MICROMECHANICS OF CONFINED POLYMER LAYERS

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Introduction

In adhesion problems it is rarely possible to ignore the geometrical loading parameters. In certain cases, such as the adhesion between the layers of a multilayered polymer film, they are an integral part of the problem. The goal of our study is to investigate the coupling effects taking place between parameters at three different length scales:

- **Molecular** : transfer of stress between layers
- **Micro** : Plastic deformation close to the interface (1-100 µm).
- **Macro** : Global geometry + Elastic properties

As a simplified model system we used an A-B-A trilayer geometry where the two outside layers were thick (1-3 mm) and the central layer was thin (0.5-100 µm).

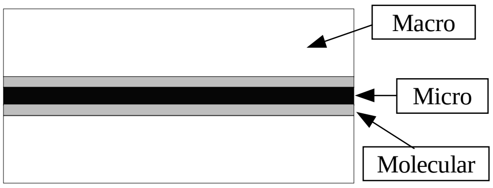

Figure 1 :Sample Geometry

The A and B polymers were polymethyl methacrylate (PMMA) and polystyrene (PS) or a blend of 80 % PS and 20 % poly2,6,dimethyl 1,4, phenylene oxide (PPO) (PS/PPO). Since PS and PMMA are immiscible, the stress at the A/B interface is transferred by a very thin (200-400 Å) layer of a PS/PMMA copolymer (random copolymer with 75% weight Styrene or 50k-50k diblock copolymer).
The copolymers were spun cast directly on the PMMA plates while the PS-based central layer, was doctor-bladed from solution onto a glass plate and subsequently transferred onto one of the PMMA plates. Eventually the two thick plates were joined at 160 °C for two hours under a light pressure producing effectively a 5-layer system. It should be noted that adding 20% w PPO to PS increased the crazing stress of the layer from 55 MPa up to 75 MPa without modifying the elastic modulus. Hence, the stress field near the crack tip was unchanged but the plasticity of the layer was modified. The outside PMMA plates were usually both 2 mm thick but asymmetric systems (3mm/1mm and 2mm/1mm) were also tested to investigate the influence of the global stress field.

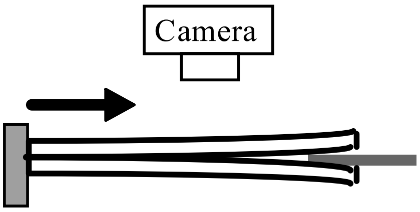

Figure 2 :Experimental Set-Up

The samples were tested in an Asymmetric Double Cantilever Beam test geometry where a wedge was inserted at constant velocity while measuring the length of the crack (various velocities were tested). The fracture toughness could be calculated using Kanninen's equations [1]. The samples were then observed microscopically (top and side) and microtome cuts were performed.

Main results

Several general comments can be made:
- The crack propagated at one of the interfaces only.
- The copolymers are necessary to obtain a good stress transfer (the fracture toughness of a trilayer without copolymers was around 30 J/m^2 independent of the thickness).
- The plastic deformation never affected the PMMA : even in the reverse geometry, the plastic deformation occurred in the PS only.
All the presented experiments were carried out at a crack velocity around 1 mm/min.
Fig 3 shows the fracture toughness of the PMMA-PS-PMMA interface as a function of the thickness of the PS layer h. Clearly in the regime investigated, G_c is strongly dependent on h. However interestingly the thickness dependence is not the same if a random copolymer (rd) or a diblock copolymer (db) is used as a stress transfer agent at the interface.

