

HOW TO OPTIMIZE THE ADHESIVE PROPERTIES OF BILAYER PRESSURE-SENSITIVE-ADHESIVES

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Introduction

Previous detailed mechanistic experiments of the debonding of PSA have shown that the failure mechanisms of PSA layers in a peel or probe test are dependent on the ratio between the interfacial resistance to crack propagation G_c and the bulk resistance to deformation represented by the elastic modulus E . PSA with high values of G_c/E form a fibrillar structure while PSA with low values of G_c/E tend to fail more interfacially¹.

Investigations of the adhesive properties of crosslinked elastomers on solid surfaces have shown that G_c is controlled both by the interface thermodynamics (through the parameter G_0 , the limiting value of the work of adhesion for vanishing crack velocities) and by the bulk dissipative properties of the elastomer². This is usually written as:

$$G_c = G_0(1 + \phi(a_T v))$$

Although the exact nature of the dissipative processes which are included in the dissipative component of G_c are not unambiguously defined, it is reasonable to think that the linear viscoelastic properties of the elastomer are a good indication of its more elastic or dissipative character. In other words a large value of $\tan \delta$ would lead to a more dissipative interfacial crack propagation.

If this conclusion is transferred to the mechanisms of debonding of PSA, which are much more viscoelastic than traditional elastomers, a more dissipative PSA layer would be more difficult to detach by an interfacial crack propagation mechanism and would readily form fibrils.

This is observed experimentally, however to make a PSA layer both soft (to satisfy Dahlquist's criterion) and dissipative, it is necessary to reduce the crosslinking level and shear resistance is typically poor. At the end a suitable optimization, where a balance between a high peel force and high tack on one hand and a good shear resistance on the other hand, is achieved.

However since the resistance to crack propagation G_c is mainly an interfacial property, while the shear resistance is mainly a bulk property, we explored the possibility to work with bilayer PSA, where an interface layer would be softer and more dissipative and the other more rigid and less dissipative.

Experimental

We performed our experiments focusing on two classes of materials, PSAs prepared from acrylic solutions and latexes. For the first class, the adhesive formulation

was a copolymer based on the following monomer composition: 2-ethyl hexyl acrylate (54%), acrylic acid (5%), ethyl acrylate (31%), and iso-octyl acrylate (10%). Additionally, the solutions contained different amounts of temperature activated crosslinking agent: the material denoted with the letter B had 0.015% of crosslinking agent while the D 0.035%. This difference in this crosslinking makes the material D more elastic than the material B. Adhesive films were made by deposition of precise volumes of solution on a substrate kept on a perfectly horizontal support. The solvents were evaporated at room temperature for a few hours. The films were then put in a vacuum oven at 130°C to allow the crosslinking reaction to take place. For bilayer systems the first layer of adhesive was prepared on a glass slide, while the second layer was first prepared on a release liner, and once dried and crosslinked, reversed and deposited onto the first layer.

The second class of materials were films prepared from acrylic latexes, where the main components were again 2-ethyl-hexyl-acrylate and methyl-acrylate. For both these latexes, denoted by the letters C and A the solid content was ~50%. For the PSA preparation, an excess amount of latex was deposited on a substrate and then doctor bladed in order to obtain the required thickness. The wet layer was then dried at room temperature for 24 hours.

Both the acrylic solutions and the latexes were provided by Cytec Surface Specialties.

In all the systems studied one layer was more dissipative (A or B), while the other one was more elastic (C or D). The top layer, in direct contact with the probe, had a thickness of ~35microns while the bottom one was approximately 75 microns thick. The results obtained for the bilayers have then been compared to those obtained from films of single layers of the materials with a thickness of ~110microns.

We performed probe test experiments on a custom-designed apparatus based on an MTS 810 hydraulic testing machine³. During the test, a flat probe approaches the PSA film on a microscope glass slide at a constant velocity. When the contact pressure of 1 MPa is reached, the probe stops during a contact time of 1s, and is then removed at a constant debonding velocity varying from 10 to 100µm/s. To test different surfaces a stainless steel probe and a probe coated with polyethylene were used. During this test a high resolution camera allows the observation of the debonding process.

Results and Discussion

We first discuss the results obtained on a polyethylene probe. In order to correctly understand the mechanical

results, we analyzed the debonding mechanisms observed for both single layers and PSA bilayers. The linear viscoelastic properties of materials A and B are shown on Figure 1. Although G'' is nearly identical for both materials for a ll frequencies.

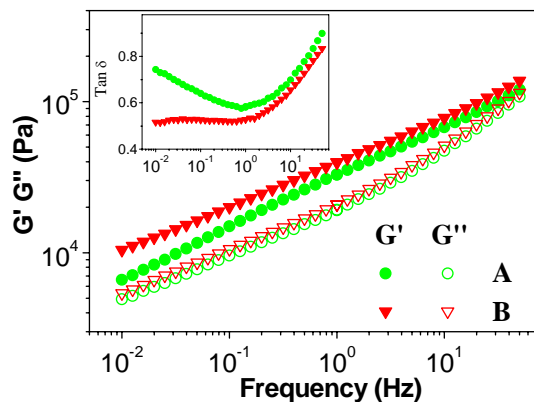


Figure 1: Linear viscoelastic properties of the two acrylic PSA (A and B) prepared from solution.

