EVALUATION OF DYNAMIC MECHANICAL PROPERTIES OF PRESSURE SENSITIVE ADHESIVE IN PAPER LAMINATES FOR POSTAGE STAMP APPLICATION: METHOD DEVELOPMENT AND ADHESIVE CHARACTERIZATION

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Introduction

Pressure-sensitive adhesives (PSA) are viscoelastic materials with flow properties playing a key role in the wetting and bond forming; their elasticity plays a key role in the storage of energy which can be used to resist the debonding process. The balance of these properties governs their time-temperature dependent responses and adhesion strength. The adhesion and other end-use properties of PSAs require a viscoelastic, non-Newtonian flow behavior which is based on the macromolecular nature of the adhesive. However, the pure PSA polymers are generally used as thin layers; therefore their flow is limited by the interactions with the solid components of the laminate (liner and face) materials. On the other hand the solid components of the laminate are commonly flexible, and/or elastic layers, allowing a relatively broad and non-uniform distribution of the applied stresses. Thus the properties of the bonded adhesive (adhesion strength) may differ from those of the pure adhesive. It remains merely difficult to introduce the properties of pure PSAs as valid evaluation information to the end-users and manufacturers.

Adhesive performance of pressure sensitive adhesives may be described in terms of both bonding and debonding. Test methods have been developed to characterize the bonding properties, such as tack tests, and debonding properties, such as peel and shear tests. In the study of dynamical mechanical properties of PSA in paper laminates that used for postage stamp application, a single lap-shear geometry previously has been used for the shearing tests. This lap-shear test determines the shear strength of adhesives in actually bonded bonding materials. The test method is primarily a comparative method for determining adhesive strengths, surface preparation parameters and adhesive environmental durability. This method provides a good basis for the evaluation of adhesives, but some modifications or additional tests are required when testing materials for specific applications.

The objectives of present work is, first, to develop a reliable testing method to characterize the dynamic mechanical properties of pressure sensitive adhesives in paper laminates for postage stamp applications; second, to evaluate the temperature and frequency responses of these PSAs; and third, to predict the long term performances from the time-temperature superposition curves generated from DMA tests at different temperatures and frequencies. A study of the influence of the thickness on the dynamical mechanical properties of these PSA products will also be investigated to determine the optimal geometry that enhances the results.
Experimental Approach

Material
The testing sample of PSA stamp was constructed by laminating a water-based polyacrylic PSA to the face paper. The face paper contains a water-soluble primer coating that could be able to water soak and remove the stamp from a bonded substrate. All individual components as well as the lamination construction have met the criteria in the USPS stamp specification, USPS-P-1238F. This kind of construction is called the unprinted laminate.

![Figure 1. Dimension of PSA in face paper laminate](image)

For each of PSA-paper layer, the paper backing is about 0.005" (0.127 mm) thick, the water soluble primer is about 0.0001" (0.0025 mm) thick, and the PSA layer is about 0.001" (0.025 mm) thick. The dimension of one PSA-primer-paper layer is shown in Figure 1. In the calculation of shear moduli of DMA tests, the thickness of the water-soluble primer was neglected because this layer is much thinner than the PSA layer and paper backing.

DMA Test Geometry (Multiple Layers of Lap-Shear Geometry)
The geometry shown in Figure 2 has been used to perform the DMA tests. The size of overlap area is about 20mm (length) × 10mm (width) × 0.85 (thickness) for an 8-layers sample. For such an 8-layer structure, there are only 7 layers of PSA coating being sheared and tested. The mechanical properties were recorded as tensile properties because the tensile test mode was used for DMA measurement. Therefore, the tensile moduli measured were converted to shearing moduli by the following relationships, and it is also schematically described in Figure 3.

\[
\Delta = \frac{P}{(w \cdot t)} \times \frac{\ell}{E} 
\]

\[
\Delta = \gamma \times (N - 1) \times h 
\]

\[
\gamma = \frac{\tau}{G} = \left( \frac{Ph}{w \cdot \ell} \right) / G = \frac{\Delta}{(N - 1)h} 
\]

\[
\Delta = \frac{P}{(w \cdot t)} \times \frac{\ell}{E} = \left( \frac{Ph}{w \cdot \ell} \right) / G 
\]

Finally,

\[
G = (N - 1) \frac{f \cdot h}{\ell^2} E 
\]

where \(P\) is the tensile force applied on the 8-layer sample during the shearing deformation;
\( \ell \) is the overlapped length of the 8-layer PSA-paper sample;
\( w \) is the width of the 8-layer PSA-paper sample;
\( t \) is the overlapped thickness of the 8-layer PSA-paper sample;
\( \Delta \) is the displacement of the 8-layer PSA-paper sample during the shearing deformation;
\( E \) is the Young’s modulus when measured using the tensile mode in DMA for the 8-layer PSA-paper sample;
\( G \) is the shear modulus of the 8-layer PSA-paper sample after converted;
\( h \) is the thickness of a single pressure sensitive adhesive;
\( N \) is the total number of layers of sample;
\( \gamma \) is the shear strain of deformation; and
\( \tau \) is the shearing stress of deformation.

