

# Isocyanurate transformation induced healing of isocyanurate-oxazolidone polymers

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**ABSTRACT:** Isocyanurate-oxazolidone (ISOX) polymers have been reported as a novel, intrinsically self-healable thermoset, and their healing mechanism under the effect of nucleophiles, such as tertiary amines and pyridines during polymerization, is thoroughly investigated in this study. This work provides evidence that the healing behavior of the polymers results part from the transformation of isocyanurate to oxazolidone on the fracture surfaces of the ISOX polymers at elevated temperatures. The isocyanurate transformation is characterized by chemical composition of the ISOX polymers before and after a predetermined healing procedure, through a combination characterization of Fourier transform infrared spectroscopy and carbon nuclear magnetic resonance spectroscopy. From the chemical composition of the ISOX polymers, an increased oxazolidone fraction is observed after the healing event, which verifies the hypothesized healing mechanism. By correlating the change in oxazolidone fraction in the polymers during the healing event, with the corresponding healing performance of the polymers, healing efficiencies of the polymers are shown to be inversely proportional to the ratio of oxazolidone to isocyanurate in the polymers. The transformation to oxazolidone is also shown to be dependent on two variables, nucleophilicity of the polymerization catalyst and duration of the postcure. The isocyanate and epoxide polymerization mechanism in the presence of nucleophiles is also investigated to explain the effect of the catalyst nucleophilicity on the chemical composition as well as the healing performance of the ISOX polymers. © 2019 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2020**, *137*, 48698.

**KEYWORDS:** crosslinking; stimuli-sensitive polymers; structure-property relationships; thermosets

Received 10 July 2019; accepted 22 October 2019

DOI: [10.1002/app.48698](https://doi.org/10.1002/app.48698)

## INTRODUCTION

Isocyanurate-oxazolidone (ISOX) polymers are prepared from the trimerization of isocyanates and their reaction with epoxides to produce two heat-resistant heterocyclic rings, specifically isocyanurate and oxazolidone, respectively, and their use has been well known in high-performance thermosets.<sup>1</sup> The network structure of the ISOX polymers can be significantly altered by the ratio and type of diisocyanate and diepoxide reactants, the employed catalyst and the presence of solvents, the combination of which act to control the fraction of the isocyanurate crosslinks and oxazolidone chain extenders.<sup>1–3</sup> While diisocyanate including methylene diphenyl diisocyanate, toluene diisocyanate (TDI), hexamethylene diisocyanate, and diepoxides such as bisphenol A diglycidyl ether, bisphenol F diglycidyl ether (DGEF) have been the most extensively used reactants for the ISOX polymers, a number of catalysts have been explored for the polymerization including tertiary amines (NR<sub>3</sub>) and imidazoles,<sup>4–6</sup> quaternary

ammonium halides,<sup>7</sup> Lewis acids,<sup>8</sup> alkoxides, and phenoxides of alkali earth metals.<sup>9,10</sup> Among these catalysts, tertiary amines have been the most commonly used ones for bulk polymerization of ISOX polymers due to their excellent catalytic efficiency as well as good miscibility with the resins.<sup>11,12</sup> For bulk polymerization of the ISOX polymers with nucleophiles such as tertiary amines, previous studies have shown agreement on the main reactions proceeding in the order of increased temperatures during the polymerization: (1) trimerization of isocyanate to isocyanurate, (2) oxazolidone formation from isocyanate and epoxide reaction, and (3) transformation of isocyanurate to oxazolidone through reaction with excessive epoxide.<sup>4,5,13</sup> The isocyanurate and oxazolidone rings lead to a dense polymer network with a reported small molecular weight between crosslinks of 79 g/mol.<sup>14</sup>

The high crosslink density endows ISOX polymers with high thermal stability and excellent physical and mechanical

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properties.<sup>15,16</sup> The aromatic isocyanurate can withstand high temperatures up to 417 °C and aromatic oxazolidone is stable up to 348 °C,<sup>17</sup> thus explaining their wide usage for improving high-temperature resistance and flame retardancy of polyurethanes.<sup>18–20</sup> In addition to the excellent thermal stability, ISOX polymers have been shown to have superior physical and mechanical properties which provide them with potential as structural adhesives, high strength foams, and composites in the automobile and aerospace industry.<sup>9,13</sup> Given these advantages of the ISOX polymers, there have been efforts to study the polymerization to achieve optimal material properties.<sup>12</sup> Recently, ISOX polymers catalyzed by a tertiary amine *N,N*-dimethylbenzylamine (BDMA) have been discovered as a novel intrinsic self-healing material.<sup>14,21</sup> Microscopic and macroscopic cracks introduced into the polymers have been effectively and repeatably healed under thermal stimulus, without additional reactants or catalyst.<sup>14</sup> The ISOX polymers were later shown to act as a self-healable matrix in carbon fiber reinforced polymer composites, demonstrating repeatable elimination of matrix delamination induced by interlaminar shear.<sup>21</sup> Stoichiometry of the diisocyanate and diepoxide has been reported to affect the healing performance of the polymers, as the resulting chemical composition of the ISOX polymers determines the ultimate materials properties including the healing performance. Given the intrinsic self-healing capacity of the ISOX polymers, a thorough study of the healing mechanism is needed. Before elucidating the healing mechanism for the ISOX chemistry, the polymerization mechanism of the ISOX polymers in the presence of a catalytic amount of nucleophiles also warrants investigation. Unfortunately, there has been no agreement for the reaction mechanism with catalytic nucleophiles in the bulk polymerization of ISOX polymers. During the initiation stage of the polymerization, the role of nucleophile, epoxide, and isocyanate was not accurately assigned. Some reports suggested that two different initiation mechanisms including zwitterions formed between the nucleophile and epoxide, and zwitterions formed between the nucleophile and isocyanate, which have reactivity dependent on temperature, are both active during the polymerization.<sup>2</sup> Others later reported that the zwitterions formed between the nucleophile and isocyanate were the catalytic species as a specific amount of nucleophile alone was able to polymerize diisocyanate into isocyanurate polymer at 80 °C.<sup>22,23</sup> Although the trimerization of phenyl isocyanate at room temperature in the presence of a catalytic amount of epoxide and  $R_4NBr/R_3N$  was also reported,<sup>24</sup> few studies in the literature have reported the nature of the catalytic species during the polymerization of the ISOX polymers.

