Structure-mechanical property relationships in acrylate networks

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Structure–mechanical property relationships in acrylate networks

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ABSTRACT: The objective of this work is to investigate the effect of the molecular mobility and resin formulation of UV-curable acrylate systems on conversion and ultimate mechanical properties. Thin single-layer films are produced from a series of nine mixtures of bisphenol A ethoxylate diacrylate, having different molecular weights (BisDA$_n$$_{-}$2, BisDA$_n$$_{-}$4, and a 50/50 mixture), with different amounts of tetraethylene glycol diacrylate (TEGDA) (0, 10, and 30 wt %). Fourier transform infrared analysis, tensile, and dynamic mechanical tests are carried out on UV post-cured resins, and the results are correlated with the amount of TEGDA. A higher content of TEGDA gives rise to an increase in conversion and glass-transition temperature. Tests on pure BisDA$_n$$_{-}$2 and mixtures of BisDA$_n$$_{-}$2 and BisDA$_n$$_{-}$4 (BisDA$_n$$_{-}$2+4) show that with increasing TEGDA content, the crosslink density increases. An increase in molecular weight of the acrylate monomer changes the final mechanical properties of UV-cured products. A material having a rubber behavior is the result of this change. Next to UV post-curing, the effect of thermal post-curing is studied. The results show that thermal treatments affect the mechanical properties mainly if the polymer has a low crosslink density. Formulations highly loaded with TEGDA lead to polymers with high crosslink density, low network mobility, and consequently low mechanical properties if thermally treated. Correlations between, on the one hand, resin formulation and process conditions and, on the other hand, the final mechanical properties of UV-cured systems are established allowing to optimize the structure–mechanical properties relationship in acrylate networks.© 2019 The Authors. Journal of Applied Polymer Science published by Wiley Periodicals, Inc. J. Appl. Polym. Sci. 2019, 136, 48498.

KEYWORDS: glass transition; mechanical properties; photopolymerization; structure–property relationships; thermosets

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INTRODUCTION

Stereolithography is one of the rapid prototyping technologies, which is capable of fabricating parts with complex geometries and good accuracy comparable to many conventionally machined components.1 Here, the starting material is a liquid resin that rapidly solidifies upon irradiation with UV light. The UV-curable resin used in this process mainly consists of a mixture of monomers with a photoinitiator that is needed to generate radicals during the photopolymerization. The mechanical properties of the three-dimensional-printed product depend on the degree of cure of the photosensitive resin and on the homogeneity along the sample thickness. Ferracane and Greener studied the effect of resin formulations on the degree of conversion and resulting mechanical properties of methacrylate resins.2 A significant correlation between degree of conversion and mechanical properties was found. The presence of unreacted monomers can further affect the stability of the product. In case of medical applications, such as dental restoratives, the uncured monomers could leach into the body, causing health issues. Therefore, an increase of monomer-to-polymer conversion would reduce the amount of leaching monomer and increase the stability of the polymer.3 Incorporation of a second monomer in the photo-curable formulation is a method to increase the maximum conversion. The viscosity of the starting formulation plays a major role herein. The addition of a diluent monomer tends to reduce the viscosity and to increase the mobility during photopolymerization.2,4 The increased mobility allows the propagation of the reacting molecules to continue for longer times before the reaction becomes
diffusion limited. As a result, the final conversion increases as well. Feilizer and Dauvillier have reported that for higher content of a triethylene glycol dimethacrylate (TEGDMA) diluent monomer in the methacrylate resin (BisGMA), the reaction slows down due to the lower reactivity of the diluent monomer. Therefore, the amount of diluent monomer that can be added is limited. Other studies have investigated the influence of the monomer molecular weight in methacrylate systems. The reactivity and therefore the final conversion decrease as the number of ethylene glycol units present in the monomer decreases due to reduced flexibility. By combining the monomer and the diluent, the conversion kinetics can be tuned. The resulting mechanical properties can be strongly affected by the nature of the monomers forming the liquid formulation. For instance, Asmussen and Peutzfeldt have observed that the diametral tensile and flexural strength increase when a diluent (TEGDMA) is added into methacrylate systems (UEDMA and BisGMA).