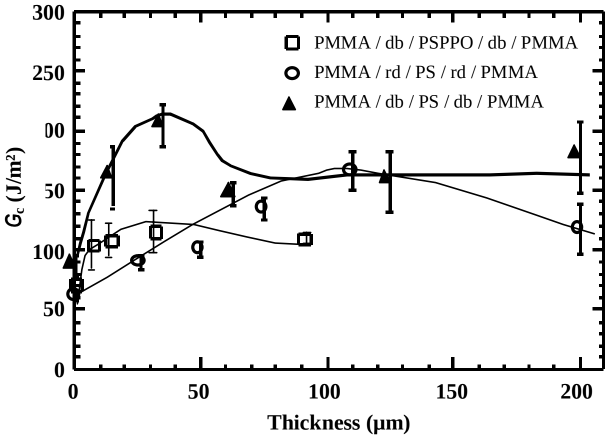

Figure 3 : Fracture toughness of PMMA/PS/PMMA assemblies as a function of the thickness of the PS layer.

Optical observations (fig 4) show that crazes develop at 45° related to the interface plane : These are very similar to the oblique crazes previously observed in PS/PMMA bilayers [2]-[3]. With both copolymers, there was a correlation between the maximum of G_c (for h around 35µm for the PS-PMMA diblock and 80 µm for the PS-r-PMMA) and the maximum density of oblique crazes inside the PS layer. This result suggests that an interfacial modification governs dissipation mechanisms far away in the layer.

For h>40 µm, a new kind of crack deviations in the PS layer appear : they start at a 90° angle relative to the interfacial plane and develop inside the volume of the layer (fig 5). They are presumably due to the internal stresses existing in the samples after their preparation [4] but don't have a great contribution to the energy dissipation as G_c increases with the number of surface cracks but does not exhibit any variation with the number of volume cracks.

The "micro" effect should also be considered. With a PS/PPO central layer and the diblock copolymer, the fracture energy became thickness independent : there were neither extended damages nor oblique crazes in the layer. That G_c value was well below the value obtained for a PS central layer since these dissipation mechanisms are inhibited. Thus, even with the same stress field and interfacial structure, the plastic deformation properties of the layer can control the fracture mechanisms.

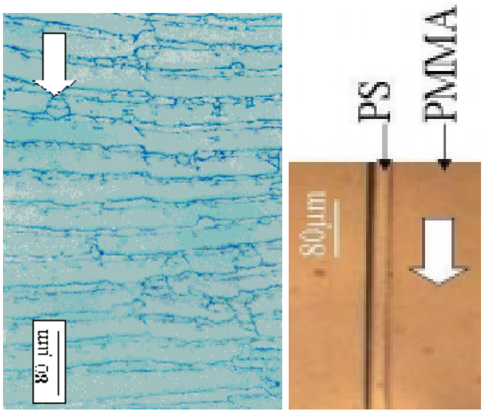

Figure 4 :Top & Side view of the fracture path Crack Deviations at 45°.

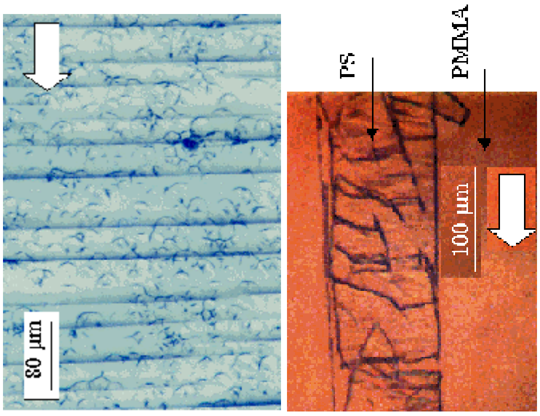

Figure 5 : Top & Side view of the fracture path. Crack Deviations at the Surface & in the Volume

The effect of the loading geometry (macro) is shown on fig 6. When the loading geometry is not symmetric, the crack clearly remains at the interface between the central layer and the thinner plate with little damages to the central layer : the fracture toughness is thickness independent beyond 0.5µm for both asymmetric geometries (3/1 and 2/1). The value of G_c for asymmetric samples is well below that obtained with the symmetric geometry since the dissipation mechanisms such as oblique crazes do not occur. Surprisingly, the symmetric system is the one where the external loading is the closest to pure Mode I but also the one where the confined layer is the most deformed. Every other ratio of beam thicknesses tends to send the fracture towards the thinner PMMA plate where it cannot go, and reduces the plastic dissipation inside the PS central layer. Presumably the « mode I » propagation is very unstable and small deviations from mode I due for example to surface roughness are enough to initiate crazes inside the PS layer.

