QUANTITATIVE AND MECHANISTIC STUDY OF THE ADHESION OF A TRIBLOCK ELASTOMER AND TACKIFYING RESIN SYSTEM USING THE PROBE TACK METHOD

J.C. Hooker[a], C. Creton[a], H. Lakrout[a],
K.R. Shull[b], and Ph. Tordjeman[c].

[a]Laboratoire PCSM-ESPCI
Paris, France
[b]Dept. of Materials Science and Engineering,
Northwestern University, Evanston, IL
[c]Groupement de Récherches de Lacq,
Elf Atochem, Lacq, France

1. INTRODUCTION

In order to extract the necessary information about the adhesion behavior of pressure-sensitive-adhesives (PSA), three general test methods can be used: 1) peel tests, 2) quick tack tests, and 3) shear tests.[1] In this study, we used a form of the quick tack test known as the probe tack method. The intrinsic nature of the probe tack method[2] and the optimization of our tack instrument[3] has allowed a more quantitative and mechanistic approach to the adhesion problem.

This study takes advantage of a model PSA composed of a blend of styrene-isoprene-styrene triblock copolymer elastomer(Vector®, Exxon) and a tackifying resin (Regalite® R101, Hercules). Although other studies using triblock/resin blends)[4,5], rubber/resin blends[6,7] or simple elastomers[8] have explored the connection between bulk rheology and adhesion and the influence of experimental parameters on tack, much less has been done to relate these observations to the micromechanisms of deformation, such as cavitation and fibrillation. Thus, the intent of this work is to formulate a more complete picture of the adhesion process by using a combination of probe tack, real-time video, and rheology that would eventually allow a more systematic approach in optimizing adhesion properties.

2. EXPERIMENTAL

2.1. Materials.

A triblock copolymer of styrene-isoprene-styrene (SIS), tradename Vector® 4211D (Exxon), and a low-molecular weight hydrocarbon resin tackifier, Regalite® R101 (Hercules), were used in this study. From GPC results, comparing to polystyrene standards, the number average molecular weight (M_n) of the Vector was determined to be 114k with a polydispersity (PD) of 1.07 and for the Regalite a M_n of 1.2k and a PD of 1.2. Analysis of the Vector by NMR indicated a styrene content of 30 wt% in agreement with the reported value.

2.2. Sample Preparation.

Blend samples of Vector/Regalite, 50:50 (wt%:wt%), for probe tack and rheological measurements were made by solution casting from toluene, followed by drying at room temperature and then in vacuum at elevated temperatures for a sufficient duration. T_g's of each phase in the Vector/Regalite system were taken from dynamic rheological temperature scans at 10 rad/s where maximums in G" occurred. The tackifying resin T_g was measured using DSC at a heating rate of 10°/min. These values are listed in Table 1.

Table 1. Vector/Regalite blend used in this study and the corresponding T_g of each phase.

Vector/Regalite (wt:wt)	Polystyrene [°C]	Polyisoprene [°C]	Polyisoprene /Regalite[°C]	Regalite[°C]
1:0	100	-53		
5:5	100		-22	
0:1				48

2.3. Probe Tack Measurements.

Details can be found in reference by Lakrout et al.[3]. Probe surfaces of bare sand-blasted stainless steel and a PDMS grafted surface were used.

3. RESULTS AND DISCUSSION

3.1. Effects of Temperature and Debonding Rate.

The effects of temperature (T) and debonding rate (V) at a given contact time (t_C = 1 sec) and contact pressure (P_C = 1 MPa) were examined. In figures 1(a) and (b), the stress-strain curves are plotted for several different conditions. As would be expected for viscoelastic materials, a comparison of the curves in figures 1(a) and (b) reveals a good correspondence between time and temperature. That is, with either an increase in debonding rate or a decrease in temperature both the adhesion energy, G_{adh}, and cavitation stress, σ_{max}, increase. The correspondence of the results for a range of temperatures and debonding rates to our rheological measurements on the same blend will be presented.