The effects of chemical structure and the presence of diluents on the mechanical properties of acrylate monomers have been less investigated. Multifunctional acrylates are known to polymerize faster than their corresponding methacrylates. Fenoli et al. have used tetraethylene glycol diacrylate (TEGDA) monomers as diluent in the starting mixture of BisDA, thus obtaining a high degree of conversion (88%). However, the mechanical part of their work only dealt with shrinkage stress and stress relaxation. Even though it is well known that a diluent allows to enhance the final conversion, its effect on the resulting mechanical properties of acrylate systems is not yet known. As an extension to our previous work on pure BisDA,

### Table 1. Composition of the Experimental Formulations

<table>
<thead>
<tr>
<th>Formulations</th>
<th>BisDA(_n=2)</th>
<th>BisDA(_n=4)</th>
<th>TEGDA</th>
</tr>
</thead>
<tbody>
<tr>
<td>BisDA(_n=2)</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>BisDA(_n=4)</td>
<td>0</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>BisDA(_n=2+4)</td>
<td>50</td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>BisDA(_n=2)-TEGDA 90:10</td>
<td>90</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>BisDA(_n=4)-TEGDA 90:10</td>
<td>0</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>BisDA(_n=2+4)-TEGDA 90:10</td>
<td>45</td>
<td>45</td>
<td>10</td>
</tr>
<tr>
<td>BisDA(_n=2)-TEGDA 70:30</td>
<td>70</td>
<td>0</td>
<td>30</td>
</tr>
<tr>
<td>BisDA(_n=4)-TEGDA 70:30</td>
<td>0</td>
<td>70</td>
<td>30</td>
</tr>
<tr>
<td>BisDA(_n=2+4)-TEGDA 70:30</td>
<td>35</td>
<td>35</td>
<td>30</td>
</tr>
</tbody>
</table>

Sample Preparation

The UV-curable formulations are prepared by mixing the monomers BisDA\(_n=2\), BisDA\(_n=4\), and TEGDA in a sonicator bath for 60 min. Thin layers of the starting liquid formulations are obtained by using a spin coater. A low spinning speed of 250 rpm for 10 s is used to initially homogenize the formulation on the silicon substrate. The layer thickness is kept constant at 80 μm, and therefore the second step, the spinning speed is regulated according to the viscosity of the different formulations.

The predictions of the final thickness at each spinning speed are reported in Figure S1 in the Supporting Information, and the values of the spinning speeds used to obtain 80-μm-thick layers are shown in Table S1 of the Supporting Information. The viscosities of the pure monomers, BisDA\(_n=2\), BisDA\(_n=4\), and TEGDA, and the mixtures are measured using a parallel-plate geometry on a Physica MCR501 (Anton Paar) rheometer at 22 °C, in a range of viscosities.

**EXPERIMENTAL**

**Materials**

The materials used for this study are three commercial acrylate monomers supplied by Sigma-Aldrich, Saint Louis, Missouri, United States. Two bisphenol A ethoxylate diacylate monomers, having two different number average molecular weights, namely \(M_n = 512 \text{ g mol}^{-1}\) (BisDA\(_n=2\)) and \(M_n = 688 \text{ g mol}^{-1}\) (BisDA\(_n=4\)), are used. A third monomer, TEGDA, with \(M_n = 302.32 \text{ g mol}^{-1}\), is added as diluent. Nine formulations, two with pure monomers and seven mixtures of BisDA\(_n=2\), BisDA\(_n=4\), and TEGDA, are prepared. Their compositions are shown in Table 1. The photoinitiator, 2,2-dimethoxy-2-phenylacetone (Irgacure 651), is added to each formulation in an amount of 3 wt %. The chemical structures are shown in Figure 1.

![Chemical structures](image)

**Figure 1.** Chemical structure of (a) BisDA\(_n\), and (b) TEGDA monomers and of (c) Irgacure 651 photoinitiator.
of shear rates from 1 to 100 s⁻¹. After spin coating, the 80-μm-thick layer of the starting formulation is UV-cured in an inert atmosphere, and by using a photomask, dog-bone-shaped samples are obtained, as described in our previous study. All the formulations are first UV-cured for 1.5 s at an intensity of 7 mW cm⁻² with an LED light (LED Cube 100 Hönle UV Technologies) to obtain the desired shape. The wafer is then washed with a solvent (acetone) for 90 s to remove the uncured resin. The tensile bars are successively UV and thermally post-cured to obtain maximally cured samples. To perform UV post-curing, the samples are irradiated at the same light intensity for different times. Next, thermal post-curing is performed in the oven at 150 °C for 30 min on samples previously UV post-cured. The specimens (tensile bars) are carefully peeled off from the wafer, and free-standing samples are thus obtained.

