

RHEOLOGICAL AND ADHESIVE PROPERTIES OF MODEL ACRYLIC ADHESIVES

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Introduction

Acrylic copolymers are widely used as pressure-sensitive-adhesives. When properly designed they combine a low glass transition temperature, low plateau modulus and excellent temperature and oxidation stability. However little published information exists on the optimal design of PSA based on acrylic copolymers.

As a part of a more comprehensive study, we present here selected results obtained by using an instrumented probe method to test the adhesive properties of model acrylic copolymers designed for PSA applications. In order to keep the system simple we have used unformulated acrylic copolymers synthesized by free radical polymerization in solution and subsequently crosslinked in the solid state with a Ti-chelate. The base monomer was always 2-ethylhexyl acrylate (EHA) while two comonomers were used: acrylic acid (AA) and stearyl acrylate (StA) as examples of a polar and an apolar comonomer. The expected effects would have been a general improvement of the adhesive properties for the AA and a decrease in adhesion in the case of StA.

Experimental

The copolymers were synthesized in solution and the weight fraction of comonomer were: 2,4 and 8% for acrylic acid and 2% AA with 10,20 and 30% stearyl acrylate. Before the crosslinking step, all copolymers had an identical weight average molecular weight of 1500 kg/mole and a degree of polydispersity varying between 5 and 8. After crosslinking they all had an insoluble fraction (as determined by Soxhlet extraction) of 60%.

Adhesive films were prepared by bar coating and subsequently crosslinked thermally. The films, prepared between two sheets of release paper were then deposited on standard microscope glass slides for the probe testing. We tested the adhesive properties with a probe test using a flat ended probe which was brought into contact with the adhesive for 1 s contact time and at a maximum compressive pressure of 1 MPa. The probe was subsequently removed at a constant velocity varying between 1 and 1000 $\mu\text{m/s}$ [1]. The surface of the probe was stainless steel polished to an average quadratic roughness around 10 nm.

From the experimental Force-displacement curve, we extracted a nominal stress (σ) vs. nominal strain (ϵ) curve

where $\sigma = F/A_0$ and A_0 is the maximum area of contact, and $\epsilon = (h-h_0)/h_0$.

In order to characterize the rheological properties of the adhesive, we also performed small-strain oscillatory tests in a parallel plate rheometer.

Results

The master curves of the elastic part of the complex modulus G' and of the dissipative factor $\tan \delta$ at 25°C are presented on figure 1 and 2 for the series of copolymers with variable amounts of AA. It is clear that the addition of acrylic acid has two effects on the small-strain rheological properties: an increase in the glass transition temperature and an increase in the plateau modulus. In the range of frequencies used for probe tack experiments (0.01-10 Hz), the dominant factor will be the increase in plateau modulus.

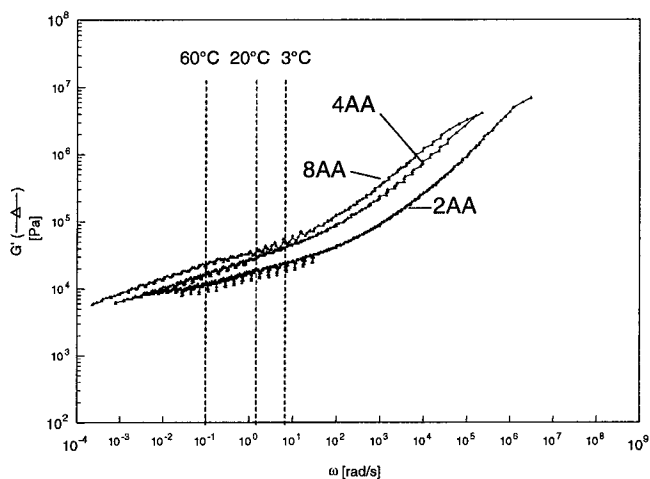


Figure 1: Elastic modulus G' of the three acrylic adhesives with variable amounts of Acrylic Acid. The dashed lines represent the reduced frequency at 25°C corresponding to 1 Hz at the marked temperature.

