

# Moisture Absorption and Desorption in a UV Cured Urethane Acrylate Adhesive Based on Radiation Source

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**ABSTRACT:** A photopolymerizable urethane acrylate (UA) adhesive was cured using two different sources: a conventional UV-lamp and a UV-emitting light emitting diode (LED). Moisture uptake in cured specimens was characterized by immersion in deionized water at 21.8, 30, 37.5, and 45°C for a period of 6 months. Additionally, desorption experiments were performed for selected specimens under vacuum at room temperature. Material degradation in the form of mass loss was observed in all samples after attainment of a maximum water uptake level, with the phenomenon being more pronounced at higher immersion temperatures. This degradation is attributed to leaching and dissolution of uncured monomers and lower weight molecular species from the samples. A two stage moisture uptake model is proposed

to account for mass loss and excellent agreement between the tested mass loss and the loss-rate parameters determined from the model is shown. Performance of specimens was characterized with dynamic mechanical thermal analysis (DMTA), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). It was found the LED source was not as effective in curing surfaces, due to which there is a higher level of mass and lower  $T_g$  from hygrothermal exposure as compared to the core regions of the LED cured specimens and the overall lamp cured specimens. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 3654–3662, 2008

**Key words:** UV Cure; lamp; LED; moisture uptake; dissolution

## INTRODUCTION

Due to distinct advantages such as solvent-free formulations and rapid rates of cure, ultraviolet (UV)-curing technology is increasingly being applied to applications involving thin film coatings and adhesives.<sup>1</sup> A UV-curable system is typically composed of reactive oligomers, reactive diluents, and photoinitiators. The photoinitiators are tailored to absorb light at specific UV-wavelengths ( $\lambda < 400$  nm), resulting in the promotion of electrons to a higher-energy orbital. This promotion of electrons results in the subsequent formation of reactive intermediates, such as free radicals, which initiate the rapid onset of polymerization between the reactive oligomers and diluents.<sup>2</sup>

The performance characteristics of UV-cured urethane acrylate (UA) materials depend largely on the extent of cure and the resulting crosslink density, which are affected by process variables such as the intensity of the impinging UV radiation, the UV exposure time, and the wavelength of the UV-sources.<sup>3</sup> Magan et al.<sup>3</sup> found that although longer wavelength UV-lasers ( $\lambda > 300$  nm) resulted in good bulk curing characteristics, they were not energetically favorable to overcome oxygen scavenging of free-radicals at the

specimen surface, leading to poor levels of surface cure. In contrast, shorter wavelength UV-lasers ( $\lambda < 300$  nm) were found to have sufficient energy for inducing surface cure, but the extent of cure in the bulk suffered as a consequence. It should be noted that these polymers are susceptible to UV from ambient light which can initiate cleavage within the polymer backbone. Further, residual photoinitiator and photoinitiator cleavage products resulting from nonoptimum curing conditions can adversely affect the photo-oxidation stability of these materials resulting in deterioration in their long-term performance characteristics.<sup>4</sup>

To date mercury arc-lamps are the most commonly used UV-source. This lamp is generally linear in shape and has multiple strong emission peaks in both the visible and UV-spectrum. Mercury arc-lamps are composed of liquid mercury and a starter gas, usually xenon or krypton. By applying a voltage drop across electrodes, discharge from the starter gas takes place until the liquid mercury has had time to vaporize and is capable of discharging in its gaseous state as well. Because the process requires vaporizing liquid mercury, these lamps are best suited for continuous operation which reduces the thermal stresses associated with heating/cooling cycles. Drawbacks of mercury arc-lamps are the need for sophisticated power-sources, fragility, high thermal output, and gradual burn-out.<sup>5</sup> Since the photoinitiators in UV-curable formulations are excited only by specific UV-wavelengths, the multi-

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ple UV-peaks arising from mercury sources may cause untoward effects leading to degradation of the polymer constituents,<sup>6</sup> requiring color filters and phosphor coatings to filter out unnecessary emission peaks.

The latest evolution in UV-source is the light emitting diode (LED) array. LEDs are compound semiconductors that emit photons of particular wavelengths when electrons and holes combine as a result of a voltage drop across electrodes. LEDs are essentially monochromatic and their emission is tunable depending on the band-gap of their particular chemistry in the solid-state. Two distinct advantages that LEDs offer over lamps are maneuverability and low-power consumption. One notable disadvantage, however, is that LEDs, at their current level of development, are not yet capable of emitting photons of similar intensity as lamps<sup>7</sup> leading to concerns related to the ability to achieve full cure, as well as preclude the effects of oxygen inhibition and scavenging.<sup>3</sup> However, LED-arrays are typically very small (<10 mm<sup>2</sup>) and have the inherent advantage of being very attractive for use in curing parts of complex geometries and where access may be limited due to their ease of placement. The UV-emission spectrum used in the current investigation is typical of indium gallium nitride (InGaN).

While the use of UV cure offers distinct advantages over methods of conventional cure, there are a number of concerns related to long-term durability especially as related to environmental exposure, with recent emphasis being focused on resistance to photo-aging.<sup>4,8-11</sup> In a number of cases, however, the materials are exposed to varying conditions of humidity and even periods of immersion in water and other solutions, resulting in the need to characterize their response to moisture uptake and desorption. In specific the increasing use of UV curable resins and adhesives used in opto-electronic components and in the assemblage of electronics to be used in harsh and changing environments with low levels of regular maintenance, as well as their increased use in LED-based rapid assembly makes the study of hygrothermal effects critical. This study focuses on the assessment of differences in moisture uptake and hygrothermal effects accruing from use of a light emitting diode (LED) or mercury arc-lamp UV source on an urethane acrylate adhesive system.