**Fourier Transform Infrared Spectroscopy Measurements**

The degree of double-bond conversion of the formulations during UV curing is measured by performing Fourier transform infrared (FTIR) spectroscopy analysis in reflection mode (Spectrum Two FTIR Spectrometer, PerkinElmer) in the range of 4000–400 cm⁻¹. Absorbance spectra are collected after each irradiation time. The double-bond conversion is determined by eq. (1):\(^{15}\)

\[
\alpha(t) = \frac{A_{\text{ref}}}{A_{\text{ref},0}} - \frac{A_{\text{acc}}}{A_{\text{acc},0}} \times 100
\]

where \(\frac{A_{\text{ref}}}{A_{\text{ref},0}}\) and \(\frac{A_{\text{acc}}}{A_{\text{acc},0}}\) represent the ratio of the second derivative of the acrylate double-bond twist at 810 cm⁻¹ and the internal reference at 829 cm⁻¹ before and after UV exposure for time \(t\). All the measurements are repeated at least two times, and the average values are shown. Error bars representing the standard deviation are smaller than the symbols and therefore omitted.

**Mechanical Properties**

Dynamic mechanical thermal analysis (DMTA) is employed on maximally cured samples to study the effect of the chemical structure on the glass-transition temperature \((T_g)\) and the crosslink density. The equipment used is a TA Instruments Q800 DMA. The tests are performed on dog-bone-shaped samples of about 80 μm thickness and 2.5 mm width. The samples are tested at a frequency of 1 Hz, in a temperature range from −50 to 150 °C with a heating rate of 3 °C s⁻¹, a strain of 0.1% and a pre-load of 0.01 N, which results in linear viscoelastic behavior. The \(T_g\) is defined as the maximum in \(\tan \delta\) and the crosslink density, \(\nu\), is calculated according to eq. (2):\(^{16}\)

\[
\nu = \frac{E'}{3RT}
\]

where \(E'\) is the storage modulus in the rubbery plateau, \(R\) is the universal gas constant, and \(T\) is the temperature.

Tensile tests are performed on maximally cured samples to study the effect of the chemical structure on the tensile behavior. Room temperature uniaxial tensile tests are performed on a micro-tensile stage (TST350 Linkam Scientific) equipped with a 20 N load cell. A Zwick/Roell testing machine equipped with a 1 kN load cell and an environmental chamber to control the temperature is used to perform tensile tests at 0 and −10 °C, respectively. The tensile tests, which are performed at a strain rate of 10⁻⁴ s⁻¹, are repeated at least two times, and the average result is shown. Error bars representing the standard deviation are smaller than the symbols and therefore omitted.

**RESULTS AND DISCUSSION**

**Effect of Material Composition**

**Viscosity of Acrylate Formulations.** In order to understand the effect of the material composition on the ultimate properties, the first step is the viscosity measurement of the initial photo-curable formulation. The viscosity affects the molecular mobility and, therefore, the diffusion of the reactive species during the photo-polymerization process. As a consequence, the degree of conversion is influenced by the viscosity of the formulation. The viscosity is a function of the intermolecular interactions between monomers.\(^{17}\) The presence of the aromatic rings in the BisDA monomers leads to an increase of the viscosity due to the π–π interactions, limiting the maximum conversion achievable.\(^{18}\) The absence of aromatic rings in the TEGDA monomer reduces the intermolecular interactions. Therefore, the addition of TEGDA monomers decreases the viscosity of photo-curable formulations.\(^{2}\)

In Figure 2, the viscosity of the photo-curable formulations is shown as a function of weight percentage of TEGDA. The viscosity-concentration dependence follows approximately the log-additivity rule.\(^{19}\) All the formulations exhibit Newtonian behavior as shown by the constant value of viscosity as a function of shear rate (see Figure S2 in the Supporting Information). Formulations consisting of mixtures of BisDA\(_n\) – 2 and BisDA\(_n\) – 4 (BisDA\(_n\) – 2 + 4) show the highest viscosity, probably due to the higher intermolecular interactions.\(^{17}\) The BisDA\(_n\) – 4 formulations show the lowest viscosity, despite their higher molecular weight. This is related to the lower amount of π–π interactions and the larger flexibility due to the higher molecular weight of the monomer.\(^{7,18}\) As expected, the viscosity is strongly affected by the chemical composition and the presence of TEGDA monomers in the photo-curable formulation.

