

ADHESION OF MONODISPERSE ACRYLIC POLYMER MELTS TO SOLID SURFACES

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1. INTRODUCTION

Recent experiments[1] have shown that the debonding of a pressure-sensitive-adhesive (PSA) from a flat punch occurred with the formation of cavities at the interface which then evolve into a fibrillar structure. In this previous study the samples were commercial acrylic adhesives (Poly Ethyl Hexyl Acrylate: PEHA) showing a broad molecular weight distribution with significant chain branching. In the present study we show that these mechanisms are still observed when the adhesive is an acrylic linear polymer (PolyNButyl Acrylate: PNBA) with a narrow molecular weight distribution. Then we investigate the effect of the molecular weight on the peak of stress, the type of rupture and the adhesion energy.

2. SYNTHESIS OF THE POLY N-BUTYL ACRYLATE

The Poly tert-Butyl Acrylate (PTBA) precursor was synthesized by living anionic polymerization at -78°C in Tetrahydrofuran in the presence of lithium chloride[2]. The PTBA was then converted into PNBA by an acid-catalyzed transalcoholysis in n-butyl alcohol with p-toluene sulfonic acid. Four molecular weights of PNBA ($M_n = 100, 180, 294$ and 860 kg/mole) were made with a degree of polydispersity varying between 1.1 and 1.3.

3. RHEOLOGICAL CHARACTERIZATION

Parallel plate rheometry provided the shear viscoelastic properties of the adhesives which were typical of linear monodisperse polymers. The main difference between the different PNBA samples was the frequency above which it became a rubber-like material. This frequency decreased with molecular weight. However, in the rubbery plateau region, the storage moduli $G'(\omega, T)$ of all

the PNBA were constant at about $G^0 \approx 0.15$ MPa, thus the average molecular weight between entanglements is $M_e = \rho RT/G^0 \approx 22$ kg/mole. Shift factors a_T were determined from the shear modulus master curves.

4. FLAT PUNCH ADHESION TEST

The flat surface of a sanded stainless steel cylinder ($\varnothing=1\text{cm}$) came into contact with an adhesive layer $75\mu\text{m}$ thick. When the pressure of contact reached 1 MPa, the position of the punch was fixed for 1s and then the probe was removed at a constant velocity. For all the PNBA samples, the tests were performed at three different temperatures ($-10, 23$ and 60°C) over four decades of debonding velocities (1 to $10^4 \mu\text{m/s}$). A mirror inclined at 45° under the transparent glass slide allowed us to observe the successive separation processes [1].

5. STRESS STRAIN CURVES AND VIDEO OBSERVATIONS

A typical stress vs. strain curve and video images of the flat punch test of PNBA are shown on Fig.1. The synchronization between image and force curve made it possible to attribute the main features of the stress-strain curves to specific micromechanisms.

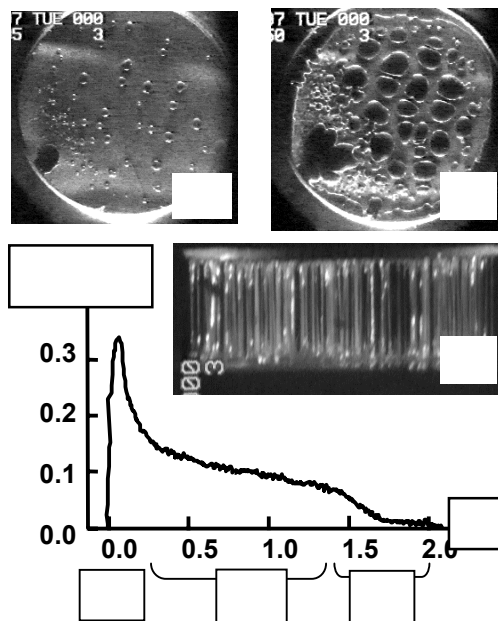


Figure 1: Synchronization of the debonding micromechanisms with the average-stress strain curve (A: cavitation, B: expansion, C: fibrillation)

After homogeneous deformation of the film under the punch ($\epsilon < 0.1$), cavities ($\varnothing=0.3$ mm) appeared randomly all over the area of contact (picture A). The slope of the nominal stress vs. strain curve decreased until it reached its zero value corresponding to the maximum value of the nominal stress σ_{max} at $\epsilon=0.1$. At this strain level all the cavities were already present ($\varnothing=1\text{mm}$). Then the stress decreased progressively to zero in an analogous way to

what is observed for low molecular weight uncross-linked polymers[3]. The pronounced plateau observed in the previous study with PEHA was never observed in this case. Again unlike the PEHA, the video records showed that the lateral growth of the cavities (in the plane of the film) and the vertical growth (out of plane) were simultaneous processes rather than sequentially separate mechanisms observed with the PEHA.

