Proc. of SPIE Vol. 2290, Fiber Optic Materials and Components, ed. H H Yuce, D K Paul, R A Greenwell (Sep 1994) Copyright SPIE

Reliability Characterization of UV-Curable Adhesives Used in Optical Devices

I.M. Plitz, O.S. Gebizlioglu , M.P. Dugan*

Bellcore
331 Newman Springs Rd
Red Bank, NJ 07701

*Anadigics, Inc.
35 Technology Drive
Warren, NJ 07059

ABSTRACT

UV (ultra-violet)-curable adhesives were identified as the underlying cause for failure of devices subjected to accelerated aging conditions. These adhesives must be resistant to degradation and dimensional/mechanical instabilities such as creep. We examined two UV-curable adhesives and found that thermal post-curing caused some shrinkage and degradation. However, post-curing also raised the adhesive glass transition temperature, thereby reducing the reliability risk associated with mechanical instability. We investigated the dimensional/mechanical stability of UV adhesives by measuring thermal expansion/contraction and creep compliance. We found that the adhesive thermal expansion and creep compliance are large enough to pose device reliability risk. Raising the glass transition temperature of UV-curable adhesives by thermal post-cure can improve optical device reliability by lowering the creep compliance.

Keywords: UV-curable adhesives, creep, glass transition temperature, device reliability

1. INTRODUCTION

As the installation of optical fiber cable increases, so does the use of passive optical devices. No longer are these components protected in telephone central offices, but they are found in outside cabinets and ONU's (Outside Optical Network) where they are exposed to the extremes of heat and humidity. With this increased potential for exposure to environmental stress, it is necessary to focus on the reliability issues associated with the choice of materials which comprise the component package.

Bellcore test programs have produced optical device failures during exposure to elevated temperatures and high levels of relative humidity.[1-3] The failure is often manifested as increased signal attenuation due to fiber movement as shown by component analysis after completion of the tests.[4] These failures typically occur at the interface between the fiber and the substrate which point to adhesive instability as the underlying cause. Other published reports indicate that mechanical changes, dimensional instability and adhesive degradation result when optical components were subjected to accelerated environmental stress testing.[5-7] The test conditions used in these programs are comparable to actual temperatures recorded under field conditions. Published reports show that metal electronic cabinets installed in the southwest reach temperatures as high as 70 °C.[8]

Generally, adhesives found in passive components are cross-linked polymers prepared from functional oligomers and monomers that are reacted through photoinitiation by ultraviolet (UV) radiation. They are used to join the fibers to optical substrates and to maintain optical alignment. Potential problems arise if the adhesive bond is weakened due to polymer degradation or mechanical stress, or if the polymer exhibits dimensional instability by shrinking or expanding in response to environmental factors. Therefore, it is important that component manufacturers choose adhesives that are chemically, thermally and mechanically stable over the service temperature and relative humidity ranges.

Bellcore requirements currently specify a minimum glass transition temperature (T_g) for adhesives used in passive devices.[9] Through the glass transition region, the coefficient of thermal expansion increases and the modulus of the polymer drops. The modulus drop depends on the cross-link density in the UV-cured adhesives. As the cross-link density increases, the modulus drop becomes smaller and occurs over a broader temperature range. Although optical adhesives exhibit higher mechanical stability than many non-cross-linked thermoplastics, their mechanical properties are time and temperature dependent. Therefore, aging affects long-term performance and can be used as a tool to predict long-term adhesive reliability. In an earlier paper[10], we reported on the mechanical behavior of two UV-curable adhesives. We found that aging these samples 500 hours at 85 °C/95% RH led to a 7-15 °C rise in T_g and resulted in a more rigid structure with no apparent degradation (no appreciable decrease in the rubbery plateau modulus). However, this finding suggested that these adhesives must shrink during aging and identified a reliability risk associated with fiber movement and loss of fiber to substrate alignment.

