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## Relationship of solvent to the photopolymerization process, properties, and structure in model dentin adhesives

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### Abstract

The ratio of the double-bond content of monomer to polymer, i.e. degree of conversion (DC) has been used frequently as a convenient means of comparing the behavior and properties of dental composites and adhesives. The purpose of this investigation was to study the relationship of photopolymerization processes, bulk properties, and structure using model dentin adhesives cured in the presence of different ethanol content as an example. There was little difference in the DC of model BisGMA-based adhesives cured in the presence of ethanol concentrations ranging from 0 to 40 wt %, but there were substantial differences in the mechanical properties. Ultimate tensile strength (UTS) and modulus of elasticity decreased with an increase in ethanol content. Polymer structure was revealed by thermal behavior in the glass transition temperature ( $T_g$ ) region; these measurements were obtained by modulated temperature differential scanning calorimetry (MTDSC) technology, which removes the competing irreversible effects associated with release of volatiles and residual curing. Glass transition temperature of model adhesives decreased substantially with an increase in ethanol content. The DC based on the quantity of remaining double bond has been used extensively to characterize and provide a relative assessment of the quality of dentin adhesives and dental composites. Since polymers differing in linearity, and therefore crosslink density, may have a similar degree of conversion, the measurement of monomer/polymer conversion does not necessarily provide complete representation of the quality or durability of the polymer structure.

### Keywords

photopolymerization; dentin adhesive; degree of conversion; structure/property relationship; glass transition temperature

### INTRODUCTION

With the development of high-powered dental curing lights, dimethacrylate resins such as BisGMA/TEGDMA can be cured quickly (<10 s) to form a strong, highly crosslinked polymer matrix that acts as the structural support for composite dental materials. The polymerization kinetics of these crosslinking polymers are complex and investigators have reported features such as autoacceleration and auto-deceleration,<sup>1</sup> trapped radical,<sup>2</sup> limited ultimate double-

bond conversion,<sup>3</sup> a reaction-diffusion-controlled termination,<sup>4</sup> primary cyclization,<sup>5,6</sup> kinetics chain length dependence,<sup>7,8</sup> and kinetics parameters<sup>9</sup> that are a function of the rate of polymerization. For a given monomer composition, the degree of conversion is an important factor because it influences the mechanical properties of the polymer<sup>10</sup> and the amount of free monomer that can be eluted from the composite.<sup>11,12</sup> Some researchers have reported that the degree of conversion, independent of cure method, has a critical effect on the final mechanical properties and wear rate of composite materials.<sup>13,14</sup> However, the relationship of photopolymerization processes, structure, and properties in dental resins are complicated. This relationship is dependent on monomer structure and functionality,<sup>15</sup> comonomer composition,<sup>16</sup> light intensity,<sup>17</sup> reaction temperature,<sup>18</sup> solvent quality,<sup>19</sup> oxygen, degree of moisture, and so forth. It is not clear that similar polymerization conversion necessarily represents the structure of the final polymer and that this parameter alone should be used when drawing conclusions about the structure/property relationships of dental resins.

A considerable number of single solution dental bonding agents currently in use contain acetone and/or ethanol as the hydrophilic carrier; these solvents could easily evaporate from the bottles because of repeated exposure to the environment during use.<sup>20</sup> The effect of solvent on the morphologic appearance of cured adhesive has been reported previously,<sup>21,22</sup> but there has been limited investigation regarding the effect of solvent on the photopolymerization process, structure, and bulk properties of the adhesive. Elliott et al.<sup>23</sup> reported the effect of solvent on the network structure of 2/98 diethylene glycol dimethacrylate/methoxyethyl methacrylate, and 2/98 diethylene glycol dimethacrylate/octyl methacrylate. These polymer hydrogels are characteristic of a more hydrophilic system; they are not representative of the more hydrophobic dentin adhesives.

Previous investigators have reported that excess solvent in the cured adhesives can lead to porous structure at the adhesive/dentin interface (Tay et al.<sup>24</sup>). These porosities may be sites where oral fluids penetrate resulting in undermining of the interface and composite restoration. In spite of these morphologic observations, our understanding of the effect of volatile solvents on the properties of dentin adhesives is limited. The present study evaluated the polymerization conversion and the mechanical properties of model dentin adhesives (mixtures of HEMA and BisGMA) as a function of concentration of ethanol in the formulations. The variation in ethanol concentration simulates the clinical condition where effective removal of residual solvent from adhesives that have penetrated the prepared demineralized dentin matrix is difficult and potentially, incomplete. The overall working hypothesis of this study was that the solvent incorporated into model BisGMA-based adhesives prior to polymerization would decrease the polymerization conversion, interrupt the formation of an adequate polymer network and result in lowered mechanical properties.

