THERMALLY ACTIVATED PARAMETERS OF SELF ADHESION IN PRESSURE-SENSITIVE ADHESIVE-LIKE NETWORKS

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Introduction

The contact mechanics of materials similar to pressure sensitive adhesive adhesives have been examined in work done by Li, et. al. [1] and by Ahn and co-workers [2]. In those measurements, the JKR theory\textsuperscript{[3]} was used to determine the intrinsic adhesion energy and the work of adhesion. In addition, that work included measurements of the adhesion energy as a function of crack propagation rate in unloading. In general, a critical rate of crack propagation was found, above which the dependence of adhesion energy on crack propagation rate exhibited power law behavior. In this work, we extend that type of experimentation to four pressure sensitive adhesive-like networks (PSA-LNs) varying in their co-monomer composition but based primarily in 2-ethyl hexyl acrylate and 1,6-hexanediol diacrylate. In addition, we carried out these measurements at three temperatures. We find that the critical crack propagation rate exhibits an Arrhenius law dependence upon temperature. This allows us to calculate an activation energy for the processes occurring during crack propagation. That activation energy was found to be on the order of the energy of a van der Waals bond.

Experimental

PSA-LNs were generated in a cylindrical form as described in two previous publications [1,4]. The general formula for the PSA-LNs was 80-90% 2-ethylhexyl acrylate, 10% 1,6-hexanediol diacrylate and 0-10% of a co-monomer. The co-monomers were: acrylic acid (AA), dimethyl amino ethyl acrylate (DMAEA) and acrylonitrile (AN). The labels given to the samples signify the amount and type of co-monomer, e.g. PSA-LN-NoAA means no co-monomer was used but PSA-LN-10AN means that 10% acrylonitrile was used. After the samples were prepared, their surface was analyzed by small spot size XPS. The surface analysis data agreed with predicted surface composition with a slight excess of hydrocarbon.

The primary apparatus was previously described [4]. For this work the apparatus was modified to include a temperature controlled chamber. We performed contact mechanics –based measurements at 0, 25 and 50\degree C under an atmosphere of dry nitrogen.

Loading and unloading measurements were performed. Loading measurements were fit to the JKR equation (Eq. 1).

\[
\alpha^3 = \frac{R}{K}(P + 3\pi W_A R + \sqrt{6 W_A R P + (3\pi W_A R)^2}) \quad \text{Eq. 1}
\]

where \(\alpha\) is the contact radius, \(P\) is the applied load, \(W_A\) is the work of adhesion, \(K\) is a stiffness constant and \(R\) is a mean radius of curvature for the samples in contact. The curves were fit to provide values of \(W_A\) and \(K\). During unloading, the adhesion energy was calculated using Eq. 2 at defined intervals

\[
G = \frac{(\frac{a}{a_0} K - P)^2}{6\pi a R} \quad \text{Eq. 2}
\]

where \(G\) is the adhesion energy. The values of adhesion energy quoted for unloading experiments are the average of two adjacent measurements. The crack propagation rates quoted for unloading measurements are determined by measurement of the difference in crack radii between the two measurements and dividing by the time interval.

Results and Discussion

A summary of the data generated in loading measurements carried out at room temperature is shown in Table 1. The values of work of adhesion provide values of the surface energy of these PSA-LNs. These values are similar to those that would be expected for compositions of this type.

Table 1 Values of work of adhesion determined from JKR loading experiments carried out at room temperature

<table>
<thead>
<tr>
<th>Sample Designation</th>
<th>(W_A), (mJ/m(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSA-LN-NoAA</td>
<td>59 ± 5</td>
</tr>
<tr>
<td>PSA-LN-10AA</td>
<td>73 ± 5</td>
</tr>
<tr>
<td>PSA-LN-10DMAEA</td>
<td>93 ± 5</td>
</tr>
<tr>
<td>PSA-LN-10AN</td>
<td>107 ± 5</td>
</tr>
</tbody>
</table>

Figure 1 shows the data taken under unloading conditions at room temperature for all four systems. As can be seen, two of the samples show a pronounced change in slope at a certain crack propagation rate. The other two samples also show a change in slope, but the transition is not as abrupt. The rate at which the slope changes is called \(v^\ast\), the critical crack propagation rate. In our measurements, \(v^\ast\) is determined by fitting low rate data to a \(G\) versus \(v\) relationship while high rate data was fitted to a log \(G\) versus log \(v\) relationship. The point at which the two curves cross is called \(v^\ast\). The low rate curve fit was extrapolated to zero rate to determine a value of \(G_{\ast}\), the intrinsic adhesion energy. Similar data was obtained for each sample at each of the three temperatures.
Attempts were made to fit our data to the relationship suggested by Ahn and Shull:

$$G = G_0 \left(1 + \left(\frac{\nu}{\nu^*}\right)^n\right)$$

where $n$ is the power law index above $\nu^*$. Our data could not be fit to this equation because of the sharpness in the transition of the crack propagation rate at $\nu^*$ and/or because of the slope in the data measured below $\nu^*$. In addition, this relationship does not explicitly provide for temperature dependence in the parameters. We also attempted to fit our data to the relationship suggested by Chaudhury and co-workers [5] that does provide for temperature dependence in $G$ versus $\nu$ data. Unfortunately, it does not provide for the existence of $\nu^*$.

Table 2 shows the temperature dependence of $G_0$ and $\nu^*$ as a function of composition. Log $\nu^*$ was plotted versus reciprocal temperature. A linear relationship was found from which an activation energy for the process occurring during crack propagation was determined. The values of the activation energy as a function of chemical composition are also shown in Table 2.

