Characterization of Optical Properties of Acrylate Based Adhesives Exposed to Different Temperature Conditions

A. Priyadarshi,[1,2] L. Shimin,[1] S. G. Mhaisalkar,[1] R. Rajoo,[2] E. H. Wong,[2] V. Kripesh,[2] E. B. Namdas[1]

[1]*School of Materials Science and Engineering, NTU, 639798, Singapore*
[2]*Institute of Microelectronics, 11–Science Park Road, Science Park 2, Singapore 117685*

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ABSTRACT: Optical adhesives combine the traditional function of structural attachment with a more advanced function of providing an optical path between optical interconnects. This article aims to characterize refractive index and birefringence of such adhesives under environmental exposure to different temperature conditions. Optical time domain reflectometery (OTDR) and prism coupling methods were employed to measure optical properties of an optical adhesive. Thermo-optic coefficient (*dn/dT*) of the adhesive was observed to decrease noticeably from -2×10^{-4}°C^{-1} to -4×10^{-4}°C^{-1} around the glass transition temperature ($T_g \sim 78$°C). It is observed that refractive indices for both T_E and T_M modes increase with increasing annealing temperature, but the birefringence ($T_E - T_M$) is decreasing. This suggests that the material has become more isotropic due to the annealing. The environmental changes in optical properties of the adhesive are discussed in the light of Lorentz–Lorenz equations. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 950–956, 2005

Key words: refractive index; temperature; annealing; OTDR; prism coupler

INTRODUCTION

In recent times, acrylate based optical adhesives are becoming important in the packaging and assembly of optical communication modules.[1–4] Optical adhesives perform dual functions of physically attaching the components and also being used in the optical path. These adhesives offer advantages in terms of low cost and amenability to mass production. In particular, UV-curable adhesives have the advantages of fast curing, within a few seconds, and do not need to be formed by mixing of multiple components. Adhesives designed for use in the optical path typically offer a very high clarity (transparency of $> 90\%$) and come with a wide refractive index range (1.40–1.70).[1] They are often utilized between light passing sections for the purpose of minimizing the reflection losses (Fresnel reflection) in packages.[1,2] The ratio (in dB) of optical power arriving at the interface to the optical power reflected back from the same interface is defined as optical return loss (ORL). Figure 1 illustrates the significance of optical adhesive in optical connectors. Return loss requirement for planar lightwave circuits (PLCs), according to Telcordia standards, is -40dB (GR-1209). The ORL at air ($n \sim 1.0$) and single mode optical fiber core ($n \approx 1.468$) interface is approximately -14.7 dB. Thus, optical adhesives are filled in the air gap to minimize the refractive index mismatch.

UV-curable acrylate adhesives consist of oligomers, monomers, additives, and photoinitiators. These formulations can be modified to provide optically clear resins with specific requirements of different properties, such as refractive index and adhesion. In general, polymeric adhesives are extremely sensitive to environmental conditions, such as temperature and moisture.[5–7] Refractive indices of various optical polymers have been studied and were found to decrease at a rate of -10^{-4}°C^{-1}.[8–12] In most of the modules that use polymeric adhesive bonds, high moisture absorption may lead to catastrophic failures. Another important factor that is known to modify properties of adhesives, such as stiffness and coefficient of thermal expansion, is annealing.[13] If the optical adhesives were to be used as an index matching material to bond two optical fibers, these changes with temperature and humidity would be deleterious to module functionality. This is because the refractive index of optical fibers consisting of inorganic materials is less sensitive to environmental conditions compared with the polymer adhesives used in optical interconnects. This causes a large mismatch in the refractive index of the fiber and adhesive, which leads to increases in ORL and noises at the interface. Furthermore, long term failure of optical modules that use adhesives in optical paths can take place due to degradation of optical properties of the adhesive in the temperature conditions.

Correspondence to: A. Priyadarshi (pb1259568@ntu.edu.sg).

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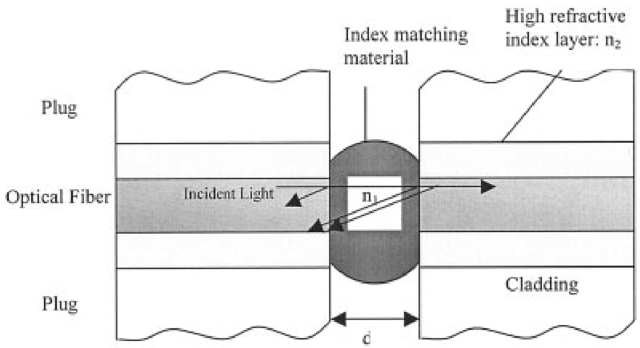


Figure 1 Schematic of an optical fiber connector employing an index matching adhesive.

