Thermomechanical Properties of Polymeric Materials and Related Stresses

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THERMOMECHANICAL PROPERTIES OF POLYMERIC MATERIALS AND RELATED STRESSES

I. INTRODUCTION

Polymeric materials are widely used for coating, embedding, and bonding in electronic assemblies as well as in structural units. In use, they are often exposed to an environment with a wide range of temperature fluctuation. Therefore, thermomechanical property data of a polymer are important for design and reliability.

One well-recognized example of concern is the stress caused by the difference between the coefficient of thermal expansion (CTE) of a polymeric conformal coating and that of the substrate electronic components. The difference, as illustrated by the bargram in Figure 1, is known to be serious enough to cause damage and functional failures. In addition, the stress can be intensified by the stiffness or modulus of the coating material. Both CTE and modulus change with temperature, and their rates of change vary through the viscoelastic state transitions. Consequently, a profile of both CTE and modulus against temperature is desirable in order to make a wise selection of materials.

Since the introduction of the thermomechanical analysis instrument (TMA) by DuPont and a number of other companies, it has been convenient to plot a spectrum of dimensional change of a material sample over a wide temperature range, from which CTE's in different temperature regions can be calculated and the glass transition temperature (Tg) can be identified. However, the profile of modulus vs. temperature has not been readily obtainable until the recent introduction of the sophisticated dynamic mechanical analysis instrument (DMA). The DMA data show not only a modulus profile but also all the transitions, including the secondary transitions which are important, yet undetectable by many other methods.

To demonstrate the data base that can be acquired with the TMA and DMA methods and to produce the data on polymeric materials used in NASA, a number of such materials were chosen for the analyses, and the data and their significance are presented in this report.

II. EXPERIMENTAL

Materials

Eight polymeric materials widely used for space applications were chosen for this work, and are listed in Table 1. The four flexible polyurethane materials are used mainly for coating and sometimes for potting. They are formulated and cured at room temperature per manufacturers' directions. The last one is a popular epoxy adhesive formulated with Shell's Epon-828 and General Mills' Versamid-140 near a ratio of 50/50 by weight. Lexan and Plexiglas are widely used as glass replacements.

Instruments

DuPont TMA-943 was used to determine the dimensional change and the CTE, and DuPont DMA-983 was used to determine the dynamic mechanical properties. Equipped with the controllers 1090 and 9900 are the necessary software to do computing and plotting. Instruments were calibrated according to manufacturer's instructions.
III. RESULTS AND DISCUSSION

Coefficient of Thermal Expansion and Glass Transition Temperature

Figures 2 and 3 give the TMA thermograms of Lexan and Conap EN11 respectively. Lexan, a thermoplastic, shows a sharp deflection at its Tg, 146°C. Its average CTE increases from 64 to 889 \( \mu \text{m/m°C} \), nearly 12 times through Tg. EN11, a flexible cross-linked polymer with a Tg around -70°C, has an average CTE a little smaller than that of Lexan below Tg (89 vs. 64 \( \mu \text{m/m°C} \)), and its CTE also increases after Tg but only 2.3 times. The large expansion rate difference between Lexan and EN11 (889 vs. 208) above Tg reflects the effect of crosslinking. Tg is generally recognized as a critical transition temperature, below which the material is hard and brittle, and above which it is rubbery.

Similarly, other materials were analyzed. Recorded in Table 2 are the CTE's and Tg's determined. Among the five thermoset materials, EN11 and Uralane have the lowest Tg and are apparently the choice coatings when hardness and brittleness are considered detrimental. Solithane and Humiseal become brittle at temperatures not much below room temperature. Since the common temperature cycling tests will go through their transition temperatures (-7°C and +5°C respectively), the thermomechanical stress created by the material, when used as a coating on electronic components, will be intensified due to CTE fluctuation in the cycling range. Adhesive Epon828/V140, which has a Tg above room temperature, is rigid and strong in bonding strength at room temperature, but its well-known toughness at room temperature or below cannot be delineated by the TMA data alone.

When the CTE's below and above their Tg are compared, the CTE's of the five thermoset materials all increase about 2 to 3 times from below to above Tg. Then, it seems preferable to use a conformal coating with a high Tg, say, a Tg higher than room temperature, so that the CTE is low around or below room temperature and a minimal CTE differential can be maintained with the substrate electronic components. However, the choice is otherwise in most cases. The reason is that although the CTE of the polymeric coating below Tg is smaller, it is still much larger than that of the metals normally used in electronics. Besides, the modulus is large at temperatures below Tg, which should warrant more serious concern (Reference 1).

