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CRITICAL ENERGY RELEASE RATE OF A BIMATERIAL ASYMMETRIC DOUBLE CANTILEVER BEAM (ADCB) WITH AN ADHESIVE LAYER.

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ABSTRACT

Goal of this research is to determine the relation between the composition of a PS-PEB block copolymer and the adhesion of a PS-LDPE interface with the block copolymer as adhesive layer. The focus of this paper is the improvement of the test method.

The Critical Energy Release Rate (G_C) of an interface between Polystyrene (PS) and Low Density Polyethylene (LDPE) is measured with an Asymmetric Double Cantilever Beam (ADCB). It was preferred to use the block-copolymers in their practical form. Therefore techniques to characterise the thickness of the block-copolymer layer which require deuteration (e.g. SIMS or FRES) could not be used and an alternative route applying ellipsometry and AFM was established.

G_C is determinated by inserting a wedge at the interface with a constant velocity. The equilibrium crack length is continuously measured during the test over the total interface length.
From the crack length and the compliance the G_C is calculated. Different models for calculating the compliance are used. The new model "beam on elastic foundation with a correction for shear deformation" is found to give the smallest variation of G_C as a function of both the beam thickness and the beam thickness ratio. Correction for non-linear elastic behaviour reduces the variation of G_C as function of the beam thickness and beam thickness ratio.

The test method is improved by:
- Developing a method to place a smooth block copolymer layer of known thickness at the interface.
- Correcting Gc calculations based on the "beam on elastic foundation" model.
- Correcting the G_C calculations for shear deformation.
- Making a start in correcting the G_C calculations for non-linear behaviour.

KEYWORDS

Critical Energy Release Rate; Asymmetric Double Cantilever Beam; Compliance model; Adhesion, Block Copolymers, Wedge Splitting Test.

INTRODUCTION

The adhesion between two different polymers is a subject of extreme relevance for many polymer applications, notably for heterogeneous polymer blending. Compatibilisation of the interface by block-copolymers is known to improve the level of adhesion. The strength of a polymer interface, reinforced by a block-copolymer, has been the subject of many investigations. Block copolymers turn out to form effective 'stitches' between the two adherents.

For practical blends, compatibilisation with thermoplastic rubber type of tri-block copolymers is often applied. In this situation both the adhesion between matrix and block-copolymer as a pure phase and its effect on the strength of the interface between matrix and dispersed phase is of importance. As a model system exemplary for such a blend, in this investigation we chose a combination of polystyrene (PS) and low-density polyethylene (PE) with a SEBS (styrene- ethylene butylene- styrene) type of block-copolymer as a compatibiliser.

Creton et al [1] developed the "wedge splitting test" which is very suitable for measuring adhesion between two rigid polymers (Fig.1). Johnson, Kendall en Roberts [2] developed the JKR test to measure the adhesion between two elastic materials. Brown [3] and Creton [4] used a JKR-type of test, which can measure the strength of an interface between a glassy polymer and a rubber reinforced with their di-block. The JKR test requires the softer component to be fully elastic up to the annealing temperature, which is not the case for PE or SEBS. Therefore the wedge splitting test was chosen. However, so far this has been applied to polymers where stiffness differed no more than 10-20 %. The Young's modulus, E, of PS and PE differ a factor of about 20.

Creton et al [1] measured the adhesion between two rigid polymers with the ADCB-test. Their results show that adhesion per block copolymer chain increases with increasing block length. A considerable increase in the adhesion was found for block copolymers with sufficient long blocks to form entanglements with the adherent substrates. Up to this block length only a small increase in adhesion was measured due to the increase in chain pull out energy with increasing chain length. If the blocks are long enough to form entanglements the fracture mechanism is chain scission with of without plastic deformation of the substrate.

Effects of and number of chains per surface area have been systematically investigated by Brown [5] for glassy, amorphous polymers reinforced by their block copolymers. His results show that interfacial adhesion increases with increasing chains per surface until the surface is saturated.

EXPERIMENTAL

Materials

One beam is made of Polystyrene (PS) the other beam is made of Low Density Polyethylene (LDPE).
The interface is reinforced with block copolymer consisting of block polystyrene, a block hydrogenated polybutadiene (PEB) and another block polystyrene. PEB has a vinylpercentage of 40-45%.