## MATERIALS AND METHODS

The monomer mixtures used in this investigation consisted of hydroxyethylmethacrylate (HEMA, Acros Organics, NJ) and 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy) phenyl]propane (BisGMA, Polysciences, Washington, PA) with a mass ratio of 40/60. This composition is similar to that used in commercial dentin adhesive formulations such as Single Bond (3M, Dental Products, St. Paul, MN). The solvent used with the model resin composition was ethanol from Fisher (Fair Lawn, NJ). The following three-component visible light photoinitiators (all from Aldrich, Milwaukee, WI) were used in this study: camphorquinone (CQ, 0.5 mol %), 2-(dimethylamino) ethyl methacrylate (DMAEMA, 0.5 mol %) and diphenyliodonium hexafluorophosphate (DPIHP 1.0 wt %); the concentration of the photoinitiator is calculated with respect to the total amount of monomer. The concentration of ethanol (0%, 5%, 10%, 20%, 30%, and 40%) was based on the total final weight of the model

adhesive. Shaking and sonication were required to yield well-mixed monomer/ethanol solutions. All the materials in this study were used as received.

### Polymerization and DC measurements

The model adhesives were cured with a commercial visible-light-curing unit: UltraLume<sup>®</sup> LED5 (Ultradent, South Jordan, UT). The degree of double-bond conversion of the model adhesives was determined using a Perkin–Elmer Spectrum One Fourier transform infrared spectrophotometer (FTIR) with a resolution of 4 cm<sup>-1</sup> in the ATR sampling mode. The change of the band ratios profile with 1637 cm<sup>-1</sup> (C=C)/1608 cm<sup>-1</sup> (phenyl) was monitored and degree of conversion (DC) was calculated by using the following equation based on the decrease in the absorption intensity band ratios before and after light curing.

$$DC = \left( 1 - \frac{\text{Absorbance}_{1637\text{cm}^{-1}}^{\text{sample}} / \text{Absorbance}_{1608\text{cm}^{-1}}^{\text{sample}}}{\text{Absorbance}_{1637\text{cm}^{-1}}^{\text{monomer}} / \text{Absorbance}_{1608\text{cm}^{-1}}^{\text{monomer}}} \right) \times 100\%$$

### Mechanical testing regimen

Round bar specimens (1.0 mm diameter × 15 mm length) cured with visible-light source (UltraLume<sup>®</sup> LED5) at 800 mW/cm<sup>2</sup> in glass-tubing molds (Wilmad Labglass, #LG-25001-100, Standard wall borosilicate tubing, 2.0 mm O.D., 1.0 mm I.D.), were used for the determination of mechanical properties. The tensile properties were determined for all samples after either 24 h storage-in-air at room temperature or 24 h storage-in-water. It is noted that these specimens did not contain ethanol after 24 h storage, as determined by FTIR spectroscopy (unpublished data). Specimens were tightly and fully attached to the upper and lower grips using cyanoacrylate cement (Zapit, Dental Ventures of America, Corona, CA) and were loaded at a cross-head speed of 0.5 mm/min using SSTM-5000 mechanical tester (United Calibration Corporation, CA) with a 150 lb load cell. The ultimate tensile strength (UTS, MPa) of each specimen was calculated as the maximum force at the point of failure divided by the specimen cross-sectional area. The elastic modulus (*E*, GPa) was measured as the slope of the linear portion of the stress–strain curve between 5% and 15% strain for all samples. Percent elongation (EL, %) was calculated as the value at the point of failure divided by the original specimen gauge length. Specimen toughness (*T*, MN/m<sup>2</sup>) was calculated as the area under the stress–strain curves. Sixteen specimens were made for each formulation; these specimens were randomly distributed into two groups, i.e. water or air-storage. Prior to mechanical testing, the specimens were carefully evaluated for defects. Specimens with defects were discarded.

### Determination of glass-transition temperature

The thermal behavior in the glass transition temperature (*T<sub>g</sub>*) region was measured with a TA Instruments model Q100 MTDSC (New Castle, DE) equipped with a Refrigerated Cooling System (RCS). To insure full evaporation of the solvent, the specimens from the same batch as above were kept *in vacuo* for one month storage prior to the measurements. The specimens were weighed (5–15 mg) in the aluminum DSC pans. In all cases, the DSC cell was purged with nitrogen gas at 50 mL/min and the specimens were heated under nitrogen purge from –80° C to 200° C at 4° C/min, with a modulation period of 60 s and amplitude of ± 2° C. The second and subsequent scans were consistent with each other but generally different from the first scan. However, only the first cycle of heating was taken into account, and the results are shown as differential reversing heat flow versus temperature. The *T<sub>g</sub>* values were reported as the temperature of the peaks, i.e. inflection points of the heat flow curves.

