Rheological Analysis of Tack

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ABSTRACT

Materials that are tacky or sticky are easily identified by touch. However, it is not so easy to quantify tack. Numerous tests have been developed to measure the degree of tack of a material, but these test do not provide much insight into the mechanisms that control tack behavior.

It is well know that surface tension and wetting contributes to the ability of a material to adhere to another surface. Also, extensive studies have shown that the bulk viscoelastic properties of materials play a major roll in tackiness.

The intent of this paper is to show the relationship between shear retardation spectra and force-displacement of adhesives measured in tension with a steel probe. Three pressure sensitive adhesives with very different tackiness are also tested in creep at different temperatures. From the probe tack test the maximum adhesion and cohesive forces, work of separation, and separation distance are all analyzed

The maximum work of separation is controlled by the bulk viscoelasticity of the adhesive providing the compliance exceeds the Dahlquist Criterion of 10^{-8} 1/Pa. This parameter best quantifies the tack of adhesives. Below this compliance adhesive failure occurs as observed from the small strains at separation. A log-log relationship between the 1/5 second compliance and the maximum separation force is found.

INTRODUCTION

We all can recognize when a material is tacky or sticky. Normally, we determine how sticky a material is by holding a material between our thumb and forefinger, and feeling how difficult it is to remove it from our fingers. Tacky and sticky can be used in the same sense. Tack, by definition (1), is the ability of a material to adhere instantaneously to a solid surface when brought into contact by a very light pressure. The formation of the adhesive bond is not directly measured, but assessed by breaking bonds. Tack is not to be confused with peel. Peel is defined as the separation of bonds of two flexible materials or of a flexible material and a rigid material by pulling the flexible material from the joining surfaces. The distinction between tack and peel is the contact time as defined by the above definition. Consequently, the test must be designed that the tack probe makes contact with the adhesive for a very short time. In contrast, peel tests require that the adhesive be in contact with the substrate for a long period of time.

There are several tests for measuring tack (instantaneous adhesives' bond strength), such as the probe tack test, peel test, rolling ball, rotating wheels, etc. It is noteworthy that none of this test can be compared with one another.

It appears that liquids will be more or less tacky within a certain range of viscosity. In general, liquids that are moderately high in viscosity are tacky. As the viscosity of liquids decrease or increase the tack decreases in both cases. Therefore, tack will reach a maximum within a certain viscosity range. Many foods are tacky, such as honey, chewing gum, syrups, flour and water, oils, creams, etc. Of course, the viscosity must be low enough to flow over the surface of the substrate in order to make good contact. Although surface tension and fluidity are necessary for good wetting and flow, these are not the only criteria for producing high tack.

For pressure sensitive adhesives (PSA), the viscoelasticity of the adhesive must be considered. The thought-provoking question is to what extent does shear viscosity and elasticity control the tack of PSA's. To answer this question, the mechanism of tack needs to be un derstood. Breaking the adhesive bond can occur either by cohesive or adhesive failure or a combination of both. We know the rheology of viscoelastic materials depends not only upon the amount and rate of deformation, but also on the kinematics (mode of deformation). The attachment and removal of a PSA to a substrate occurs primarily in compression and tension modes and to a lesser extent shearing is introduced.

The rheology of PSA's are normally measured in shear to determine their elasticity and viscosity in their linear viscoelastic regions. One reason for this is that shear measurements are relatively simple to make compared to extensional measurements. However, numerous researchers have made correlations of the shear rheology with both tack and peel of PSA. In particular, the storage modulus G' has been correlated with these PSA properties. The Dahlquist's Criterion considers compliance J, which is the inverse of shear modulus (2) .

One might expect a problem relating linear viscoelastic rheological data to large mechanical deformations, especially when the modes of deformation are different. Analysis of the retardation spectrum in the short time period of the tack measurement may give insight into the structural components that control tack. Is the tack controlled by surface tension or bulk rheology? Furthermore, can shear rheology be related to the probe tack of PSA's? In order to answer these questions, three unsupported films with very different tack properties were evaluated. These are free film adhesives about 0.15 mm thick. Shear creep measurement leading to retardation spectra identifies the bulk viscoelastic properties of these adhesives. The tack probe test measures their tack properties.