The mean molair mass between entanglements, Me, is according to Wu [6] for PS 18.7 kg/mol and for PE 1.39 kg/mol.
The moleculair weight of the PS block is 7.3 kg/mol. This is 0,4 x Me_{PS}. The moleculair weight of the PEB block is 33,9 kg/mol. With a vinylpercentage of 40 this gives a moleculair weight of the back bone of PEB of 27,1 kg/mol. This is 19,5 x Me_{PE}.

Sample preparation

The sample preparation procedure was as follows. The PS and PE material were compression moulded to the required thickness in a vacuum mould. The temperature was 220°C.
One side of the mould was covered with a smooth chromed metal plate as is used for photographic purposes. Plates were then machined to produce beams of the proper dimensions (width: 10 mm, length 45 mm), taking care that the smooth surface was not damaged or polluted.

The block copolymer was dissolved in toluene and spin coated on a silica wafer at standard spinning conditions. The thickness of the layer was measured by ellipsometry. The layer was then picked up from the wafer by placing the PS beam (dried at 90°C) with its smooth surface on the wafer and annealing in an oven at 130°C (under nitrogen, 150 mbar) for 1 hour. AFM images of the wafer clearly show that this procedure practically removes all the block-copolymer from the wafer. The layer thickness measured with AFM is equal to the ellipsometry measurement.
Thickness variations were obtained by changing the concentration.

After applying the block-copolymer to the PS, the PE part of the specimen was stacked on the interface, and the whole specimen was annealed in an oven (48 hours at 130 °C, 125 mbar nitrogen) to obtain adhesion.

Experiments
The wedge splitting test is used (see figure 1), as mentioned in the introduction.

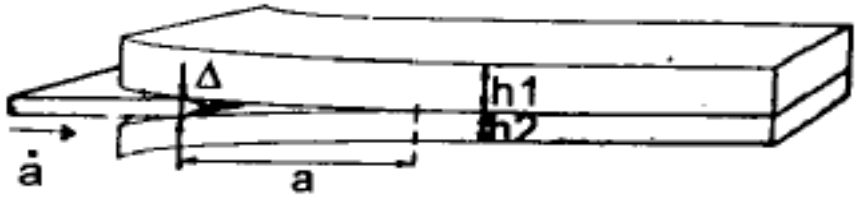

Figure 1: Wedge splitting test with an Asymmetric Double Cantilever Beam specimen.

The specimen is called "Asymmetric Double Cantilever Beam" because both beams have different thickness (h1 and h2 in figure 1) to minimise the tendency of the crack to propagate in a mode II direction. In order to test the most suitable ratio between the thickness (h) of both homopolymer beams several combinations of h_{PE} and h_{PS} were tested.
To determine G_C a wedge is inserted at the interface with a constant velocity of 0.1 mm/min. The equilibrium crack length is continuously measured during the test over 12 mm of the total interface length.
A video recording of 2 seconds is made every 1.51 minute, resulting in about 60 recordings of the crack length.

The inserting force on the wedge is measured during the experiment. It is found that this force is constant if the crack length is in equilibrium. An interval of 2.5 mm is choosen in which the inserting force fluctiations are minimal. During this interval 16 recordings of the equilibrium crack are made. These recordings are used for measuring the crack length.
The crack length is measured in the middle and on both sides (at a distance of the side of 20% of the specimen width). The avarage crack length is calculated from these meassurements. This avarge value is the avarage of the measurements of both sides and the measurement in the middle.
From the crack length, a, and the compliance, C, the critical energy release rate, G_C is calculated for each beam:

$$G_{C_i} = \frac{\Delta^2}{2b(C_1 + C_2)^2}\frac{dC}{da} \tag{1}$$

In which Δ is the wedge thickness and b is the sample width.
Summation (i = 1..2) gives the G_C of the specimen.

The deflection of the beam and the load on the beam are not measured. Therefore a model is needed to calculate the compliance.

One model is the "simple beam model" in which the beams are considered to be clamped at the crack tip. The equation for G_c based on the "simple beam" model is:

$$G_C = \frac{3\Delta^2}{8a^4}\frac{\Pi E_i h_i^3}{\Sigma E_i h_i^3} \tag{2}$$

During the experiments other models are developed (see next section).