In this work, the healing mechanism of the ISOX polymers based on an understanding of the polymerization mechanism in the presence of catalytic nucleophiles of  $NR_3$ /pyridine is investigated. The individual role of the nucleophile, epoxide, and isocyanate, during the initiation period of the polymerization, is studied as forming nucleophile/epoxide/isocyanate zwitterions at room temperature. Stronger nucleophiles lead to faster formation of the zwitterion and stronger catalytic effect for the trimerization of the isocyanate at the early stage of the polymerization. At higher temperatures as the chain mobility improves, further conversion of isocyanate and epoxide leads to oxazolidone and more isocyanurate, and higher extent of polymerization. However, full

polymerization of the ISOX polymers is reached before depletion of isocyanate and epoxide because of the heavy steric effect resulting from dense distribution of isocyanurate crosslinks in the polymer network. Upon damage, the steric effect is reduced and transformation to oxazolidone from isocyanurate and epoxide can continuously proceed at the fracture surfaces under thermal stimulus. To verify this hypothesis, the healing performance of the polymers is correlated to the chemical composition of the ISOX polymers, which is characterized by combined characterization of Fourier transform infrared (FTIR) spectroscopy and carbon nuclear magnetic resonance (NMR). The healing performance of the ISOX polymers is quantified by measurement of healing efficiencies of the polymers, and the chemical composition of the ISOX polymers is adjusted through the variation of the catalyst nucleophilicity and the duration of postcure at 250 °C after the initial curing of the polymers at 200 °C.

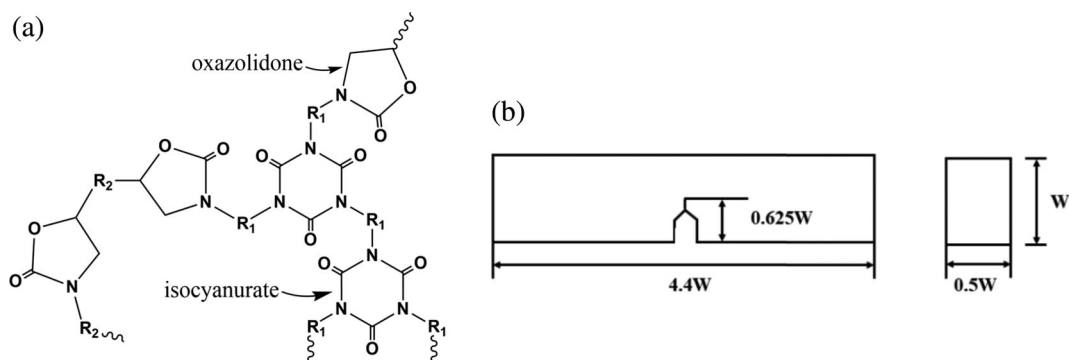
## EXPERIMENTAL

### Polymerization of the ISOX Polymers with Tertiary Amines/Pyridine

Two monomers used for the polymerization, DGEBF and tolylene-2,4-diisocyanate (TDI), were purchased from Momentive and Acros Organics, respectively. For the three catalysts, *N,N*-dimethylbenzylamine was purchased from Acros Organics, 1,4-diazabicyclo [2.2.2] octane (DABCO, 99%) was purchased from Sigma Aldrich and 2-dimethylaminopyridine (2-DMAP, 98%) was purchased from TCI America. 1,4-butanediol diglycidyl ether (BDE), phenyl glycidyl ether (PGE) and *p*-tolyl isocyanate (PTI) were purchased from Fisher and all the chemicals were used as received. The ISOX resin was prepared by first mixing TDI and DGEBF in a 1/1 M ratio using a vortex mixer for 10 min; then, a 0.1 wt % of DABCO/BDMA/2-DMAP was added and mixed thoroughly with the TDI/DGEBF mixture before transferring the resin into a RTV664 silicone mold and degassing the resin under vacuum. To note, DABCO, BDMA, and 2-DMAP were added separately into the ISOX resins and the corresponding ISOX polymers were named DABCO, BDMA, and 2-DMAP polymer, respectively. The network structure of the polymers is shown in Scheme 1(a). The degassed ISOX resin was initially cured at 80 °C for 1 h and subsequently at 200 °C for 12 h, before a 250 °C postcure was applied for predetermined durations between 0 and 10 h. A DV2T viscometer from Brookfield was used to run viscosity tests on the ISOX resins under ambient conditions. A fixed volume of TDI and DGEBF was mixed thoroughly for 10 min before the addition of 0.1 wt % of each catalyst, and then, a rotating spindle was immersed in the resin immediately to monitor the gelling process.

### Healing Efficiency Measurement of the ISOX Polymers

Three-point bend fracture testing according to ASTM D5045 was used to evaluate the healing performance of the ISOX polymers. After the samples were postcured at 250 °C, they were individually machined into a single edge notched bending (SENB) geometry for the test, as shown in Scheme 1(b). A sharp notch was then introduced to the specimen by repeatedly sliding a fresh razor blade across the precrack before placing the specimen on two stationary rollers for the SENB test. The SENB specimen was loaded at a low displacement rate of 0.1 mm/min, and the test



**Scheme 1.** (a) Network structure of the isocyanurate-oxazolidone polymers. (b). Geometry of single edge notched bending samples ( $W = 15$  mm).

was stopped once the specimen was fractured into two pieces. It should be noted that a piece of high-temperature resistant Kapton tape was applied to the top of each specimen (under the middle loading pin), to allow the specimen to be assembled without dislocation between the two pieces of the fractured specimen. The fractured specimen was wrapped in aluminum foil to help create a uniform temperature throughout the specimen before a healing procedure of  $200\text{ }^\circ\text{C}$  for 2 h under 200 psi and then  $200\text{ }^\circ\text{C}$  for 2 h under 100 psi was applied. The healed samples with the two rejoined surfaces were then retested using the three-point bend test under the same conditions, as the maximum loading during the first SENB test and the result of the second SENB test were recorded for each specimen for calculation of the healing efficiency. To note, the healing efficiency of each sample was averaged from at least eight specimens. The load was applied in the direction of the crack during the healing procedure, to solely maintain contact between the two fracture surfaces of the SENB specimen.

