

Reliability characterization of adhesives used in passive optical components

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1.0 INTRODUCTION

The number of passive optical devices, connectors and splices used in optical fiber systems to the home and work place is increasing at an accelerating rate. The extent to which the manufacturing and packaging of these components relies on heat-curable epoxy-based and UV (Ultraviolet)-curable (epoxy acrylate or urethane acrylate-based) adhesives is unprecedented in the telecommunications industry. The use of these materials introduces new reliability issues which must be resolved; the most important of these is the ability of the components to function satisfactorily for long periods of time under adverse environmental conditions. Ongoing reliability tests, in which optical components are subjected to elevated temperatures and high relative humidity, are generating device failures which focus attention on optical adhesives. Specifically, device analysis has demonstrated that degradation in mechanical properties of these adhesive materials is the principal failure mechanism operating in these devices.

2.0 RELIABILITY ISSUES

Optical adhesives are ubiquitous materials which can be tailored to perform several functions in the various component technologies. Rigid adhesives are used as structural elements in fused biconic tapered technology to provide support for the fiber, in slab waveguiding technology to maintain alignment between the fiber and the substrate, and in connectors to secure and align the fiber within the ferrule. Flexible adhesives are employed to accommodate movement of sub-component parts. Index matching adhesives are used to fill gaps in the optical path. Epoxy-based adhesives are used as packaging material to provide a moisture barrier and stress relief for the fiber leads.

Commercial optical devices are available in plastic packages with ports for optical fiber leads. Since a variety of polymeric materials play an essential role in the device packaging, overall reliability of an optical device depends strongly on the long-term performance of these materials. While packaging materials are used to isolate device components from the environment, they also serve to fix active and passive components within a package. In the device reliability program that we have undertaken at Bellcore, we have addressed the dimensional stability and creep of polymeric materials used in devices and connectors. In this report, we focus our attention on the reliability of adhesives used for positioning fibers in the device and maintaining fiber-laser or fiber-substrate alignment.

Optical Adhesives Performance and Reliability

All optical adhesive materials must be chemically, thermally and dimensionally stable over the entire service temperature range and retain their adhesive strength at high temperatures and high levels of relative humidity. Optical adhesives that are used to join fibers to substrates in devices must support mechanical loads while maintaining fibers in position. In other words, they must be resistant to creep (flow under constant stress or load) over a wide range of operating conditions.

Optical adhesives are thermosetting (cross-linked) polymers. They are applied as viscous liquids that contain monomers, prepolymers and initiators and form cross-linked polymers by chemical reactions. The polymerization and cross-linking reactions are initiated either by heat or ultraviolet (UV) radiation. One can

obtain a wide range of adhesive physical characteristics by modifying the type and composition of components in the prepolymer mixture. As cross-linked materials, optical adhesives exhibit higher mechanical stability than many thermoplastics. Nevertheless, their mechanical properties are time and temperature-dependent, and they are known as viscoelastic (a term describing their intermediate position between viscous liquids and elastic solids) materials.

Adhesives Mechanical Behavior and Glass Transition Temperature

Adhesives can exhibit the features of a brittle glassy solid, an elastic rubber or a viscous liquid depending on the temperature and time scale of mechanical measurement. At low temperature or short times, they are glassy with a modulus of 10^9 - 10^{10} Pa (Pascal or $N\ m^{-2}$). At high temperatures or long measurement times, they are rubber-like with a 10^6 - 10^7 Pa modulus. Between the glassy and rubbery behavior, adhesives show a transition region through which physical and mechanical properties change dramatically. This is known as the glass transition region and identified by the glass transition temperature, T_g . The glass transition in polymers is a resonance phenomenon. At T_g , a major resonance occurs when the applied test frequency equals the natural frequency of long-range molecular motions. As the test frequency increases, faster (higher kinetic energy) motions become possible only at higher temperatures. Through the glass transition region, the specific volume-temperature profile shows an increase in slope with increasing temperature, the coefficient of thermal expansion exhibits a step increase and the modulus drops as illustrated in Figure 1. For cross-linked polymers, the magnitude of the modulus drop depends on the cross-link density (number of molecular cross-linkages in unit volume of material). As the cross-link density increases, the modulus drop becomes smaller and occurs over a broader temperature range.

In addition to time and temperature dependence, adhesive mechanical behavior depends on strain and strain-rate, too. For small strains, these materials obey Hooke's law (stress is proportional to strain) and show linear viscoelastic behavior. A commonly used technique, DMA (Dynamic Mechanical Analysis) takes advantage of the linear viscoelastic response for describing time and temperature dependence of mechanical behavior. The physical basis of the DMA technique and experimental measurement options are presented in Figure 2 and in the Appendix. This technique furnishes storage modulus (elastic component of the mechanical behavior), loss modulus (viscous component), and loss tangent ($\tan \delta$, a ratio of loss modulus to storage modulus) in a test where a small oscillatory strain or stress is applied to a specimen over a broad temperature and deformation-rate range. A key feature of this test is that the specimen structure remains unperturbed throughout the experiment.