## MATERIALS AND TEST METHODS

A specialized urethane acrylate adhesive (Dymax OP-52)\* was used in this investigation. The system

\*Commercial names are provided for purposes of reference only and is not intended to imply recommendation, endorsement, or implication that the product identified is necessarily the best available.

has high optical clarity indicative of aliphatic urethane formulations with reactive sites being the C=C double bonds found in the acrylate backbone connected to the carbonyl group. The system has a viscosity of 5000 cP, a 1.9% linear shrinkage and a glass transition temperature of 64°C when fully cured. An inherent benefit of such a formulation is that the reactive acrylate monomers are typically of low molecular weight, eliminating the need for organic solvents to control the viscosity of the system. However, this also makes it more susceptible to leaching of the lower molecular weight species as a result of hygrothermal exposure. For the purposes of this investigation test specimens were fabricated in two forms. The first geometry was a molded bar-specimen with average dimensions after preparation of 33 mm × 7.5 mm × 2.5 mm. The second geometry was a half-dome with an average radius of 5.6 mm at the base and peak average thickness of 2.0 mm. These two sample geometries will, hereafter, be called "bars" and "droplets", respectively.

The polymerization of a UV-curable polymer requires a suitable radiation source capable of activating the photoinitiators to produce free-radicals within the prepolymer formulation. The selection of proper UV-emitting equipment, however, is not trivial. For example, if a particular photoinitiator (i.e. formulation) is activated by UV radiation with a wavelength of 250 nm, but the UV-source emits radiation at 300 nm, no polymerization will take place because the energy for photolysis will not have been reached. Therefore it is of critical importance that the UV-source be matched to the activation requirements of the photoinitiator, or vice versa. It is also important that any additional filler in the prepolymer formulation be transparent to the incoming radiation so that the cure efficiency can be maximized. To assess two commonly used sources of radiation, the samples were cured with either a mercury arc-lamp or a LED. To cure the bars, a mercury lamp was held in a static fixture with sample exposure lasting for about 1 min. The LED device was fixated to an automated tool that scans the LED over the sample for about one and a half minutes. The differences in UV-emission energy is 0.35 W/cm<sup>2</sup> for the mercury lamp and 0.05 W/cm<sup>2</sup> for the LED. Prior to use, the bar-samples were pretreated by polishing away the hard (due to lamp exposure) or tacky (due to LED exposure) surfaces, which were slightly voided, until smooth and defect-free. A Struers Roto-Pol-22 with 330 grit SiC sandpaper was used to polish the specimens. It should be noted that the bar specimens had a slightly lower glass transition temperature ( $T_g$ ) compared to the droplets: lamp source cured bar and droplet specimens were determined using differential scanning calorimetry (DSC) to have  $T_g$ s of 46.5°C and 51.3°C, respectively, whereas

the corresponding levels resulting from LED cure were. 46.9°C and 51.2°C, respectively. It can be seen that the  $T_g$ s resulting from the use of the lamp and LED are comparable for both sets of specimens, indicating equivalent levels of activation. The higher  $T_g$  of the droplet specimens is attributed to the small thickness of these specimens.

The as-received samples cured with the lamp had a yellowish tint compared to the relatively transparent LED-cured samples. Additionally, the samples cured with the lamp were noticeably harder and smoother at the surface than the LED cured samples, which were tacky and slightly viscous.

For the aging experiments, polished bar-samples and as-received droplet-samples were placed in pierced polyethylene bags and submerged in water baths containing deionized (DI) water maintained at temperatures of 21.8°C, 30°C, 37.5°C, and 45°C. The moisture uptake in the samples was determined gravimetrically by periodically removing the samples from the baths, blot-drying them with paper towels and weighing them using an electronic balance with an accuracy of 0.01 mg, prior to re-immersing them in the appropriate baths. A minimum of five coupons were used at each aging condition.

Desorption tests were performed at room temperature under vacuum (25 mmHg) for selected bar specimens, which had been immersed in deionized water for 6 months at temperatures of 21.8°C and 45°C, representing the lowest and highest temperatures of immersion considered.

Dynamic Mechanical Thermal Analysis (DMTA) tests were performed on polished bar specimens in 3-point bending mode using a Rheometric Scientific dynamic mechanical thermal analyzer. Specimens were tested at 1 Hz in single frequency mode with a heating rate of 3°C/min from -20°C to 120°C, and preload strain of 0.01%. The peak of the loss tangent curve was used as an indicator of the glass transition temperature ( $T_g$ ).

DSC tests were conducted on 10–20 mg samples cut from dried film heated at a rate of 10°C/min from -50°C to 120°C, designated as the first run. Consequently, each sample was cooled down to -50°C quickly (~50°C/min), and then heated again with the same parameters as the first run (designated as second run). An N<sub>2</sub> atmosphere (10 mL/min) was employed for both heating and cooling processes.

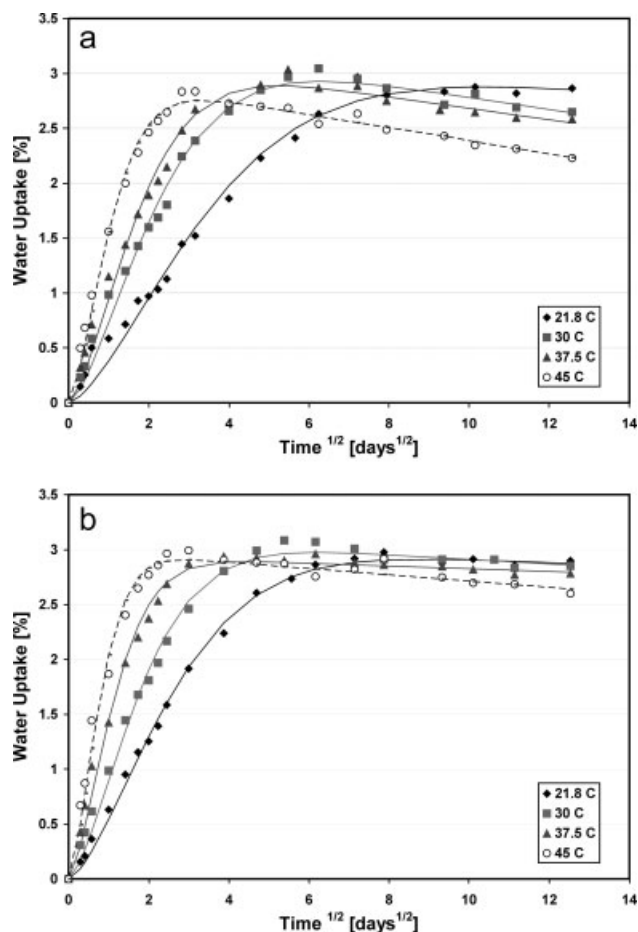
Specimens for Thermogravimetric analysis (TGA) were cut from droplet specimens with an initial sample weight in the range of 8–10 mg. TGA was performed with a Mettler Toledo instrument (TGA/SDTA 851<sup>o</sup>) with dry nitrogen gas (25 mL/min) being introduced into the test furnace to provide an inert atmosphere. The experiments were performed