#### Carbon NMR Spectroscopy and FTIR Spectroscopy

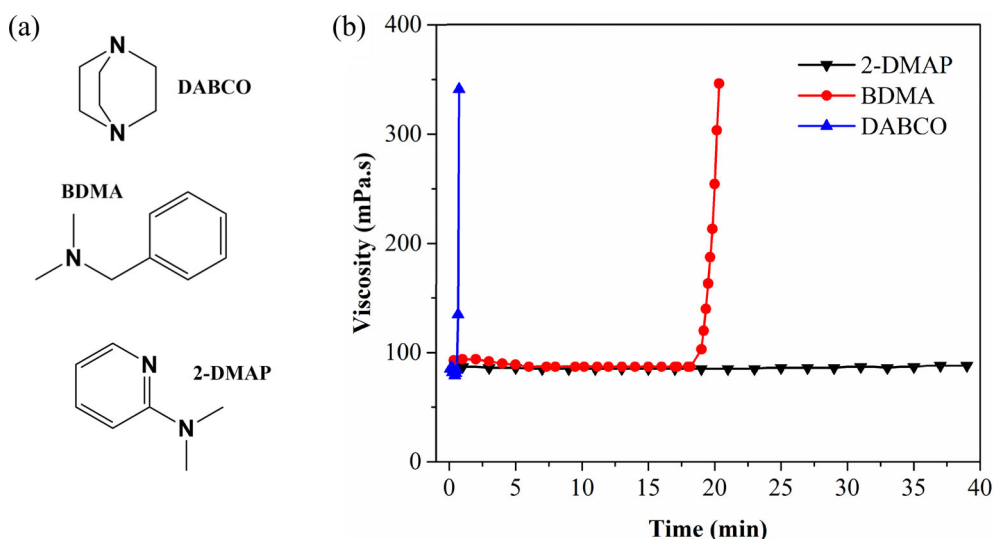
A Varian vnmr 500 MHz instrument with a Varian 5 mm PFG OneNMR probe was used for the carbon NMR test in this work. Proton decoupling was used to get rid of the nuclear overhauser

effect effects. A spectrum window of  $-40$ – $210$  ppm was used to ensure that all peaks of interest fall within 60% of the center of the spectrum. For quantification analysis, an acquisition time of 5 s and a  $90^\circ$  pulse with a relaxation delay of 25 s was used. Each sample used 256 scans to get a reasonable signal to noise ratio and dimethyl sulfoxide ( $\text{DMSO}-d_6$ ) was used as solvent. FTIR spectra were recorded over a range from  $600$  to  $4000\text{ cm}^{-1}$  with a Nicolet iS50 spectrometer using a diamond ATR from Thermo Scientific. Each spectrum was collected under 16 scans with a resolution number of 4.

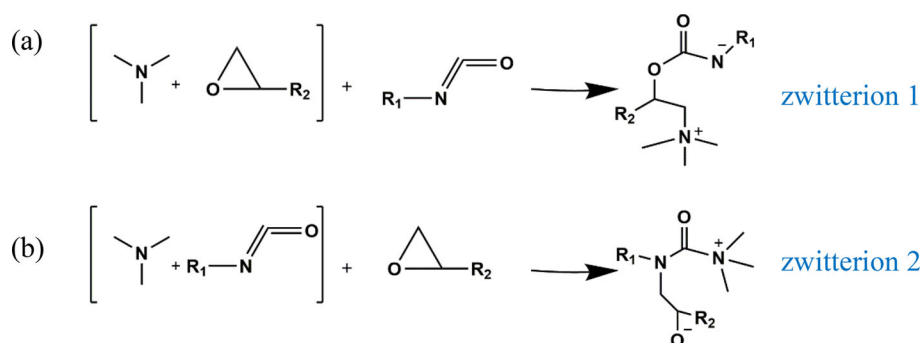
## RESULTS AND DISCUSSION

### Polymerization Mechanism of the ISOX Polymers

The polymerization mechanism of the ISOX polymers is first investigated to understand the healing mechanism. The initiation stage of the polymerization, isocyanurate formation, isocyanate-to-oxazolidone, and isocyanurate-to-oxazolidone transformation are studied under the catalytic effect of tertiary amines/pyridines. DABCO, BDMA, and 2-DMAP are applied individually for the polymerization. Lewis basicity of the utilized nucleophiles, DABCO, BDMA, and 2-DMAP decreases from top to bottom in Figure 1(a), as indicated by their  $pK_a$  values.<sup>25,26</sup> When epoxide



**Figure 1.** (a) Chemical structure of the three nucleophiles added for the polymerization. (b) Viscosity measurement during the gelling process of the three ISOX polymers. [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]



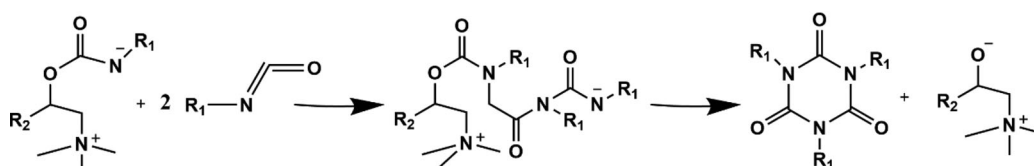
**Scheme 2.** Zwitterion formation as initiation mechanism of (a) tertiary amines/pyridine first attacks the epoxide and (b) tertiary amines/pyridine first attacks the isocyanate. [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

or isocyanate is solely present in the reaction, the nucleophiles cannot initiate strong polymerization and the reaction takes more than 24 h to gel. While in the presence of epoxide and isocyanate, the gel time for the BDMA polymer is around 20 min, as shown by the gel point measurement results for the three ISOX polymers shown in Figure 1(b). The initiation of the polymerization, started by the zwitterion formation from the nucleophiles, epoxide, and isocyanate, is discussed in detail below.