3.0 ADHESIVES CHARACTERIZATION

We examined two ultraviolet (UV)-curable and two thermally curable adhesives for this report. Sample codes and curing conditions are presented in the following table.

Table 1
Sample Descriptions

Sample	Sample Code	Cure Condition
UV-Curable Adhesive 1	UVC1	5 Minutes
UV-Curable Adhesive 2	UVC2	30 Minutes
Heat-Curable Adhesive 1	HC1	10 Min. / 100°C
Heat-Curable Adhesive 2	HC2	10 Min. / 100°C

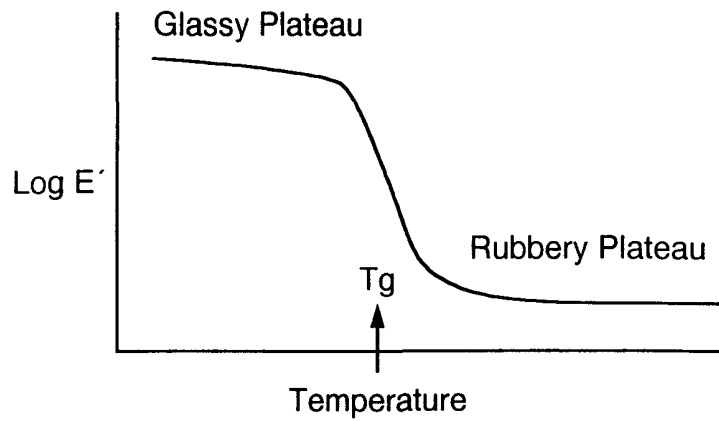


Figure 1. Stiffness Modulus vs. Temperature; the material exhibits rigid glassy behavior at temperatures below T_g , and becomes markedly softer above T_g .

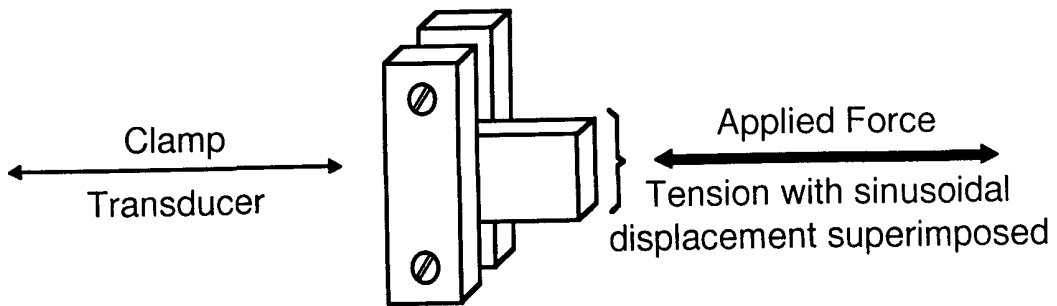


Figure 2a. The test sample for Dynamic Mechanical Analysis is mounted in slight tension (without deformation) with a superimposed sinusoidal displacement.

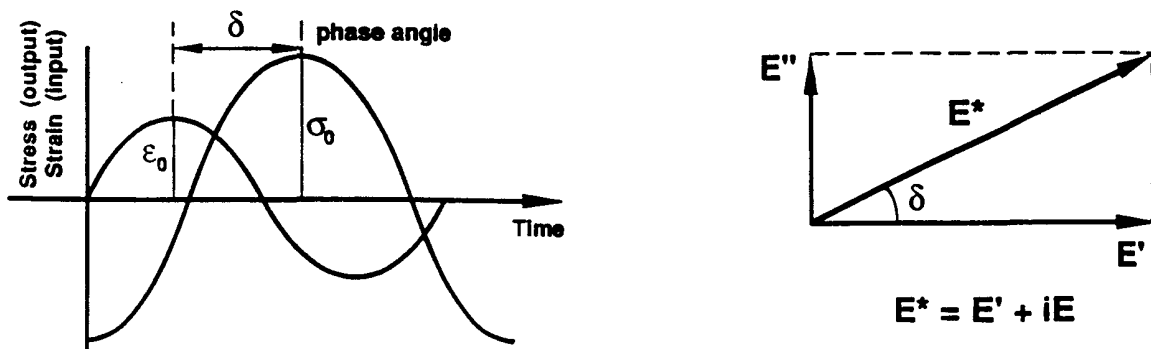


Figure 2b. The complex relationship between the input strain and the measured stress.

For ultraviolet curing, a Black-Ray B-100A UV source (with a peak intensity at 365 nm) was used. Thin UV-curable and thick heat-curable adhesive films were prepared for dynamic mechanical measurements. For 30-100 μ m thick films, tension mode was used while for 1-2mm thick, relatively stiff adhesive samples, bending mode was chosen. In both cases, accurate film dimensions measured on well-defined sample geometries enabled us to obtain accurate storage moduli, E' , and loss tangent, $\tan \delta$, values. For DMA analysis, we used Polymer Laboratories DMTA (Dynamic Mechanical Thermal Analyzer⁽¹⁾) Mark II. The tensile samples were 10 mm wide and 15 mm long. Only, 5 mm of the sample total length was used as free length for tensile measurements. Peak-to-peak displacement was 10 μ m. For clamped bending experiments, sample thickness, width and free length were 1-2 mm, 10 mm, and 5 mm, respectively. Samples were deformed in single cantilever bending with peak-to-peak bending displacement of 32 μ m. Test frequencies were 1 and 10 Hz, and thermal scan rate was 2 $^{\circ}$ C per minute.