RESULTS: INFLUENCE OF BEAM THICKNESS (RATIO) AND COMPLIANCE MODEL ON G_C

Rutten has tested several combinations of h_{PE} and h_{PS} with a block copolymer (see materials) layer of about 21 nm [unpublished graduation thesis, Hogeschool Venlo HLO polymeerchemie, the Netherlands, in co-operation with Shell].
The layer thickness is uncertain because the method to place a smooth block copolymer layer of known thickness at the interface (see sample preparations) was not yet established by that time.
Rutten spincoated the block copolymer layer on the smooth PE surface. To estimate the layer thickness a block copolymer layer was spincoated under the same conditions on a silica wafer. The thickness of this layer is measured by ellipsometry.
Rutten used specimens with beam thickness of 2, 4 and 8 mm. Creating specimen with h_{PE}/h_{PS} of 2/8, 4/8, 2/2, 4/4, 8/2 and 8/4. Two specimen of each geometry.

His data were used to determine the most suitable ratio between the thickness (h) of both beams. The G_C-value of these specimens were calculated applying the equations based on the Kanninen's elastic foundation model [7] proposed by Creton [1]. In a similar range of thickness ratio data Creton showed that a minimum occurred, which was attributed to the lowest tendency of the crack to propagate in a mode II direction at this minimum. However our data showed a monotonously increasing Gc as a function of the thickness ratio.
When investigating the possible cause for this difference the original elastic foundation solution by Kanninen was revisited. It was found that where Creton relates the stiffness of the beam foundation to the stiffness of the beam under consideration. The stiffness has to be related to the stiffness of the opposite, supporting beam as originally intended by Kanninen. The equation for G_C based on the "beam on elastic foundation" model then change to:

$$G_C = \frac{3\Delta^2 E_1 h_1^3 E_2 h_2^3}{8a^4}\left(\frac{E_1 h_1^3 (1+0.64\frac{h_1 S_1}{a})^2 + E_2 h_2^3 (1+0.64\frac{h_2 S_2}{a})^2}{\left(E_1 h_1^3 (1+0.64\frac{h_1 S_1}{a})^3 + E_2 h_2^3 (1+0.64\frac{h_2 S_2}{a})^3\right)^2}\right) \tag{3}$$

with

$$S_{1,2} = \left(\frac{E_{2,1} h_{2,1}^3}{E_{1,2} h_{1,2}^3}\right)^{\frac{1}{4}} \tag{4}$$

Figure 2 shows the results of this calculation. Every point is the average of 2 measurements (2 specimens of each geometry).

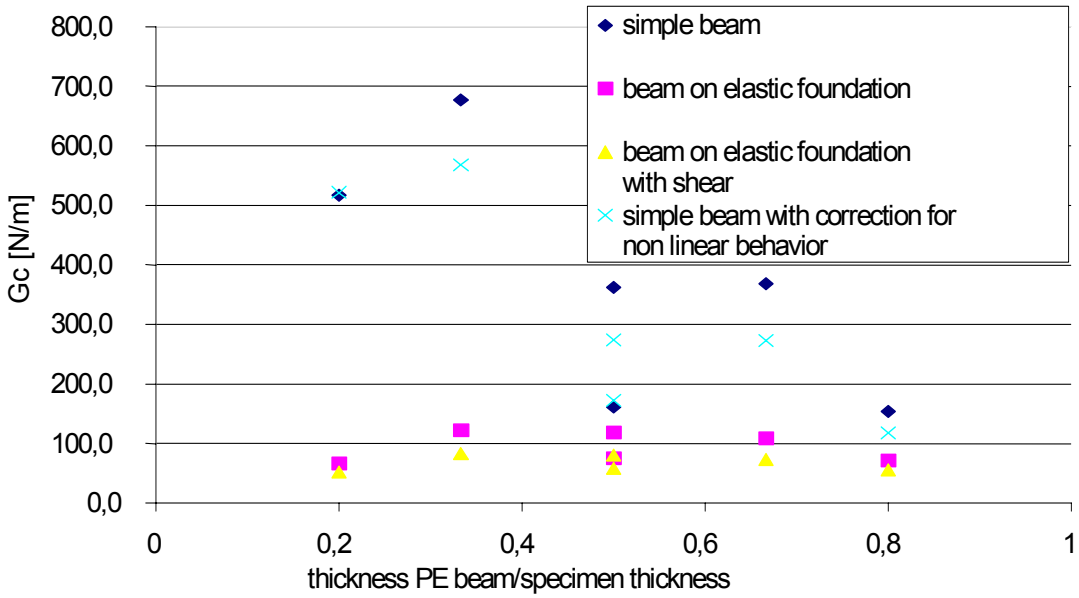

Figure 2: Critical energy release rate for different beam thickness ratio's and different compliance models. For thickness ration ratio's of 0,2 (h_{PE}/h_{PS} = 2/8), 0,33 (h_{PE}/h_{PS} = 4/8), 0,5 (h_{PE}/h_{PS} = 2/2 and h_{PE}/h_{PS} = 4/4 the lowest values of Gc at this thickness ratio are the values for 2/2), 0,66 (h_{PE}/h_{PS} = 8/4), 0,8 (h_{PE}/h_{PS} = 8/2),