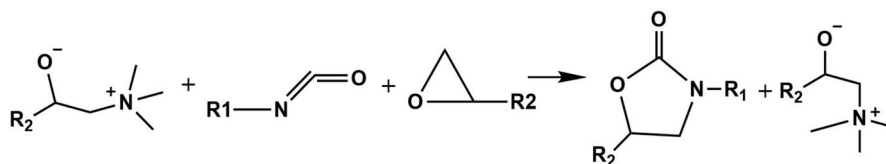
During the initiation stage of the polymerization, two zwitterions can be active depending on the initial nucleophilic reaction induced by the nucleophiles. The nucleophiles attack the epoxide first and zwitterion 1 forms, while the nucleophiles attack the isocyanate first and zwitterion 2 forms, as shown in Scheme 2. Zwitterion 1 is the true active species during the initiation, suggested by both experimental evidence and simulation evidence. At room temperature, 1 mmol PTI, 1 mmol IPGE, and 0.1 wt % BDMA were mixed in DMSO- $d_6$  and immediately characterized under proton NMR. Based on the proton NMR spectrum of the mixture, the formation of the ring-opening product of PEG was confirmed by the presence of three new peaks at 3.57, 3.72, and 5.12 ppm (Figure S1 in Supporting Information). The proton signal of CH in the epoxide ring showed a downfield shift from 3.33 to 5.12 ppm, suggesting zwitterion 1 as the active species. In the case of zwitterion 2, a new chemical shift at lower field would be expected however it was not observed. Previous research<sup>27</sup> has reported a lower activation energy of 14.6 kcal/mol for zwitterion 1 and 34.3 kcal/mol for zwitterion 2, which further supports that zwitterion 1 is the true initiating species for the polymerization. For nucleophiles with varied nucleophilicity, the stronger ones lead to faster formation of the initiating species, resulting in significantly reduced gel time. As can be seen in Figure 1(b), the polymer with DABCO catalyst, the strongest nucleophile, gels in less than 1 min, making it difficult to degas for the preparation of the SENB samples without internal bubbles.

Following the formation of the catalytic species, trimerization of the isocyanates dominates the first stage of the polymerization and is the only species detected after the first curing step at 80 °C. As shown in Scheme 3, the nitrogen anion of the isocyanate acts as the nucleophile, attacks two free isocyanates, and forms the cyclic isocyanurate, releasing the epoxide/tertiary amine for the formation of another isocyanurate. Unlike the full conversion in the model compound cases to be discussed in this section, the isocyanate-to-isocyanurate conversion in the polymer is hard to reach 100%, as the steric effect from the increasing crosslink density gets stronger while the trimerization is progressing. As a result, a large portion of isocyanate remains trapped in the polymer network and is available for the formation of oxazolidone during the second step of the cure at 200 °C for 12 h. It should be noted that the trimerization rate increases with stronger nucleophiles due to the more rapid formation of the zwitterions. In other words, more isocyanurate forms during the first stage of the polymerization, given the same polymerization time at 80 °C.

Steric effects within the ISOX polymers get weakened as the temperature increases from 80 to 200 °C during the second curing step of the ISOX polymers, leading to higher molecular mobility which allows more isocyanurate formation with the left isocyanate during the trimerization stage. Meanwhile, oxazolidone formation predominates at this temperature, which is demonstrated by two model compounds discussed below. As shown in Scheme 4, the released zwitterion after the formation of isocyanurate combines with epoxide and isocyanate to give oxazolidone in the polymer network at 200 °C. For the ISOX polymers polymerized under the stronger nucleophiles, less oxazolidone is expected to form during this stage as more isocyanate has been converted to isocyanurate at the trimerization stage with faster trimerization rate. For the isocyanurate-to-oxazolidone transformation, the speculated mechanism is shown in Scheme 5, where the residual nucleophiles



**Scheme 3.** Trimerization mechanism (isocyanate to isocyanurate).



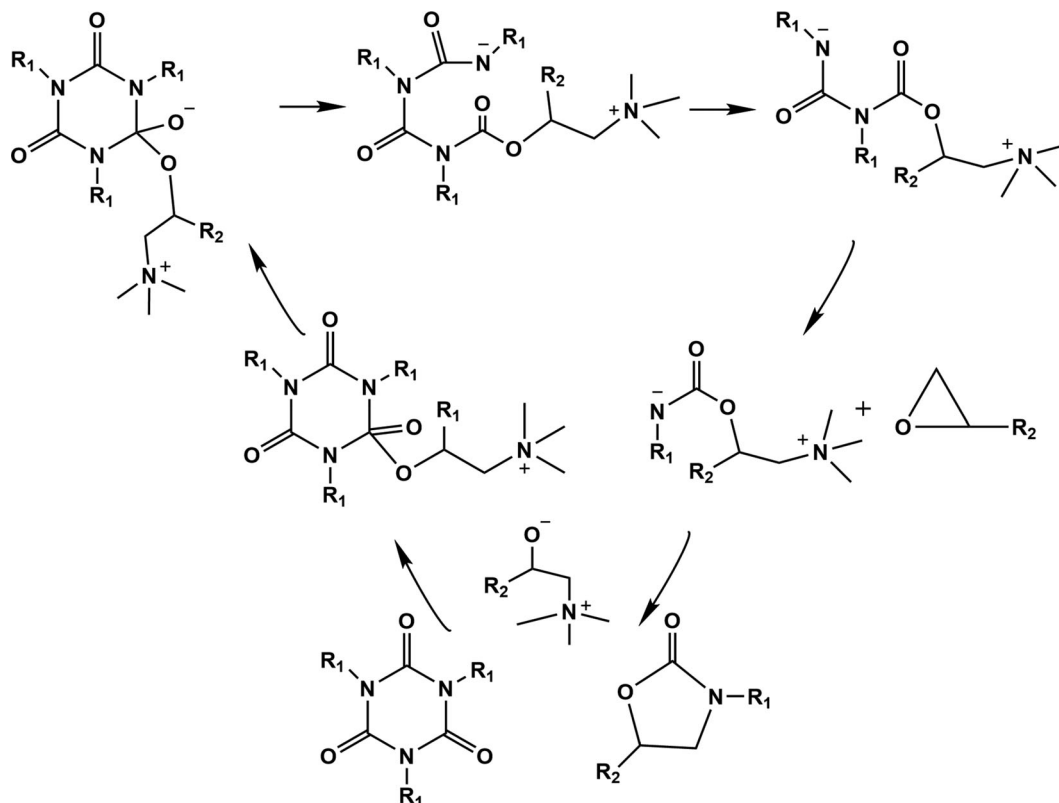
**Scheme 4.** Isocyanate-to-oxazolidone transformation.

decompose the isocyanurate and yield oxazolidone and isocyanate. The resulting free isocyanate then further transforms into oxazolidone in the presence of nucleophiles and epoxides, leading to more oxazolidone formation. As this process continues, more oxazolidone is obtained in the polymer network, before an equilibrium between the isocyanurate and oxazolidone is finally reached at this temperature.