EXPERIMENTAL

The probe tack test device is made of steel. The adhesive is attached to a 19 mm flat bottom plate. The probe is 5 mm in diameter and is flat, i.e., the edge is not rounded. The ARES rheometer is used to make the tack measurements. The unsupported PSA about 0.15 mm thick are attached to the bottom plate.

The probe is placed about 0.05 mm above the adhesive. The test was programmed to lower the probe at 0.1 mm/s for 2 sec and then reversed direction at the same rate. The load was measured as a function of time. The creep tests were made using the SR5 controlled stress rheometer. All measurements were made in the linear viscoelastic region. Tests were performed at 0, 25, 60 and 80°C using 25 mm parallel plates. The peltier was used to control the temperature of the sample.

DISCUSSION OF RESULTS:

Numerous studies have been made correlating shearing rheology to the tack and peel adhesion of PSA's. Chu (3) reported on the dynamic mechanical properties and 180° peel, Quick Stick, and Polyken Tack. Low frequency storage modulus G'(0.1 rad/s) and high frequency G' (100 rad/s) correlate well with tack and peel, respectively. Dale (4) and others reported good correlations with tan delta. Giordano (5) also showed the relationship between tack and G'. Low G' PSA's generally have higher tack.

Dahlquist did extensive creep measurements. He recognized that compliance and retardation spectra play a significant role in the quick stick or tack of PSA. He is credited with recognizing that in order for a PSA to have suitable tack it must have creep compliance above 10^{-8} 1/Pa. This is known as the Dahlquist's Criterion. Creep and retardations spectra were made to determine the viscoelastic properties of these PSA's.

Crosby and Shull (6) studied of PSA's using a probe test to analyze the failure mechanism of a filled and unfilled adhesive. They investigated the energy release rate and the relative effects of bulk and
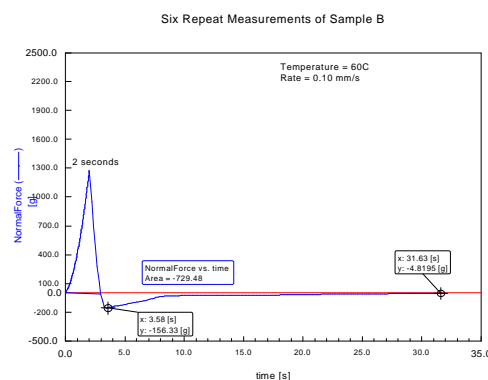

Figure1: Typical data from a tackprobe test V
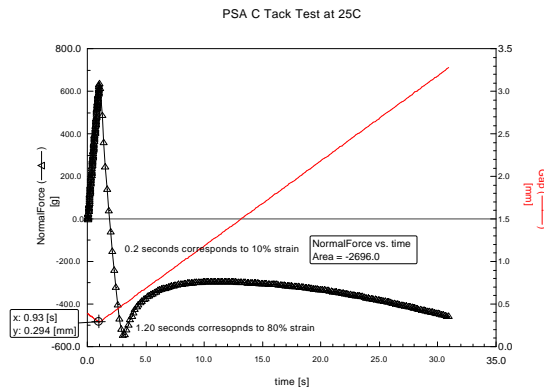
PSA C Tack Test at 25C

Figure 2: Tack probe data of sample C at 25°C

interfacial processes. Zosel (7) studied the degree of crosslinking of PDMS on it's the tack behavior and found that a maximum tack strength occurs when the adhesive is lightly crosslinked. This structure results in a stress-strain curve with a large shoulder followed by the stress maximum and a high strain to break. From high speed photography the formation of fibrillar structures within the adhesive were observed. Good and Gupta (8) analyzed the mechanism of filament elongation and the mode of separation, i.e., adhesive versus cohesive failure.

Again, it must be emphasized that the rheological data in this report is obtained in the time scale of the probe tack test. Also, the PSA compliance data are obtained in their linear viscoelastic region, and yet the probe tack data are occurring in their non-linear viscoelastic regions above a strain of 10 %, which corresponds to a time of 0.2 seconds.