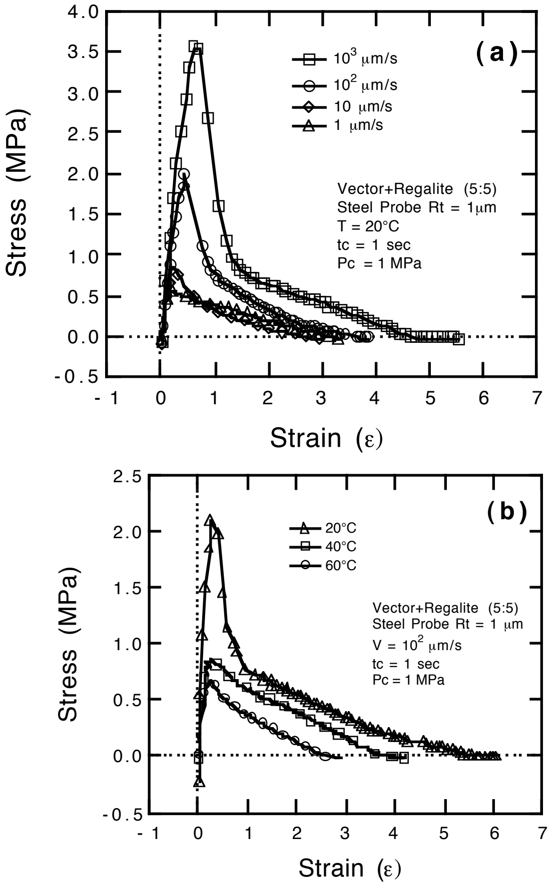


Figure 1. Stress-strain curves for the 50:50 Vector/Regalite system at (a) constant T = 20°C and (b) constant V = 100 µm/s using the rough probe.

Another interesting fact can be drawn from the shape of the curves in figure 1. Almost all the curves lack a significant plateau or shoulder following the maximum in stress, indicating the lack of extensive fibrillation. Such behavior is consistent with the relatively high modulus of this material over the temperatures and debonding rates used. Furthermore, the mode of separation for all conditions was adhesive.

To elucidate the mechanisms of deformation and rupture of the adhesive joint, images were taken during the bonding and debonding stages. The characteristic size of the cavities, in general, were much smaller than observed in the polyacrylate systems, concurrently, the walls being significantly thicker, as well. Separation then occurred by the formation of penny-shaped cracks which propogated towards the edges. This is in contrast to the polyacrylate systems where the cavities grew to form a honeycomb shape with very fine walls, followed by extension of the walls into fibrils, and separation by either a cohesive or adhesive mechanism. [3] More detailed results of the cavity formation and growth will be presented from the use of a higher magnification system.

3.2. Contact Time Effects.

In figure 2 are results of G_{adh} and σ_{max} as a function of contact time for the Vector/Regalite (5:5) system at 20°C and a debonding rate of 100 µm/s. An increase in σ_{max} is observed with increasing contact time and appears to level off around 50 sec, although it is not certain if that is the case for G_{adh}. This suggests that the tests performed in the section above were in a contact limited regime. Thus, further experiments will be performed under conditions which are not contact time limited to determine to what extent the contact limited results are appropriate for characterizing our adhesive system.

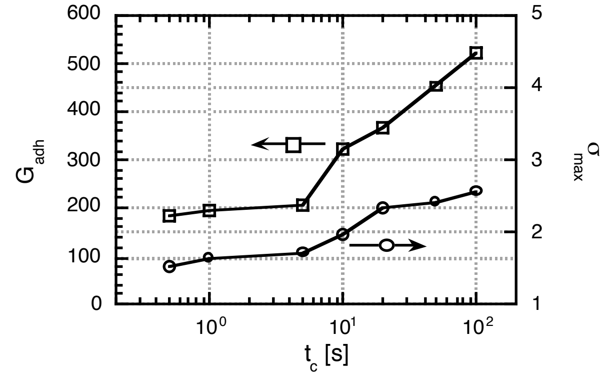


Figure 2.

In figure 3 there are a series of curves in which only the contact time has been changed. The curves for contact times of less than 10 sec do not differ greatly in shape. However, as the contact time increases, not only does σ_{max} increase, but the presence of the plateau region becomes significant indicating the growth of fibrils.