Instead of showing a minimum a maximum is found. Furthermore data are still varying strongly with thickness and thickness ratio. It was then decided, given the relatively small ratio between beam length and thickness to include shear deformation in the elastic energy term. Resulting in the equation for C for beam 1 and 2 based on the "beam on elastic foundation with correction for shear stress" model:

$$C_{1,2} = \frac{4\left(\frac{aS_{1,2}}{0.64h_{2,1}}+1\right)^3}{E_{1,2}bh_{1,2}^3\left(\frac{S_{1,2}}{0.64h_{2,1}}\right)^3} + \frac{1.2a}{G_{1,2}bh_{1,2}} \tag{5}$$

Combination with equation 1 gives the energy release rate of each beam.
Beside the shear deformation the non-linear behaviour is another complication. Tensile tests show that PS behaves linear under the ADCB test conditions. The behaviour of PE however is non-linear. The beginning of the stress strain curve (tensile test acc. to DIN 53455-5, 50 mm/min) can be described by a power law:

$$\sigma = E_0 \varepsilon^n \tag{6}$$

In which σ is the stress, ε is the strain, E_0 and n are fitparameters. Fitting the stress strain curve from ε = 0.003 up to ε = 0.008 results in: E_0 = 4.02 (±0.82) x 10^7 N/m^2 en n = 0.663 ± 0.040.

Combination of this power law and the equation that Williams [8] derived for a DCB gives the energy release rate of one beam:

$$G = \frac{2n}{b(n+1)} P^{\frac{n+1}{n}} \left(\frac{2(n+2)}{bE_0h^{n+2}}\right)^{\frac{1}{n}} a^{\frac{n+1}{n}} \tag{7}$$

In which P is the force on the beam at the wedge. Summation gives the total G.

P has to be determinded by iteration:

$$\left(P_1 C_{n1}\right)^{\frac{1}{n_1}} + \left(P_2 C_{n2}\right)^{\frac{1}{n_2}} = \Delta_1 + \Delta_2 = \Delta_{tot} \tag{8}$$

The results of the Gc calculations are shown in figure 2 for every model. Every point is the average of 2 measurements (2 specimens of each geometry, 16 x 3 measurements pro specimen). The data still vary with thickness and thickness ratio. Table 1 shows the variation for each model.

Table 1:
Variation of Gc with thickness ratio, varation of Gc for given thickness ratio (h_{PE}/h_{total} = 0,5) but different beam thicknesses (h_{PE}/h_{PS} = 2/2 and h_{PE}/h_{PS} = 4/4) and the maximum variation of Gc for two specimen with identical geometry calculated with the four models.

Model	Gc variation with thickness ratio	Gc variation for same thickness ratio (= 0.5)	Meassurement variation
Simple Beam	523	200	145
Simple Beam with correction for non linear behavior	450	101	102
Beam on Elastic Foundation	56	43	36
Beam on Elastic Foundation with corr. for shear defformation	31	22	21

The new model "beam on elastic foundation with a correction for shear deformation" is found to give the smallest variation of G_C as a function of both the beam thickness and beam thickness ratio. Both variations are less than 150% of the maximum measured variation in Gc for two specimens with identical geometry.

Correction for non-linear elastic behaviour reduces the variation of G_C as function of the beam thickness.

The optimal optimal beam thickness ratio (pure mode I) is not derived from these experiments. Decided is to use a beam thickness ratio for which the compliamce of both beams is equal according the "simple beam model" (beam thickness: PE 5.5 mm, PS 2 mm).

CONCLUSIONS

- A method is established to place a smooth block copolymer layer of known thickness at the interface without deuteration.
- The new model "beam on elastic foundation with a correction for shear deformation" is found to give the smallest variation of G_C as a function of both the beam thickness and beam thickness ratio.
- Correction for non-linear elastic behaviour reduces the variation of G_C as function of the beam thickness.

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