From the Newtonian viscosities these samples should have very different flow behavior when making contact with the steel tack probe. Samples A, B,and C have viscosities of $5x10^7$, $3,4x10^5$ and $4,8x10^4$ Pa s, respectively.
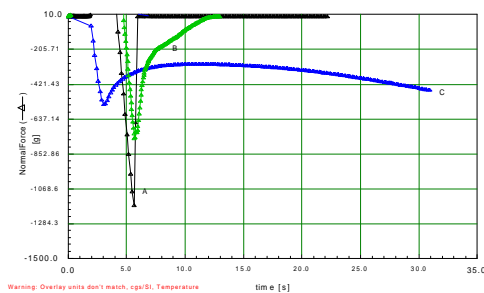

Fugure 3: Comparison of tack probe data of sample A, B, C at 25°C

Figure 1 shows a typical probe tack test result. The 0.15 mm adhesive attached to a flat steel plate was compressed and released at a rate of 0.1 mm/s. It was squeezed in the time scale of 1 to 2 seconds and then pulled in tension. The maximum release force is 1.53 N and the area is 7.15 N s under the force versus. time plot. The separation time was 31 seconds. This corresponds to a separation distance of 3.1 mm. and 2100 % strain at separation

Figure 2 shows the force-time plot of Sample C being pulled apart by the tack probe. Note the time scales. At 0.2 s the sample was strained 10 %. At 1.2 seconds the sample yielded at 80 % strain and began to flow where fibrils are produced. The sample stretched to beyond 2000 % without separating.

Figure 3 shows the tack curves for the three PSA samples A, B and C. All were tested at room
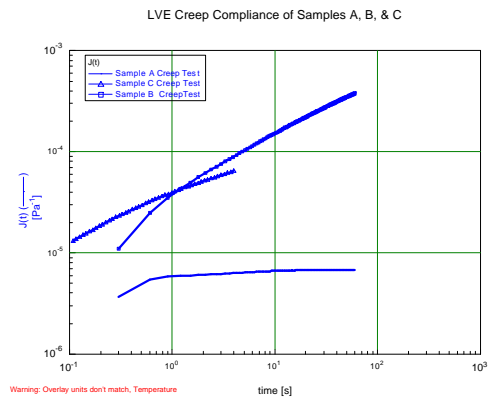

Figure 4: Creep compliance of sample A, B, C

temperature. Observe that Sample C has the most tack as defined by the largest area under the tack curve and the longest separation time. Sample B is intermediate in its degree of tack and has a yield force between Sample A and Sample C. Both failed cohesively. The Sample A has an adhesive failure and does not elongate when it separates.

Figure 4 shows the compliances of the three samples tested at 25 °C. Samples were tested in creep at different stress levels for each temperature to establish their linear viscoelastic regions.

Figure 5 shows the short time strain for Sample B tested at 60 C during the creep experiment. The strain corresponding to 0.2 seconds is 10 %. This is in agreement with strain and time of the force-time
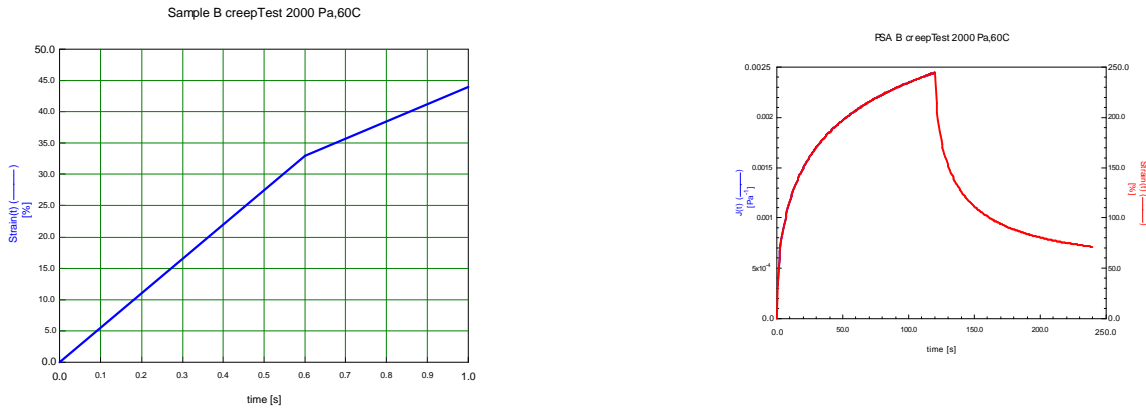
Figure 5: Expaneded view of the creep recovery curve of sample B tested at 60 °C

plot of the tack probe test. Table 1 lists the tack probe test data for all the measurements.