More interesting is the other configuration, with the more elastic layer directly in contact with the steel surface (A+C or B+D). In this case we observed a liquid-like behaviour with the formation of fibrils and fingers at the same time. However the presence of the thin layer of a more elastic adhesive on top influenced significantly the failure and we observed an adhesive fracture, with no residues of PSA left on the probe.

By considering the true contact area between the probe and the films, we obtained the *nominal stress-vs-strain* curves for all the system studied. The curves typically showed a peak in stress, corresponding to the beginning of cavitation, followed by a decrease of the stress to an almost constant value (plateau), due to the growth of fibrils. For the more elastic PSAs a strain hardening, where the stress value increases again, was observed. The adhesion energy was conventionally defined as the integral under the stress-strain curve.

On steel the materials C and D present a high value of the maximum stress σ_{max} and a marked strain hardening before the detachment. The films A and B have a lower peak and a low value of stress in the plateau. Since these materials are more viscoelastic and less crosslinked, fibrils formed can stretch more before being finally fractured and thus the extension of the plateau, ϵ_{max} , reaches high values of strain and failure is cohesive.

The bilayers A+C and B+D, if compared respectively to A and B, show an increase in σ_{max} and in the level of the plateau. Moreover they present a very similar σ_{max} , thus the adhesion energy is higher. These results imply that the configuration (more dissipative layer)+(more elastic layer) could be used to improve the adhesion on high energy sur

Different results were found on polyethylene. In Figure 3 the *stress-vs-strain* curves obtained are displayed for the adhesives made from acrylic solutions. The adhesion energy of B on PE is much higher than that of the D film where no plateau is observed. As shown in the figure, both bilayer configurations improve the adhesion energy. The bilayer B+D, compared to single layers B and D, shows a higher peak and an increase in the plateau level, while the extension ϵ_{max} remains similar to the one found for B. The best tack results are obtained with the bilayer D+B, that combines a soft dissipative layer near the interface with the probe with a more cohesive layer as backing: this film shows a higher and longer plateau. It should also be observed that in this case a small strain hardening is also observed before the detachment, due to the elasticity of the D layer on the bottom of the PSA. The adhesion energy in this case is substantially increased relative to either B or D alone.

From these results we can conclude that a bilayer configuration, where a more dissipative layer is on top of a more elastic one, could be used to improve adhesion on low energy surfaces.

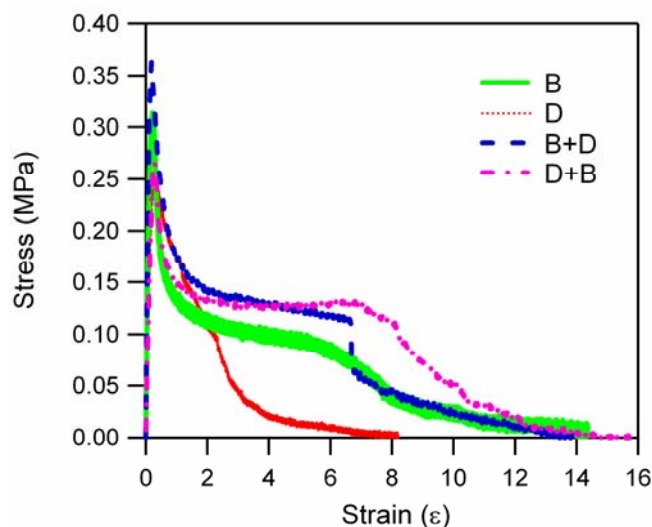


Fig.3: Nominal stress-vs-strain curves obtained for the single layers of materials B and D, and for the bilayers B+D and D+B on polyethylene. The debonding speed was 10microns/sec.

Conclusions

To conclude, our results show that adhesive properties can be significantly modified by using bilayer systems, and that the use of a gradient in composition is an interesting option to improve adhesion. The adhesion properties of the two layers are very important in determining the adhesion of the bilayer, and to enhance the adhesion a very dissipative layer and a more elastic one are needed. The order of the layers plays an important role. On high energy surfaces like steel the combination dissipative (backing)+ elastic(top) layer appears to increase the work of adhesion of

the PSA: in this case, while we observe a liquid-like debonding, the mechanism is not cohesive, and the presence of the more elastic layer on the top avoids the transfer of the adhesive on the probe.

The opposite configuration, with the dissipative layer on top of the elastic one, gives better results on a low energy surface like polyethylene, where the composition gradient in the film improves considerably the adhesion.

References

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