This isocyanurate-to-oxazolidone transformation in model compound reaction is further studied. For model compound 1 (1PTI/1BDE/BDMA), an epoxide excessive reaction was conducted by adding 0.1 mol% of BDMA in PTI and BDE in a 1:1 M ratio. The chemical composition of the product under different reaction temperatures was investigated. As shown in Figure 2, the FTIR spectrum of the product after an 80 °C reaction shows the formation of isocyanurate (absorption band corresponding to the stretching C=O vibration at 1710  $\text{cm}^{-1}$ ) at this temperature, while no oxazolidone was detected (absorption band corresponding to the stretching C=O vibration at 1750  $\text{cm}^{-1}$ ).<sup>14</sup> When the reaction temperature was further increased to 150 °C, oxazolidone formed while the isocyanurate

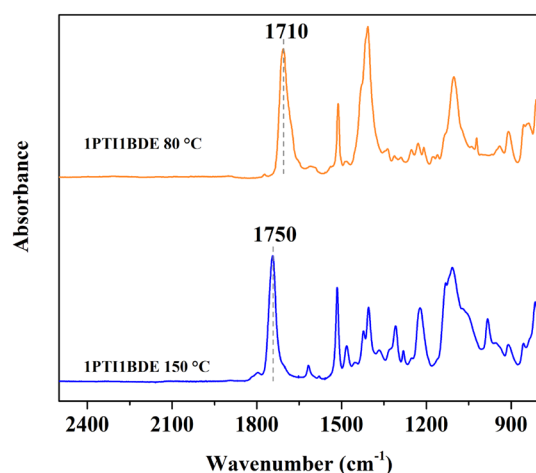
disappeared, as shown by the FTIR spectrum, indicating the isocyanurate-to-oxazolidone transformation at this elevated temperature. Carbon NMR was used to further confirm the isocyanurate trimerization at 80 °C and the isocyanurate-to-oxazolidone transformation at 150 °C. For the carbon NMR spectrum of the model compound 1 after the 80 °C reaction [Figure 3(a)], the resonance at 149 ppm corresponds to isocyanurate carbonyl carbons and other resonance can be found in Supporting Information. The presence of the signal at 149 ppm in the model compound 1 after the 80 °C reaction indicates the formation of isocyanurate, and the transformation to oxazolidone from isocyanurate after the 150 °C reaction was observed from the presence of the signal at 154 ppm and the absence of the signal at 149 ppm, as shown by Figure 3(a,b). The absence of isocyanurate after the 150 °C reaction from both FTIR and carbon NMR proved the instability of isocyanurate in the presence of excessive epoxide in solution.

Equilibrium between isocyanurate and oxazolidone is then observed in the case of model compound 2 (1PTI/1PGE/BDMA) with a lower molar ratio of epoxide, where PTI reacts with equal molar ratio of a monoepoxide (epoxide glycidyl ether, PGE). In



**Scheme 5.** Isocyanurate-to-oxazolidone transformation.





**Figure 2.** FT-IR spectra of IPTI/1BDE/BDMA reaction after 80 °C (dash line represents isocyanurate absorption band at 1710  $\text{cm}^{-1}$ ) and then 150 °C (dash line represents oxazolidone absorption band at 1750  $\text{cm}^{-1}$ ). [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