Table 1 lists the yield forces (the units of grams are used as force instead of dynes in this study), areas calculated from the force-time plot, and break strains where the sample separates from the probe. Samples that separate with an area in the range of 100 gram's or less are taken as failing adhesively. Larger area relate to yielding processes and cohesive failure occurs,

Next, consider the retardation spectra of these three samples. As shown in Figure 6, observe that spectra of Sample A, B and C extend beyond the time period of the tack probe test. The deformation time at a strain of 10 % is 0.2 seconds. This strain is the upper limit of the linear viscoelastic region in both shearing and elongational modes of deformation. This is rather important to know, since the Deborah number controls the viscous or elastic response during the separation process of the adhesive and/or cohesive failure processes. The

Deborah number is the ratio of the characteristic relaxation or retardation time to the stimulus time. If the Deborah number is high, greater than one, then the deformation will be elastic. For a typical viscoelastic material the time necessary for the molecular rearrangement to take place is comparable to the time scale of the experiment. If the deformation
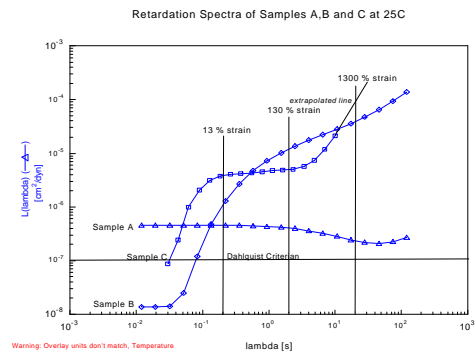

Figure 6: Retardation spectra of samples A, B, C tested at 25 °C

Sample	Yield Force, Grams	Area Gram.s	Break Strain %	Compliance cm.sq/dyne xe7
A(25C)	1170	1120	120	4.52
A(80C)	200	102	180	6.0
B(0C)	344	52	20	0.125
B(25C)	740	1450	470	12.87
B(60C)	156	729	2100	324
C(25C)	545	2700	>2000	38

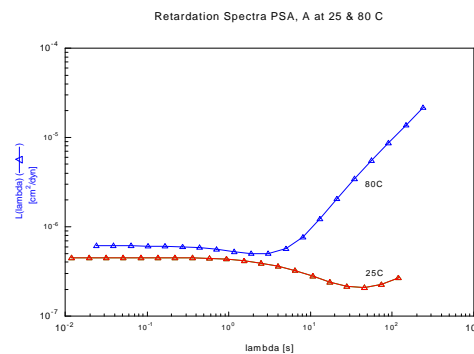Table 1: Yield forces and brfeak stgrain for samples A, B, C at various temperatures

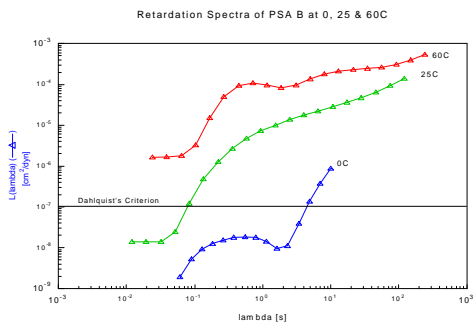Figure 7: Retardation spectra of sample A, tested at 25 and 8 °C

Figure 8: Retardation spectra of sample B tested at 25 and 60 ºC

rate is very fast, in the time scale of 0.001 to 0.01 seconds, both Samples B and C will behave like elastic solids. When the Deborah number is close to one the material is typically viscoelastic.

Observe that these retardation spectra in Figure 6 show characteristic transition, plateau, and terminal zones. The retardation spectrum for Sample A shows only a plateau, where as Sample C shows all three zones. Sample B only shows transition and plateau zones. The Sample A has the lowest compliance in the stimulus range of the tack probe tester, and is constant over the measured retardation times from 0.001 to 100 seconds. This is not conducive to large deformations as is seen from the tack probe test result. A broad rubbery plateau indicates that the sample may be lightly cross-linked and will deform elastically over a wide range of release rates. It cannot elongate due to its high cohesive strength and failure will occur adhesively. PSA C exhibits all three zones, transition, plateau, and terminal. This provides it with a good balance of adhesion and

cohesion. At very fast release rates and shorter times below 0.03 second, it will have poor tack because the compliance is too low according to the Dalhquist's Criterion. Conversely, at the longer times it will act more fluid-like and flow easily due to the compliance increase at the longer times corresponding to the terminal zone. Elongation at separation will be high because the adhesive will flow and filaments will be produced. The Sample B shows the terminal and plateau zones of the spectrum. Most important it has a very broad plateau and for this reason its viscoelastic and tack behavior will be more rate dependent than adhesives that have a flatter plateau in their retardation spectrum. It also will behave solid-like below 0.04 seconds and becomes more compliant at the long time. It cannot elongate as far as samples C at this temperature because the time scale of the terminal zone is too long for the stimulus time of the tack probe test