There are two types of tests carried out using DMA. The first type of test is the frequency sweep / isothermal temperature test, in which the data was obtained by controlling the temperature at the room temperature and the frequency is changed at 100 Hz, 10 Hz, 1 Hz and 0.1 Hz, in order. The second type is the frequency sweep / temperature step test, in which the data was recorded by sweeping the frequency at 100 Hz, 10 Hz, 1 Hz and 0.1 Hz at temperatures from -50 to 60 °C at 5 °C increments. At each step, the sample was soaked for 5 minutes before the test starts in order to have thermal homogeneity.

**DMA Results and Data Analyses:**

**Effects of PSA Thickness on Dynamic Mechanical Properties**

As discussed above, the multi-layer structure is used to measure the shearing deformation properties of the PSA coating layer. But the details of interpreting this geometry need to be fine-tuned to get the optimal responses in the dynamical mechanical tests. Therefore, different layers of PSA-paper structure (2, 4, 6, 8, and 10 layers) were tested using the frequency sweep / temperature step over the same frequency and temperature ranges. The 2-layer structure is actually the conventional lap-shear geometry. The sample preparation and testing procedures are also the same as discussed earlier. The Tan Delta versus temperature curves at 4 different frequencies of these structures for PSA-1 are shown in Figure 4-8. One notices that the values of tan delta are sensitive to the thickness of layers of lap-shearing geometry. For the conventional lap-shear geometry which has no extra layers between two arms, the tensile strength of the backing paper, which behaves as an elastic material contributes significantly to the total strength obtained from the mechanical tests, especially at very high frequency. Consequently, one observes that the value of tan delta at 100 Hz is notably higher than those obtained at lower frequencies. The advantage of the multi-layer geometry is that the addition of the extra layers into the shearing arms promotes the shearing motion between the inter-layers and reduces the tensile deformation of the two arms. Therefore, it could decrease part of the work dissipated which is caused by tensile and bending deformations of the backing papers. There is no Tan delta jump obtained at 100 Hz in Figure 5, in which the sample contains two extra layers. If the number of extra layers was increased, the value of tan delta will also distinctly increased, as shown in the third plot in which the sample contains four extra layers. This suggests that the shearing motion on each layer is eventually enhanced by adding more layers. When adding more layers, the value of tan delta was slightly increased. This result may suggest that the lap-shearing geometry with overall 6-8 layers (extra 4 or 6 layers) is an optimum condition for testing these postage stamp PSAs.

The relationship of the peak value of Tan delta at 1 Hz and the average shearing strain of each layer versus the total number of layers of samples is described in Figure 9. The shearing strain was calculated
from Equation (3). It is clear that when the average shear strain of each layer decrease, the peak value of Tan delta increases with increase in the total number of PSA-paper layers. This curve shows that a PSA-paper structure with 5-10 layers is appropriate for conducting these tests.

Figure 2. Test Geometry for multi-layer of lap-shear DMA test.
Figure 3. Scheme of PSA deformation in paper lamination
Figure 4. The plot of shear tan delta versus temperature of 2-layers PSA-1 sample

Figure 5. The plot of shear tan delta versus temperature of 4-layers PSA-1 sample
Figure 6. The plot of shear tan delta versus temperature of 6-layers PSA-1 sample

Figure 7. The plot of shear tan delta versus temperature of 8-layers PSA-1 sample
Figure 8. The plot of shear tan delta versus temperature of 10-layers PSA-1 sample

Figure 9. The relationship of Tan delta and strain versus number of PSA-paper layers
Figure 10. PSA -1 Lap-shear test

Figure 11. PSA-1 paper Tensile Test
Frequency Sweep/Isothermal Temperature
The shear properties from the frequency sweep/isothermal temperature tests of the 8-layer PSA-paper sample and the tensile properties of a single bare paper backing sample of PSA-1 are shown in Figure 10 and 11 at nine different frequencies from 0.01 to 100 Hz at room temperature. These data are the average numbers of a number of repeated tests. In Figure 10, one can observe the storage modulus and loss modulus increase with increasing frequency. The storage modulus ranges from 0.01 to 0.1 MPa, which is about 1 time higher than the loss modulus at each frequency. Tan delta was found to be fairly flat in the range from 0.4 to 0.46 but with a transition at around 2 Hz. However, the properties of single bare paper backing sample were quite different from that of the 8-layer PSA-paper sample as shown in Figure 11. Comparatively, the storage modulus and loss modulus of a single bare paper backing did not have a distinct change with the frequency sweep. Their values are about 5-6 orders of magnitude higher than that of 8-layer PSA-paper samples. The value of Tan delta was in the range of 0.03 to 0.05, which is 1 order of magnitude lower than that of the 8-layer PSA-paper samples and is a typical value of an elastic material.