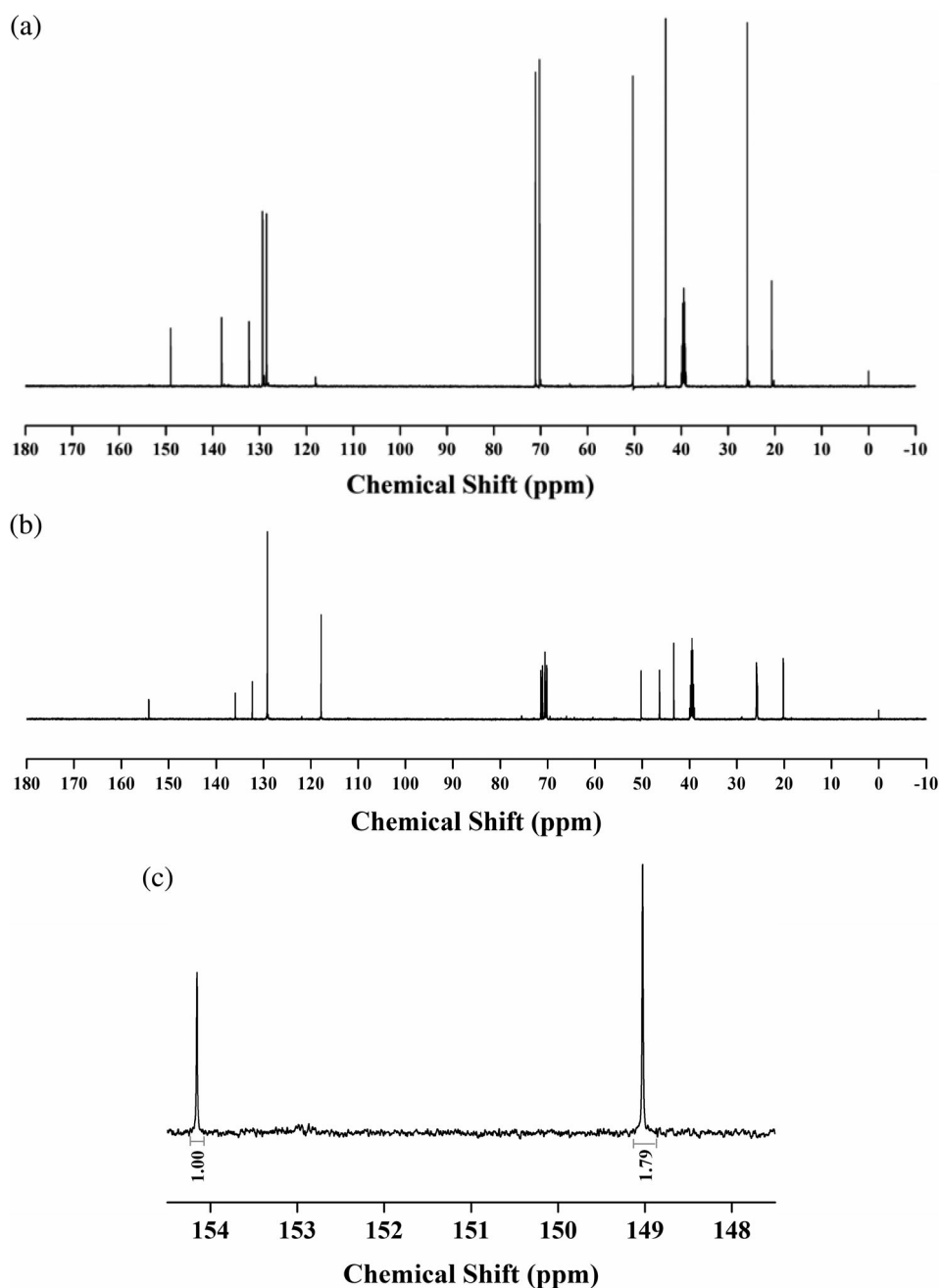
this isocyanate/epoxide equivalent case, both isocyanurate and oxazolidone were detected in the product by FTIR and carbon NMR after a 200 °C 1 h reaction following the reaction scheme for model compound 1 (reaction first at 80 °C 1 h and then at 150 °C 3 h). The coexistence of isocyanurate and oxazolidone indicates that the conversion between these two rings reached an equilibrium. The higher reaction temperature of 200 °C was not applied for model compound 1 because only oxazolidone was detected in the product after the 150 °C reaction and no further isocyanurate-to-oxazolidone transformation was expected. The carbon NMR data from model compound 2 are then used to characterize the isocyanurate-to-oxazolidone transformation in the case where reaction equilibrium of the two rings is not restricted by molecular mobility. Based on the integration of the signal at 149 and 154 ppm, the conversion of isocyanurate to oxazolidone was 36% and the conversion of isocyanurate to isocyanurate was 64% in the product of model compound 2 after the 200 °C 1 h reaction, as shown in Figure 3(c). The integration is used for developing a working curve for measurement of the isocyanurate-to-oxazolidone transformation in the case where molecular mobility is limited; for example, in the ISOX polymer network. To further verify this instability of isocyanurate in the polymeric system, a yellow, transparent solid TDI polymer was first prepared and then placed in a vial filling with DGEBA. The mixture of the polymer and DGEBA was kept at 200 °C overnight, and in this epoxide excessive case, the mixture eventually turned into an orange, homogenous and viscous liquid after it was slowly cooled to room temperature. Oxazolidone was then detected both under FTIR and carbon NMR in the product while no isocyanurate from the TDI polymer was left. Again, the equilibrium between the isocyanurate and oxazolidone in the ISOX polymers will be quantified through a working curve developed in this work.

To investigate the isocyanurate-to-oxazolidone transformation in the ISOX polymers, a working curve, as shown in Figure 4(a), is

developed through combined analysis of FTIR and carbon NMR data taken from three model compounds. The three model compounds are specifically 1PTI/1BDE/BDMA (model compound 1), PTI/1PGE/BDMA (model compound 2), and 3PTI/1BDE/BDMA (model compound 3). Model compound 3 represents the case of excessive isocyanate, while model compounds 1 and 2, as discussed above, represent the case of excessive epoxide and the equivalent stoichiometry case, respectively. For each case, the reaction product was characterized both by FTIR and carbon NMR. As shown in Figure 4(b), the NMR spectrum of the model compound 3 (3PTI/1BDE) showed that the ratio of oxazolidone to isocyanurate is 0.383 (1/2.61), which is represented by the  $x$  axis of the leftmost point in the working curve. The corresponding  $y$  axis of the same data point represents the ratio between absorbance of oxazolidone at 1750  $\text{cm}^{-1}$  and absorbance of isocyanurate at 1710  $\text{cm}^{-1}$  from the FTIR spectrum, as shown in Figure 4(c). The other three data points were collected from model compounds 1 and 2, and the working curve correlating the carbon NMR and FTIR results was obtained using a linear regression analysis and was used for quantitative composition characterization of the ISOX polymers in the next section.