4.0 RESULTS and DISCUSSION

In Figures 3 and 4, we show DMTA spectra for adhesive samples described in Table 1; Figures 3a and 3b are for samples UVC1 and UVC2 while Figures 4a and 4b are for the two-part thermally curable epoxy adhesives HC1 and HC2. All four spectra show a plot of storage modulus E' on the left ordinate and loss tangent $\tan \delta$ on the right ordinate against temperature on the abscissa. We first examine common features of all four spectra. At the beginning of each thermal scan at about -75 $^{\circ}$ C, all samples are glassy with a storage modulus of about 2 GPa (2×10^9 N m⁻² or Pa = 258 kpsi). As temperature rises at 2 $^{\circ}$ C min⁻¹ rate, log modulus of all four samples drops nearly linearly toward the glass transition region. Through this region, the storage moduli drop about two orders-of-magnitude to a rubbery plateau region. The loss tangent ($\tan \delta$), however, goes through a peak at T_g and remains near zero in the rest of the temperature scan shown in the figures 3 and 4. Table 2 presents a comparison of E' and $\tan \delta$ spectra at 1 Hz frequency and selected temperatures for the sample adhesives. The temperatures selected are -50 $^{\circ}$ C (about 10 $^{\circ}$ C lower than the lowest temperature used in the Bellcore temperature cycling test), T_g , and a temperature at which E' attains its lowest value in the entire spectrum.

Table 2
Dynamic Mechanical Properties of Sample Adhesives

Sample	T_g ($^{\circ}$ C)	E' @ -50 $^{\circ}$ C	E' @ T_g	E'_{min}	$\tan \delta$ @ T_g	$\tan \delta$ @ E'_{min}
UVC1	41	1.41 GPa	56.23 MPa	15.84 MPa	1.05	0.03
UVC2	34	0.71 GPa	39.81 MPa	10.00 MPa	1.10	0.10
HC1	84	1.78 GPa	56.23 MPa	15.84 MPa	0.88	0.02
HC2	128	1.58 GPa	63.09 MPa	0.50 MPa	0.65	0.07

In Table 2, we first note that T_g values for UV-curable adhesives are lower (34-41 $^{\circ}$ C) than the T_g 's for heat curable adhesive samples (84-128 $^{\circ}$ C). In Figures 3 and 4, T_g values shift upward with test frequency. For a tenfold (one order-of-magnitude) increase in frequency, T_g shifts 5-6 $^{\circ}$ C for samples UVC1, UVC2 and HC1 while HC2 exhibits a 9 $^{\circ}$ C shift. The observed T_g shifts are similar to 5-7 $^{\circ}$ C shift per decade (tenfold) of frequency in linear amorphous polymers⁽²⁾. The third column of the Table gives the storage moduli at -50 $^{\circ}$ C where all adhesives are in the glassy region. E' values at this temperature are of the same order of magnitude and very typical of glassy polymers. In the fourth column of Table 2, storage moduli at T_g are 18-25 times lower than those at -50 $^{\circ}$ C. The lowest E' values attained at the end of glass transition are shown in the fifth column of the table. These values are about two orders-of-magnitude smaller than those at -50 $^{\circ}$ C. For uncross-linked polymers, the storage modulus drop from the glassy to the rubbery region is

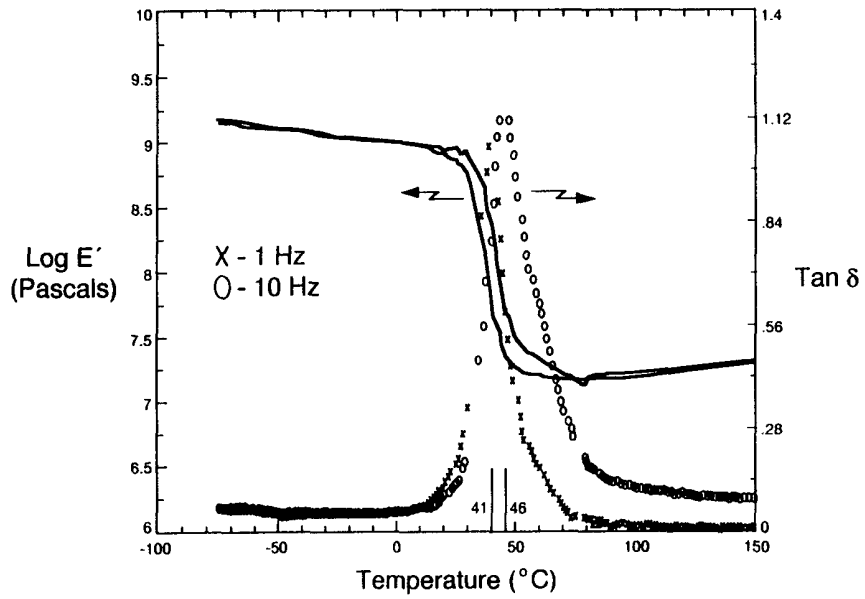


Figure 3a. UVC-1 after five minute UV exposure.