On the other hand the incorporation of stearyl acrylate does not have much effect on the glass transition temperature but has an effect on the modulus which decreases with increasing StA content (not shown here). Since in this regime E' is controlled by the average molecular weight between entanglements, one can deduce from these results

that M_c increases with increasing StA content and decreases with increasing AA content.

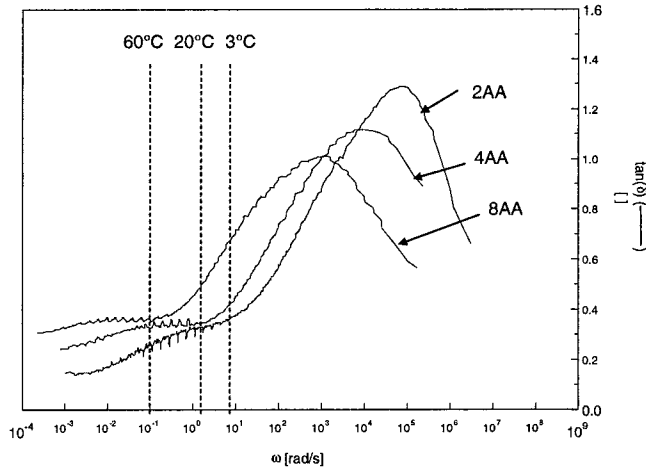


Figure 2: Dissipative factor $G''/G' = \tan \delta$, of the three acrylic adhesives with variable amounts of acrylic acid. The dashed lines represent the reduced frequency at 25°C corresponding to 1 Hz at the marked temperature.

Representative σ - ϵ curves at room temperature for the three different AA contents are shown on figure 3 for a debonding velocity of 1000 $\mu\text{m/s}$. The change in monomer composition has an important effect of the peak stress σ_{max} and on the plateau stress. On the other hand the maximum extension of the plateau (ϵ_{max}) is not much affected, within experimental reproducibility, by the change in comonomer. A similar remark can be made for the copolymers with increasing StA content shown on figure 4.

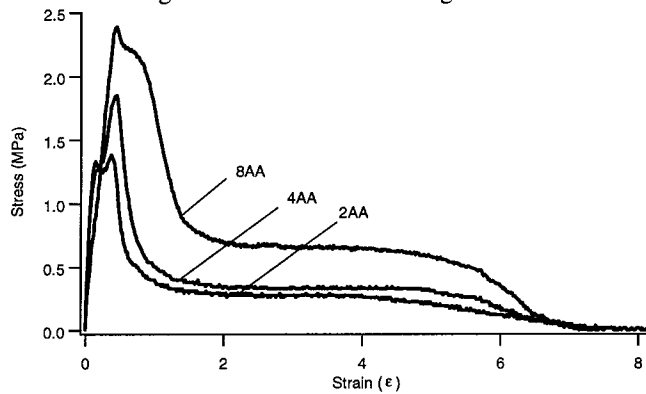


Figure 3: Representative σ - ϵ curves for the three acrylic adhesives with variable amounts of AA. $V_{deb} = 1000 \mu\text{m/s}$, $T = 22^\circ\text{C}$.

In order to further analyze the results provided here we have performed tack tests at different temperatures (3°C and 60°C). We have attempted to apply the time-temperature superposition principle to the main parameters that can be extracted from the probe tests, namely, σ_{max} , the peak stress, ϵ_{max} the maximum extension at failure and W_{adh} the adhesion energy.