**Conversion Evolution.** The monomer-to-polymer conversion of the nine formulations as a function of irradiation time is obtained through FTIR spectroscopy on dog-bone-shaped specimens. All...
the samples are first UV-cured for 1.5 s and successively UV post-cured for 3, 5, 10, 50, 100, 150, and 200 s. The acrylate C=C twist peak at 810 cm$^{-1}$ is monitored. The spectra for the maximally UV post-cured formulations based on pure BisDA$_{n=2}$, BisDA$_{n=4}$, and BisDA$_{n=2+4}$ monomers are shown in Figure 3 (a). The peak at 810 cm$^{-1}$ shows a shoulder in maximally UV-cured samples that is related to the amount of C=C double bonds left. The height of the acrylate peak increases as the average molecular weight of the monomers decreases. A plausible explanation is that, although the UV-curing conditions are the same, the total amount of remaining C=C double bonds is higher in case of lower molecular weight monomer, BisDA$_{n=2}$, due to the higher initial concentration of reactive groups. Moreover, this effect can be caused by the higher viscosity that limits the mobility of the network, leading to a maximum conversion value of 74% with BisDA$_{n=2}$ formulations. As the polymer vitrifies, the propagation of the reacting species slows down and polymerization ceases.4

Figure 3(b) presents the evolution of the conversion for formulations of pure BisDA$_{n=2}$ and mixtures of BisDA$_{n=2}$ and TEGDA. The obtained conversion values are 74% for formulations of BisDA$_{n=2}$, 77% for BisDA$_{n=2}$:TEGDA 90:10, and 85% for BisDA$_{n=2}$:TEGDA 70:30. The presence of TEGDA leads to a reduction of the initial viscosity, thereby increasing the segmental movements of the radicals during the initial stage of the photopolymerization.20 This increase in mobility promotes the diffusion of the reacting species giving rise to monomer-to-polymer conversion. As a result, relatively less unreacted monomer is present in the final product. In case of formulations based on BisDA$_{n=4}$ monomers, there is almost no effect on the final conversion if TEGDA is added. In these systems, the viscosity does not play a role because a maximum conversion of 95% is already reached without adding TEGDA to the pure BisDA$_{n=4}$ monomer, as shown in Figure 3(c). Formulations with BisDA$_{n=2+4}$ monomers present an intermediate behavior [Figure 3(d)]. The overall final conversion is higher compared to that of the

![Figure 3](image-url)
BisDA\(_n = 2\) formulations. The addition of TEGDA leads to a slight increase in monomer conversion. The pure BisDA\(_n = 2 + 4\) mixture is characterized by a maximum conversion of 84%, followed by BisDA\(_n = 2 + 4\) TEGDA 90:10 and BisDA\(_n = 2 + 4\) TEGDA 70:30 being 84 and 89%, respectively.

**DMTA Results.** The results of the thermal–mechanical characterization of maximally cured samples (UV 200 s), performed by DMTA are shown in Figures 4 and 5. The storage modulus and tan \(\delta\) measured on maximally UV-cured samples of the pure BisDA\(_n = 2\) monomer and mixtures of BisDA\(_n = 2\) and TEGDA are given in Figure 4(a). The storage modulus of the different formulations shows similar behavior in the low-temperature range. However, at temperatures above 50 \(^\circ\)C, the rubber plateau increases as the amount of TEGDA increases. As shown in Figure 3(b), the TEGDA content leads to an increase of the final conversion due to the higher mobility of the monomers; therefore, a more crosslinked network is obtained, as depicted by the higher rubber plateau. The peak of tan \(\delta\) is considered as the \(T_g\). The fact that only one clear transition peak is observed confirms that the different monomers are miscible on a molecular level. Moreover, the heterogeneity of the network, determined by the breadth of tan \(\delta\),\(^{21}\) seems not to be affected by the different formulations. The curves show a slight increase of \(T_g\) with increasing TEGDA content (Figure 4(a)). The same behavior is observed for UV maximally cured samples composed of mixtures of BisDA\(_n = 2 + 4\) and TEGDA monomers, see Figure 4(b). Here, the samples are characterized by lower values of \(T_g\) due to the presence of the high-molecular-weight monomer.