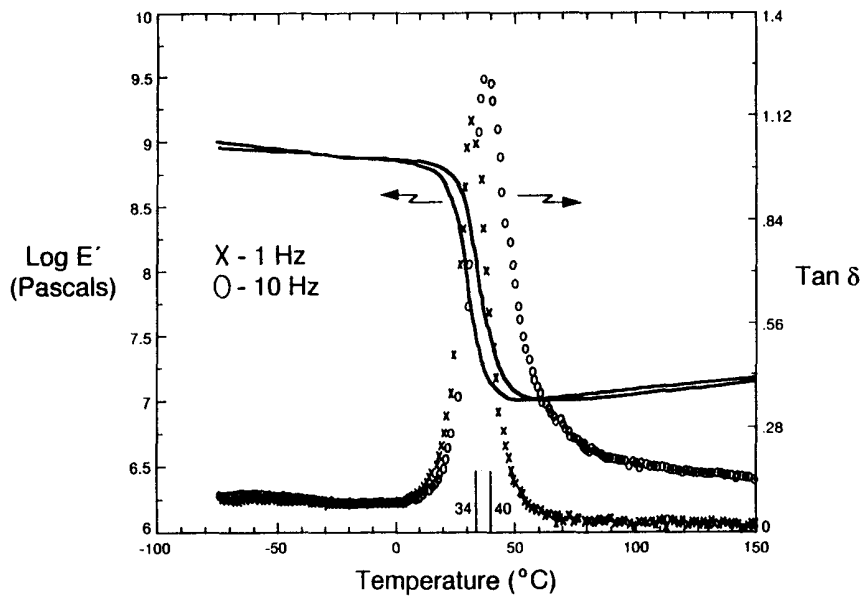


Figure 3b. UVC-2 after thirty minute UV exposure.

Figure 3. Mechanical behavior of ultraviolet curable adhesives after the manufacturers' recommended cure.