at a 10°C/min heating rate over the temperature range of 25–600°C.

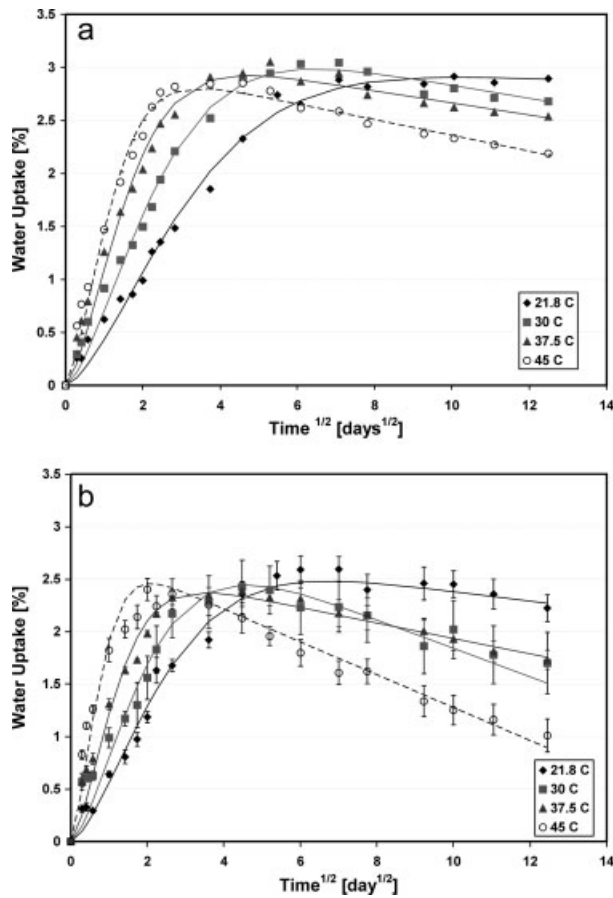
## RESULTS AND DISCUSSION

The response of immersion in deionized water in terms of weight change of the lamp and LED cured bar and droplet specimens are shown in Figures 1 and 2, respectively. For all specimens the initial weight gain increases linearly as a function of the square root of immersion time. After reaching a maximum level of water uptake ( $M_m$ ), the weight change exhibits a linear decrease with increasing time of immersion. This mass loss is attributed to the leaching of unreacted monomers and lower molecular weight species<sup>12,13</sup> which is in line with the findings of Dolez et al.<sup>14</sup> who reported that the amount of unreacted acrylic monomer within a photopolymerized resin varied with curing time and temperatures.

In classic Fickian diffusion the weight change levels off asymptotically following an initial linear increase.<sup>2</sup> The observed weight loss of the present UA system indicates that the long-term diffusion



**Figure 1** Water uptake curves for specimens cured with the UV Lamp source. (a) Bar specimens (b) Droplet specimens.



**Figure 2** Water uptake curves for specimens cured with the LED source. (a) Bar specimens (b) Droplet specimens

behavior deviates from the classic Fickian response on attainment of a equilibrium level. To determine the diffusion coefficient and to further evaluate the

equilibrium water content, a two stage diffusion model was applied following,<sup>15-17</sup> wherein the first stage of water absorption and diffusion (initially linear) was attributed to the water concentration gradient (Fickian diffusion mechanism), while the second stage (conventionally attributed to relaxation dominated additional weight gain following the first stage<sup>15-17</sup>) was assigned in the present case to mass loss due to leaching and dissolution of unreacted and lower molecular weight species. The relation is thus the same as that proposed by Bao et al.<sup>15</sup>

$$M_t = M_\infty(1 + k\sqrt{t}) \left\{ 1 - \exp \left[ -7.3 \left( \frac{Dt}{h^2} \right)^{0.75} \right] \right\} \quad (1)$$

where  $M_t$  is the water uptake at time  $t$ ,  $M_\infty$  is the quasi-equilibrium water uptake, and  $D$  is the moisture diffusivity, with the difference that  $k$  represents the rate constant of degradation, rather than the relaxation term, and is thus negative.