Tests performed on specimens with pure BisDA\(_n = 4\) and mixtures of BisDA\(_n = 4\) and TEGDA are not reproducible at temperatures above 30 \(^\circ\)C. The samples show failure during the test in the rubber region, probably due to the presence of small defects on the specimen that propagate fast in case of a weaker material, for UV maximally cured samples composed of mixtures of BisDA\(_n = 2 + 4\) and TEGDA monomers, see Figure 4(b). Here, the samples are characterized by lower values of \(T_g\) due to the presence of the high-molecular-weight monomer.

**Tensile Behavior.** The influence of the chemical structure of the photo-curable formulation on the mechanical properties is investigated. Tensile tests are performed at room temperature on maximally UV-cured (200 s) dog-bone-shaped specimens at a single strain rate of \(10^{-3} \text{ s}^{-1}\). Figure 6(a) shows the effect of adding TEGDA in BisDA\(_n = 2\) based systems. The yield stress is not affected by the TEGDA content, but a different post-yield behavior is observed. When increasing the TEGDA amount, the strain hardening clearly rises, which indicates that the material has a higher network density, as also seen in the DMTA results (Figure 4).\(^{23}\) The tensile behavior of BisDA\(_n = 2 + 4\) samples is reported in Figure 6(b) in which a similar trend is observed. The low \(T_g\)'s of those samples result in a rubbery response of the material if tested at room temperature. Therefore, the tensile behavior of these formulations is tested below \(T_g\) to verify that the rubber behavior observed in the mechanical response is only a result of the relative difference between the testing temperature and the \(T_g\). The testing temperatures chosen are 0 \(^\circ\)C and −10 \(^\circ\)C, respectively, for BisDA\(_n = 2 + 4\) and BisDA\(_n = 4\) formulations where the samples are in the glassy state (see Figures 4 and 5). When performing tensile tests at −10 \(^\circ\)C (\(T_g \approx 25 \text{ °C}\)) on samples based on BisDA\(_n = 4\) monomer, it is found that the mechanical response, including the yield stress, increases upon increasing the TEGDA content, as shown in Figure 7(a). It is evident that even a small amount of TEGDA monomer in the system strongly affects the mechanical properties. This means that the presence of monomers with low-molecular weight in a loose network influences the chain interactions and, therefore, the stress at which the material starts to flow. The mechanical response of the BisDA\(_n = 2 + 4\) samples tested at 0 \(^\circ\)C (\(T_g \approx 25 \text{ °C}\)) is shown in Figure 7(b). Here, an intermediate behavior is observed: the overall mechanical response increases if 10 wt % TEGDA is added into the system, while further addition leads.
to a change in the post-yield behavior, as observed for BisDA<sub>n</sub> = 2 based samples. Adding a small amount of monomers with low-molecular weight in BisDA<sub>n</sub> = 2+4 systems reduces the network mobility and leads to an increase in \( T_g \) and yield stress (see Table II and Figure 7), whereas a higher amount affects the network structure leading to an increase in crosslinking density.

![Figure 5](image-url)  
*Figure 5. (a) Storage modulus as function of temperature of pure BisDA<sub>n</sub> = 4. The dog-bone-shaped specimen is shown in the inset.(b) tan δ of mixtures of BisDA<sub>n</sub> = 4 and TEGDA. [Color figure can be viewed at wileyonlinelibrary.com]*

<table>
<thead>
<tr>
<th></th>
<th>0 wt %&lt;sup&gt;a&lt;/sup&gt;</th>
<th>10 wt %&lt;sup&gt;a&lt;/sup&gt;</th>
<th>30 wt %&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \nu (\text{mol m}^{-3}) )</td>
<td>( T_g (°C) )</td>
<td>( \nu (\text{mol m}^{-3}) )</td>
</tr>
<tr>
<td>BisDA&lt;sub&gt;n&lt;/sub&gt; = 2</td>
<td>3 869</td>
<td>47</td>
<td>4 944</td>
</tr>
<tr>
<td>BisDA&lt;sub&gt;n&lt;/sub&gt; = 4</td>
<td>-</td>
<td>14</td>
<td>-</td>
</tr>
<tr>
<td>BisDA&lt;sub&gt;n&lt;/sub&gt; = 2+4</td>
<td>3 547</td>
<td>29</td>
<td>4 192</td>
</tr>
</tbody>
</table>

<sup>a</sup> TEGDA concentrations.