Eventually only small areas of polymer stayed bonded to the probe and the side view of the picture C shows the extension of such fibrils ($\varnothing \approx 0.5\text{mm}$) which eventually failed cohesively.

5.1. Part A: Maximum of stress and molecular features

The driving force for the cavitation process in a predominantly elastic medium is the release of elastic energy[4,5]. If this idea is extended to a viscoelastic material, one expects the critical stress for unstable growth of cavities to be proportional to the real part G' of the dynamic shear modulus of the adhesive. Since in our experiments the maximum stress is the parameter most directly related to the cavitation process, we tried to build master curves of σ_{\max} using the shift factors of the dynamic shear measurements. Fig.2 shows that the σ_{\max} values for the PNBA 294 kg/mole polymer do not fall on a single line.

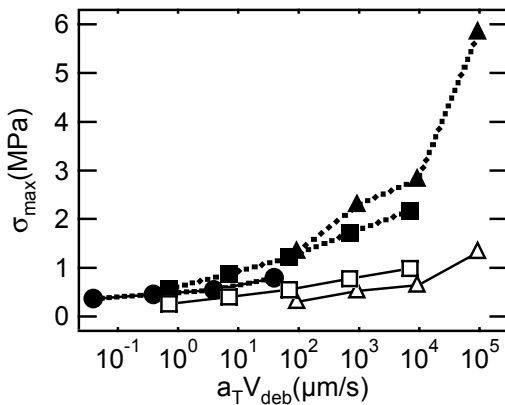


Figure 2: σ_{\max} master curve before (empty symbols) and after the area of contact correction (filled symbols) (PNBA 294 kg/mole, $T_{\text{ref}}=20^\circ\text{C}$, \bullet 60, \blacksquare 23, \blacktriangle -10°C)

This lack of time-temperature superposition might be due to a different real area of contact between the probe and the film during the bonding stage. The real area of contact of an elastic film on a rough surface depends on two parameters: the elastic modulus at the bonding frequency (G') and the relaxation properties of the polymer which govern the change of the real area of contact A_I with time for a given imposed displacement. Commercial acrylic adhesives like PEHA have a very broad spectrum of relaxation times, and in particular, low molecular weight fractions provide the fast relaxation

times necessary to achieve a large real contact area within a short contact time (typically 1s). In the case of the monodisperse PNBA's, these low molecular weight fractions are absent and the contact area depends mostly on the elastic properties of the polymer at the bonding frequency. Creton & Leibler[6] proposed that

$$A_I \propto \frac{P_c}{G} \text{ if } G \geq 0.1 \text{ MPa}$$

for an elastic material. Based upon this assumption, an approximate correction has been applied to the nominal area of contact:

$$A_I(T) \propto A_I(T_0) \frac{G(T_0)}{G(T)}$$

when the temperature changed from T_0 to T . We considered that at $T_0=60^\circ\text{C}$ the area of contact was maximum. The filled points on figure 2 show that after the correction if σ_{\max} is plotted as a function of $a_T V$, the points reasonably fit a master curve for the PNBA 294 kg/mole. So our conclusion is twofold: cavitation process is indeed governed by the viscoelastic properties of the adhesives and low molecular weight fractions in PSA's are important for the formation of the contact.

Part C: Maximum strain and type of rupture

After considering the cavitation process, we now focus on part C of the curve, i.e. the fibril stability and the fracture. The microscopic mechanism occurring during this process is the elongation of the fibrils. The question here is how does the molecular weight of the polymer affect the extension of the fibrils before fracture?

Let's begin with a very general picture of the type of fracture: for all the PNBA's except the highest molecular weight (860 kg/mole) whose separation was always adhesive, the rupture was cohesive at low reduced strain rates, and became adhesive at high reduced strain rates. The distinctive feature of these linear monodisperse

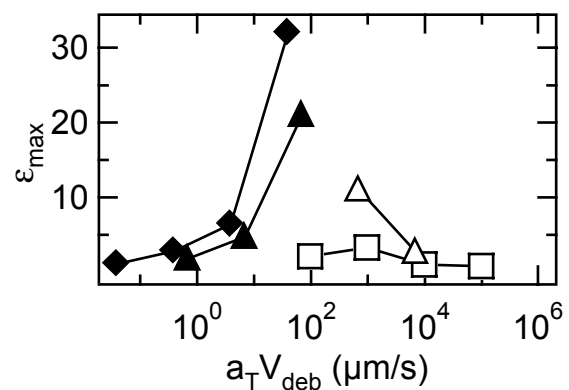


Figure 3: ϵ_{\max} master curve with adhesive (empty symbols) and cohesive (filled symbols) fracture (PNBA 294 kg/mole, $T_{\text{ref}}=20^\circ\text{C}$, \bullet 60, \blacksquare 23, \blacktriangle -10°C)

samples is that the transition from cohesive to adhesive failure with increasing strain rate always corresponded to

a maximum in the value of ϵ_{\max} vs. strain rate as shown on Fig.3. However the strain rate at which the cohesive-adhesive transition and the maximum in ϵ_{\max} occurred increased when the molecular weight decreased. A simple qualitative picture by of the deformation and failure of a single fibril may explain this result. Indeed the failure may occur by