In the present work, the refractive index of a commercial UV-curable optical adhesive is characterized for temperature and annealing conditions. Optical time domain reflectometery (OTDR) and prism coupling methods were employed to measure optical properties of the adhesive. The thermomechanical properties of the adhesive were studied by DMA, TMA, and DSC measurements. The optical adhesive used in the study is ABLELUX OGRFI146T, manufactured by Ablestik. The adhesive is acrylate based consisting of oligomers, monomers, additives, and photoinitiators, and is suitable for application in the light passing section in optical modules. The effect of temperature on the refractive index as well as the effect of annealing on the refractive index and birefringence of the optical adhesive is reported in this study.

REFRACTIVE INDEX MEASUREMENTS

OTDR

An OTDR based on the principle of Michelson's interferometer is used to determine the ORL at the fiber-adhesive interface. OTDR is a nondestructive technique capable of performing *in situ* measurements and requires access to only one end of the fiber. It injects a short, intense laser pulse into the optical fiber and measures the backscatter and reflection of light as a function of time.[14] Figure 2 shows the schematic of the ORL measurement principle using the OTDR. Rayleigh scattering and Fresnel reflection are physical causes of signal reflection. Backscattered light provides a signature from which information about signal strength is deduced. Interpretation of the OTDR measurement features is aided by knowledge of the fiber backscatter and reflection mechanism together with familiarity with the measurement process. The backscattered signal typically is very weak and may suffer from interference from noise. To overcome this problem, the process of sending a pulse and receiving the echo is repeated many times to improve the signal-to-noise ratio through averaging. Pulse width, which is 5ns to 10ns, decides the spatial resolution and sensitivity of the measurement.

The concept of return loss is employed to calculate the refractive index from the reflected signal obtained from the OTDR. When light is transmitted from medium 1 to medium 2 (e.g., from a fiber to an adhesive), a portion of the incident light is reflected back (Fresnel reflection) into medium 1 due to mismatch in refractive indices (Fig. 1). The reflection coefficient (RC) is then given by:

$$RC = \frac{(n_1 - n_2)}{(n_1 + n_2)} \tag{1}$$

The percentage of light reflected (R) is as follows:

$$R = RC^2 = \left[\frac{n_1 - n_2}{n_1 + n_2}\right]^2 \tag{2}$$

Return loss (RL) is then obtained by converting the percentage of light reflected to dB:

$$RL = -10\log_{10}R \tag{3}$$

Note that a larger return loss number implies a more favorable condition of lower reflected power.

Prism coupler method

The prism coupler is used to explore the dependence of the refractive index on annealing temperature. The prism coupler is a direct method of measuring the refractive index and the thickness of a thin film by measuring the angle at which modes can be prism coupled into the film.[15] It employs optical waveguiding techniques to promptly and precisely measure both the thickness and refractive index of films. The output light of the prism coupler source first passes through a prism polarizer with an extinction ratio of

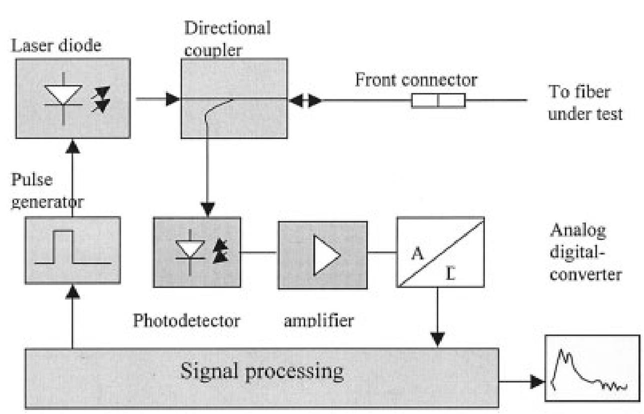


Figure 2 Schematic of the measurement principle of an OTDR.