![Figure 6](image-url)  
*Figure 6. Stress–strain response for (a) UV post-cured BisDA<sub>n</sub> = 2 samples and (b) UV post-cured BisDA<sub>n</sub> = 2 + 4 samples measured at 23°C. [Color figure can be viewed at wileyonlinelibrary.com]*
Effect of Thermal Post-Curing

Conversion Evolution. The presence of uncured monomers in the UV-cured networks suggests that further polymerization of trapped reactive species is possible by giving mobility to the system. All the samples are first UV post-cured and successively thermally cured for 30 min at 150 °C. The effect of the thermal treatment on the conversion as a function of UV irradiation time is reported in Figure S3 in the Supporting Information. The final conversion values are given in Table III for all the studied formulations. Even if the thermal treatment could let the trapped reactive species react with their unreacted neighbors, the results, when compared to the corresponding UV post-cured samples, reveal that the final conversion is not affected by the thermal post-cure, as shown in Figure S3 in the Supporting Information. The difference between the given data in Table III and the final conversion values of UV post-cured samples (Figure 3) is below 2%, which is within the experimental error, and therefore not indicated in the table.

DMTA Results. In our previous study, we showed that thermal post-curing leads to an increase in $T_g$ and, consequently, improved mechanical properties. This effect is mainly due to a thermodynamically more stable arrangement of the UV-cured network due to the increment in mobility given by the thermal treatment. Moreover, this increase in $T_g$ might be partially attributed to the evaporation of small molecules during the thermal treatment. The molecules act as plasticizer, lowering the $T_g$. During the sample preparation, the specimens are washed with solvent (acetone) to remove the uncured resin; therefore, molecules of acetone might still be present in the network structure. These molecules evaporate when the sample is thermally treated, leading to an apparent increase in $T_g$. The overall increase in $T_g$ is most probably a combination of both solvent evaporation and network arrangement mechanisms. Moreover, analysis on samples dried in the oven (45 °C for 30 min) prior to DMTA tests confirms that the evaporation of volatiles does not affect the final network structure. The storage modulus in both glassy and rubber states remains the same when DMTA test on a dried sample is compared with that of the corresponding UV post-cured sample, see Figures S4 and S5 in the Supporting Information.

In order to study the chemical formulation dependence and the effect of thermal post-curing on the $T_g$ samples UV and thermally post-cured (30 min at 150 °C) are examined with DMTA. The $T_g$ values are reported in Table IV. Samples prepared with BisDA$_{\text{n}=2}$ monomers show, as expected, an increase in $T_g$ when subjected to thermal post-curing, but this rise in $T_g$ is less visible if the TEGDA monomer is added to the initial formulation. It has been shown that the presence of TEGDA in the BisDA$_{\text{n}=2}$ networks leads to an increase in crosslink density (Table II), thereby limiting the mobility of the network and resulting in a more stable structure. This result suggests that thermal post-curing does not strongly affect UV-cured samples having a high crosslink density. On the other hand, tests performed on the samples prepared with mixtures of BisDA$_{\text{n}=4}$, BisDA$_{\text{n}=2+4}$, and TEGDA monomers show a slight increase in $T_g$ as the TEGDA content increases. This behavior is linked to the looser

Table III. Conversion Values for the UV (200 s) and Thermally (150 °C for 30 min) Post-Cured Formulations

<table>
<thead>
<tr>
<th>Conversion (%)</th>
<th>0 wt %a</th>
<th>10 wt %a</th>
<th>30 wt %a</th>
</tr>
</thead>
<tbody>
<tr>
<td>BisDA$_{\text{n}=2}$</td>
<td>74 ± 0.1</td>
<td>78 ± 0.6</td>
<td>84 ± 0.8</td>
</tr>
<tr>
<td>BisDA$_{\text{n}=4}$</td>
<td>93 ± 0.4</td>
<td>93 ± 0.1</td>
<td>95 ± 0.1</td>
</tr>
<tr>
<td>BisDA$_{\text{n}=2+4}$</td>
<td>86 ± 0.1</td>
<td>84 ± 0.3</td>
<td>88 ± 0.1</td>
</tr>
</tbody>
</table>

The difference compared to samples only UV post-cured is within the experimental error (2%).

a TEGDA concentrations.
structure of the network of these samples that allows the thermal treatment to affect the final mechanical properties, even at high conversion values.