Modulus and Transitions Measured by DMA

The DuPont dynamic mechanical analysis measures the mechanical responses of a material as it is deformed (flexed) under a periodic stress (0.1 to 2.0 mm amplitude; 0.001 to 85 Hz frequency) in a wide temperature range from -150°C up. The responses are expressed in storage modulus and loss modulus, from which transition temperatures and Tan delta can be identified or calculated. Tan delta or quantitative damping is defined as the ratio of loss modulus to storage modulus. Modulus may be either flexural or shear depending on the ratio of length-to-thickness of the specimen. The storage modulus is a measure of the energy stored elastically during deformation. The loss modulus, the imaginary viscous property like that of a liquid, reflects the material's tendency of converting mechanical energy into heat when stressed. The loss is due to internal friction and is sensitive to many kinds of molecular motion, transitions, relaxation processes, structural heterogeneities, and the morphology of multi-phase systems if multiple phases exist (References 2 and 3).

Figure 4 is a DMA thermogram of adhesive Epon828/V140 run at a fixed 1-Hz frequency and a fixed amplitude of 0.4 mm. It shows flexural storage modulus E', loss modulus E'', and Tan delta against temperature. From -140°C to 83°C, the value of E' decreased from 5.1 to 0.08 GPa with a sharp drop that starts around 52°C. The sharp drop is reflected by a large loss peak at 71°C. This peak is called \( \alpha \)-transition, a primary transition closely related to the glass transition.
Secondary Transitions and Toughness

In Figure 4, there are two smaller loss peaks at lower temperatures called β- and r-transitions, respectively, in decreasing-temperature order. The presence of r-transition is further confirmed by a DMA run at the natural resonant frequency with a fixed amplitude of 0.2 mm as shown in Figure 5. It is known that a DMA run at the resonant frequency can detect subtle transitions better than that run at a fixed frequency. However, the loss peak temperatures obtained are different from that determined at a fixed frequency because the modulus, hence the peak temperatures, is known to change with frequency. For this reason, a DMA run at a fixed frequency, preferably 1 Hz, is generally accepted for material comparison.

Beta- and r-transitions are considered secondary transitions, and are related to the motion about the chain backbone of a relatively small number of monomer units or to motions of side groups. They are important because nearly all tough ductile glassy polymers and those with high impact strength have prominent secondary transitions (Reference 4). This explains why Epon828/V140 compound is an adhesive with room- and below-room-temperature toughness even though it has a Tg higher than room temperature.

The importance of secondary transitions in relation to toughness may also be demonstrated by the DMA thermograms of Lexan and Plexiglas. Lexan is known to be a tough glass replacement. Although its Tg by DMA shown in Figure 6 is as high as 155°C, it has a β-transition at a temperature as low as -72°C. In contrast, the β-transition of Plexiglas is at 31°C, which is above room temperature as shown in Figure 7. To improve its toughness at room temperature, an impact-improved grade, Plexiglas DR100, has been introduced. Its β-transition shown in Figure 8 is lowered to 16°C.

Coating Material's Modulus Changes Over Tg

The DMA thermograms of the four polyurethane coating materials, EN11, Uralane 5753LV, Solithane-113/113-300, and Humiseal-2B74 were recorded and are included in the Appendix. Their storage shear moduli, G', are compared in Figure 9, which exhibits distinctively that EN11 and Uralane belong to one group whose modulus remains very small when the temperature is decreased to as low as -30°C. In contrast, Solithane and Humiseal retain their high modulus up around room temperature, but will go through their transitions with an abrupt and tremendous modulus drop when temperature is further raised. Therefore, when exposed to common temperature cycling, the modulus of the first two will likely remain low whereas that of the second two will undergo a large fluctuation through their transitions in every temperature cycle. The high modulus and its fluctuation alone could cause stress, and inflict damage to or affect function of the substrate components. The adverse effect would be worse when combined with the stress produced by the difference in CTE's as pointed out earlier.

Figure 10 shows the difference of the two groups of coating materials in terms of loss modulus peaks. Solithane and Humiseal have high α-transition peak temperatures and their β-transition peaks are also weak in intensity, which is associated with their toughness.

Table 3 lists some modulus data for the purpose of comparison. The modulus of all materials increases with decreasing temperature, but the increase is as abrupt as 14 to 32 times through the α- or glass transition, which occurs in a small temperature range of 20 to 30°C. This clearly indicates that the effect of modulus fluctuation through Tg should be a serious concern and a desirable material should have a low glass transition temperature, preferably as low as below the expected temperature exposure range, if such a thermomechanical stress is to be avoided.
**Tg's Measured by DMA and TMA**

