

Direct Observation Of Cavitation And Fibrillation Processes In Model Acrylate PSA's

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INTRODUCTION

While some progress has been made recently on the understanding of the adhesion of Pressure-Sensitive-Adhesives[1,2], the microscopic mechanisms which are responsible for their ability to adhere on almost any substrate are still not known in detail. Zosel has pointed out that a necessary condition to have good pressure-sensitive adhesive properties is the development of a fibrillar structure upon debonding[3]. In order to further investigate that aspect, we have developed in our laboratory a probe tack experiment, schematically described on figure 1, which allows the observation of the deformation mechanisms of the adhesive in real time, while the force-displacement curve is being acquired.

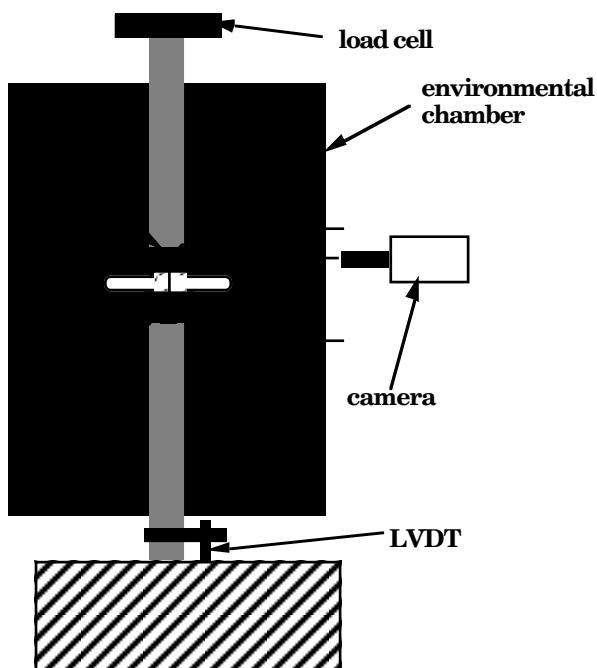


Figure 1: Schematics of the instrumented probe tack apparatus

In that experimental geometry, a flat ended probe of 1 cm diameter is brought in contact with an adhesive film approximately 100 μm thick previously applied onto a glass substrate. The time of contact and mean pressure are controlled and the probe is then removed at constant velocity. The tensile force exerted by the adhesive on the probe and the probe displacement are recorded during the whole experiment. The use of a glass substrate allows the observation (through the substrate) of the deformation mechanisms of the adhesive and in particular of the nucleation and growth of cavities during the debonding phase as well as the identification of the time at which these different stages occur in the force-displacement curve. The very low compliance of the instrument can be precisely measured and subtracted from the experimental curve to obtain the true deformation curve of the adhesive film. This high rigidity also provides a much better reproducibility in the results relative to a commercial probe tack instrument.

MODEL SYSTEMS

We use several acrylate polymers as our model PSA's. Two emulsion polymers of poly (2-ethylhexyl acrylate) with and without 2% acrylic acid comonomer (PEHA-AA and PEHA respectively) have been provided by Elf-Atochem and are representative of a latex-based adhesive. These polymers are however difficult to characterize on a more molecular level since they have a very wide molecular weight distribution including some very high molecular weights. In order to have better control over the molecular structure, we also synthesized by anionic polymerization several poly (tert-butyl acrylates) of different molecular weights (from 6k to 800k). The tert-butyl group was then substituted with an n-butyl group by a transesterification reaction. This synthesis route leads to polymers which contain a small amount (a few percent) of acrylic acid groups. In order to remove completely these acid groups we reacted the polymer with diazomethane to methylate the side groups. These polymers have a very well defined molecular structure and will be used to investigate in more detail the effect of molecular weight, molecular weight distribution and of the presence of acrylic acid on the adhesive properties.

EXPERIMENTAL PROCEDURE

In our experiments, the temperature (-20 $^{\circ}\text{C}$ to 50 $^{\circ}\text{C}$) and the debonding rate (1 $\mu\text{m/s}$ -1 cm/s) were the main experimental parameters which were varied. The contact pressure was usually fixed at 1 MPa and the time of contact was fixed at 1 s.

The results will be presented as stress vs. strain where the stress is the force divided by the true area of contact (as obtained from the video) during the compression phase, and the strain is the displacement of the probe normalized by the initial thickness of the film. A typical curve for PEHA-AA is shown on figure 2. From such a curve one can extract

the maximum stress, maximum strain and adhesion energy per unit area of contact.