In this report, we will examine the effects of aging two UV-cured adhesives at 85 °C and <30% relative humidity. We will also determine the effect of thermally post-curing these adhesives and we will consider the creep behavior of the post-cured samples at 40 °C and relate these effects to the dynamic mechanical behavior. We will discuss the theory of creep behavior characterization and demonstrate how the mechanical behavior of UV-cured adhesives affects the long-term reliability of passive optical devices.

2. EXPERIMENTAL MATERIALS AND METHODS

We evaluated two commercially available UV-curable adhesives for this study, UV1 and UV2. They were cured using a Black-Ray-B-100A UV source with a peak intensity at 365 nm. Films were prepared by drawing a layer of uncured resin across a quartz plate using a 0.003 inch draw bar. After UV exposure, samples were subjected to thermal post-curing or were aged for six weeks at 85 °C. Test specimens were cut from these films for dynamic mechanical analysis with a DMTA (Dynamic Mechanical Thermal Analyzer). The theory and experimental methods of dynamic mechanical analysis were discussed elsewhere.[10]

Table 1
Sample Descriptions

Sample	Sample Code	Film Thickness (μm)	Conditions
Adhesive 1 Control	UV1	100	5-minute cure (as per manufacturer directions)
Adhesive 1 Post-Cured	UV1a	200	UV1 post-cured @ 45 °C for 12 hours
Adhesive 1 Aged	UV1b	100	UV1 aged 6 weeks @ 85 °C
Adhesive 1 Aged	UV1c	100	UV1 aged 6 weeks @ 85 °C/85% RH
Adhesive 2 Control	UV2	100	20-minute cure (as per manufacturer directions)
Adhesive 2 Post-Cured	UV2a	300	UV2 post cured @ 45 °C for 12 hours
Adhesive 2 Aged	UV2b	100	UV2 aged 6 weeks @ 85 °C
Adhesive 2 Aged	UV2c	100	UV2 aged 6 weeks @ 85 °C/85% RH

We used a Polymer Laboratories DMTA Mark III to record storage modulus (E') and the loss tangent (tan δ). Test frequencies were 1 and 10 Hz, and the heating rate was 2 °C/min. The glass transition temperature (T_g) was defined as the temperature of the DMTA tan δ peak. Thermal expansion profiles were determined between -25 °C and 125 °C with a 2 °C/min. heating rate. Isothermal creep measurements were carried out at 40 °C under a constant stress of 0.3 MPa (42 psi).

3. RESULTS AND DISCUSSION

3.1 Post-curing and aging

We reported earlier[10] that two commercial UV-curable adhesives exhibited substantially lower transition temperatures, T_g, than two thermally-curable adhesives. In this paper, we show that thermal post-cure at 45 °C can raise the T_g and improve the dimensional/mechanical stability of UV-curable adhesives for optical device applications. Figure 1 presents DMTA spectra of the storage modulus, E', and loss tangent, tanδ, for sample UV1a. The modulus-temperature profile shows three distinct regions: the glassy region where the glassy storage modulus E'_g is about 2.2 GPa, the glass transition region through which the storage modulus E' drops about two-orders-of-magnitude, and the rubbery plateau region. A storage modulus at the rubbery plateau of nearly 10 MPa signifies the cross-linked structure of the adhesive sample. In the glass transition region, the modulus-temperature profile shows an inflection at the glass transition temperature while tan δ-temperature profile goes through a maximum. As shown in this Figure, T_g depends on the test frequency and shifts 5-7 °C per decade of frequency.

In Table 2, we present a comparison of dynamic mechanical properties (glassy storage modulus E'_g, storage modulus E' at T_g, rubbery plateau storage modulus E'_r, loss tangent (tan δ) at T_g, and the rubbery plateau loss tangent) to demonstrate the effects of thermal post-cure. The thermal post-cure at 45 °C resulted in increased values of T_g, E'_g and E' at T_g, and decreased tanδ peak value. The effect on the rubbery plateau modulus, E'_r, appears to be mixed; while the UV1 sample showed a decrease by a factor of two, the UV2 sample exhibited a rise in E'_r by a factor of 2.4. If the thermal post cure resulted in only additional cross-linking, this would lead to a substantial rise in the rubbery plateau modulus, E'_r, and we would expect only a minimal change in the glassy modulus E'_g and the modulus E' at T_g.[11] Thus, the trends of Table 2 suggest shrinkage (a drop in specific volume) for both samples and some degradation during thermal post-cure for the UV1 samples. From the standpoint of dimensional/mechanical stability, however, thermal post-cure gives the samples higher transition temperatures and therefore reduces the adhesive-related reliability risk in device applications.