**Tensile Behavior.** Finally, the effect of thermal post-curing on the mechanical properties is examined. When comparing, for example, the stress–strain curve of maximally UV-cured BisDA<sub>n</sub> = 2 samples and the one UV and thermally post-cured, a twofold increase in yield stress is observed (Figure 8(a)). This effect is strongly correlated with the increase of the T<sub>g</sub>. A strong influence on the large strain response is also observed. Thermally treated samples are more brittle when compared with the corresponding UV post-cured samples; therefore, the failure occurs at lower strain, see Figure 8(a). Figure 8(b) shows the effect of the thermal post-cure on BisDA<sub>n</sub> = 2 with TEGDA, tested at room temperature. For all the samples, the yield stress is increased after thermal treatment, but the effect is less strong on samples with higher TEGDA content. These results are in agreement with the evolution of T<sub>g</sub> (Table IV). UV and thermally post-cured samples with pure BisDA<sub>n</sub> = 4 and mixtures of BisDA<sub>n</sub> = 2 + 4 and TEGDA show a rubber behavior if tested at

Table IV. T<sub>g</sub> Values for the UV (200 s) and Thermally (150 °C for 30 min) Post-Cured Formulations

<table>
<thead>
<tr>
<th></th>
<th>0 wt %&lt;sup&gt;a&lt;/sup&gt;</th>
<th>10 wt %&lt;sup&gt;a&lt;/sup&gt;</th>
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<tbody>
<tr>
<td>BisDA&lt;sub&gt;n&lt;/sub&gt; = 2</td>
<td>77 (+26)</td>
<td>67 (+17)</td>
<td>53 (+2)</td>
</tr>
<tr>
<td>BisDA&lt;sub&gt;n&lt;/sub&gt; = 4</td>
<td>17 (+3)</td>
<td>19 (+4)</td>
<td>24 (+6)</td>
</tr>
<tr>
<td>BisDA&lt;sub&gt;n&lt;/sub&gt; = 2 + 4</td>
<td>35 (+6)</td>
<td>37 (+2)</td>
<td>38 (+1)</td>
</tr>
</tbody>
</table>

Values in brackets represent the difference compared to samples only UV post-cured.

<sup>a</sup> TEGDA concentrations.

![Figure 8](image-url)
ambient temperature due to the low values of the $T_g$. For this purpose, the stress–strain behavior of thermally post-cured samples is studied by performing tensile tests well below $T_g$, where the samples are in the glassy region. Tensile tests performed at $-10{^\circ}C$ on mixtures consisting of BisDA$_n$ = 4 and TEGDA are reported in Figure 8(c). Thermal treatment results in an increase of the mechanical response, independent of the TEGDA content. From Figure 8(d), it follows that the effect of the thermal post-curing on mixtures of BisDA$_n$ = 2 + 4 with TEGDA is strongly affected by the TEGDA content. Samples with higher TEGDA content show a similar behavior as observed in mixtures of BisDA$_n$ = 2 and TEGDA. The cured network is more dense, and therefore, the effect of the thermal post-cure is less.

A schematic representation of the envisioned crosslinked networks is shown in Figure 9. The network is strongly affected by the chemical structure. By increasing the molecular weight of the monomer, a looser network is formed. Addition of short TEGDA monomers leads to the formation of a more dense structure, and this effect is more pronounced in case of BisDA$_n$ = 2 formulations. Thereby, the higher crosslink density limits the mobility of the network during thermal post-curing, resulting in a more stable structure.