1. disentanglement of the polymer chains
2. fracture of the polymer chains
3. debonding of the fibril from the punch

In the first process, the maximum strain of the fibril ϵ_{\max} is controlled by the product $\tau_d d\epsilon/dt$ where τ_d is the terminal relaxation time of the polymer ($\tau_d \propto M^3$ and decreases with temperature) and $d\epsilon/dt$ is the local strain rate ($d\epsilon/dt \propto V_{\text{deb}}$). This means that both the fibril stress σ_{fibril} and ϵ_{\max} increase continuously as $V_{\text{deb}} M^3$ increases because disentanglement becomes more difficult. If the failure mechanism is not disentanglement but debonding (process 2 or 3) the critical stress σ_r sustainable by the interface fibril/punch is the rupture criterion. one expects σ_r to be constant so in this regime, ϵ_{\max} decreases with $V_{\text{deb}} M^3$ since

$$\epsilon_{\max} \propto \frac{\sigma_r}{V_{\text{deb}} M^3}$$

The transition from one mechanism to another occurs when the fibril stress just increases above σ_r . At this point, ϵ_{\max} reaches its maximum value. If σ_r is independent of temperature and σ_{fibril} is uniquely dependent on $V_{\text{deb}} M^3$, the value of $a_T V_{\text{deb}}$ at which this transition is observed should scale with M^{-3} .

This is qualitatively observed but not quantitatively. The main reason being the fact that the prediction of ϵ_{\max} in the cohesive regime from shear rheometry is not correct. Elongational rheometry, a technique which is much more sensitive to molecular weight and architecture should be used instead.

5.3. Part B: Formation of fibrils

We will finally consider the part B of the process described on figure 2. In order to form a fibrillar structure, the growth rate of the cavities out of the plane of the film must be higher than the in-plane growth rate. We have evidence that this ratio is also controlled by a product $V_{\text{deb}} \tau$ (where τ is no longer clearly identified with the terminal relaxation time) and goes through a maximum at an intermediate value[7]. The two limiting cases being interfacial dewetting ($V_{\text{deb}} \tau \ll 1$) and brittle interfacial fracture ($V_{\text{deb}} \tau \gg 1$). The transition from fibrillar fracture to brittle fracture was fairly abrupt and for PNBA samples occurred at roughly the same value as the cohesive to adhesive transition. This result has an important practical implication: with such monodisperse polymers one could not have a fibrillar (and therefore dissipative) and adhesive (and therefore no residual

polymer on the surface) fracture, which would make them useless as PSA's.

6. ADHESION ENERGY AND MOLECULAR FEATURES

The adhesion energy is the integral under the stress-strain curve which can be divided into two parts. Firstly, the energy dissipated under the peak is directly related to the maximum nominal stress which is a non-trivial function of the shear modulus due to the poor bonding conditions discussed earlier. And secondly, the tail of the curve is related to the dissipative processes occurring during the lateral and vertical growth of the cavities.

A first experimental result is that master curves of W_{adh} as a function of $a_T V_{\text{deb}}$ cannot be constructed since the temperature has an influence on both the bonding and debonding stage for these materials. This is in contrast with the results obtained with emulsion acrylics where master curves could readily be constructed [1].

A second important observation is that for the PNBA linear polymers, the adhesion energy is mostly correlated with the maximum extension of the fibrils related to the second stage of the tack experiment. In fact the adhesion energy is proportional to the maximum strain (ϵ_{\max}). Clearly the more the fibrils can extend without breaking the higher will be the adhesion energy. It is therefore of great practical relevance to be able to control this maximum extension with well-tuned elongational properties of the adhesive.

7. CONCLUSIONS

Experimental results of probe tack tests on linear monodisperse PNBA polymers have shown that a large spectrum of relaxation times is a necessary condition for the performance of a PSA. If short relaxation times are absent (i.e. no low molecular weight fraction), the contact with the substrate is not achieved within short contact times, while if long relaxation times are absent, a fibrillar and adhesive fracture cannot be achieved.

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