Table 2
Dynamic Mechanical Properties of Sample UV-Curable Adhesives

Sample	T_g (°C)	E'_g (GPa)	E' @ T_g (MPa)	E'_r (MPa)	Tanδ @ T_g	Tanδ @ E'_r
UV1	41	1.41	56.23	15.84	1.05	0.03
UV1a	50	2.26	84.64	7.96	0.74	0.04
UV2	34	0.71	39.81	10.00	1.10	0.10
UV2a	46	3.52	133.63	23.55	0.83	0.01

In addition to the initial mechanical properties of the UV-curable adhesives, environmental factors such as temperature and humidity may affect the long-term performance and reliability of these materials in devices. In Table 3, we show the dynamic mechanical properties of the samples exposed to two aging environments for six weeks: 1) 85 °C/95% relative humidity (RH), 2) 85 °C with <30% humidity. We showed earlier[10] that the samples UV1c and UV2c, exposed to 85 °C/95% RH for 500 hours (about 3 weeks), did not degrade. The T_g and the glassy moduli of the aged samples suggested that these samples had become more rigid. The rubbery plateau moduli, however, indicated that this stiffening did not result from cross-linking, but rather suggested shrinkage most likely due to the loss of adhesive components by volatilization. The samples aged at 85°C

with low humidity exhibited the highest T_g of all UV-curable adhesives examined to date. Their moduli are also the largest of all adhesive samples we have investigated. The rubbery plateau modulus E'_r of the sample UV2b suggests substantial cross-linking while E'_r of the sample UV1b indicates some degradation. A more definitive assessment of the effects of aging treatments requires a detailed examination of the adhesive formulations (components and compositions).

Table 3
Dynamic Mechanical Properties of Adhesives after Aging

Initial Values

Sample	Tg (°C)	E'_g (GPa)	E' @ Tg (MPa)	E'_r (MPa)	Tanδ @ Tg	Tanδ @ E'_r
UV1	41	1.41	56.23	15.84	1.05	0.03
UV2	34	0.71	39.81	10.00	1.10	0.10

Samples Aged Six Weeks @ 85 °C

Sample	Tg (°C)	E'_g (GPa)	E' @ Tg (MPa)	E'_r (MPa)	Tanδ @ Tg	Tanδ @ E'_r
UV1b	57	3.57	136	4.93	0.80	0.02
UV2b	57	3.03	125	31.0	0.81	0.004

Samples Aged Six Weeks @ 85 °C / 85% RH

Sample	Tg (°C)	E'_g (GPa)	E' @ Tg (MPa)	E'_r (MPa)	Tanδ @ Tg	Tanδ @ E'_r
UV1c	48	1.58	82.5	17.8	0.89	0.01
UV2c	49	1.41	75.0	15.8	0.87	0.02

3.2 Thermal expansion and creep measurements

As shown in the preceding paragraphs, UV-curable adhesives exhibit transitions in or close to the service temperature range of optical devices. Therefore, to minimize the risk of adhesive dimensional/mechanical instability that may result in fiber movement and consequent signal attenuation, the following two adhesive characteristics should be considered in optical device design:

1) Large thermal expansion coefficient relative to glass, ceramic and metallic components in optical devices.
2) Creep under constant mechanical stress.

