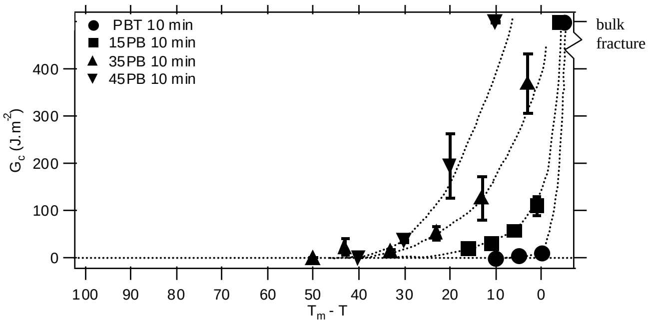

Figure 2. Fracture toughness G_c at room temperature PBT and copolymers. Contact time : 10 min

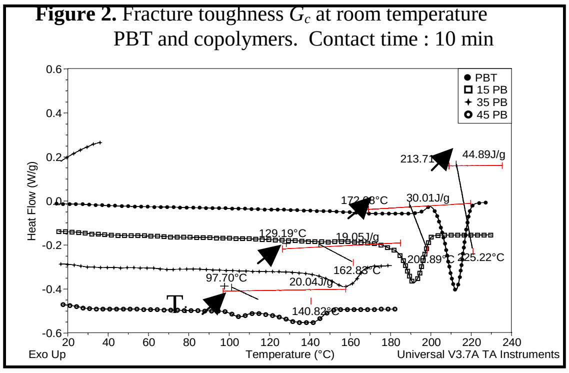

Figure 3. DSC PBT, 15, 35 and 45PB ramp : 5°C/min

Optical observations (**Figure 4.**) show two different structures depending on the temperature of contact : for T_c=T_m, we observe spherulites across the interface while for a contact below T_m we observe a transcrystalline zone similar to the morphology at the surface of the assembly. Optically, it appears that the temperature of contact has to be superior or equal to T_m to obtain a difference between the structure at the interface and the surface structure. Nevertheless, from a TEM image of the interface for $T_{contact}$<T_m, it appears that lamellae are running across the interface.

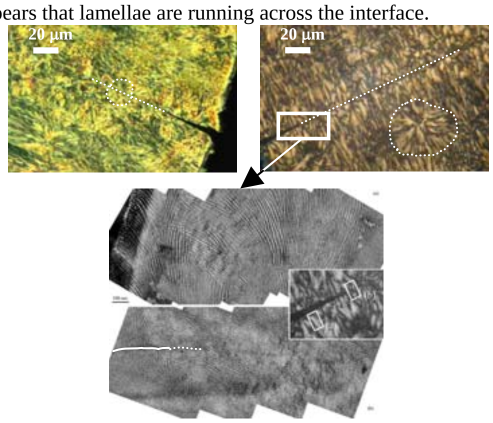

Figure 4. Optical and electronic microscopy on 15PB. (1) $T_{contact}$=T_m , (2) $T_{contact}$<T_m

Those obsevations and DSC results shows that a certain degree of melting is necessary to obtain measurable adhesion.

In the case of the 45PB it is possible to obtain an amorphous sample at room temperature by quenching the sample after molding.

New experiments have been be carried out at T>T_g but with amorphous samples put in contact at room temperature and then heated up to $T_{contact}$.

Better Adhesion is found in the amorphous case (**Figure 5.**) and becomes measurable at lower contact temperature. But still, adhesion is surprisingly weak at temperatures such as T_m-80 and T_m-60, which correspond respectively to T_g+30 and T_g+60. Optical and electron microscopy observations must be done near the interface in order to understand the reasons of this weak adhesion.

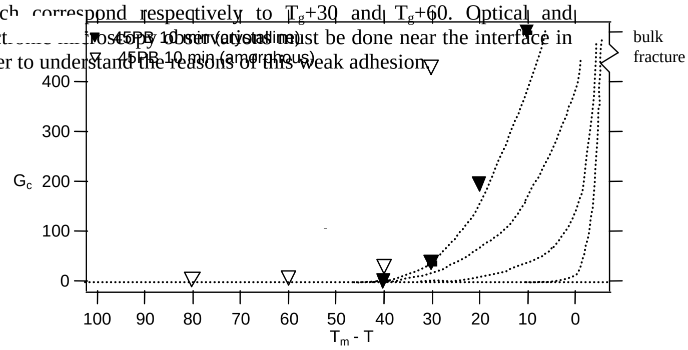

Figure 5. Fracture toughness G_c at room temperature
full symbol : contact between crystalline 45PB
open symbol : contact between amorphous 45PB

Conclusions

For highly crystallized polymers like PBT or 15PB, it is necessary to be nearly at the melting point to obtain any adhesion at all and then the increase in adhesion with contact temperature is very sharp. Adhesion for less crystalline copolymers like 35PBI and 45PBI appears much more progressively with contact temperature and can be significant at temperatures down to 30°C below T_m. This difference in behavior may be related to the width of the DSC melting peak, which is wider in the case of the last two copolymers. The presence of crystallites even in small amounts strongly decreases the mobility of the chains at the interface preventing the necessary interdiffusion which would increase adhesion. Adhesion only becomes significant when enough chains recover their full mobility i.e. during the melting of the first crystallites.

For a contact between amorphous 45PB, it possible to get adhesion at a temperature as low as T_m-80. The value of G_c at this temperature is very small in comparison with other results on amorphous polymers put in contact above T_g. A detailed study on 45PB cold crystallization should be performed on order to understand this weak adhesion in a case where interdiffusion is expected to occur before crystallization.

Acknowledgements

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