The great magnitude of change in modulus has made the determination of Tg's by the modulus measurement such as the DMA method very important from a practical point of view. Amazingly, the DMA method used in this work gave Tg's, as recorded in Table 3, 20 to 30°C higher than those values in Table 2 obtained by the TMA method. In general, it is recognized that the Tg values of a material often differ greatly, sometimes as much as 10 to 20°C, in literature from different sources. The observed variation may be attributed to the thermal history of the sample and to the methods of measurement (Reference 5). Also, the glass transition occurs over a temperature range rather than at a single, sharply defined temperature. It should be noted from the DMA and TMA thermograms that the temperature range, which the transition goes through, is quite wider in DMA than in TMA. This can be understandable since one polymer property's change, as a consequence of the polymer structural transition, may take place in a pace quite different from that of another property change of the polymer. In this work, the DuPont DMA instrument was used, which requires a much larger thermal capacity, both in the specimen and the sample clamping device, than the TMA instrument. The large capacity could cause significant thermal lag in temperature monitoring. For this reason and the fact that the TMA method is based on the conventional volume-temperature measurement, the Tg's determined by TMA shall be accepted as being more accurate and being comparable with those reported in literature. The loss modulus peaks by the DMA method in this work should be considered only as transition references, and the peak temperature values of the α-transition may be off from the material's true Tg.

**IV. CONCLUSION**

The thermomechanical properties of a polymeric material determined by the TMA and DMA methods are very useful information in relation to thermomechanical stresses particularly when the material is used as a coating or a potting material of electronics or other sensitive parts. The combined profile of the CTE and the modulus changes over a wide temperature range clearly shows the drastic effect of the glass transition on both the CTE and the modulus of a polymer, and the damaging potential due to such effect. The TMA method can also detect secondary transitions and it provides a convenient means for the study of a polymeric material's toughness.

Among the four polyurethane coating materials examined in this work, EN11 and Uralane-5753LV belong to one class with subzero glass transition temperatures, so low that they are likely below the temperature range of the common temperature cycling tests. In contrast, the glass transition temperatures of Solithane 113/113-300 (compound 1) and Humiseal-2B74 are near room temperature. Hence the electronics or other sensitive parts under either of these coatings will endure dangerously not only the thermomechanical stress due to the CTE change of the coating, but also the dramatic stress caused by the 26-32 times change of the modulus in each temperature cycle which goes through their Tg's.

**Acknowledgement**

The assistance provided by Mr. Andrew Mattie in preparing samples for the experiments is gratefully acknowledged.

**REFERENCES**


Table 1
Materials

<table>
<thead>
<tr>
<th>NAME</th>
<th>CHEMICAL CLASS</th>
<th>CURE SCHEDULE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lexan</td>
<td>Polycarbonate</td>
<td>(Thermoplastic, G.E.)</td>
</tr>
<tr>
<td>Plexiglas, regular</td>
<td>Acrylic polymer</td>
<td>(Thermoplastic, Rohm &amp; Haas)</td>
</tr>
<tr>
<td>Plexiglass-DR100</td>
<td>Acrylic polymer</td>
<td>(Thermoplastic, impact improved)</td>
</tr>
<tr>
<td>Conap EN11</td>
<td>Polyurethane</td>
<td>Room temperature for 7 more days</td>
</tr>
<tr>
<td>Uralane 5753LV</td>
<td>Polyurethane</td>
<td>Room temperature for 7 more days</td>
</tr>
<tr>
<td>Solithane-113/113-300</td>
<td>Polyurethane</td>
<td>Room temperature for 7 more days</td>
</tr>
<tr>
<td>Compound #1</td>
<td></td>
<td>Room temperature for 7 more days</td>
</tr>
<tr>
<td>Humiseal 2B74 (100/85 by wt.)</td>
<td>Polyurethane</td>
<td>Room temperature for 7 more days</td>
</tr>
<tr>
<td>Epon828/V140 (50/50 by wt.)</td>
<td>Epoxy</td>
<td>70°C for 3 hrs plus 80°C for 1 hr</td>
</tr>
</tbody>
</table>

Table 2
Thermomechanical Analysis Data

<table>
<thead>
<tr>
<th>Material</th>
<th>Tg, °C (duplicate)</th>
<th>Avg. CTE below Tg, m/m°C</th>
<th>Avg. CTE above Tg, m/m°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lexan</td>
<td>146, 148</td>
<td>64.3 (-140 ~ 130°C)</td>
<td>889 (146 ~ 168°C)</td>
</tr>
<tr>
<td>Plexiglas (regular)</td>
<td>110, 111</td>
<td>54.4 (-120 ~ 80°C)</td>
<td>3696 (114 ~ 121°C)</td>
</tr>
<tr>
<td>Epon828/V140</td>
<td>42, 43</td>
<td>63.5 (-140 ~ -40°C)</td>
<td>165 (60 ~ 130°C)</td>
</tr>
<tr>
<td>Conap EN11</td>
<td>-70, -68</td>
<td>88.8 (-140 ~ -80°C)</td>
<td>212 (-50 ~ 100°C)</td>
</tr>
<tr>
<td>Uralane 5753LV</td>
<td>-59, -62</td>
<td>90.6 (-130 ~ -70°C)</td>
<td>218 (-50 ~ 100°C)</td>
</tr>
<tr>
<td>Solithane-113/113-300, Compound #1</td>
<td>-7, -7</td>
<td>98.5 (-140 ~ -80°C)</td>
<td>247 (10 ~ 120°C)</td>
</tr>
<tr>
<td>Humiseal-2B74 (100/85)</td>
<td>5, 5</td>
<td>87.7 (-140 ~ -80°C)</td>
<td>225 (20 ~ 120°C)</td>
</tr>
</tbody>
</table>