Adhesives in optical devices are used to fix fibers onto metallic and/or ceramic substrates. To assess the reliability risk associated with this potential thermal mismatch, we examined the linear thermal expansion of the adhesive samples post-cured at 45 °C. Figures 2a and 2b present thermal expansion profiles for samples UV1a and UV2a in the temperature range of -25 °C to 125 °C. Although the thermal expansion profiles appear similar for these samples, the thermal contraction profile over the temperature range from 125 °C to 25 °C for sample UV1a (the higher T_g sample) exhibits a lower hysteresis than sample UV2a (lower T_g sample). This hysteresis arises from viscoelastic relaxations through the glass transition region. It should be noted that the hysteresis behavior is very sensitive to the sample T_g. Over the entire temperature range, the total thermal strain (based on the room-temperature length of the adhesive samples) remains below three percent. From the thermal expansion profiles of Figures 2a and 2b, we determined the following values for the coefficient of linear thermal expansion (α) over the glass transition region:

Sample UV1a: $\alpha = 2.4 \times 10^{-4}\ °C^{-1}$ at T_g (1Hz) = 50°C

Sample UV2a: $\alpha = 2.4 \times 10^{-4}\ °C^{-1}$ at T_g(1Hz) = 46°C

Considering the two to three orders-of-magnitude lower thermal expansivity of non-polymeric device components[12], the adhesive thermal expansion/contraction may lead to thermal mismatch-induced failures unless device design allows for differential thermal expansion/contraction by the judicious choice of materials and component dimensions.

A second and equally important source of adhesive-related reliability risk is the creep of an adhesive under constant stress in the service environment. Creep is a slow continuous deformation of a viscoelastic material under constant load/stress. An adhesive's response to mechanical stress is intermediate between the elastic response (instantaneous deformation under load and complete recovery after the load removal) of a solid such as a metal or a ceramic at room temperature, and the viscous response of a liquid (flow under load with no recovery). The viscoelastic response is strongly dependent on the rate and time of loading as well as the magnitude of the mechanical stress. At low mechanical stresses where the stress remains directly proportional to strain at any given time, the response is termed linearly viscoelastic. Most viscoelastic materials are linear over certain ranges of stress, strain, time, temperature and nonlinear over larger values of some of these variables. For instance, under a short time of loading, many polymers exhibit linear response even at stresses where considerable nonlinearity occurs if the loading time is longer.[13] Creep is generally described in three stages: primary creep where the rate of deformation decreases with time, and the response is linearly viscoelastic; the second stage, where the deformation rate is nearly constant, although polymeric materials do not exhibit a pronounced secondary creep; and the third stage called tertiary creep where deformation occurs at an increasing rate and ends in fracture. Although creep usually occurs under combined stresses, it is usually studied in one of three deformation modes: uniaxial tension, compression and shear. For polymers, it is customary to report linear viscoelastic creep in a plot of creep compliance (creep strain divided by stress) against time at the temperature of the creep experiment. For linear creep, the creep compliance is independent of stress, and the creep compliance-logarithm of time plot exhibits a characteristic sigmoidal shape.

In optical device applications, adhesives may be subjected to a combination of multiaxial tensile/compressive and shear deformations. We, however, used uniaxial tensile deformation to measure the tendency of adhesives for linear viscoelastic creep. Figure 3 shows uniaxial tensile creep compliance (D) - time profiles taken at 40 °C under a constant stress of 0.3 MPa (43 psi) for the samples UV1a and UV2a. Both samples exhibit an initial instantaneous creep and reach a limiting compliance within about 30 minutes. Sample UV1a shows a lower limiting creep compliance of 0.055 MPa^{-1} (a limiting creep strain of 0.020) when compared with sample UV2a (a limiting compliance of 0.070 MPa^{-1} and a limiting creep strain of 0.016). Under the relatively mild conditions used in these creep experiments, the magnitudes of creep compliances measured are expected to adversely impact device reliability. A uniaxial tensile creep strain of 0.016 is equivalent to a 16-μm displacement (elongation) of a 1 mm-long adhesive strip, and tolerances in fiber positioning in an optical device are only within a fraction of a micrometer. The most important points that emerged from the creep compliance-time profiles of Figure 3 are that 1) creep compliance drops with increasing T_g, and 2) the measured creep compliances are significant at 40°C and 0.3 MPa, conditions likely to be encountered in the service environment. These results corroborate the rationale for the minimum T_g criterion proposed earlier[10] for reducing the reliability risk associated with adhesive creep in optical devices. According to this criterion, the glass transition temperature of an optical device adhesive should be about 40°C higher than the maximum service temperature. If the adhesive T_g is kept well above the service temperature range, the creep compliance becomes smaller, thereby reducing the adhesive creep-related reliability risks.