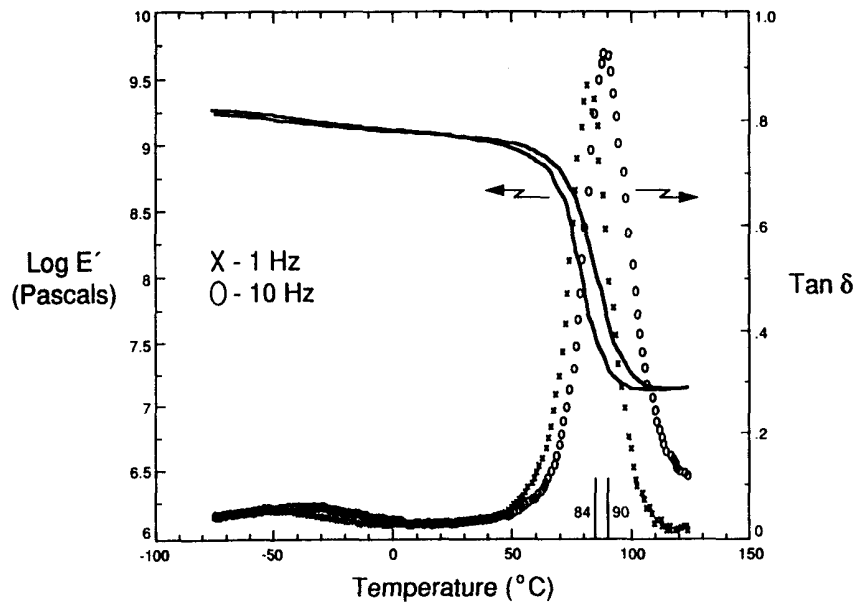


Figure 4a. HC-1

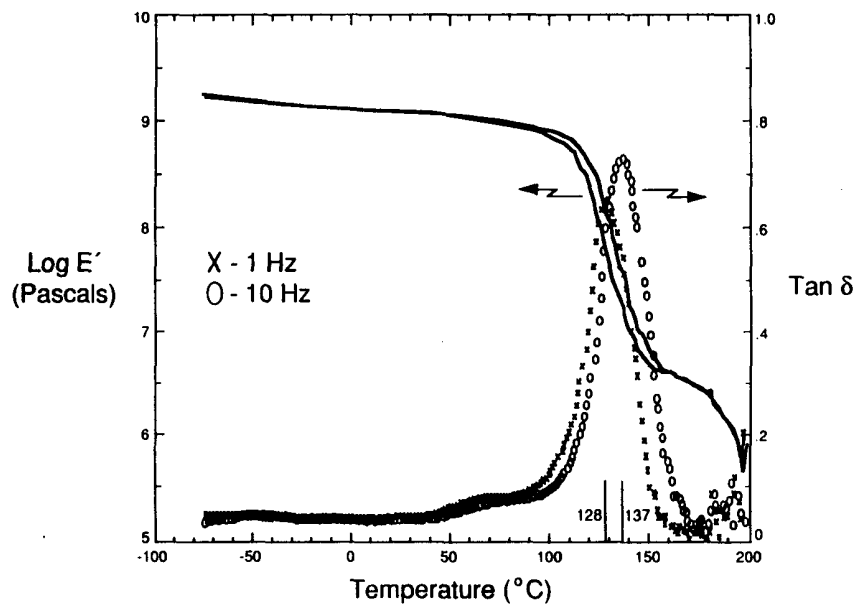


Figure 4b. HC-2

Figure 4. Mechanical behavior of thermally curable adhesives cured at 100°C for ten minutes. Note that the Tg's are than those of the UV-curable adhesives.

typically three orders-of magnitude. The smaller drop in E' values through the glass transition suggests that molecular motions are impeded, thereby confirming that the samples are cross-linked. One further evidence of cross-linking in these samples is that E' becomes constant or slowly increases with temperature in the rubbery plateau region. E'_{\min} is called the rubbery plateau modulus and can be used to estimate the cross-link density of the samples via the rubber elasticity theory.⁽³⁾ Except for sample HC2, E'_{\min} values are similar and suggest comparable cross-link densities. The storage modulus E'_{\min} for HC2 appears to be too low and suggests sample degradation during the DMTA experiment. In the last two columns of Table 2, we list $\tan \delta$ values at T_g and at the temperature of E'_{\min} . A lower $\tan \delta$ value for the sample HC2 suggests a more rigid internal structure compared to other samples. A high T_g value with low $\tan \delta$ is highly desirable for the reliability of optical adhesives. At the T_g where the volume relaxation rate is at its maximum value, materials tend to flow to relieve internal stresses and external loads. Thus, in the glass transition and rubbery plateau regions, dimensional instabilities (via expansion/contraction phenomenon) and creep (flow under constant load) pose serious reliability risks. In selecting adhesives for devices, therefore, one should avoid materials that exhibit transitions such as glass transition and relaxations in the service temperature range. From the figures 3 and 4, we propose that the maximum service temperature be below the temperature in the glassy region where E' -T profile at 1 Hz diverges from E' -T profile at 10 Hz. This can be translated to the following quantitative rule:

$$T_{\text{service,max}} (^{\circ}\text{K}) / T_g (^{\circ}\text{K}) \leq 0.9$$

For instance, a $T_{\text{service,max}} = 75^{\circ}\text{C}$ would require an adhesive with the $T_g \geq 114^{\circ}\text{C}$. In applying this rule, one should use a DSC (Differential Scanning Calorimeter)-measured T_g instead of the T_g determined by DMA since the DSC-measured T_g ⁽⁴⁾ is lower than the DMA-measured T_g under similar thermal scan rates.

Adhesives Mechanical Behavior and Cure Schedules

Figure 5 shows a DMTA spectrum for a film of UVC1 adhesive cured only for 3 minutes. Although this spectrum appears similar to the spectrum of a 5-minute cured UVC1 sample shown in Figure 3a, we note some significant difference in properties. Table 3 presents these differences for 1 Hz spectra.

Table 3
Effects of Cure Time on Dynamic Mechanical Properties

UV Exposure	T_g ($^{\circ}\text{C}$)	E' @ -50°C	E' @ T_g	E'_{\min}	$\tan \delta$ @ T_g	$\tan \delta$ @ E'_{\min}
3 Minutes	26	1.49 GPa	35.48 MPa	5.62 MPa	1.17	0.28
5 Minutes	41	1.41 GPa	56.23 MPa	15.84 MPa	1.05	0.03

The sample with 3-minute UV exposure has a lower T_g . The glassy moduli of the samples are comparable. The most significant differences between the two samples appear in the last four columns of this table. The 3-minute UV-exposure results in lower moduli and higher $\tan \delta$ values. This result suggests that the cross-linked network formed by 3-minute exposure is loose and compliant. In cross-linked polymers of a given chemical structure, there are two strong indicators of the extent of cross-linking or network tightness (rigidity): the ratio of glassy modulus to rubbery plateau modulus and the ratio of $\tan \delta$ at T_g to $\tan \delta$ for the rubbery plateau. Table 4 gives a comparison of these characteristic ratios.

Table 4
Effects of Cure Time on the Characteristic Ratios

UV Exposure	E' @ -50°C / E'_{\min}	$\tan \delta$ @ T_g / $\tan \delta$ @ E'_{\min}
3 Minutes	265	4
5 Minutes	89	35

The modulus ratios suggest that 3-minute exposure gives a much lower extent of cross-linking. A lower $\tan \delta$ ratio confirms that 3-minute exposure results in a loose structure. We can conclude that underexposure in UV-cross-linked adhesives results in lower T_g , under-cured materials and presents a reliability hazard.