## RESULTS AND DISCUSSION

### Degree of conversion of model adhesives cured in the presence of different concentrations of ethanol

The preparation of model adhesives is a free radical chain growth crosslinking copolymerization of HEMA and BisGMA.<sup>25,26</sup> In this study, the round-bar glass-tubing molds were used in place of the widely used hour-glass shaped molds such as those made from Teflon, vinyl polysiloxane impression, or wax materials.<sup>25,26</sup> The advantages of the glass tubing molds included easy preparation of smooth surface beam specimens without the need for polishing, without air bubbles, and without evaporation of the solvent. The reproducibility of the data indicates the suitability of this method for determining the tensile properties of these photo-cured polymer specimens. The round-bar specimens were cured with a visible-light source (UltraLume<sup>®</sup> LED5). This light source was used because of its large output footprint (with size of 10–13 mm), which facilitates the preparation of beam specimens with gauge length less than 13 mm. The degree of conversion of these specimens before and after 24 h storage was determined by FTIR in the ATR sampling mode.

As shown in Figure 1, the monomer/polymer conversion of specimens cured in the absence of ethanol for 40 s is 48%. These specimens experienced an increase in conversion to 73% and 81% after 24 h storage in air and water, respectively. The difference in DC before and after storage indicates that the reaction continues after the light is extinguished. Even though no new radicals are being formed by initiation, the free radicals that are present when the light is turned off continue to propagate and terminate.

Interestingly, the difference in DC before and after storage is less when the initial DC is higher. As an example, the DC of specimens made without ethanol increased from 48 to 73% while the conversion of the specimens made with 20 wt % ethanol increased from 72 to 80% after 24 h storage in air. The reason may be that, at low conversion the network is less reacted, and this greater mobility allows for more dark-cure as compared to samples that are more highly converted. The specimens containing 10 wt % ethanol content show the maximum conversion (87%), and the specimens cured in the presence of 40 wt % ethanol and stored in air had the lowest value (69%). This observation implied that (1) after the photopolymerization, the remaining postcureable methacrylate double bonds continued to react whether stored in air or water (2) the degree of methacrylate double bond conversion of these specimens is approximately 70–80%.

### Tensile properties of model adhesives cured in the presence of different concentrations of ethanol

The mechanical properties of model adhesives cured with varying concentrations of ethanol were evaluated. Previous investigators reported that highly cross-linked dimethacrylate systems exhibit similar network structure and properties as a function of double bond conversion, regardless of the method or rate of cure.<sup>14</sup> Since the kinetics and network formation of crosslinking systems are quite complex, a thorough understanding of polymer network structure and mechanical property evolution is still an open question. In this study, the DC values of the model adhesives were similar irrespective of the differences of ethanol content, but there were substantial differences in the mechanical properties.

Table I and Figure 2 show the tensile properties of model adhesives cured in the presence of different concentrations of ethanol. FTIR spectra of these specimens show that ethanol had evaporated after 24 h storage. Following air or water storage, the ultimate tensile strength (UTS) of model adhesives without ethanol were (mean and standard deviation)  $70.2 \pm 7.2$  MPa and

57.1 ± 6.1 MPa, respectively. The tensile strength of the model adhesives cured in the presence of 40 wt % ethanol was so low that an accurate measurement could not be completed.

The decline in UTS with ethanol content follows a complex trend. For example, in a comparison of the specimens stored-in-water, it is noted that those samples cured in the presence of 5 wt % ethanol had ~60% of the strength of specimens produced without ethanol. For specimens stored-in-water there is a continued gradual decrease in UTS with ethanol content until 30 wt % ethanol content. At this concentration, there is a precipitous drop in UTS. In comparison, for those specimens stored-in-air there are minimal differences in the UTS for samples cured in the presence or absence of 5 wt % ethanol. For specimens stored-in-air, but cured in the presence of 10 wt % and higher ethanol concentrations there is a substantial decrease in the UTS. Water storage of the model adhesives generally yields lower UTS values than the stored-in-air groups.

The influence of ethanol content in the model adhesive formulation on the modulus of elasticity shows results comparable to those for the tensile strength. The modulus of stored-in-air specimens cured in the presence of 20 wt % ethanol is only half the value of those specimens made without ethanol. The moduli of elasticity decreased with an increase in ethanol content. For model adhesive specimens formulated with the same concentration of ethanol, moduli were lower for the water-stored as compared to the air-stored samples.