### Healing Mechanism of the ISOX Polymers

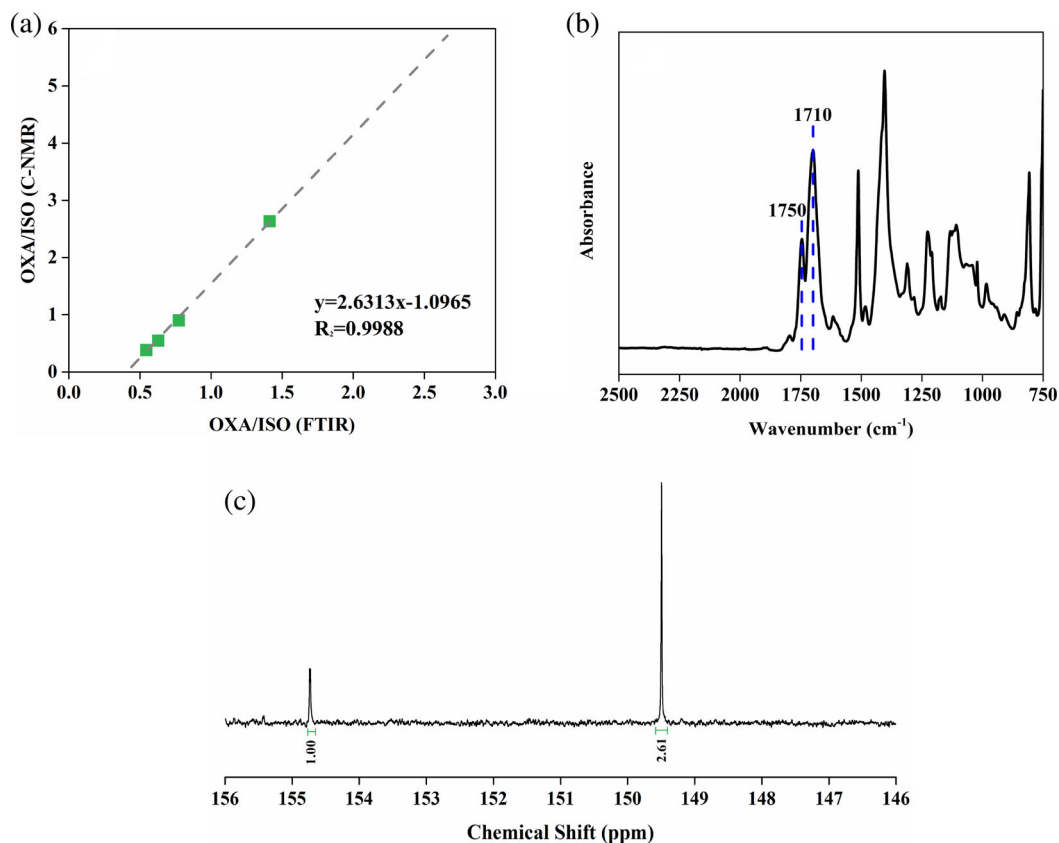
The healing mechanism of the ISOX polymers is discussed in this section based on the understanding of the polymerization mechanism in the previous section. Varied healing behaviors of the ISOX polymers are quantified and correlated to the compositional variation of the polymers characterized utilizing the developed working curve. By correlating the healing efficiencies of the polymers and the corresponding chemical compositions of the polymers, the healing mechanism is revealed to correlate with the isocyanurate-to-oxazolidone transformation. The chemical composition of the ISOX polymers is tuned with postcure time at 250 °C and nucleophiles with varied nucleophilicity. When the postcure time at 250 °C is increased from 0 to 10 h, reduced healing efficiencies are observed for both the BDMA polymer and the 2-DMAP polymer, as can be seen in Figure 5. The healing efficiency decreases from 74 and 57%, respectively, for the BDMA polymer and the 2-DMAP polymer, to 62 and 56% following an additional 2 h postcure at 250 °C. The reduced healing efficiency observed with increased postcure time is believed to be a result of the greater oxazolidone fraction in the polymer network, and therefore depends on the efficiency at which each nucleophile participates in the isocyanurate-to-oxazolidone transformation during polymerization. As supported by the discussion on the polymerization mechanism in the previous section, the isocyanurate-to-oxazolidone transformation increases with increased postcure at 250 °C, leading to less isocyanurate available for transformation to oxazolidone. However, the measured healing efficiency of the BDMA polymer is always higher than that of the 2-DMAP polymer. The healing efficiency of the 2-DMAP polymer, decreased to 20% after a post-curing time of 10 h at 250 °C, while that of the BDMA polymer, catalyzed by the stronger nucleophilic catalyst, reached a constant healing efficiency of 40% when the 250 °C postcure is increased to 10 h. The changing healing behavior of the ISOX polymers catalyzed with different nucleophiles indicates different extent of isocyanurate transformation on the fracture surfaces of the



**Figure 3.** (a) Carbon NMR spectrum for IPTI/1BDE/BDMA after 80 °C reaction (500 Hz, DMSO- $d_6$ , 149.01, 138.12, 132.26, 129.38, 128.55, 118.10, 71.05, 70.24, 50.32, 43.35, 25.92, and 20.69 ppm). (b) Carbon NMR spectrum for IPTI/1BDE/BDMA after 150 °C reaction (500 Hz, DMSO- $d_6$ , 154.22, 135.97, 132.36, 129.20, 117.83, 70.56, 50.25, 46.37, 43.32, 25.88, and 20.21 ppm). (c) Carbon NMR spectrum for IPTI/1PGE/BDMA after 80 °C 1 h, 150 °C 3 h, and 200 °C 1 h reaction (500 Hz, DMSO- $d_6$ , 154.17, 149.04 ppm).

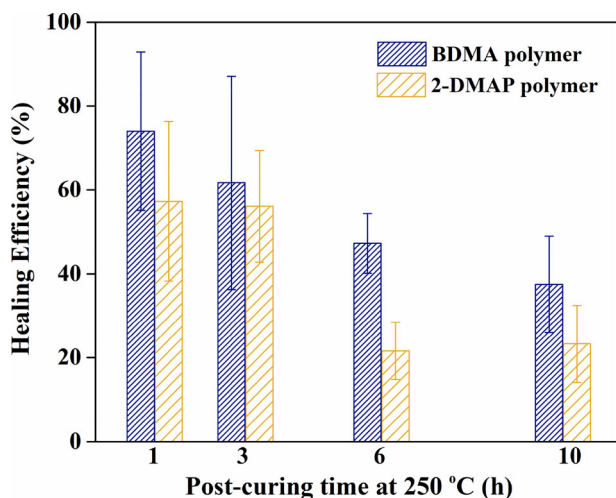
polymers. To verify this explanation, the developed working curve is used for measurement of the isocyanurate transformation on the fracture surfaces of the ISOX polymers. It should be noted that the healing efficiency of polymers cured using DABCO, the strongest nucleophilic catalyst among the three nucleophiles considered here, is not shown in Figure 5 since the polymerization rate is too fast to prepare SENB samples without bubbles for the measurement of healing efficiencies.

To fully understand the healing mechanism of the ISOX polymers, it is important to know the chemistry on the fracture surfaces of the polymers. As isocyanurate-to-oxazolidone transformation occurs during both the curing and the healing process at 200 °C, the chemical composition of the fracture surfaces within the cured ISOX polymers and healed ISOX polymers is characterized through the working curve. From the FTIR spectrum of each sample, the conversion of isocyanate to oxazolidone