The solid lines in Figures 1 and 2 show the good fit between experimental data and this expression. For purposes of calculation of parameters for the dome-type specimens, the dimensions were normalized to that of a cube with equivalent surface area with the height of the cube being equal to the height of the dome. Diffusion and degradation characteristics for the specimens are summarized in Table I. As can be seen the value of the diffusion coefficients increase with temperature of immersion with the droplets having a slighter higher set of values than the bar specimens, irrespective of source of radiation. It is noteworthy that the absolute value of  $k$ , representing the rate of deterioration, does not show

**TABLE I**  
Diffusion Parameters Determined with the Two-Stage Diffusion Model for Specimens Immersed in Water

| Specimens          | Immersion temperature (°C) | $M_{max}$ (%) | $M_\infty$ (%) | $\Delta m$ (%) | $k$ ( $10^{-5}/s^{1/2}$ ) | $D$ ( $10^{-7} mm^2/s$ ) |
|--------------------|----------------------------|---------------|----------------|----------------|---------------------------|--------------------------|
| Lamp cured bar     | 21.8                       | 2.94          | 3.19           | 0.25           | -2.8                      | 1.64                     |
|                    | 30                         | 2.63          | 3.33           | 0.7            | -5.61                     | 3.6                      |
|                    | 37.5                       | 2.55          | 3.2            | 0.65           | -5.51                     | 6.66                     |
|                    | 45                         | 2.2           | 2.98           | 0.78           | -6.78                     | 17.72                    |
| Lamp cured droplet | 21.8                       | 2.8           | 3.00           | 0.20           | -1.65                     | 1.74                     |
|                    | 30                         | 2.75          | 3.12           | 0.37           | -2.28                     | 3.84                     |
|                    | 37.5                       | 2.7           | 2.95           | 0.25           | -2.44                     | 9.13                     |
|                    | 45                         | 2.51          | 3              | 0.49           | -3.25                     | 20.34                    |
| LED cured bar      | 21.8                       | 2.9           | 3.09           | 0.19           | -1.77                     | 1.88                     |
|                    | 30                         | 2.7           | 3.45           | 0.75           | -6.1                      | 3.78                     |
|                    | 37.5                       | 2.5           | 3.23           | 0.73           | -5.97                     | 8.16                     |
|                    | 45                         | 2.2           | 3.1            | 0.9            | -8.15                     | 13.17                    |
| LED cured droplet  | 21.8                       | 2.1           | 2.84           | 0.74           | -5.49                     | 1.76                     |
|                    | 30                         | 1.7           | 2.28           | 0.58           | -14.46                    | 3.22                     |
|                    | 37.5                       | 1.7           | 2.67           | 0.94           | -9.38                     | 7.72                     |
|                    | 45                         | 0.98          | 2.84           | 1.86           | -18.75                    | 18.63                    |

$M_{max}$ , weight change after immersion determined directly from Figures 1 and 2;  $M_\infty$ , equilibrium water uptake,  $k$  and  $D$  determined from curve fitting with eq. (1);  $\Delta m = M_\infty - M_{max}$ . Standard deviations for  $k$  and  $D$  are in the order of 5%.

as clear a trend, although the rate of deterioration indicated by specimens immersed in deionized water at 45°C (the highest temperature of immersion) is higher than that shown by the specimens immersed at the lowest temperature, 21.8°C. It is pointed out that leaching and dissolution of uncured monomers and lower molecular weight species is a complicated process, combining the diffusion of the species from bulk to the surface, the diffusion of the water molecules into the specimen and the interactions between the constituent species with water and the cured polymer structures. The comparable  $k$ -values for lamp and LED cured bar specimens suggest that the two sources result in only a slight difference in bulk cure characteristics. However, for lamp cured specimens, the bar samples exhibit a  $k$ -value higher than those of the droplet samples, which is believed to be due to the greater degree of surface cure with the lamp source. The LED UV cured bar specimens show a roughly comparable  $k$ -value to the lamp cured bar samples; however, the LED cured droplets possess a much higher  $k$  value than all other samples. This is believed to be due to the under-cured surfaces associated with the LED source.

$M_{\max}$  is determined directly from Figures 1 and 2 and represents the total weight change during immersion. As mentioned above,  $M_s$  represents the equilibrium water uptake regardless of the extraction of uncured monomers. Therefore, the value of the difference ( $\Delta m = M_s - M_{\max}$ ) represents the amount of leached and dissolved monomer mass during the period of immersion. The greater the value of  $\Delta m$ , the greater is the volume of unreacted monomers leached out. It is worth reiterating that the bar specimens had their surfaces removed via grinding and polishing. Therefore, the diffusion parameters of the bar specimens are more closely related to the behavior of the material in the bulk, while the diffusion parameters of the droplets are heavily influenced by their "as-cured" surface characteristics. The lamp cured droplets exhibit a low  $\Delta m$  compared to the bar specimens (Table I), indicating the use of the UV lamp as a radiation source results in a greater degree of surface cure. It is interesting that the values of  $\Delta m$  of the lamp cured bar samples are slightly lower than those of LED cured bar specimens, which suggests that the lamp source is also more effective for curing the bulk of the specimen. The difference is even more pronounced in the droplet samples suggesting that the LED source is not completely effective in curing the surface primarily due to the effects of oxygen inhibition and scavenging.<sup>3</sup> The sticky surfaces of LED cured samples further support this assumption.

It is noted that the LED cured droplets display the lowest values of  $M_s$  (2.28% ~ 2.84%), while the other

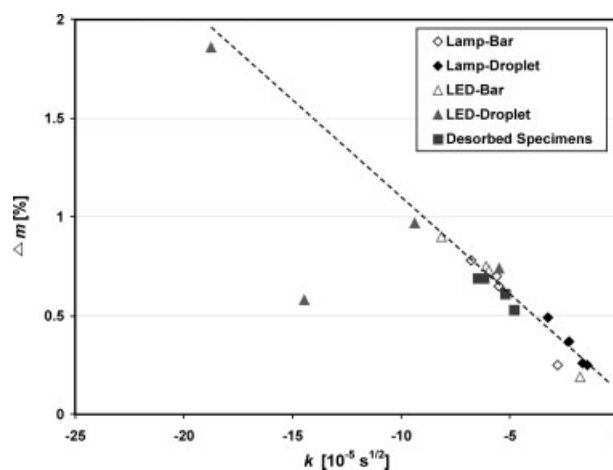
specimens exhibit comparable values (~ 3%) as shown in Table I. These are in line with the results reported earlier by Clayton et al. of saturation water uptake values between 1.5 and 3.1 wt % for urethane acrylates consisting of polyether [polytetramethylene oxide] and polyester [polycaprolactone] diols of various molecular weights end-capped with toluene 2,4 di-isocyanate/2-hydroxyethyl acrylate.<sup>18</sup> It is also noted that the equilibrium water content appears to be largely insensitive to the immersion temperatures for both lamp and LED cured specimens. The temperature dependence of the equilibrium water content is determined by the polarities of the molecular structures and the insensitiveness to the immersion temperature suggests the moderate polar properties of the current UA networks.<sup>2</sup>