<table>
<thead>
<tr>
<th>Sample designation</th>
<th>$G_0$ at 0°C (mJ/m$^2$)</th>
<th>$\nu^*$ at 0°C (nm/sec)</th>
<th>$G_0$ at 25°C (mJ/m$^2$)</th>
<th>$\nu^*$ at 25°C (nm/sec)</th>
<th>$G_0$ at 50°C (mJ/m$^2$)</th>
<th>$\nu^*$ at 50°C (nm/sec)</th>
<th>$Q_A(\nu^*)$ kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSA-LN-NoAA</td>
<td>76</td>
<td>425</td>
<td>66</td>
<td>496</td>
<td>58</td>
<td>604</td>
<td>1.2 ± 0.2</td>
</tr>
<tr>
<td>PSA-LN-10DMAEA</td>
<td>194</td>
<td>129</td>
<td>169</td>
<td>188</td>
<td>100</td>
<td>203</td>
<td>1.6 ± 0.2</td>
</tr>
<tr>
<td>PSA-LN-10AA</td>
<td>177</td>
<td>144</td>
<td>132</td>
<td>201</td>
<td>96</td>
<td>233</td>
<td>1.7 ± 0.1</td>
</tr>
<tr>
<td>PSA-LN-10AN</td>
<td>241</td>
<td>149</td>
<td>195</td>
<td>212</td>
<td>178</td>
<td>259</td>
<td>2 ± 0.2</td>
</tr>
</tbody>
</table>
The data in Table 2 clearly shows that $G_0$ decreases with increasing temperature. This is expected. The literature says that surface energy should decrease at a rate of about 0.1 mJ/°C m$^2$ [6]. However, the change in $G_0$ with temperature is significantly higher than that, except for PSA-LN-NoAA. $\nu^*$ increases with increasing temperature. We also note that the material having the lowest polarity, PSA-LN-NoAA, has the lowest $G_0$ (it is almost the same as $W_a$) and the highest $\nu^*$ at each temperature. For data showing $G$ versus $\nu$, the effect of temperature is to shift the curves to the right and down. The effect of having higher polarity monomers in the material is to shift the curve up and to the left.

We also can look at the value of the activation energy determined from the temperature dependence of $\nu^*$. The values are between 1 and 2 kcal/mole, with the highest activation energy found for the most polar monomer. These activation energies are on the order of the values expected for van der Waals interactions.

**Conclusions**

Contact mechanics of acrylic pressure sensitive adhesive-like networks were examined at three different temperatures over a range of sub-micron-per-second rates of interfacial separation. Self-adhesion energies measured as a function of crack propagation rate were found to exhibit a transition to markedly stronger rate dependence above a certain critical rate of crack propagation, $\nu^*$. For each of the four systems tested, this rate was found to be a thermally activated parameter. To our knowledge, the above finding is the first of its kind to be reported in the field of polymer adhesion.

As temperature increases, the dependence of the adhesion energy on the crack propagation rate shifts to the right (higher rates) and down (lower energy). As the level of intermolecular interaction in the bulk and interface increases, the dependence of adhesion energy on crack propagation rate seems to shift to the left (lower rates) and up (higher energy.) We also found that there is a measurable dependence of $G$ on $\nu$ at rates below $\nu^*$. A finding that is difficult to model using Eq. (3).

The activation energy determined from the dependence of the critical crack propagation rate on temperature was found to be on the order of the energy to break van der Waals attractions (~ 2 kcal/mole.) The materials used in this study are chemically very similar to the chemistry of commercial acrylic pressure sensitive adhesives, albeit at a much higher crosslink density than that used in commercial PSAs. Thus, despite the fact that the magnitude of van der Waals attractions are quite low, they are the source of the quite measurable adhesive bond strength of pressure sensitive adhesives.

**Acknowledgements**

The authors would like to thank: Dr. Afshin Falsafi (3M) for constructing the JKR apparatus, Dr. Lihua Li (Advanced Materials) for producing results that motivated this work, Prof. Christopher W. Macosko (U. of MN) for critical feedback at the inception of the work, Dr. Phillip J. Cole (Sandia National Labs) for ongoing feedback and review of our previous publications, Dr. David Giles (U of MN) for assistance with rheological measurements, and Mr. Gary Korba (3M) for XPS surface composition analysis. Support from the 3M Company for one of us (YSG) is appreciated as is support from the NSF under Grant DMI-0103169 for another of us (WWG).

**References**

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Dr. Pocius has been actively involved in many aspects of adhesion science including mechanical testing, surface science and surface analysis as well as in adhesive and primer formulation for over 27 years. He has given hundreds of presentations in the area of adhesion science and has taught in a number of workshops and short courses including that of the Adhesion Society, the Adhesives and Sealants Council and the University of Wisconsin at Milwaukee. He is co-author of the American Chemical Society Audio Course on Adhesion and Adhesives. Dr. Pocius has published over 50 papers and articles and holds 19 US Patents. He has published a book entitled “Adhesion and Adhesives Technology – An Introduction” which is now available in a 2nd Edition. He has received several “Best Paper” Awards from SAMPE and was also winner of SAMPE’s Delmonte Award for Excellence for his development of water-based primers for the aerospace industry. He is an active member of the Adhesion Society having been an Executive Committee Member, a Program Chair, a Session Chair and an Exhibition Chair. Dr. Pocius was the Chair of the 1998 Gordon Conference on the Science of Adhesion and was co-program chair of the 2nd World Congress on Adhesion and Related Phenomena, February 2002. In 2000, he was elected to be a “Robert L. Patrick Fellow of the Adhesion Society.” He was elected to the 3M Carlton Society in 2000. In late 2001, Dr. Pocius was selected to be Adhesives Age “Person of the Year.”

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