Effects of Aging on Mechanical Behavior

Optical adhesives are required to retain their original characteristics throughout the service life of fiber optic devices. We now examine the effects of 500 hours of aging three adhesive samples (two UV-curable and one heat-curable) at 85 °C / 95 % RH (Relative Humidity) on their dynamic mechanical behavior. Figures 6a-6c show DMTA spectra for adhesive samples UVC1 and UVC2 and HC2. We note that the T_g 's rose 7 and 15 °C for UVC1 and UVC2 samples, respectively, whereas the T_g for the sample HC2 dropped about 20 °C. Table 5 gives a comparison of moduli and loss tangent at 1 Hz for these samples before and after aging.

Table 5
Effects of Aging on the Dynamic Mechanical Properties

Sample	T_g (°C)	E' @ -50°C	E'_{min}	$\tan \delta$ @ T_g	$\tan \delta$ @ E'_m
UVC1	41	1.41 GPa	15.84 MPa	1.05	0.03
UVC1 (Aged)	48	1.58 GPa	17.78 MPa	0.89	0.01
UVC2	34	0.71 GPa	10.00 MPa	1.10	0.10
UVC2 (Aged)	49	1.41 GPa	15.84	0.87	0.02
HC2	128	1.58 GPa	3.16 MPa	0.65	0.07
HC2 (Aged)	106	0.87 GPa	11.54 MPa	0.6	0.01

From this table, we observe that the aging treatment resulted in similar characteristics for the UV-cured samples; the T_g 's, E' 's and $\tan \delta$ values appear to converge to those of a high T_g , more rigid material. The characteristic ratios for the sample UVC1, however, did not change with aging. For instance, the E' ratio for the aged UVC1 sample is 89, the same as that of the UVC1 sample before aging. This suggests that the aging treatment did not affect the cross-link density of the adhesive. Nonetheless, the $\tan \delta$ value drops from 1.05 to 0.89 (the ratio of $\tan \delta$ at T_g to $\tan \delta$ at E'_{min} increases from 35 for this sample before aging to 89 after aging), confirming that the aged sample has become more rigid. These comparisons suggest that aging leads to a stiffening of the adhesive structure with the loss of lower molecular weight components that may be volatilized during the aging treatment. From a reliability standpoint, this result implies shrinkage of the adhesive film during the aging process. However, it also means that the adhesive sample evolves to a physically more stable, higher- T_g material during the 500-hour aging treatment.

The last two rows show a comparison of dynamic mechanical properties for the sample HC2 before and after 500-hour aging at 85 °C / 95% RH. We caution the reader that these comparisons are tentative since our results are preliminary on the effects of aging heat-curable samples. For instance, a 22 °C drop in T_g is too large to be associated with any physical changes in the adhesive structure. Furthermore, this T_g drop is not consistent with a large decrease in the characteristic storage modulus ratio (from 500 for the unaged sample HC2 to 75 after aging). Nearly nine-fold drop in the modulus ratio suggests that substantial cross-linking occurred during aging and must have resulted in a large T_g increase. Tentatively, our preliminary results indicate some degradation of the adhesive sample HC2 after 500 hours at 85 °C / 95% RH.

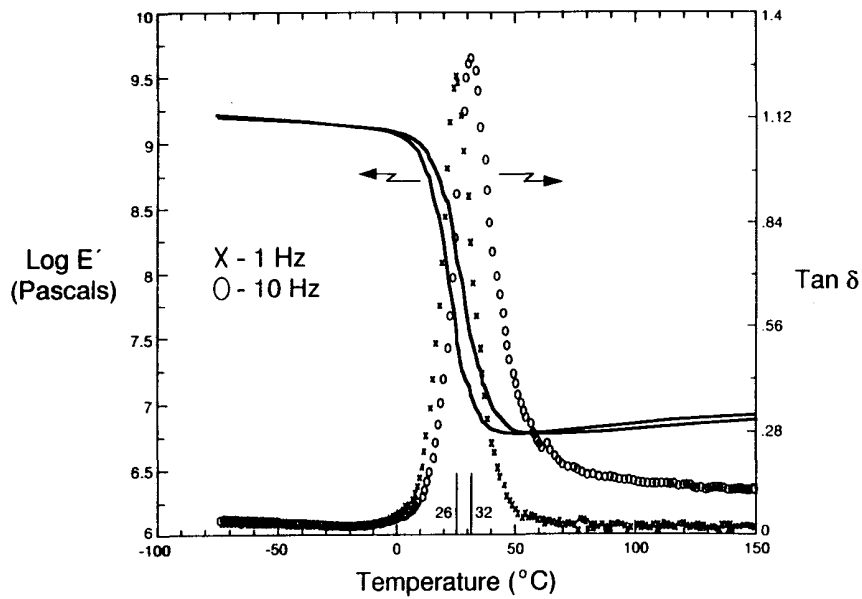


Figure 5. UVC-1 after a reduced cure of three minutes exposure. Note that the Tg is lower than the sample shown in Figure 3a.