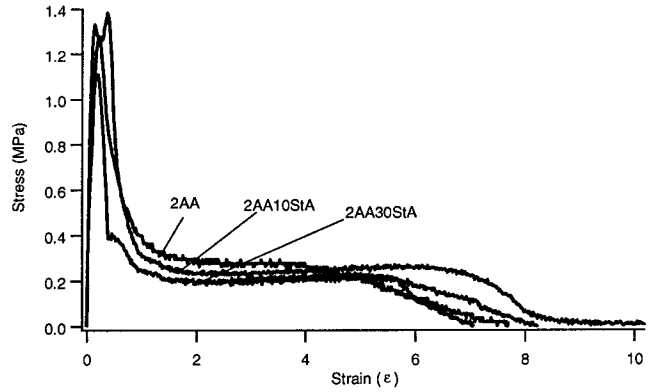


Figure 4: Representative σ - ϵ curves for the three acrylic adhesives with variable amounts of stearyl acrylate and 2% AA. $V_{deb} = 1000 \mu\text{m/s}$, $T = 22^\circ\text{C}$.

The shift factors obtained from the rheological measurements have been used to shift the data along the debonding rate axis. For the peak stress σ_{max} , the situation is quite clear: the peak stress increases with reduced V_{deb} and is directly correlated with the change in elastic modulus G' (compare figures 5 and 1)

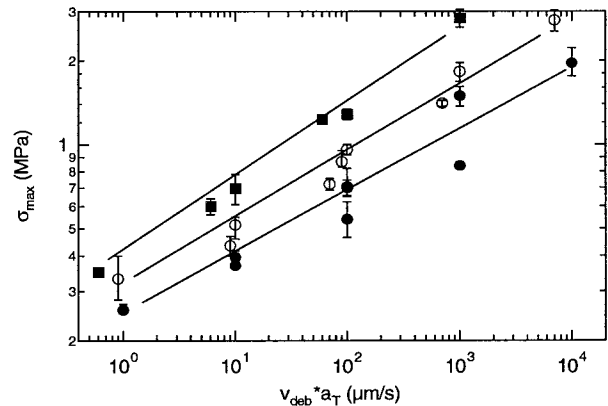


Figure 5: Peak stress σ_{max} as a function of reduced debonding velocity for the three adhesives containing variable amounts of AA. (\blacksquare) 8AA; (\circ) 4AA; (\bullet) 2AA. The lines are guides for the eye

However the video observations of the debonding process show that three types of mechanisms of debonding can occur depending on average strain rate and temperature. At low temperature/high strain rate, failure occurs by brittle fracture at the interface after the rapid nucleation of some cavities. This type of mechanism is only observed for the 8AA at $T = 3^\circ\text{C}$ and $V_{deb} = 1000 \mu\text{m/s}$ and causes an abrupt drop in stress after the peak stress without any fibrillation plateau. In the second regime, at intermediate temperatures and strain rates, a marked plateau in stress is observed after the peak stress (figure 1) and the observed maximum extension is mostly controlled by the degree of crosslinking of the adhesive with a slight effect of the monomer composition. Finally at low strain rate/high temperature the plateau becomes less and less marked and the maximum extension decreases with decreasing reduced V_{deb} . The most revealing method to characterize this be-

havior is to monitor the maximum extension ϵ_{max} which varies with $a_T V_{deb}$ as shown on figure 6 for the series with variable acrylic acid content.

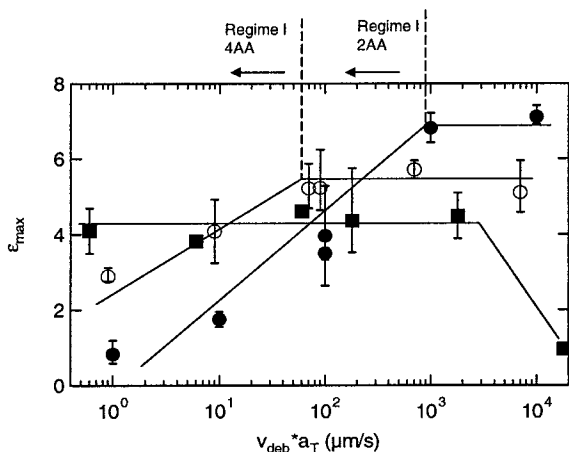


Figure 6: Maximum extension ϵ_{max} as a function of reduced debonding velocity for the three adhesives containing variable amounts of AA. (\blacksquare) 8AA; (\circ) 4AA; (\bullet) 2AA. The lines are guides for the eye. The dashed lines represent V^* for the 4AA and 2AA copolymer.