As mentioned above, the value of  $\Delta m$  is expected to have a correlation with the observed mass loss which is indicated by  $k$  as a measure of the degradation rate in the second-stage. As shown in Figure 3, good linearity is found between  $\Delta m$  and  $k$ . The deviation for the LED droplets is likely due to removal of portions of the uncured, sticky, surface during blot drying. The linearity between  $\Delta m$  and  $k$  also demonstrates the validation of the assumption related to the two stage mass change model.

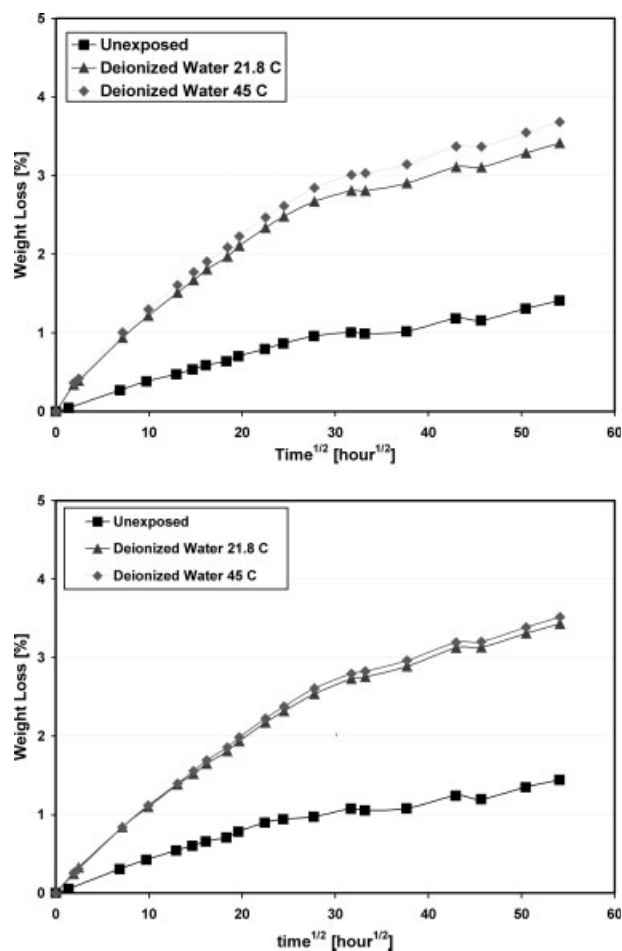
The activation energy,  $E$ , for diffusion can be calculated according to the Arrhenius relationship

$$D = D_0 \exp(-E_a/RT) \quad (2)$$

where  $D_0$  is a constant,  $R$  is the universal gas constant, and  $T$  is the absolute temperature in Kelvin by plotting  $\ln(D)$  versus  $1/T$ . Values of  $E_a$  of 82.7 kJ/mol and 83.9 kJ/mol were determined for the lamp cured bar and droplet specimens, respectively,



**Figure 3** Plot of  $\Delta m$  vs.  $k$  for water absorption and desorption. (Note: desorption is only for specimens immersed in deionized water at 21.8 and 45°C. All data presented in this diagram are listed in Tables I and II).



**Figure 4** Moisture desorption curves. (a) Cured with the UV Lamp source (b) Cured with the LED source.

whereas values of 84.6 kJ/mol and 84.8 kJ/mol were determined for the LED cured bar and droplet specimens, respectively. The relatively close set of values indicates only minor differences in diffusion mechanisms as a function of UV-source and specimen type.

To further elucidate the mechanism of moisture transport in UV-cured UA samples, vacuum desorption tests were performed at room temperature on selected samples that had been aged in deionized-

water for 6 months. Figure 4(a,b) show the mass loss curves for lamp and LED cured specimens, respectively. As a comparison, unexposed samples maintained under ambient conditions were also tested and are shown in the plots. It was found that the weight loss initially increased linearly over the first month, and then continued to increase at a slower rate as a function of the square root of drying time. This is contrary to the common desorption curves of epoxy specimens,<sup>19</sup> where the weight loss is seen to stabilize after an initial linear change. The discrepancy is hypothesized to be due to the uncured monomers. The two-stage diffusion model (eq. 1) was applied to desorption and parameters are summarized in Table II. In the Table the maximum weight loss,  $M_{\max}$ , represents the total weight drop after vacuum drying,  $M_s$  is the equilibrium weight loss after the first desorption stage,  $k$  is related to the rate of the second stage weight loss, which is assigned to the uncured monomers, and  $D$  represents the moisture desorption diffusivity.