An overview of the mechanical properties of the nine formulations is reported in Figure 10. DMTA and tensile tests on maximally UV post-cured samples allow us to study the effect of the chemical structure of the photo-curable formulation on the ultimate mechanical properties. Figure 10(a,c) shows the evolutions of $T_g$ and yield stress as a function of the TEGDA content for UV post-cured samples. An increase in $T_g$ with TEGDA content is reported for all sets of samples. The increase is less pronounced in case of BisDA$_n$ = 2 samples, where an increase of 4 $^\circ$C is obtained when 30 wt % of TEGDA is added in the systems. On the other hand, BisDA$_n$ = 2 + 4 formulations show an increase of 8 $^\circ$C, see Table II. The TEGDA content has a strong effect on the yield stress of BisDA$_n$ = 4 samples. Adding a higher amount of low-molecular-weight TEGDA monomers in a loose BisDA$_n$ = 4 network results in structures with a shorter distance between the crosslinks, as shown in Figure 9. This effect influences the chain interactions, and therefore, the sample needs a higher stress to flow. The effect of thermal post-curing is summarized in Figure 10(b,d). A decrease in both glass-transition and yield stress with increasing TEGDA content is observed for pure BisDA$_n$ = 2 samples. The TEGDA content in the system increases the crosslink density, reducing the mobility of the network, and therefore, the thermal post-treatment is less effective, see Figure 9.

The yield stress evolutions observed in Figure 10(c,d) are the results of tensile tests performed at a testing temperature that keeps the $T_g - T \approx 25$ $^\circ$C. BisDA$_n$ = 2 and BisDA$_n$ = 2 + 4 formulations show an overlap of the yield stress dependence on the TEGDA amount for both UV and UV and thermally post-cured samples. This behavior indicates that the distance to $T_g$ determines the mechanical response. On the other hand, BisDA$_n$ = 4 formulations are characterized by a lower mechanical response even if the tensile tests are performed at the same $T_g - T$. This confirms that a different polymer network structure is formed with BisDA$_n$ = 4 formulations.

This study shows that the ultimate mechanical properties are strongly affected by the chemical structure of the photo-curable formulations. An increase in molecular weight of the acrylate monomer can change the properties of the UV-cured product. A material having a rubbery behavior is the result of this change.
Moreover, when the BisDA monomer is used with TEGDA, there is an improvement in monomer-to-polymer conversion and in the resulting ultimate mechanical properties. The effect of thermal post-curing is strongly dependent on the chemical composition.

CONCLUSIONS

The effect of resin composition of UV-curable acrylate systems on the ultimate mechanical properties is investigated. To improve the molecular mobility during the photopolymerization process, TEGDA is added as a diluent in the systems. A systematic set of nine liquid starting formulations based on bisphenol A ethoxylate diacrylate, having two different molecular weights (BisDA$_n$ = 2 and BisDA$_n$ = 4), mixed with TEGDA monomers is characterized. Thin dog-bone-shaped samples are prepared via stereolithography on which the evolution of monomer conversion with irradiation time has been studied. The monomer-to-polymer conversion depends on the viscosity of the formulation. With a decrease in viscosity, an increase in conversion is observed, which depends on the type of BisDA or the amount of added TEGDA. The more mobile the monomers, the less tendency for vitrification. As a result, the final conversion is higher. By performing tensile tests and dynamic mechanical tests on UV post-cured samples, the yield stress and $T_g$ are correlated with the amount of TEGDA. Formulations based on BisDA$_n$ = 2 show that by increasing the TEGDA amount, a slight increase in $T_g$ is observed, while the yield stress remains unaffected. In those systems, addition of TEGDA leads to an increase of the crosslink density, which is confirmed by the increase in strain hardening as observed in the stress–strain response. BisDA$_n$ = 4 and BisDA$_n$ = 2 + 4 formulations show a rubber behavior if tested at ambient temperature due to the low $T_g$. For this purpose, we performed tensile tests well below $T_g$, where the samples are in the

![Graphs showing Tg and yield stress as function of TEGDA amount for UV post-cured and UV and thermally post-cured samples.](image-url)
glassy state. For the higher molecular weight monomer, BisDA\textsubscript{n} = 4, an increase in both yield stress and \( T_g \) is observed by increasing amount of TEGDA. Formulations based on mixtures of BisDA\textsubscript{n} = 2 with BisDA\textsubscript{n} = 4 and TEGDA show an intermediate behavior. Next to UV curing, the effect of thermal post-curing is studied. This effect is more pronounced in resins with lower crosslink density. The resins with BisDA\textsubscript{n} = 2, which are thermally post-cured, show a decrease in yield stress and \( T_g \) with increasing TEGDA amount. On the other hand, for less dense networks, the thermal post-curing increases \( T_g \) and consequently the yield stress with an increasing amount of TEGDA. The correlations between molecular mobility in the resin formulations and mechanical response of the cured resins allow to tune the material composition of photo-curable systems used in the stereolithography process for desired mechanical properties.

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