Specimens stored-in-air and cured without ethanol showed the lowest elongation (4%). As seen from Table I, with the increase of ethanol content in the adhesive formulation, the elongation of model adhesives stored-in-air increased from 4 to 21%. The values of specimens stored-in-water were maintained at about 8% regardless of the ethanol concentration in the adhesive formulation. With the exception of the model adhesive formulations that did not include ethanol, the toughness values of the water-stored samples were lower than the air-stored specimens. The toughness values of the water-stored samples decreased with increasing ethanol content. The air-stored samples did not present such a consistent pattern in the toughness values as a function of ethanol concentration, e.g. the toughness values of specimens cured in the presence of 20 wt % ethanol were nearly 40% higher than those cured in the absence of ethanol.

The mechanical property measurements suggest that the polymer crosslinking structure may change with ethanol content, although the polymer presents with a similar degree of conversion. It is well known that chain polymerization of multivinyl monomers results in pendant double bonds on the growing polymer chains. These pendant double bonds can react with propagating radicals by three different reaction mechanisms<sup>5</sup>: primary cyclization (in which the macroradical attacks the pendant double bond in the same chain), secondary cyclization (in which the radical attacks double bonds pendant on other chains already incorporated in the network), and intermolecular crosslinking. Primary cyclization causes small loops to be formed in the network, which causes microgels and heterogeneity to occur in the polymer. These small cycles do not contribute significantly to the overall network structure.<sup>6</sup> In contrast, intermolecular crosslinking reactions, which are responsible for the aggregation of the microgels, lead to the formation of the macrogel and contribute to the overall strength of the network.

Adding solvent to the reaction increases the probability of cycling, due to the diluted concentration of monomer, and slowed rate of polymerization causing the local radical on its own chain to remain longer in close proximity to pendant double bonds. The presence of cyclization in hydrogels has already been indicated by the heterogeneity which is seen with small-angle neutron scattering in a poly(acrylic acid) and methylene bisacrylamide copolymers.<sup>27</sup> In addition, delayed gel-point conversion from what is predicted by the classical

Flory–Stockmayer theory is evidence of the existence of significant cyclization reactions. The solvent concentration during polymerization will also change the gel-point conversion of polymer because of varying degrees of cyclization, which is demonstrated by the photopolymerization kinetics presented in this study.

Characterization of the structure/property relationship of adhesives as a function of solvent concentration provides information that is integral to our understanding of the behavior of these materials under clinically relevant conditions. For example, it is clear that in a clinical setting the repeated opening of the container and exposure of the adhesive to the environment will allow solvent/water to evaporate. As solvent/water evaporate from the adhesive, the monomer-to-water ratio increases and lowers the vapor pressure of water, thus reducing the ability of solvent/water to evaporate from the adhesive. It is likely that residual solvent/water will be trapped within the adhesive resin upon curing. The concentration of solvent/water in the adhesive formulation will thus vary with time and this variation in composition will impact the mechanical properties. Additionally, clinical protocols for dentin bonding recommend application of the adhesive to a wet demineralized dentin substrate. With wet bonding, the channels between the demineralized dentin collagen fibrils are filled with water, solvent, conditioner, etc. and the only mechanism available for adhesive resin infiltration is diffusion of the adhesive into whatever fluid is in the spaces along the collagen fibrils. The solvent/water may be trapped within the interstices of the demineralized dentin matrix spaces. Since the adhesive polymerizes *in situ*, the solvent/water within the interstitial spaces may be trapped within the adhesive. These factors could impact the clinical behavior of the adhesive and its ability to provide a durable seal at the material/tooth interface.<sup>28,29</sup>

### Structural differences revealed by thermal analysis

When designing a cross-linked polymer for a specific application, it is important to understand the network formation and the resulting material properties as each application has specific material requirements. The material properties, such as the molecular weight between crosslinks, swelling, and diffusion of a solute within its mesh, are all determined by the extent of crosslinking in the network. The degree of polymer crosslinking may be assessed by swelling tests, hardness test,<sup>30</sup> mechanical property test (e.g., DMA<sup>31</sup>), and the measurements of the glass transition temperature (e.g., DSC or TG<sup>32</sup>). However, testing of the specimens at elevated temperatures increases the mobility of the radicals and additional polymerization ensues. For example, the DSC analysis of photo-initiated acrylate-based polymer resin is complicated by the heterogeneity of crosslinking structure, various composition (cross-linked polymer, oligomer, monomer, organic solvent, initiator, water), and post-cured reaction when heating, which shift with temperature. The result is often a complex thermal curve that may include superimposed glass transitions, evaporation and curing peaks.<sup>33</sup> Definitely, minor differences in  $T_g$  cannot be determined using conventional DSC. Some researchers chose to utilize iniferter molecules, such as XDT (*p*-xylylene bis(*N,N*-diethyl dithiocarbamate)) in the presence of ultraviolet light to create partially cured networks that contain no trapped radicals.<sup>34,35</sup> This method combined with dynamic mechanical analysis (DMA) provided insight into the network structure of the formed polymer.<sup>36</sup> However, the iniferter-based system polymerizes much more slowly than conventional initiator systems due to lower rates of radical generation and the presence of the dithiocarbamyl radical which consumes carbon radicals via termination.<sup>36</sup> The polymerization kinetics have been greatly changed by the iniferter, the behavior of this system is not representative of conventional dental resin systems, which are visible-light cured and unstable with trapped radicals.