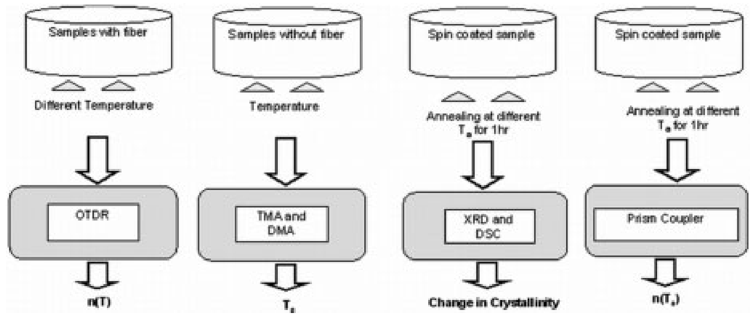


Figure 3 Refractive index, thermomechanical, and change in crystallinity measurement methods for different conditions of temperature, and annealing treatments.

10^{-6}. The polarizer serves two functions: it ensures that the laser output is linearly polarized, and by rotating it the relative intensities of T_E and T_M modes is adjusted. Each mode leaves the output prism at an angle determined by the effective index within the waveguide. The prism coupler has a higher index accuracy of ±0.0001 compared to the OTDR, which has an accuracy of only ±0.001.

EXPERIMENTAL

Figure 3 explains the experimental flow diagram for different characterizations.

Sample preparation

Samples were prepared in two different ways for the characterization:

a. Cylindrical shaped: Cylinder-shaped specimens (diameter 5 mm and height 2 mm) on the tip of a single mode fiber (SMF) were prepared using a Teflon mold.
b. Spin coated film: Optical adhesive was spin coated onto SiO_2 coated wafers. The optical adhesive was fully cured using a UV light source of 100mW/cm^2 intensity for 60s.

Thermomechanical analysis

UV-DSC of raw and cured samples was performed to check if samples were fully cured. The differential photocalorimeter (DPC), as an accessory, with the thermal analyzer and 2920 differential scanning calorimeter was used for the UV-DSC. Samples were irradiated with ultraviolet light (wavelength 365nm) and power of 60mW/cm^2. The temperature dependent coefficient of thermal expansion (CTE) and tan δ of the optical adhesive were determined experimentally by a thermal mechanical analyzer (TMA, TA instrument model 2940) and a dynamic mechanical analyzer (DMA, TA instrument model 2980).

Temperature study

To investigate the temperature dependence, samples (with fiber) were placed in a Teflon insulated temperature chamber that had a temperature uncertainty of 1°C. A schematic of the experimental setup is shown in Figure 4. The return-loss at a wavelength of 1550nm

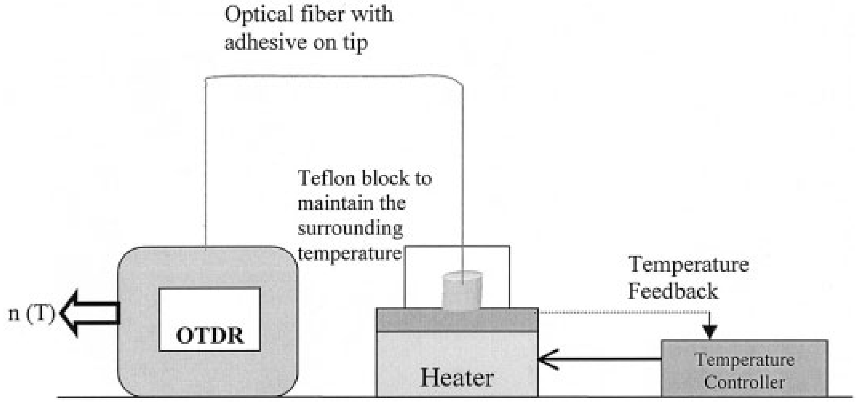


Figure 4 Schematic of the experimental setup for refractive index measurement with OTDR at different temperatures.

was measured at different temperatures with OTDR (model AQ7410B). The refractive indices were then calculated from these return loss values [Eqs. (1)–(3)].

Annealing study

A spin coated wafer, with the adhesive, was diced in square shape (2cm × 2cm) and exposed to different annealing conditions as follows:

i. The sample was annealed at 60°C for 1 h.
ii. The sample was quenched to room temperature using liquid nitrogen.
iii. Steps i and ii were repeated for different temperatures of 70°C, 80°C, 90°C, 100°C, and 200°C.

The refractive index and birefringence of the diced samples were measured with a prism coupler (Metricon model 2010 prism coupler). Finally, thermal DSC and XRD (thin film mode) measured crystallinity of the annealed samples. DSC measurements were performed with increasing temperature from 0 to 250°C at a heating rate of 10°C/min. XRD was performed in thin film mode from 0 degree to 30 degrees.