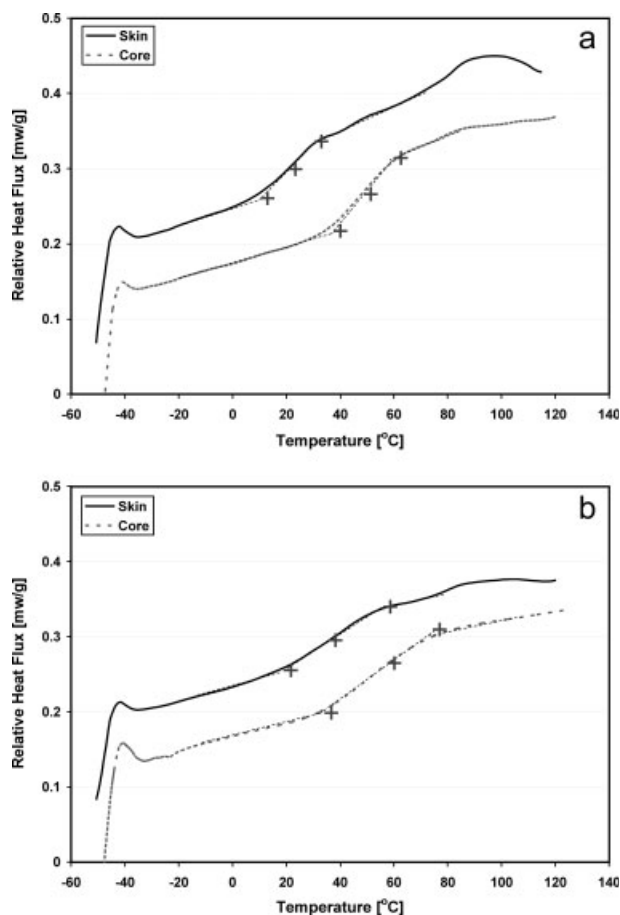
The weight loss indicated by the unexposed specimens as a result of vacuum assisted desorption includes the water absorbed by specimens during the water cooled polishing process and the storage period, and uncured monomers. It can be seen from Table II that the unexposed lamp cured specimen exhibit a lower monomer loss ( $m$ ) than the unexposed LED specimen, while the  $k$  and  $D$  values are similar. In the case of the specimens tested after 6 months immersion in deionized water, the LED cured specimens showed slightly higher  $\Delta m$  values, consistent with the conclusion that the LED cured specimens possess a higher concentration of uncured monomers. It is of interest to note that the desorbed specimens show a relation of  $\Delta m$  vs.  $k$  along the same linear plot as the immersed specimens (as shown in Fig. 3). This further supports the assumption that the  $k$  is directly related to the mass loss rate.

The extent of cure is dependent effectiveness of the UV radiation source and this in turn influences the effects of mass uptake and loss due to immersion in deionized water. In particular it was seen that the use of the LED source resulted in a lower degree of

**TABLE II**  
Diffusion Parameters Determined with the Two-Stage Diffusion Model for the Specimens Dried under Vacuum

| Specimens      |                    | $M_{\max}$ (%) | $M_s$ (%) | $\Delta m$ (%) | $k$ ( $10^{-5}/s^{1/2}$ ) | $D$ ( $10^{-7}$ mm <sup>2</sup> /s) |
|----------------|--------------------|----------------|-----------|----------------|---------------------------|-------------------------------------|
| Lamp Cured Bar | Unexposed          | 1.34           | 0.75      | 0.59           | 20.67                     | 3.45                                |
|                | DI Water at 21.8°C | 3.36           | 2.83      | 0.53           | 4.8                       | 2.8                                 |
|                | DI Water at 45°C   | 3.64           | 3.03      | 0.61           | 5.22                      | 3.2                                 |
| LED Cured Bar  | Unexposed          | 1.44           | 0.79      | 0.65           | 21.72                     | 3.2                                 |
|                | DI Water at 21.8°C | 3.43           | 2.74      | 0.69           | 6.47                      | 3.4                                 |
|                | DI Water at 45°C   | 3.52           | 2.83      | 0.69           | 6.19                      | 3.3                                 |

$M_{\max}$ , maximum weight loss in 6 months;  $M_s$ , equilibrium water uptake,  $k$  and  $D$  determined from curve fitting with eq. (1);  $\Delta m = M_{\max} - M_s$ . Standard deviations for  $k$  and  $D$  are in the order of 5%.



**Figure 5** DSC curves for unexposed LED cured specimens (a) First run from  $-50^{\circ}\text{C}$  to  $120^{\circ}\text{C}$  at a rate of  $10^{\circ}\text{C}/\text{min}$  (b) Second run conducted after immediate cooling.

cure on the specimen surface due to the oxygen inhibition which in turn contributes to the higher mass loss seen in these specimens on extended periods of immersion in deionized water. To further investigate the effects of cure in lamp and LED cured specimens, DSC tests were performed on samples scraped from the skin and core regions of cured droplets. Figure 5(a,b) show the DSC curves from two runs on LED cured skin and core samples. The glass transition temperatures determined from the mid-point of the transition steps are listed in Table III. It is clear that the skin of the LED cured droplet possesses a much lower  $T_g$  ( $\sim 18.9^{\circ}\text{C}$ ) than the core ( $\sim 51.2^{\circ}\text{C}$ ), which further explains the existence of the sticky surface on LED cured samples. The wider peak plateau of the skin specimens at about  $100^{\circ}\text{C}$  [Fig. 5(a)] can be attributed to the evaporation of the amount of uncured monomer and absorbed water molecules. In the second DSC run, the  $T_g$  of both skin and core specimens is seen to increase, with the increase being significant for the skin samples, which can be traced to the loss of plasticization effects due to the evaporation of monomers and water molecules during the heating process itself.

In contrast, specimens from the lamp cured droplets exhibit a reverse trend vis-à-vis the  $T_g$  of skin and core specimens. As shown in Figure 6(a,b) and Table III, the lamp cured specimens indicate a slightly higher  $T_g$  in the skin than in the core, supporting the contention that the UV lamp, with shorter wavelength UV of  $\lambda < 300\text{ nm}$ , is more effective at the surface.<sup>3</sup> Compared to the LED cured specimens, the lamp cured specimens showed higher overall  $T_g$ s.