We used a novel modulated temperature DSC method to obtain the thermal properties of model adhesives and to provide related information on the degree of crosslinking. To our knowledge, this approach has not been reported before for the photo-cured polyacrylate resins which have

pendant methacrylate double bonds. Perhaps the greatest DSC advance in the recent decade has been that of Modulated DSC, in which a small temperature modulation is applied to the underlying linear temperature program. By applying Fourier Transform analysis to the resultant heat flow signal, it is possible to separate out rapidly reversing processes, such as specific heat and  $T_g$ , from kinetically controlled processes, such as evaporation, crystallization and crosslinking reactions.

Figure 3(a) shows the results obtained in the MTDSC analysis for the model adhesives synthesized cured without ethanol. Prior to measurement by DSC, the sample was only partly cured with the DC at about 50%, having vitrified during the curing process at room temperature. As the sample is heated, it enters the glass transition region. The glass transition temperature, which is a reversible phenomenon, is clearly observed as a step change on the reversible component of the heat-flow curves. As the temperature is raised further, the thermal energy provides sufficient molecular mobility to recommence the curing process, causing a shift in the transition region. The non-reversible component showed a large exotherm peak arising from the simultaneous thermal curing. As the temperature is raised still further, the reaction finally ceases as the system approaches full cure. This is corroborated by the results in Figure 3(b), obtained after the sample had been heated again. The observed exotherm is substantially smaller, since curing has essentially been completed in the first run. It may be noted that the concurrence of the positions of both the glass transition and the enthalpic peak would not have been detected under conventional DSC conditions, since the exotherm would have obscured it completely.

Figure 4 shows the reversing Heat Flow signals of model adhesives cured in the presence of different ethanol content. The derivative reversing heat flow could be used to show clearly the glass transition. It is seen that with the increase of ethanol content from 0% to 30 wt % in the adhesive formulation,  $T_g$  of model adhesives with similar DC decreased about 30° C and  $T_g$  width becomes larger and larger. This behavior could be attributed to the heterogeneous nature plus the broad distribution of relaxation times and mobilities in the crosslinking network.<sup>36</sup> As stated before, the reactions of the pendant double bonds with radical centers located on the same macromolecule do not contribute to the overall crosslinking density however, they do facilitate microgel formation. Microgels, which are typically formed near initiation sites, quickly become regions of very low radical mobility. However, other portions of the formed network, which have experienced less polymerization, possess far more mobile microenvironments. This nonideal network development causes an inhomogeneous distribution of chain mobilities and local free volume that leads to a broad distribution of relaxation times.<sup>6</sup> The greater the concentration of solvent the more primary cyclization, heterogeneity, formation of microgels, and delays in the gel point. Thus, the gradual broadening of the glass transition with increasing ethanol content in the adhesive formulation is attributed to an increase in the heterogeneity of the network.

## CONCLUSIONS

The photopolymerization degree of conversion and the mechanical, thermal properties of a model dentin adhesive cured in the presence of different concentrations of ethanol have been studied. The model adhesives showed a similar degree of monomer to polymer conversion irregardless of the concentration of ethanol, but there were substantial differences in the mechanical properties.  $T_g$  transition in the reversing heat flow curve is accurately obtained by taking advantage of the capabilities of the MTDSC technology to remove the competing irreversible effects associated with the release of volatiles and residual curing. The decrease in the glass transition of specimens (stored-in-air) with an increase in ethanol content and the broadening of  $T_g$  width could be due to the increased heterogeneity of the crosslinking network.