In addition to the stress vs. strain curve, we recorded the bonding and the debonding stage and this provided considerable amounts of information on the precise evolution of the mechanisms with time.

In particular, we observed that in all cases, the maximum stress corresponded to the widespread nucleation of cavities, at the interface between the probe and the film. The appearance of these cavities is a direct result of the negative hydrostatic pressure applied to this very constrained film. A characteristic view of these cavities is shown on figure 3.

The average size and size distribution of these cavities was characterized as well as the kinetics of their growth.

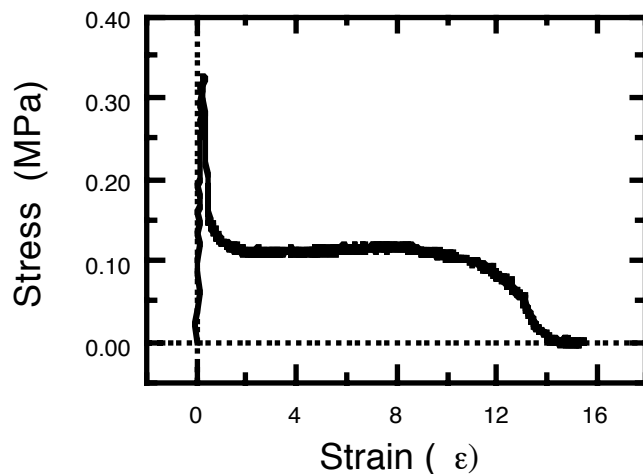


Figure 2: Typical stress-strain curve of a PEHA-AA adhesive

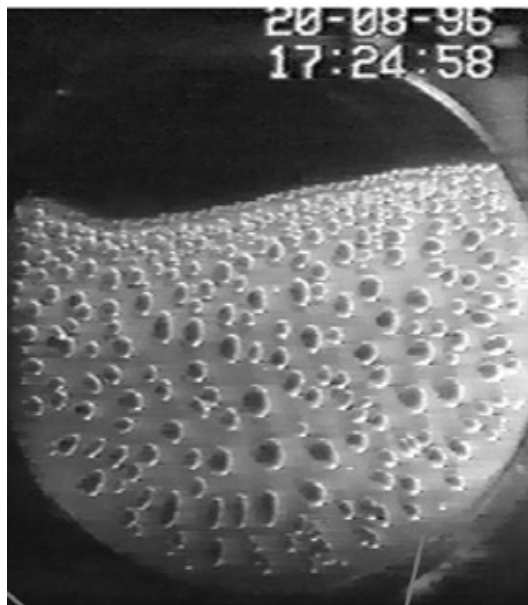


Figure 3: Typical cavities nucleated at the interface between the probe and a PEHA-AA film.

RESULTS

As pointed out earlier by Zosel[3,4], one can differentiate three main types of curves. A "brittle" curve or type I, where the stress decreases quickly to zero after reaching a maximum; a fibrillar curve or type II, which is illustrated on figure 2, and a cohesive fracture curve or type III, where the stress decreases continuously from the maximum to zero at a moderate rate.

We observed the type I curve at low temperatures and high strain rates but curiously also at the highest temperatures and lowest rates for the PnBA polymers and for the PEHA. The type II curve was observed for PEHA and PEHA-AA at intermediate temperatures and rates, while type III curves were observed mostly for the PnBA polymers at high temperatures and intermediate debonding rates.

For almost all experimental conditions one can make the following observation:

The cavitation stress increases with debonding rate and with decreasing temperature. This variation is well correlated with that of the storage shear modulus G' measured in a parallel plates rheometer so that one can easily construct a master curve using the same shift factors a_T obtained rheologically. This result is in agreement with the analysis done by Gent and coworkers[5,6] on the cavitation of crosslinked rubber.

This correlation between G' and the cavitation stress is no longer true for very low temperatures where the area of contact may not be complete.

The same master curve can be built for the adhesion energy provided that one remains within the range of conditions where the type of stress-strain curve remains the same.

It is not possible to apply t-T superposition for the adhesion energy of two different types of curves.