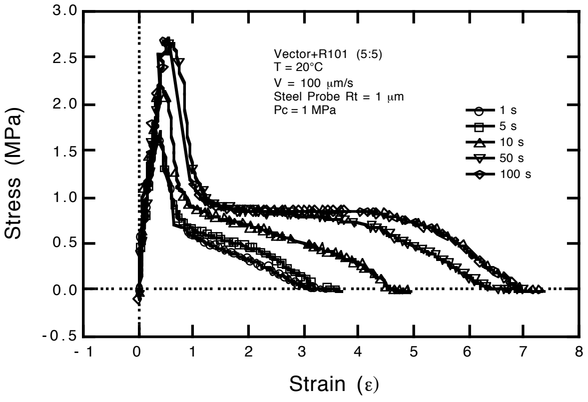


Figure 3. Stress-strain curve of the 50:50 Vector/Regalite system where only the contact time, t_c, was changed.

It obvious that there is an increase in the adhesion between the adhesive and adherend contributing to enhanced fibril extension, but it is unknown whether this stems from only an increase in contact area or if some fundamental change in specific interactions occurs.

3.3 Effects of Adherend Surface.

In order to examine the effects of surface properties on adhesion, a probe with a thin layer of grafted PDMS was compared to that of a bare rough stainless steel probe. Figure 4 gives a comparison of the stress-strain curves for an untreated and treated surface at equivalent conditions (T = 20°C, V = 100 μm/s, t_c = 1s, P_c = 1 MPa). As is evident for this set of conditions, there is a significant lowering of the adhesion properties with the modified PDMS surface. This was done for several different debonding rates and the values obtained for G_{adh} and σ_{max} are plotted in figure 5. In all cases, the stress and adhesion energy are much lower for the PDMS modified surface. This suggests that the Vector/Regalite system is very sensitive to surface interactions and that bulk properties play a lesser role in adhesion to the PDMS surface. The extent to which the difference in adhesion is due to specific interactions or surface roughness will be determined. More detailed results on surface effects will be presented in terms of other types of probe surfaces (e;g; glass) and the changes in debonding mechanism which occurs.

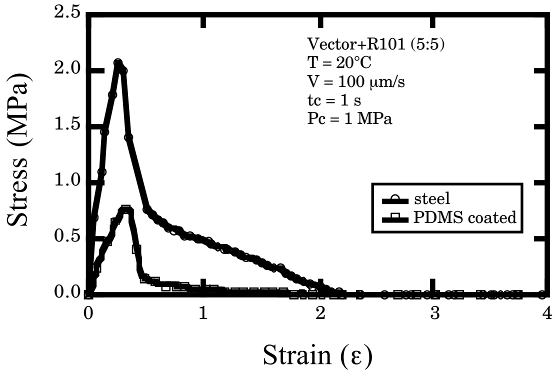
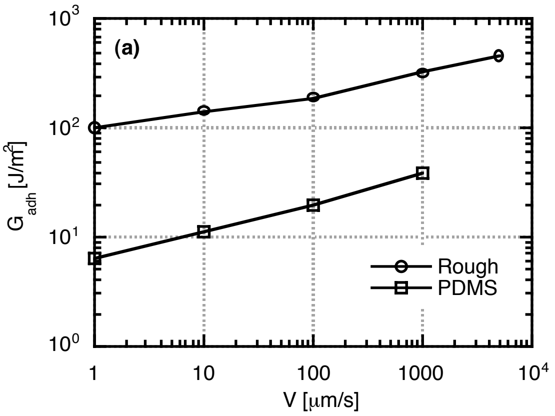


Figure 4. Stress-strain curve of the 50:50 Vector/Regalite system for an untreated and treated probe at equivalent conditions.



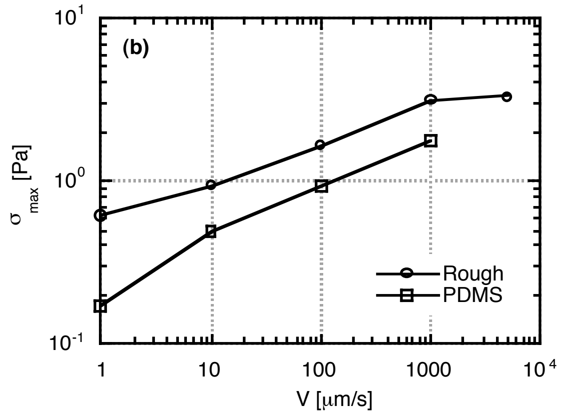


Figure 5. (a) G_{adh} and (b) σ_{max} versus V for the 50:50 Vector/Regalite system, comparing the results for a rough and PDMS surface.

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