4. SUMMARY AND CONCLUSIONS

As the installation of optical devices becomes widespread in outside, unprotected areas of the telecommunications network, it is necessary to focus on the reliability issues associated with the material properties of components that comprise the device package. UV-curable adhesives were previously identified as the underlying cause for failures of devices subjected to accelerated aging conditions. Adhesives used in the optical devices must be resistant to degradation and dimensional/mechanical instabilities such as creep. In this report, we examined two UV-curable adhesives after subjecting

them to thermal post-cure and accelerated aging. We found that post-curing these adhesives caused some shrinkage as well as some degradation. However, thermal post-curing also raised the adhesive glass transition temperature, thereby reducing the reliability risk associated with dimensional/mechanical instabilities. Thermal aging also led to a rise in the adhesive T_g.

We investigated the dimensional/mechanical stability of UV-curable adhesives by measuring thermal expansion/contraction profiles and uniaxial tensile creep compliances. The measured linear thermal expansion coefficient of 2.4×10^{-4} °C^{-1} indicated a potentially large thermal expansion mismatch. The measured uniaxial tensile creep compliances of 0.055 MPa^{-1} to 0.070 MPa^{-1} at 40 °C also suggested potential adhesive deformation that may pose significant reliability risks in the operation of optical devices. We showed that the creep compliance at 40 °C decreased with increasing T_g. This result confirmed the rationale for the minimum T_g criterion introduced in the Bellcore requirement for fiber optic branching components.[9] The long-term reliability of optical devices can be improved by maximizing the adhesive T_g to reduce creep compliance.