NOTES: The first two materials are thermoplastics. All the rest are thermosets cured at room temperature for more than 7 days except Epon828/V140 which was cured at 70°C for 3 hours and 80°C for 1 hour. No effect on Tg and CTE was found by post-curing them at 65°C for 24 hours. Tg and CTE are symbols for glass transition temperature and coefficient of thermal expansion respectively.
Table 3
Modulus Changes at Glass Transitions by DMA\(^1\)

<table>
<thead>
<tr>
<th>Material</th>
<th>(1) Before Tg Deflection</th>
<th>(2) After Tg Deflection</th>
<th>Ratio (1)/(2)</th>
<th>Transitions, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>α− (Tg)(^2)</td>
</tr>
<tr>
<td>Lexan</td>
<td>1.7 (142°C)</td>
<td>0.07 (162°C)</td>
<td>24</td>
<td>155</td>
</tr>
<tr>
<td>Plexiglass (regular)</td>
<td>1.9 GPa (104°C)</td>
<td>0.14 GPa (126°C)</td>
<td>14</td>
<td>119</td>
</tr>
<tr>
<td>Epon828/V140 (51/49)</td>
<td>2.1 (52°C)</td>
<td>0.08 (84°C)</td>
<td>26</td>
<td>71</td>
</tr>
<tr>
<td>Conap EN11</td>
<td>497 MPa (-53°C)</td>
<td>35 MPa (-18°C)</td>
<td>14</td>
<td>-39</td>
</tr>
<tr>
<td>Uralane 5753LV</td>
<td>575 (−52°C)</td>
<td>22 (−18°C)</td>
<td>26</td>
<td>-40</td>
</tr>
<tr>
<td>Solithane−113/113−300, Compound #1</td>
<td>315 (9°C)</td>
<td>9.8 (36°C)</td>
<td>32</td>
<td>25</td>
</tr>
<tr>
<td>Humiseal-2B74 (100/85)</td>
<td>362 (16°C)</td>
<td>14 (49°C)</td>
<td>26</td>
<td>37</td>
</tr>
</tbody>
</table>

NOTES:
1. Dynamic mechanical analysis.
2. The α-transition corresponds to Tg. The transition temperatures by the loss modulus peaks are about 20 to 30°C higher than those determined by TMA as shown in Table 2.
3. The loss modulus peak temperature of Lexan, 153°C (±2°C), was used as a standard for DMA temperature calibration.
4. Weak in intensity.
Figure 1. Coefficients of Thermal Expansion of Various Materials  
Figure 2. TMA of Lexan
Figure 3. TMA of Conap EN11
Sample: EPON828/V140 51/49; 70C/3H CURE
Size: 39.71 x 13.89 x 3.36 mm
Method: POLYCARB 5C/MIN SUBZERO-2
Comment: 1 HZ; TEMP CALIBD;

-139.6°C
5.113 GPa

-122.2°C

-41.37°C
2.084 GPa

52.17°C

70.87°C

83.55°C
0.07837 GPa

Amplitude (p-p) = 0.40 mm

Temperature (°C)

Figure 4. DMA of Epon828/V140, Fixed Frequency Mode
Figure 5. DMA of Epox828/V140, Resonant Mode
Figure 6. DMA of Lexan
figure 8. DMA of Plexiglas DR100, Impact Improved
Figure 9. DMA: Comparison of the Storage Moduli of Polyurethane Coatings
Figure 10. DMA: Comparison of the Loss Moduli of Polyurethane Coatings

Amplitude (p-p) = 0.40 mm
Frequency: 1 Hz Fixed
Appendix

DMA Thermograms of Polyurethane Coatings
Figure A-1. Conap EN11
Figure A.2. Uralane 5753LV
Figure A-3. Solithane-113/113-300, Compound 1
Figure A-4. Humiseal-2B74
The thermomechanical properties of a number of widely used polymeric materials were determined by thermomechanical analysis and dynamic mechanical analysis. A combined profile of the coefficient of thermal expansion and the modulus change over a wide temperature range obtained by the analyses shows clearly the drastic effect of the glass transition on both the CTE and the modulus of a polymer, and the damaging potential due to such effect.