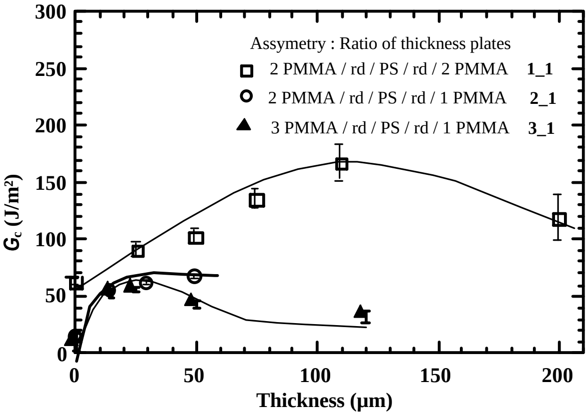

Figure 6 : Fracture toughness of PMMA/PS/PMMA assemblies. Effect of the mode mixity of loading

This system is very sensitive to even slight modifications of the stress fields. This is once more illustrated by the effect of the cooling mode : Samples of PMMA /rd/ 110 µm PS / rd / PMMA were cooled after pressing using 4 different modes (fig 7).

Once again, the maximum of G_c could be correlated with the presence of oblique crazes since the standard cooling process was the one that led to the maximum of residual shear across the interface.

- At very slow cooling rates, little residual shear stress is expected since the rubbery PS layer can reorganize to accommodate the differences in volume expansion.
- At very fast cooling rates, large tensile stresses in the center of the sample are obtained but very few additional interfacial shear stresses due to the T_g mismatch will be present since both the PS layer and the PMMA layer close to the interface cannot relax the stresses and as a result are both in tension.
- At intermediate cooling rates, one expects the central layer to be in tension and the T_g mismatch to be responsible for additional shear stresses at the interface.

Based on these results, the thermal residual stresses appear to modify the phase angle at the interface and favor the formation of oblique crazes in the PS layer

Conclusions

Despite the peculiar properties of PS (low crazing stress), this study clearly illustrates that the problem of a confined layer is controlled by the three length scales. In this system, every slight modification of the stress field can have a major influence on the global dissipation mechanisms and completely modify the measured G_c

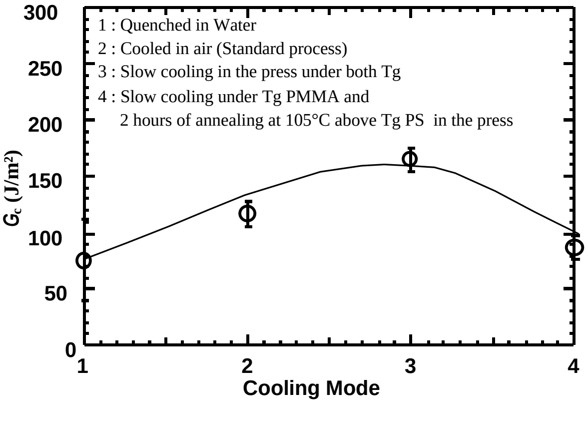

Figure 7 : Effect of the Cooling Modes on the fracture toughness.

- The **mode mixity** governs the adhesion mechanisms even if the elastic mismatch is very low. It has been also seen in other studies with PS/PMMA. [2] - [3].
- The **plastic deformation properties** of the layer are also an important factor controlling the fracture mechanisms : even with the same stress field, the plasticity of the layer plays a major part in the dissipation mechanisms.
- There is also an **interfacial control** of the micromechanisms. Not only does the nature of the interfacial molecular layer modify the maximum thickness of the main craze[5] but it also modifies the initiation process of oblique crazes ahead of the main crack.

References

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