Temperature Step/Frequency Sweep
The results of frequency sweep/temperature step tests for the 8-layer PSA-paper sample of PSA-1 are shown in Figure 12, 13 and 14 for the storage modulus, loss modulus and tan delta at 4 different frequencies over the temperature range from -50 to 60 °C. On each plot, there are three distinct responses, which are the glassy, transition and flow regions. From the Loss Modulus versus temperature curves, the glass transition temperatures (T_g) were observed to be -15.04 °C at 0.1 Hz, -4.92°C at 1 Hz, 4.97 °C at 10 Hz, and 15.06°C at 100 Hz. The shape of the curves at different frequencies is very similar to each other. But the curves are shifted to higher temperatures at higher frequency, as expected for a viscoelastic polymer. This is because the material behaves “stiffer” at higher frequency and “softer” at lower frequency. The shearing storage moduli decreased from around 1 MPa in the glassy region to about 0.1 MPa in the flow region. The moduli obtained in the flow region were consistent with Dahlquist’s criteria for pressure sensitive adhesives. The glass transition temperatures from the peaks in the tan delta versus temperature curves are slightly different from those from the loss modulus curves. The tan delta value increased from less than 0.1 in the glassy region to about 0.6 in the transition region and decreased to 0.3-0.5 in the flow region depending on the frequency.

Time-Temperature Superposition (tTs) Curves of PSA-1
The master curves of time-temperature superposition (tTs) of the 8-layer PSA-paper geometry of PSA-1 were generated from the tTs shifting of the curves in Figure 12-14 and they are shown in Figure 15, 16 and 17 for the storage modulus, loss modulus and tan delta, respectively. They are constructed in the frequency space and correspond to room temperature by using a computer program based on Williams-Landel-Ferry (WLF) equation. The WLF equation considered the equivalency of time and temperature in the context of free volume theory for an activated flow process in viscoelastic materials such as pressure sensitive adhesives. The WLF equation yields an equivalent frequency for a given temperature relative to a reference temperature and experimental frequency:

\[
\ln a_T = \frac{-C_1(T - T_o)}{C_2 + (T - T_o)}
\]

where \(a_T\) is the shifting factor at \(T\), \(C_1\) and \(C_2\) are constants for a given polymer, and \(T_0\) is the reference temperature. The activation energy \(E_a\) can be calculated from the Arrhenius relationship of the shifting factor with temperature from the following equation:
\begin{equation}
\ln a_T = \frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \tag{7}
\end{equation}

with \( R \) being the gas constant. The frequency of the master curves of PSA-1 ranges from 1E+12 to 1E-4 Hz and the activation energy was about 36 kcal/ mol. These master curves could be used to predict the adhesion performance of the PSA-1 samples in a very large frequency range, especially at some extremely low and high frequencies that cannot be obtained via traditional experiments.

\textbf{Figure 12.} The plot of shear storage modulus versus temperature of PSA-1
Figure 13. The plot of shear loss modulus versus temperature of PSA-1

Figure 14. The plot of shear tan delta versus temperature of PSA-1
Figure 15. The tTs master curve of shear storage modulus versus temperature of PSA-1

Figure 16. The tTs master curve of shear loss modulus versus temperature of PSA-1

\[ T_{\text{ref}} = 23^\circ C, \Delta E = 36 \text{ kcal/mol} \]
**Figure 17.** The tTs master curve of shear tan delta versus temperature of **PSA-1**

**Conclusions**

The lap-shearing geometry with multiple layers is proven as a reliable testing method which utilizes the dynamical mechanical properties of polyacrylic pressure sensitive adhesive (PSA) for characterization. The effect of thickness on dynamical mechanical properties for testing sample has been investigated; and the results indicated that the multi-layer geometry with 5-10 layers could be an appropriate structure for DMA tests in order to get enhanced responses. The time-temperature superposition (tTs) curves have been produced at the room temperature according to the temperature step/frequency sweep tests on DMA. These tTs curves could be used to predict either the short-term or long-term performances of these PSAs when applied in the postage stamp.
References:


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