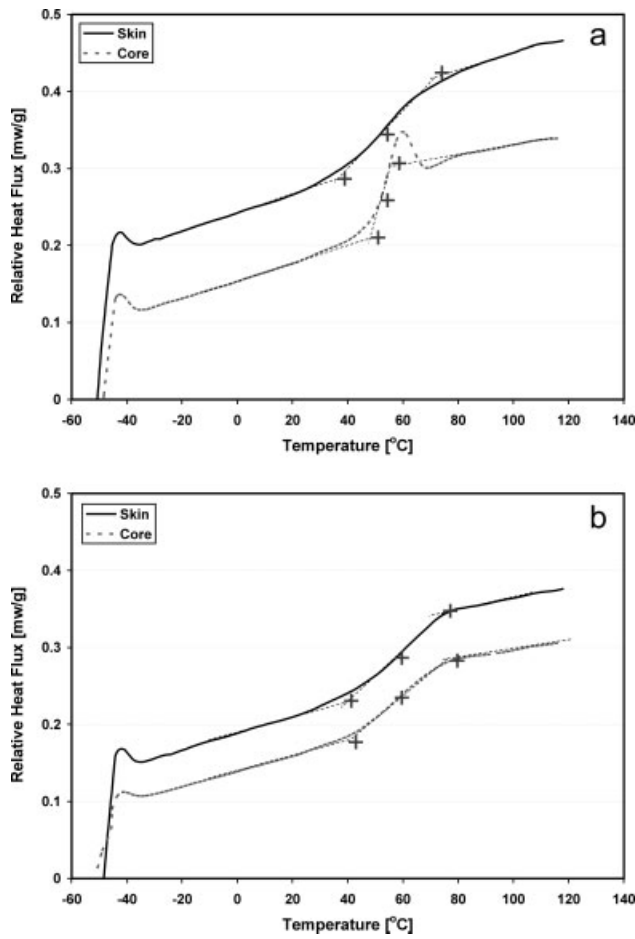
Using the Fox-Loshaek expression<sup>20</sup> to relate the cross-link density to glass-transition temperature it can be seen that there are distinct differences in the extent and efficiency of cure resulting from the two different sources. The lamp-cured specimens show a higher cross-linked surface and a slightly lower cross-linked bulk, whereas the LED-cured samples indicate a higher cross-linked bulk (at about the same level as that from the lamp) but a significantly lower cross-linked surface. It is noted that Magan et al.<sup>3</sup> had earlier reported on the presence of higher amounts of uncured monomers at the surface of processed specimens. These effects clearly affect moisture uptake response. The relative difference in cross-link density as well as the presence of uncured monomer based on source type (Lamp and LED) clearly affect long-term hygrothermal stability and ageing response as shown from the uptake results (Tables I and II), emphasizing the need for further studies of effects of moisture and environment.

TGA profiles as shown in Figure 7 provide further validation for the lower extent of cure at the surface of specimens cured by the LED source since these specimens start to lose weight at a much lower temperature in comparison to the other samples. For example, by  $200^{\circ}\text{C}$ , the LED cured samples lose about  $\sim 5\text{ wt } \%$ , while the others lose less than  $1.3\text{ wt } \%$ .

DMTA tests were performed to investigate the effects of hygrothermal ageing on the viscoelastic behavior of the polymer. Tests on unexposed samples showed a slighter lower  $T_g$  and rubbery modulus for the LED cured samples which are in line with the lower cross-linkage of those specimens.<sup>19,21</sup> Typical changes in storage modulus and loss tangent curves of LED specimens as a result of immersion in deionized water are shown in Figure 8(a,b), respec-

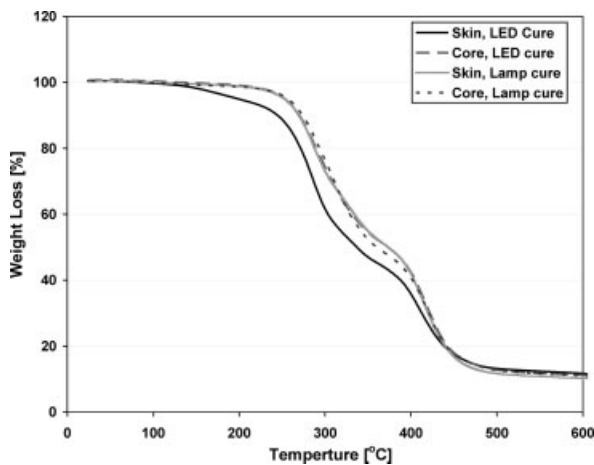
**TABLE III**  
Glass Transition Temperature ( $^{\circ}\text{C}$ ) Detected from DSC Curves (Mid-Point)

| Run     | Lamp cured UA |      | LED cured UA |      |
|---------|---------------|------|--------------|------|
|         | Skin          | Core | Skin         | Core |
| 1st run | 53.4          | 51.3 | 18.9         | 51.2 |
| 2nd run | 57.7          | 55.3 | 34.6         | 53.3 |



**Figure 6** DSC curves for unexposed UV Lamp cured specimens (a) First run from  $-50^{\circ}\text{C}$  to  $120^{\circ}\text{C}$  at a rate of  $10^{\circ}\text{C}/\text{min}$  (b) Second run conducted after immediate cooling.

tively. It is seen that the  $\tan \delta$  height is decreased with immersion and the peak is also shifted to lower temperatures. With increase of ageing time, the single  $\tan \delta$  peak splits to double peaks. Such changes are commonly encountered when using DMTA to