RESULTS AND DISCUSSION

Dependence of refractive index on temperature

Figures 5(a) and (c) show the refractive index (n) of optical adhesive and tan δ (DMA) against temperature. This refractive index plot shows that n decreases with temperature. The refractive index measured at 25°C was 1.463 for $\lambda = 1550$ nm, in agreement with the data sheet values for the adhesive materials. The calculated thermo-optic (TO) coefficient (dn/dT) is plotted in Figure 5(b). In a temperature range of 20–70°C, the thermo-optic coefficient is almost constant, with a value of -1.8×10^{-4}/°C, and changes drastically to a lower value -4.2×10^{-4}/°C in a 75–120°C range. To understand the drastic changes in the thermo-optic coefficient between the 70°C and 75°C temperature range, DMA measurements to investigate the glass transition temperature of the adhesive were performed. The tan δ curve for the adhesive is shown in Figure 5(c). The tan δ graph shows a peak at ~ 78°C, corresponding to the glass transition temperature. This glass transition temperature (Tg ~ 78°C) of the adhesive is in the same range as the observed discontinuity in the TO coefficient between the 70°C and 75°C temperatures.

The drastic change of thermo-optic coefficient around the glass transition temperature suggests that the change of the refractive index may have a relationship with density.[16] Moreover, according to the Lorentz–Lorenz law, the refractive index is related to density by the following equation:

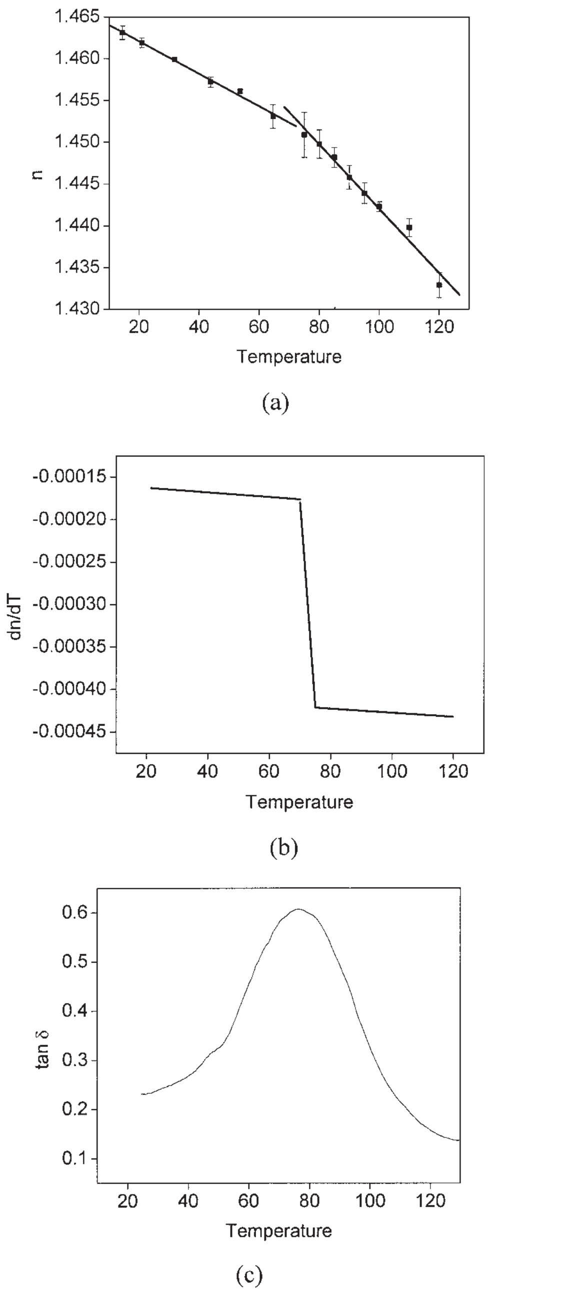
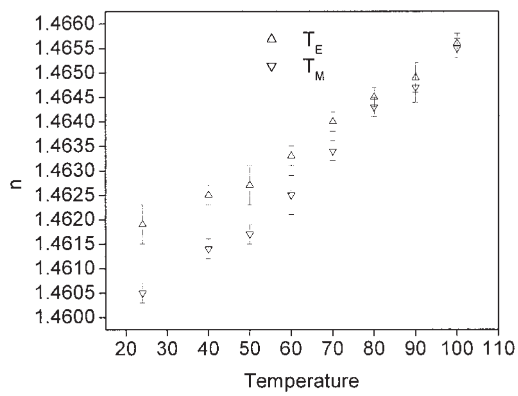