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Figure 1

Tensile Storage Modulus and Loss Tangent Profiles For Sample UV1a

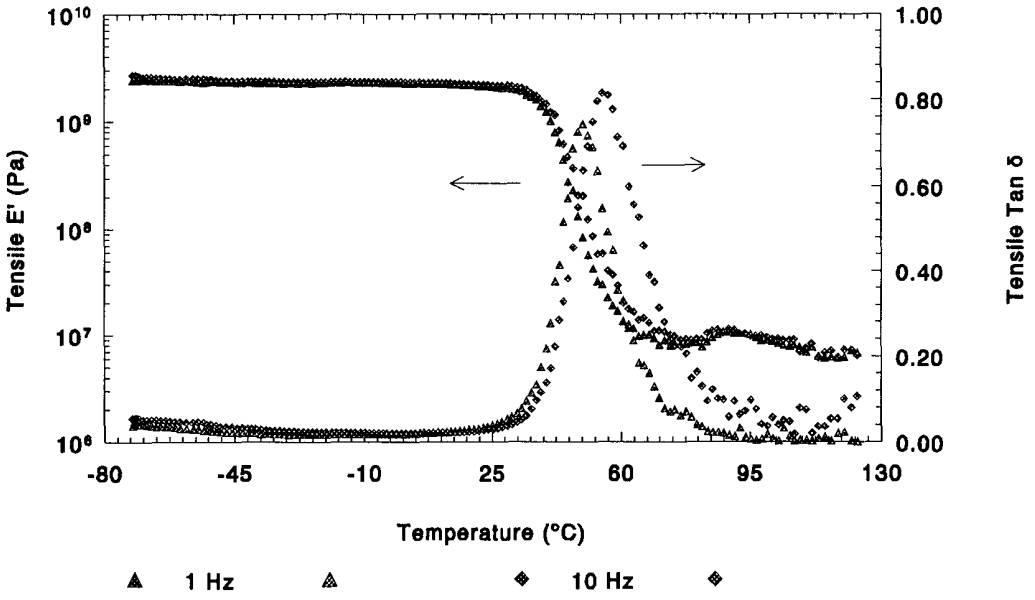

Figure 2a

Thermal Expansion Profile For Sample UV1a

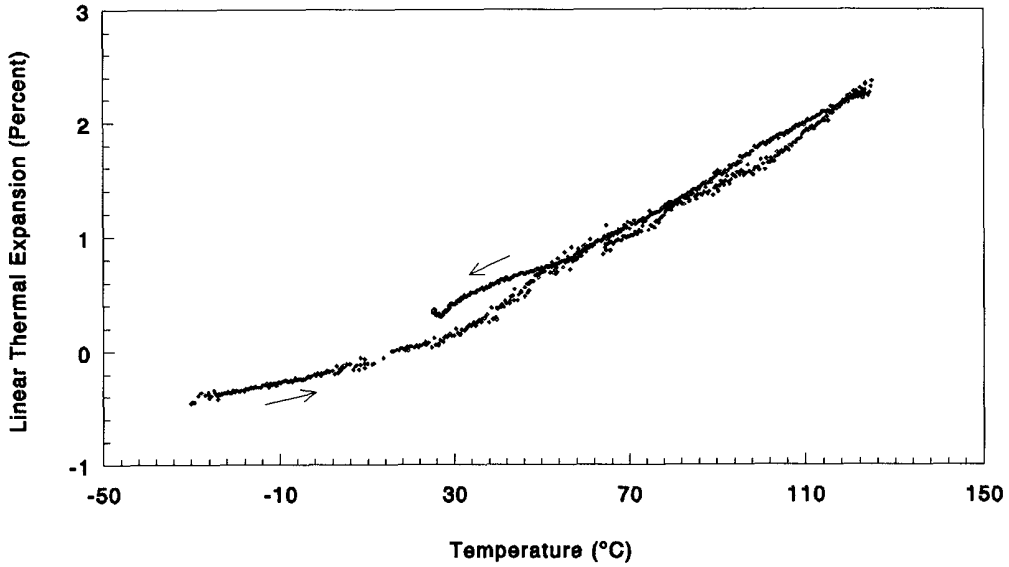

Figure 2b

Thermal Expansion Profile For Sample UV2a

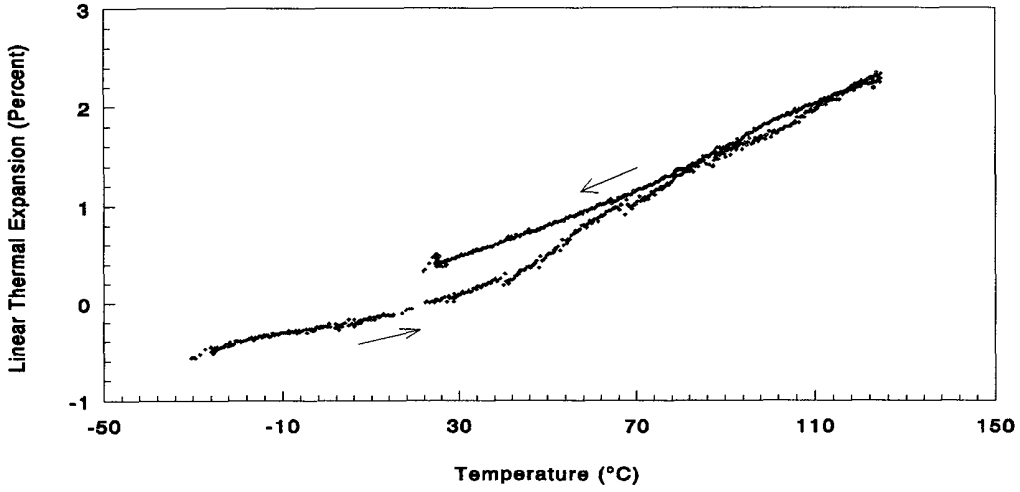

Figure 3

Tensile Creep Compliance vs Time at 40°C