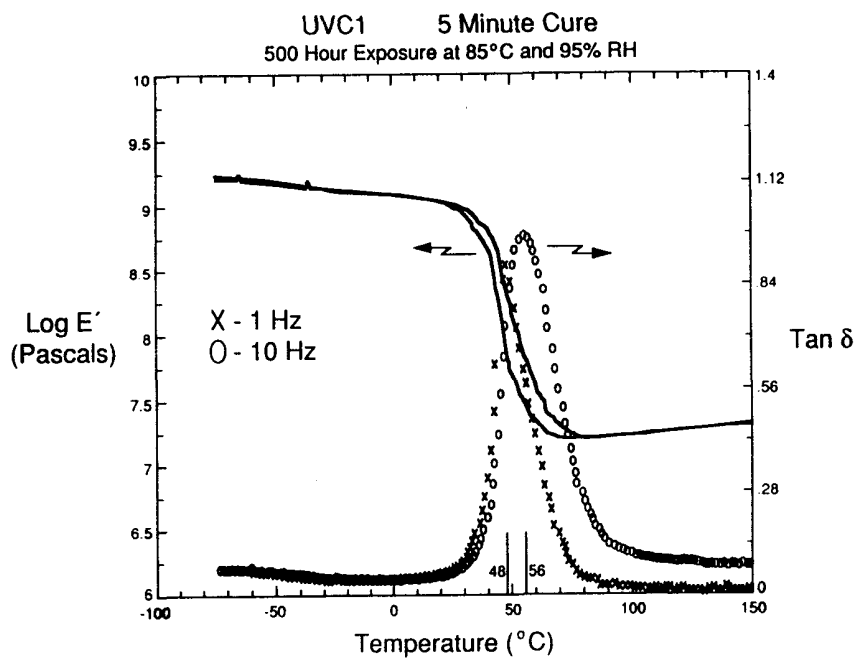


Figure 6a. UVC-1 showing an increase in Tg indicating that continued curing is occurring during this test. Compare with Figure 3a.

Figure 6. Mechanical behavior of adhesive samples after exposure to test conditions of 85°C and 95% relative humidity.

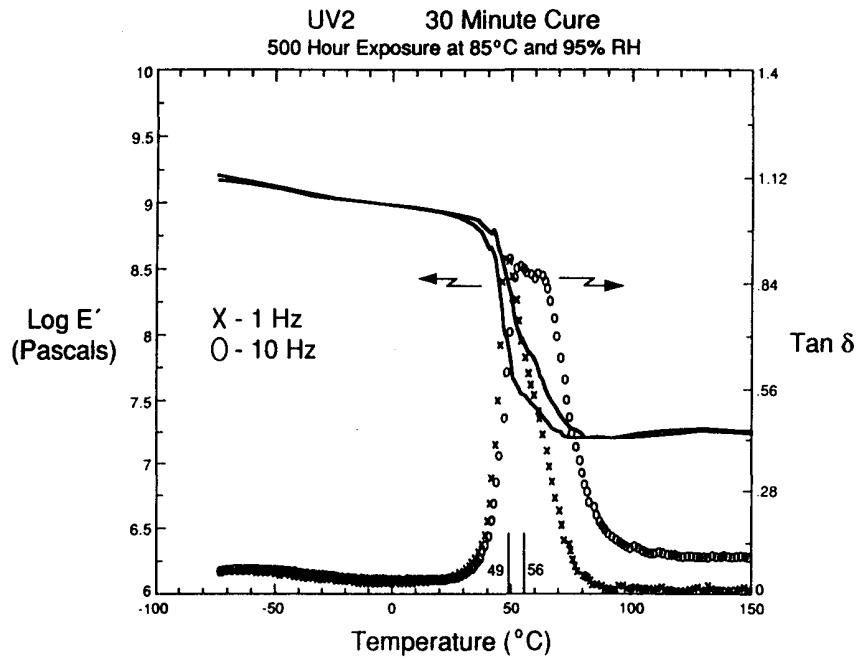


Figure 6b. UVC-2 showing an increase in T_g indicating that continued curing is occurring during this test. Compare with Figure 3b.