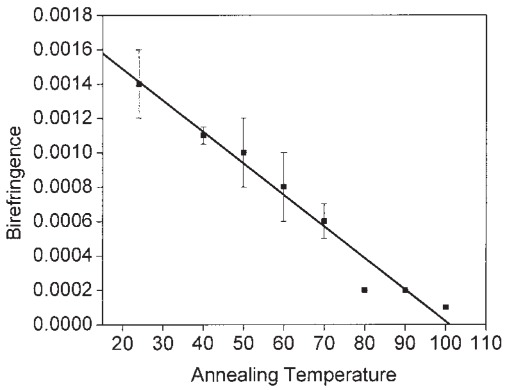
Figure 5 (a) Temperature (in °C) dependence of the refractive index, (b) variation of dn/dT versus temperature, and (c) tan δ (DMA) graph for optical adhesive.

$$(n^2 - 1)/(n^2 + 2) = \rho RD/M \quad (4)$$

where RD is molar refraction, M is molecular weight, and ρ is the density of the material. Molar refraction and molecular weight remain nearly constant with changes of temperature and pressure. Change in refractive index takes place by virtue of the density factor, which is a function of temperature and pres-



(a)



(b)

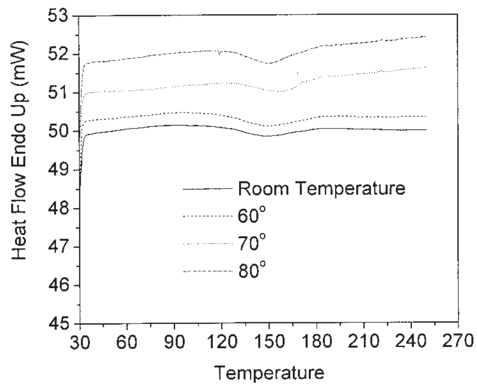
Figure 6 Plot of annealed temperature (°C), versus (a) refractive index (both T_E and T_M modes) and (b) birefringence for constant annealing of the samples for 1 h.

sure. This relationship is consistent with the results obtained; as temperature increases, the adhesive refractive index decreases because volume increases due to its high coefficient of thermal expansion (75×10^{-6}/°C), as measured by DMA and TMA, thus resulting in lowering of the density.

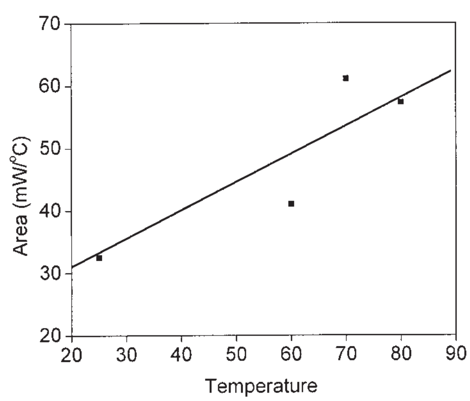
Dependence of the refractive index on annealing temperature

The refractive indices of the optical adhesive were obtained with the prism coupler for different annealing temperatures, as shown in Figure 6(a). The TE mode of the prism coupler measures the refractive index of the adhesive for the electric field vibrating parallel to the material surface. On the other hand, the TM mode measures the index for electric field vibration perpendicular to the material surface. In both the TE and TM modes, refractive index was observed to increase with annealing temperature.

This increase in refractive index may be attributed to change in the density of the material according to the Lorentz–Lorenz law. Change in density can take place due to physical aging and the process of orientation, leading to an increase in crystallinity. Physical aging is a time and temperature dependent phenomenon, which results in volume relaxation leading to density increase of materials.[17] Volume relaxation of acrylate based polymer due to annealing was determined by measuring the change in refractive index of the material.[18] Thermal DSC (for short-range order[19,20]) and XRD (for long-range order) results rule out the possibility of refractive index increase due to the crystallinity change (Figs. 7 and 8). From the DSC data, the amount of heat absorbed ($-\Delta H$) in the annealed sample was measured (Fig. 7). The amount of residual crystallinity present in the adhesive after annealing is calculated with the help of $-\Delta H$. Residual crystallinity increases with increasing annealing temperature [Fig. 7(b)]; thus, the amount of short-range crystallinity present in the samples decreased with increasing annealing temperature. The adhesive is getting more and more amorphous with higher annealing temperature. Similarly, the XRD result (Fig. 8) shows



(a)



(b)

Figure 7 (a) Thermal DSC of samples annealed for 1 h, and (b) Change in the trough area of the thermal DSC curve. The trough areas of the thermal DSC correspond to the heat because of the change in short range crystallinity.

no sign of long-range crystallinity in the adhesive. Thus, overall crystallinity has decreased by annealing, which results in the density going down.