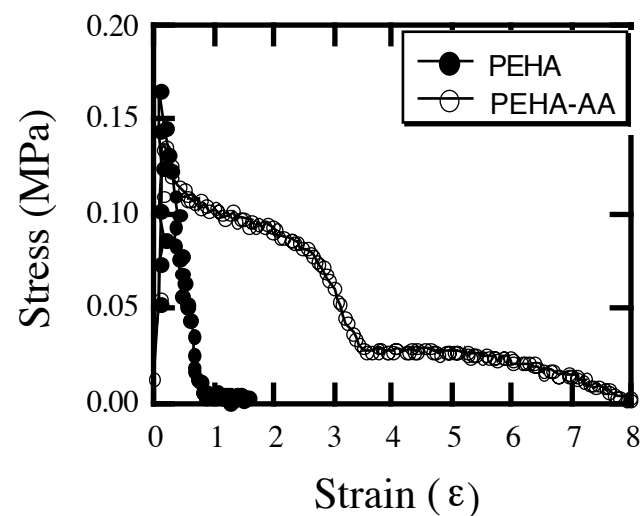


Figure 4: Stress-Strain curves of two PEHA adhesives at 50 °C and 1 μm/s

The combined use of the stress-strain curve and of the video give us a better insight into those observations. In particular it is possible to explain the type I curve that one observes at high temperatures by a viscous liquid behavior of dewetting under pressure. As an example, the stress-strain curves of PEHA-AA and PEHA at 50 °C and 1 μm/s are shown along with a snapshot of their debonding pattern.

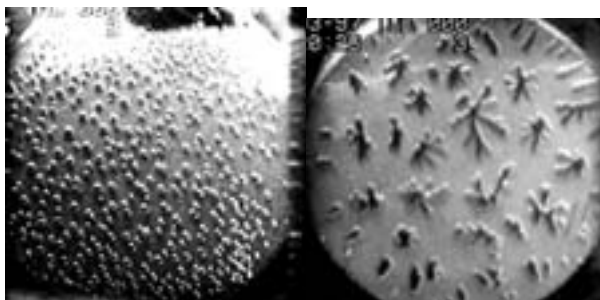


Figure 5: Snapshots of the debonding pattern of a PEHA-AA (left) and a PEHA (right). The corresponding stress-strain curves are shown on figure 4.

From the systematic observation of the video sequences a general pattern emerges: For the acrylate PSA's the cavities initially formed expand and form a honeycomb structure with very fine walls between the cavities. These walls are stretched in the tensile direction and will form a fibrillar structure which will grow at a relatively constant stress (for the emulsion polymers) and eventually fail, either by the fracture of the cell walls (cohesive fracture) or by the debonding of these walls from the probe (adhesive fracture). Within this general pattern, the size and shape of the cavities as well as the maximum elongation of the fibrils are strongly influenced by the experimental conditions and by both the nature of the probe surface and the rheological properties of the adhesives. Some general trends will be presented.

Effect of the Surface of the Probe

Interestingly, for those relatively soft adhesives, the cavitation stress is not influenced much by the nature of the surface of the probe (steel, glass, polystyrene, polydimethylsiloxane) but is more influenced by the roughness of the substrate. On the other hand the adhesion energy and in particular the eventual mode of failure of the fibrils (cohesive or adhesive) are more strongly influenced by the nature of the probe surface. We were not able however to directly correlate the surface energy of the probe surface with the measured adhesion energy, suggesting therefore that other parameters are relevant such as the molecular mobility at

the interface[7] or the degree of interpenetration between the probe and the adhesive (for polymeric probe surfaces).

Effect of the Molecular Structure.

For the two emulsion polymers prepared from a latex, the presence of 2% acrylic acid had a profound influence on the adhesive properties. The maximum extension of the fibrils was greatly decreased by the presence of AA comonomer. On the other hand the value of the stress on the plateau was increased by the presence of AA.

Concerning the microstructure, the cavities formed with the PEHA-AA were much smaller than for the PEHA. This was interpreted as a sign of a stronger interaction with the surface of the PEHA-AA.

The eventual failure of the bond occurred much more adhesively for the PEHA-AA polymer than for the simple PEHA. While this results appears counterintuitive, it simply reflects the fact that the strain hardening of the PEHA-AA fibrils is much more pronounced than for the PEHA.

The molecular structure of the model PnBA shows several differences with that of the PEHAs. These polymers were monodisperse and of lower molecular weight than the PEHA's. Furthermore the samples were prepared by casting from solution.

Despite the fact that the study of these materials is so far less extensive than that of the PEHA's emulsion polymers, several points can already be made:

The energy of adhesion shows a relatively sharp maximum with molecular weight. The low molecular weight sample ($M_n = 100$ k) behaves in a liquid like manner and the high molecular weight sample ($M_n = 800$ k) does not form any fibrils. The deformation occurs through the formation of cavities similar to those obtained with the emulsion polymers. However the maximum extension of the fibrils is greatly reduced. More systematic trends on the effect of molecular weight, of the presence of AA as a side group and on the effect of the probe surface will be presented.

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