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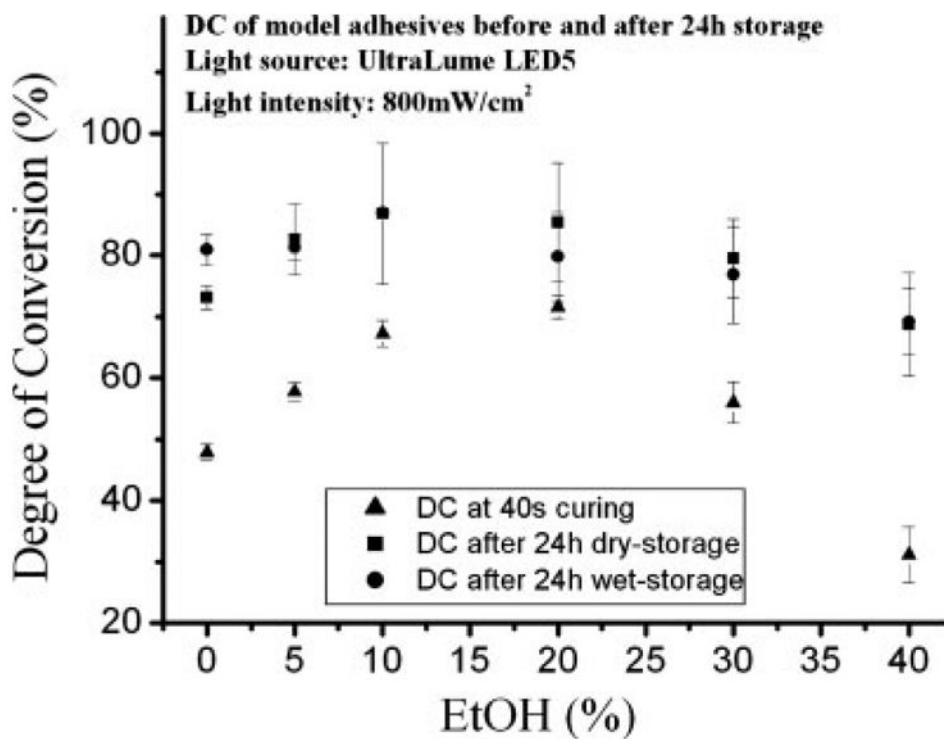
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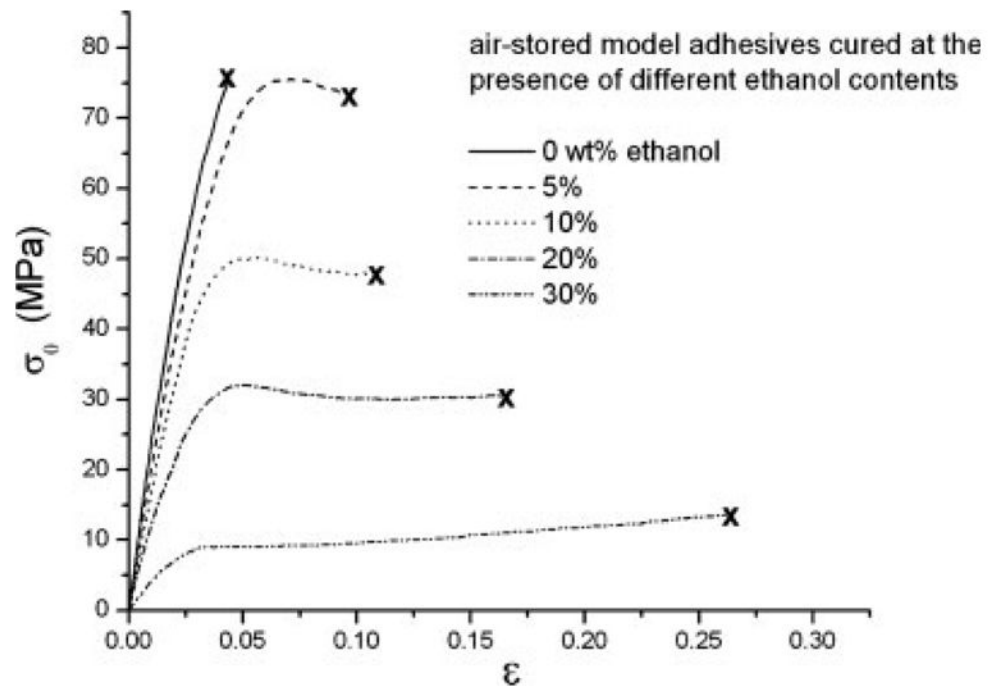
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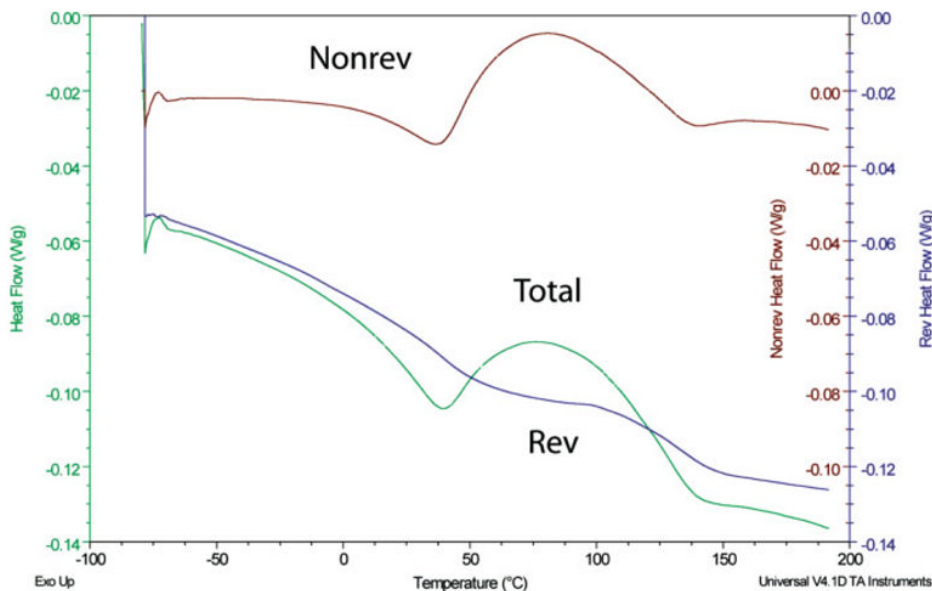
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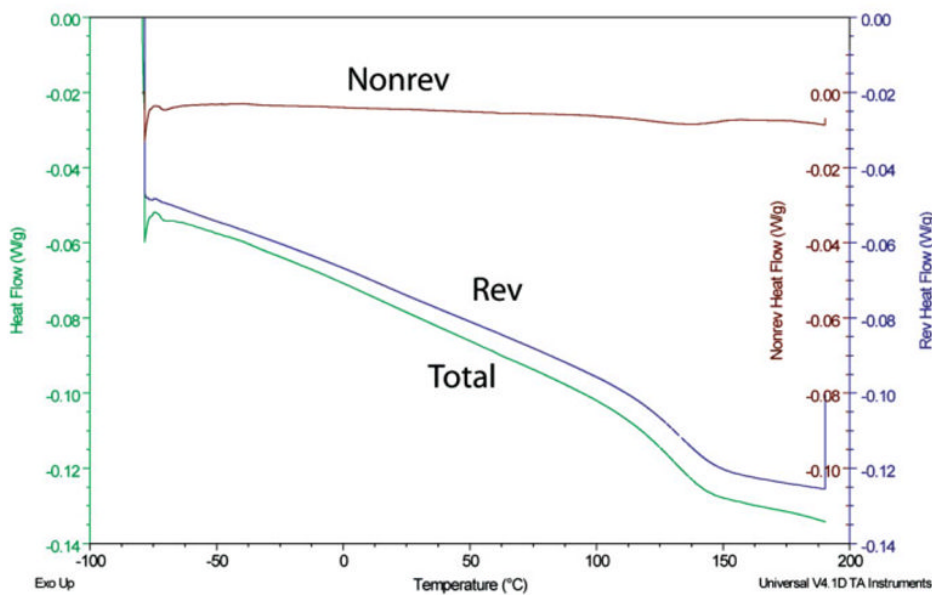
**Figure 1.** DC of model adhesives before and after 24 h storage measured by FTIR spectroscopy for the ethanol contents of 0 wt %, 5 wt %, 10 wt %, 20 wt %, 30 wt %, 40 wt % in the adhesive formulation (UltraLume<sup>®</sup> LED5, 800 mW/cm<sup>2</sup>).