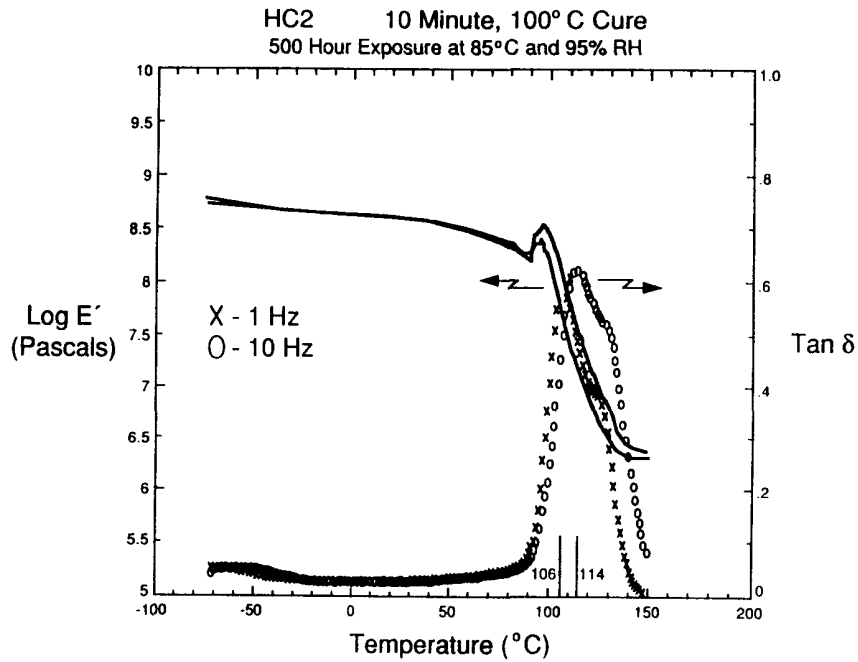


Figure 6c. The T_g of sample HC-1 has dropped indicating some degradation has occurred as a result of exposure to the elevated temperature and high relative humidity. Compare with Figure 4b.

Figure 6. Mechanical behavior of adhesive samples after exposure to test conditions of 85°C and 95% relative humidity.

5.0 CONCLUSIONS

Optical adhesives are essential components of fiber optic devices. They are used to hold such device components as lasers, modulators and optical fibers positioned and aligned with respect to each other. For reliable operation of these devices, optical adhesives must retain their original characteristics, that is, they must be chemically, thermally and dimensionally stable. Moreover, the adhesive materials must resist creep under thermomechanical loads. In this report, we examined major optical adhesive reliability issues by an evaluation of dynamic mechanical properties for two UV-curable and two heat-curable adhesive materials. We used DMTA (Dynamic Mechanical Thermal Analyzer) to compare general features of dynamic mechanical properties for these adhesives. We found that UV-curable materials had lower T_g than the heat-curable samples. The UV-curable adhesive T_g 's are several degrees above room temperature, and the rubbery plateau falls within the service temperature range. These results indicate that UV-curable adhesives are not suitable as structural elements in optical device applications. From a comparison of storage moduli and loss tangent, we developed a rule for dimensional stability and creep resistance of these materials. According to this rule, the maximum service temperature for a given adhesive should be about 40 °C lower than its T_g . We also examined the effects of lower-than optimal UV exposure on the adhesive dynamic properties. We determined that underexposure results in reduced T_g and presents a reliability hazard. Finally, we examined the effects of 500-hour aging at 85 °C /95% RH on the UV-curable and heat-curable adhesive mechanical properties. For the UV-curable adhesive samples, the aging treatment caused 7-15 °C increase in T_g and resulted in more rigid materials with no apparent structural degradation. These observed changes, however, suggest that UV-curable adhesives must undergo some shrinkage during aging and indicate a significant reliability risk for loss of fiber position and alignment. For the heat curable samples, our preliminary results suggest that some degradation occurred as a result of the exposure to elevated temperature and high relative humidity. Tests to study this degradation are in progress.

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APPENDIX

Dynamic Mechanical Analysis

For an oscillating (sinusoidally varying) strain, stress also varies cyclically, but lags behind strain for a viscoelastic material as shown in the following expressions

$$\varepsilon = \varepsilon_0 \sin \omega t \quad (1)$$

$$\sigma = \sigma_0 \sin(\omega t + \delta) \quad (2)$$

where δ is the phase angle or phase lag describing the relative angular displacement of stress and strain shown in Figure 1. Expanding the equation for stress gives

$$\sigma = \sigma_0 \cos \delta \sin \omega t + \sigma_0 \sin \delta \cos \omega t \quad (3)$$

The stress in Eq.3 is resolved into two components; the first term on the right gives the component in-phase with strain, and the second term containing $\cos \omega t$ is 90° ($\pi/2$) out-of-phase with the strain. Hence we define two dynamic moduli: E' which is in-phase with the strain and E'' which is out-of-phase with the strain.

$$E' = \frac{\sigma_0}{\varepsilon_0} \cos \delta \quad E'' = \frac{\sigma_0}{\varepsilon_0} \sin \delta \quad (4)$$

Eq.3 can be rewritten as follows

$$\sigma = \varepsilon_0 E' \sin \omega t + \varepsilon_0 E'' \cos \omega t \quad (5)$$

The phase angle δ is defined as

$$\tan \delta = \frac{E''}{E'} \quad (6)$$

Rewriting Eqs.1 and 2 in complex notation,

$$\varepsilon = \varepsilon_0 \exp(i\omega t) \quad \sigma = \sigma_0 \exp i(\omega t + \delta) \quad (7)$$

we obtain the following expression for complex modulus E^*

$$E^* = E' + i E''$$

E' and E'' are called the storage modulus (real part of the complex modulus) and loss modulus (imaginary part of the complex modulus), respectively. Experimentally, moduli can be measured in tension, compression, bending for viscoelastic solids, and in shear for viscoelastic liquids.