Another reason for increase in the refractive index could be incomplete curing during sample preparation. It might get compensated during the annealing process of the samples. A UV-DSC plot of heat flow for the raw and cured material is presented in Figure 9. The raw sample gave off a large amount of heat during the curing process, as indicated by the trough (see Fig. 9). However, no trough is present for cured samples, suggesting that no reaction took place during the entire UV exposure (Fig. 9). Thus, it can be concluded that the samples were all completely cured during sample preparation and that the variation of refractive index with annealing temperature was not due to residual curing processes. Thus, the change in refractive index due to annealing results from the volume relaxation of the adhesive.

Figure 6(b) shows the variation of birefringence with annealing temperature as measured by a prism coupler. Birefringence was calculated from the difference in refractive index between the TE and TM modes [Fig. 6(a)]. The adhesive film has a temperature-dependent birefringence, with the quantity $\Delta(n_{TE} - n_{TM}) / \Delta T$ having a value of 1.86×10^{-5} °C^{-1}. The relation between the polarization and temperature is largely linear. Anisotropy in the optical property of the adhesive is determined by the chemical configuration and conformation of a polymer chain. Birefringence of a material provides information about the crystallinity and orientation of the polymer molecular chains. As depicted in Figure 6(b), the birefringence of the adhesive decreases with increasing annealing temperature. This means that the optical adhesive has become more isotropic due to the heat treatment, and thermal DSC also shows the decrease in short-range crystallinity (Fig. 7).

The presence of residual stresses also results in distortion of the molecular chain and induces birefringence in the polymeric materials. Residual or internal stresses caused by the curing process in the adhesive

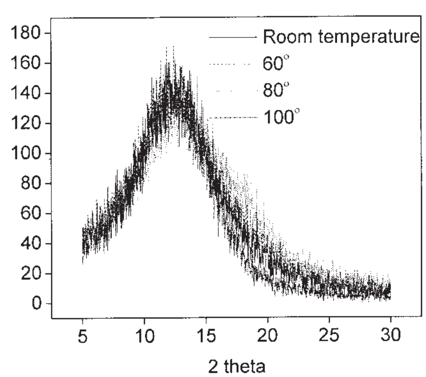


Figure 8 XRD of optical adhesive annealed at different temperatures.

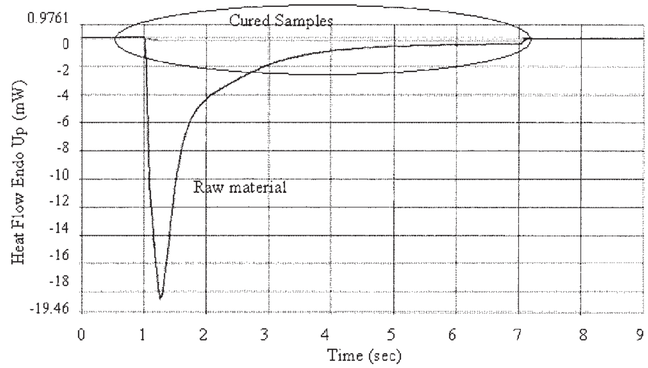


Figure 9 UV-DSC plots for uncured and cured adhesive samples. Only the raw material is showing the heat flow change, and cured samples don't show any change in heat flow.

get relaxed with time during the annealing. Decrease in the birefringence can take place due to stress relaxation in the adhesive film also. The subsequent slow progression of the polymer towards equilibrium, termed structural recovery, takes place by the annealing process and helps in reducing the adhesive birefringence of the adhesive material.

CONCLUSIONS

Methods for characterizing the optical adhesive in different environmental conditions were demonstrated in this work. Return-loss by OTDR and prism coupling methods were employed to measure/calculate the optical properties of an optical adhesive. The impact of different temperature and annealing conditions on the refractive index of the adhesive was examined and discussed in this publication. It was observed that refractive indices decreased with increase in temperature, and this decrease of refractive indices was because of the density change of the material. As opposed to the temperature dependence, the annealing temperature dependence of the refractive index has a positive relationship. This is suggested to result from volume relaxation. The molecular orientation also results in a more isotropic material, as evidenced by the decrease in birefringence with annealing temperature. These optical property characterization methods provide useful insights into the reliability of optoelectronic devices and components assembled with optical adhesive.

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