**Figure 2.** Stress–strain relationship of model adhesive samples cured in the presence of different ethanol contents.



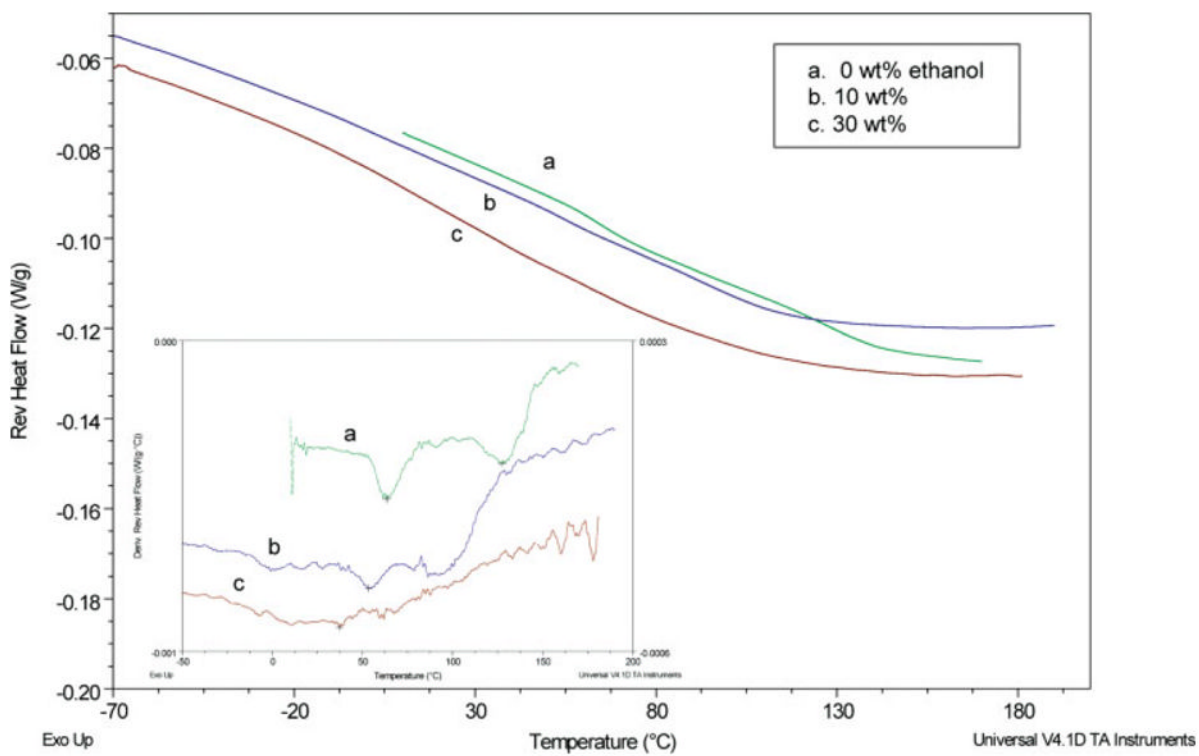
(a)