**Figure 4.** (a) Working curve for quantification of the ISOX polymers from combination of the carbon NMR and the FTIR techniques, measured from the model compounds 1, 2, and 3. (b) FTIR absorbance spectrum for 3PTI/1BDE/BDMA after 80 °C 0.5 h, 150 °C 3 h, and 200 °C 1 h reaction [ $A(\nu_{CO} 1750 \text{ cm}^{-1}) = 0.185$ ,  $A(\nu_{CO} 1710 \text{ cm}^{-1}) = 0.339$ ,  $A(\nu_{CO} 1750 \text{ cm}^{-1})/A(\nu_{CO} 1710 \text{ cm}^{-1}) = 0.546$ ]. (c) Carbon NMR spectrum for 3PTI/1BDE/BDMA after 80 °C 0.5 h, 150 °C 1 h, 200 °C 1 h reaction (500 Hz, DMSO- $d_6$ , 154.73, 149.50 ppm), OXA/ISO = 0.383. [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

was measured, with the results shown in Figure 6(a). To continuously track the transformation to oxazolidone under high

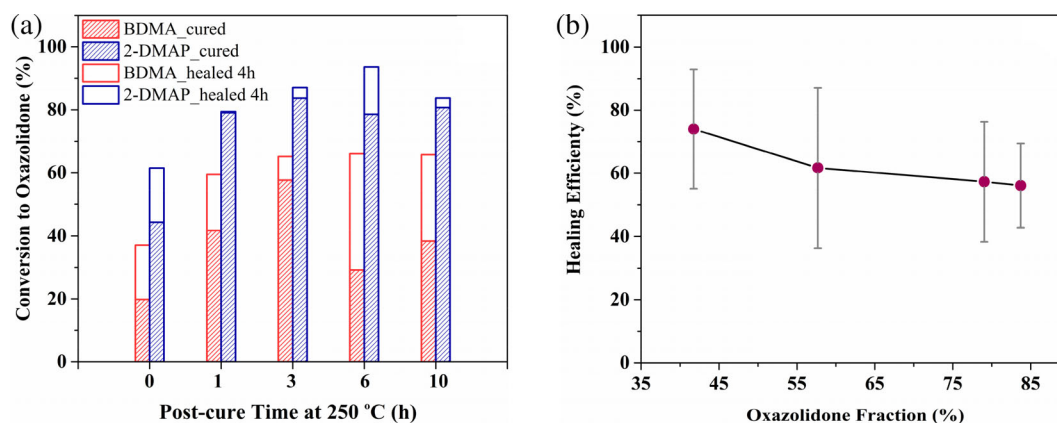


**Figure 5.** Healing efficiencies measured for the BDMA polymer and 2-DMAP polymer with increased postcure time at 250 °C. [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

temperatures, the cured samples were further postcured at 250 °C for varying durations ranging from 0 to 10 h before the characterization of the chemical composition. A thermal treatment at 200 °C for 4 h, which is the same as the healing procedure, was applied to the ISOX polymers following the SENB tests, to investigate the representative chemistry during the healing process. As shown in Figure 5(a), a higher conversion to oxazolidone was observed for the fracture surfaces within the healed samples than that of the cured samples. The increase in conversion to oxazolidone indicates isocyanurate-to-oxazolidone transformation during the healing process. The transformation is restricted in the cured polymers due to the heavy steric effect. However, this steric effect is reduced in the presence of chain scission at the fracture surfaces, which partially accounts for the strong healing behavior of the ISOX polymers.

With different nucleophiles added during the polymerization, varied healing performance was observed for the BDMA polymer and the 2-DMAP polymer, due to the difference in the capacity of the polymers to accomplish the isocyanurate-to-oxazolidone transformation at the fracture surfaces. For the BDMA polymer, stronger zwitterions are present for the isocyanurate transformation to oxazolidone at the fracture surfaces during the healing process, resulting in more oxazolidone formation and a





**Figure 6.** (a) Isocyanurate transformation within the ISOX polymers with varying postcure time at 250 °C, calculated from the working curve for the BDMA polymer and the BDMA polymer after 4 h at 200 °C, the 2-DMAP polymer and the 2-DMAP polymer after 4 h at 200 °C. (b) Healing efficiency measurement for the cured BDMA polymer with varying oxazolidone fractions. [Color figure can be viewed at wileyonlinelibrary.com]

corresponding higher healing efficiency of the BDMA catalyzed polymer. As shown in Figure 5(a), the new oxazolidone formation within the BDMA catalyzed polymer during the 200 °C 4 h healing process is higher than that of the 2-DMAP polymer for different postcure times. Regarding the nucleophiles applied for the polymerization, the healing efficiencies of the ISOX polymers decrease with the increased oxazolidone fraction of the polymers, as can be seen in Figure 5(b), further validating that the isocyanurate-to-oxazolidone transformation as a contributing factor in the healing mechanism. It can be noted that the purpose of postcuring the ISOX polymers in this work is to understand the relationship between the healing performance and the chemical composition of the polymers. To achieve optimal healing performance of the ISOX polymers, postcure at 250 °C is not preferred as it leads to increased oxazolidone conversion. Although the postcure is expected to improve toughness of the polymers because of the increased amount of oxazolidone in the network as chain extenders, it is considered a trade-off between healing capacity and the mechanical properties of the polymers.

## CONCLUSION

In this work, the healing mechanism of the ISOX polymers was investigated based on the understanding of the polymerization mechanism. Polymerization of ISOX polymers begins with nucleophiles attacking the epoxide before the zwitterion of the nucleophile/epoxide/isocyanate initiates polymerization. By varying nucleophilicity of the catalyst, ISOX polymers with different chemical compositions were prepared and characterized using a combination of FTIR spectroscopy and carbon NMR spectroscopy. This work has shown that the starting ratio of isocyanurate and oxazolidone in the polymer affects the healing process and that the presence of a high fraction of oxazolidone leads to reduced healing performance of the polymers. Furthermore, polymers with a high extent of isocyanurate-to-oxazolidone transformation during the healing process demonstrate higher strength recovery. This transformation is restricted in the cured ISOX polymers because of the heavy steric effect, given the high density of isocyanurate cross-linkers in the polymer network. However, the weakening of the steric effect on the crack surfaces at high

temperatures in the presence of epoxide is an important reason for the occurrence of the isocyanurate-to-oxazolidone transformation during the healing and is therefore concluded to be important to the preparation of polymers with high healing efficiencies. To conclude, the healing behavior of ISOX polymers is complex and the results provided here offer important contributions which have not been demonstrated through prior results.

## ACKNOWLEDGMENTS

The authors gratefully acknowledge the support from both the Army Research Office (Award Number: W911NF-12-1-0014) and the National Science Foundation (Grant Number: CMMI-1762369).

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