Two regimes are clearly visible: at low reduced velocity (regime I) ϵ_{max} increases with V_{deb} while at high reduced velocity, ϵ_{max} becomes roughly independent of V_{deb} . These regimes are identical to those observed for styrenic block copolymer based PSA[2] and can be interpreted in terms of competition between interfacial crack propagation and extension of the fibrils. For a given applied stress on the probe, the velocity of crack propagation directly depends on the rate of energy dissipation at the edge of the propagating crack which is characterized by the parameter G_c [3]. The extension of the fibrils depends on the other hand directly on the nonlinear elastic properties of the adhesive in extension, which are not known. As a simplification, we will assume that the Young's modulus E is the controlling parameter there, i.e. the lower the modulus and the larger the extension for a given applied tensile stress.

The measured maximum extension of the fibrils in regime I depends then on the ratio G_c/E which has the dimension of a distance. A high value of G_c/E favors a high ϵ_{max} while a low value favors interfacial debonding and a low ϵ_{max} . Since the rate dependence of G_c is always more pronounced than that of E [4], a low V_{deb} favors interfacial crack propagation. On the other hand in regime II, G_c has increased significantly and as a consequence the interfacial crack propagation has slowed down or stopped altogether (this can be seen by noting that the size of the cavities tends to stabilize), ϵ_{max} becomes independent of V_{deb} and is controlled mainly by the nonlinear elastic properties of the adhesive in extension, i.e. for these acrylic adhesives, mainly by their degree of crosslinking.

We define a critical reduced velocity at room temperature: V^* for the transition between a variable ϵ_{max} and a constant ϵ_{max} value. When comparing different adhesives at a given

V_{deb} , a high G_c/E causes V^* to be low while a low G_c/E causes the opposite effect.

The effect of the comonomers in the composition can be seen on figure 7, where V^* is plotted for the different compositions used in this study. Clearly AA shifts the useful range towards low frequency implying good long term strength (permanent applications) while StA shifts the range slightly towards high frequencies (removable applications)

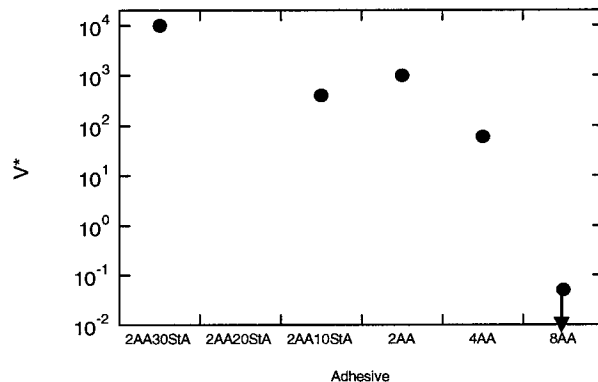


Figure 7: Critical reduced probe velocity at which a transition between an interfacial debonding mechanism to a bulk debonding mechanism is observed for different adhesives. (see text). For the 8AA, V^* is outside of the experimental range, as shown by the arrow.

Conclusion

We have shown that by changing the monomer composition of the acrylic PSA it is possible to shift the useful range of the adhesive in the temperature-frequency domain. In particular the addition of AA significantly increases the interfacial interactions and extends the useful range of the adhesive to higher temperatures, while the addition of StA has the opposite effect by extending the useful range of the adhesive to lower temperatures. One should be however cautious in interpreting this data as evidence that, given enough time, all PSA will eventually reach the interfacial debonding mechanism and spontaneously detach from the substrate. It is unclear at the moment whether the time-temperature equivalence which we have assumed here really applies in all cases and further investigation is needed.

References

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