(b)

**Figure 3.**

(a) Typical MTDSC plots showing total heat flow and its two components, i.e., reversible and non-reversible heat flows. Note that the glass transition region, which is very clear in the reversible heat flow component, is overlapped by the non-reversible heat flow component and would not be observed in the total heat flow curve, i.e., the one usually measured by conventional DSC. (b) MTDSC plots of the sample examined in (a), re-run under similar conditions. Note the disappearance of the exothermic peaks in the total and non-reversible heat flow curves. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 4.** Reversing heat flow signals of model adhesives cured in the presence of different ethanol contents of (a) 0 wt %; (b) 10 wt %, (c) 30 wt %. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

TABLE I  
Mechanical Properties of Model Adhesives as a Function of Concentration of Ethanol in the Adhesive Formulation

EtOH Content (wt %)	Storage and Test Condition	Ultimate Tensile Strength (MPa)	Modulus of Elasticity (GPa)	% Elongation	Toughness (MN/m <sup>2</sup> )	Degree of Conversion After 24 h storage
0	In air	70.2 ± 7.2 (6)	2.45 ± 0.21 (6)	4.22 ± 0.21 (6)	1.71 ± 0.30 (6)	73.2 ± 1.9 (8)
0	In water	57.1 ± 6.1 (5)	1.91 ± 0.13 (5)	7.05 ± 1.08 (5)	2.97 ± 0.65 (5)	81.0 ± 2.5 (8)
5	In air	68.8 ± 2.9 (7)	2.01 ± 0.14 (7)	8.57 ± 3.42 (7)	4.59 ± 2.40 (7)	82.7 ± 5.8 (8)
5	In water	33.0 ± 3.2 (6)	1.31 ± 0.05 (6)	8.16 ± 0.86 (6)	2.27 ± 0.28 (6)	81.3 ± 2.2 (7)
10	In air	49.0 ± 2.6 (7)	1.65 ± 0.08 (7)	9.23 ± 3.65 (7)	3.75 ± 1.80 (7)	86.9 ± 11.5 (10)
10	In water	31.5 ± 1.5 (7)	1.16 ± 0.12 (7)	8.42 ± 3.50 (7)	2.18 ± 1.13 (7)	87.0 ± 0.7 (8)
20	In air	30.8 ± 1.5 (7)	1.24 ± 0.13 (7)	15.75 ± 4.10 (7)	4.41 ± 1.21 (7)	85.5 ± 9.7 (8)
20	In water	24.0 ± 0.8 (8)	0.99 ± 0.04 (8)	8.66 ± 2.80 (8)	1.26 ± 0.69 (8)	79.8 ± 7.3 (8)
30	In air	10.5 ± 4.7 (6)	0.38 ± 0.13 (6)	20.82 ± 12.59 (6)	1.52 ± 1.13 (6)	79.6 ± 6.4 (8)
30	In water	13.6 ± 4.5 (8)	0.61 ± 0.16 (8)	9.40 ± 4.24 (8)	1.04 ± 0.50 (8)	76.9 ± 7.9 (8)
40	In air	—	—	—	—	68.8 ± 8.4 (8)
40	In water	—	—	—	—	69.2 ± 5.4 (4)

Gauge Length: 8.52 mm, rate: 0.5 mm/min, Specimen: 1-mm Round-Bar, determined after 24 h storage in air or in distilled water.