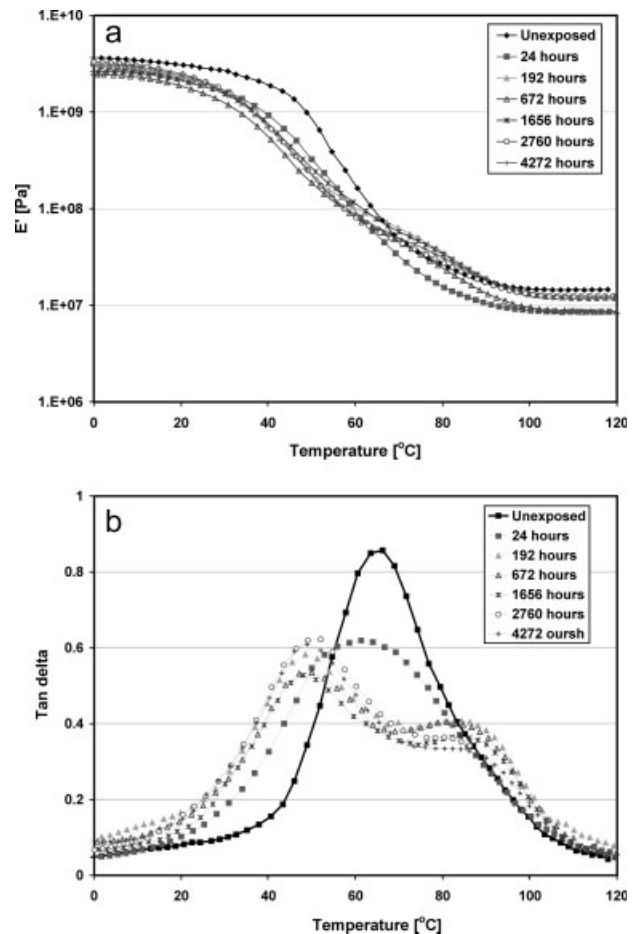
**Figure 7** TGA curves.

study the hygrothermal ageing of polymers and polymer composites cured using conventional sources of heat<sup>19,22–25</sup> and the lower temperature peak is attributed to the plasticization effect of the water ingress, while the higher peak is assigned to the drying effect of the DMTA ramp,<sup>19,23</sup> or the inhomogeneous nature of water ingress in some systems.<sup>24</sup>

Figure 9(a,b) show the variation of the lower  $T_g$ s with the period of immersion in deionized water as a function of temperature. For all ageing conditions, the  $T_g$ s initially decrease dramatically and then level off. A similar trend has also been reported for temperature cured epoxy or epoxy composites<sup>19,25</sup> and is interpreted in terms of the plasticization of the resin phase. As with the results of DSC reported earlier in the paper, the lamp cured specimens possess a slight higher  $T_g$  ( $52 \sim 54^{\circ}\text{C}$ ) than LED cured specimens ( $48 \sim 50^{\circ}\text{C}$ ) over all periods of this investigation.

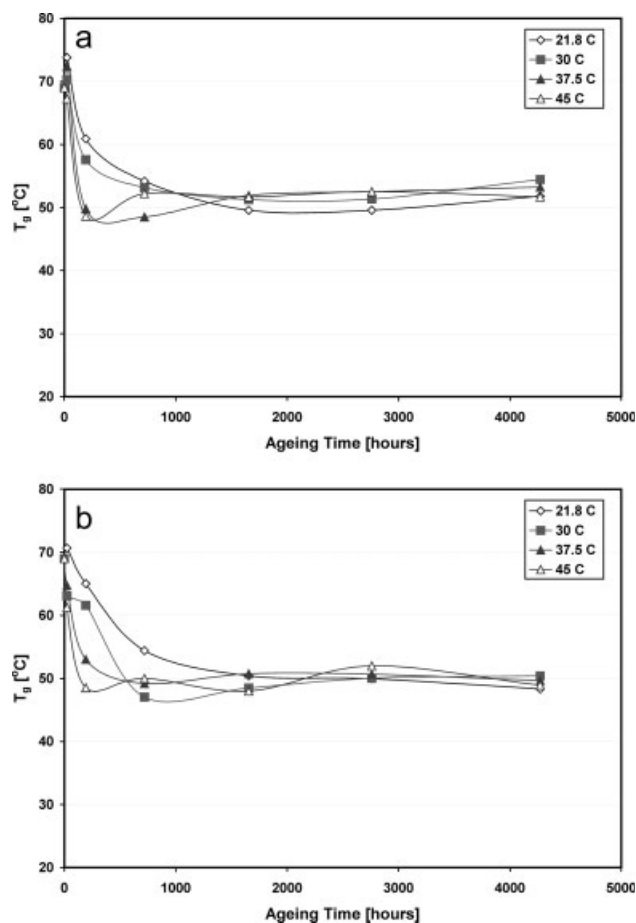
**SUMMARY**

Moisture diffusion behavior of urethane acrylate samples cured using either a traditional mercury



**Figure 8** Typical DMTA results for LED specimens aged in deionized water at  $45^{\circ}\text{C}$  (a) Storage modulus (b) Loss tangent.





**Figure 9** Variation in glass transition temperature as a function of immersion time in deionized water (a) Cured with the UV Lamp source (b) Cured with the LED source.

arc-lamp or a LED UV source is investigated. Both droplet and bar geometry specimens were used to assess response during water immersion and desorption under vacuum. Specimens cured with both sources exhibit an observable mass loss as a result of hygrothermal ageing due to the leaching and dissolution of unreacted monomers and lower molecular weight species. LED cured droplet specimens displayed a much higher mass loss over the six-month period of immersion in deionized water at all temperatures considered compared to all other specimens. This is attributed to the lower effectiveness of curing of the LED UV-source, which is also supported by the lower  $T_g$  and relatively poor thermal stability of the specimen surfaces. A two stage diffusion model was modified to describe both the moisture uptake and mass loss behavior observed during this study and results are shown to match well with

the model. Good linearity is found between mass loss ( $\Delta m$ ) and mass loss rate ( $k$ , determined from the two stage model) validating the application of the two stage mass change model to describe the moisture absorption (or desorption) process with mass loss during the second-stage. DSC results reveal that the surface of LED cured specimens exhibits a much lower  $T_g$ , indicative of the lower effectiveness of cure due to the LED on the specimen surfaces. In addition, both DMTA and DSC results indicate that the lamp source is more effective in curing the surface and the bulk.

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