Attempts were made to improve the tack of Samples A by increasing the temperature. Sample A was heated to 80 ºC and tested in both creep and tack. Observe, in Table 1 that the maximum tack yield force decreased from 1170 at 25 ºC to 1.96 N at 80 ºC. Adhesive failure occurred because the area decreased to 1 N s for some unknown reason. Sample B was tested at 60 ºC. Compared to room temperature, the yield force decreased from 7.16 to 1.53 N. When tested at 0 ºC the maximum adhesive force was 3.38 N. The area was only 0.5 N s, indicating that no yielding occurred.

Increasing the temperature of Sample A did little in the way of improving its tack. The retardation
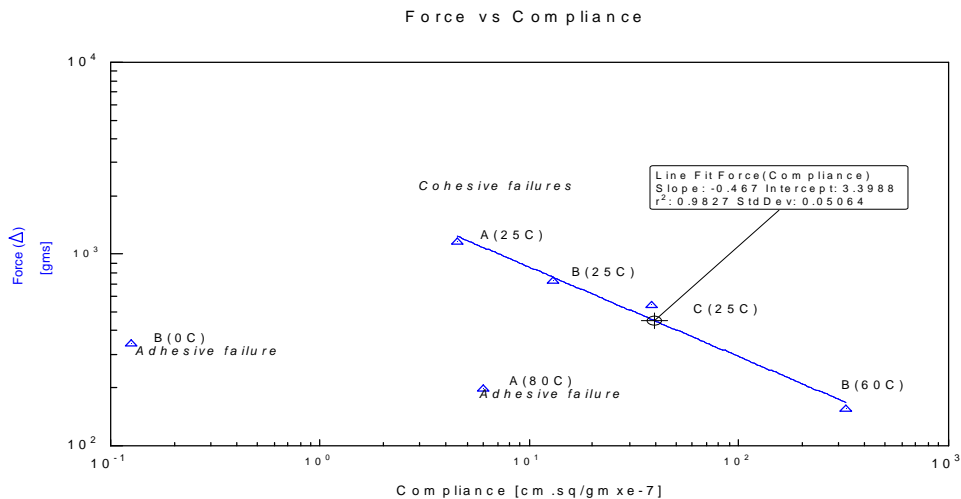

Figure 9: Plot of log force against log 1/5 second creep compliance for all samples

spectra can provide a partial explanation for this. The compliance shifted in this time period the rubbery plateau still persists between 25 and 80 ℃. The decrease in the compliance at the long time of Sample A is not realistic. However, this is outside the range of interest and not important for this analysis.

Comparing the retardation spectra of Sample B at 0, 25 and 60 ℃ show the consistent trend where the retardation times are shifted to lower compliance with decreasing temperature and longer times. Plots are shown in Figure

Most striking with this compliance -tack probe analysis is the agreement between the yield and maximum force and the compliance measured at 0.2 seconds. Figure 9 show a linear relationship between logarithm force and log of 1/5 second compliance. Samples that have areas of work of separation greater than 0.981 N s were fitted to a linear least squares plot. These data correspond to cohesive failures. The correlation coefficient of 0.982 shows the agreement is good. The other two data sets are not included because the are adhesive type failures

CONCLUSIONS

In conclusion, tack, which is a property of "quick stick", is quantified by the work of separation no matter whether it is due to adhesive or cohesive failure. When the bulk adhesive meets the Dahlquist's Criterion the adhesive will separated cohesively and high tack well be realized? When the adhesive's compliance is above the 10^{-8} 1/Pa the probe test can be predicted from shear creep data providing measurements are made in the same time periods, which corresponded to 0.2 seconds in this study. A log-log linear relationship was found between the 1/5 second compliance and the tack probe maximum force

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