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Synthesis and Characterization of Thermosetting Furan-Based Epoxy Materials with Improved Thermomechanical Properties

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Abstract

Biobased alternatives to petroleum-based thermosetting polymers have recently drawn increasing attention due to their positive impact on the economy and environment. These alternatives should mimic the rigid, aromatic characteristics of incumbent high-performance thermosetting materials. Furanyl derivations from cellulose and hemicellulose are considered to be promising candidates for phenyl replacements. The preparation of furan-based diepoxies is challenging, and proper property comparisons of thermosets prepared with furanyl and phenyl-based epoxy analogs are critical. In this work, analogous furanyl and phenyl-based diepoxies were synthesized, and thermosets were prepared using standard amine hardeners. A structure-property relationship investigation indicates that furan-based thermosets possess improved $T_g$ ($\Delta = 8-16 \text{ °C}$) and improved glassy modulus ($\Delta = 0.1-0.6 \text{ GPa}$) compared to their phenyl analogs. The furan ring has thus been proven a viable building block for bio-based high-performance epoxy resins, with potential for applications in other thermosetting fields.

1. Introduction

Due to their excellent thermomechanical properties, thermosetting polymers are widely used for applications such as polymer composites, electrical insulation materials, surface
coatings and adhesive glues.\textsuperscript{1} Generally, these excellent thermomechanical properties are contributed from the formation of a cross-linked network when cured with hardeners.\textsuperscript{2} In particular, epoxy resins are one of the most utilized thermosets due to their outstanding performances.\textsuperscript{3}

A high percentage of thermosetting resins are currently derived from non-renewable resources, mainly from petroleum feedstocks. Nowadays, because society has a growing concern regarding the fluctuating price of fossil fuels and a heightened awareness of environmental protection, increasing interest has been paid to utilizing renewable resources to manufacture thermosetting materials.\textsuperscript{2, 4} Bio-based resources can be a promising candidate to be utilized for preparing thermosetting materials with comparable properties to those of incumbent petroleum-based thermosets.\textsuperscript{5} Several biomass resources have been explored as feedstocks for renewable thermosetting materials, such as plant oil,\textsuperscript{6} cellulose,\textsuperscript{7} hemicellulose\textsuperscript{8}, lignin,\textsuperscript{9} starch\textsuperscript{8} and chitin.\textsuperscript{10} These biomasses can be converted into low-molecular-weight chemicals that possess specific building blocks, and are further transformed into monomers that are useful for preparing thermosetting materials. These building blocks include triglyceride-derived fatty acids,\textsuperscript{6} hemicellulose-derived isosorbide,\textsuperscript{8} lignin-derived polyphenols,\textsuperscript{9} cellulose and hemicellulose-derived furans.\textsuperscript{7} Triglyceride-derived chemicals possess aliphatic chains that endure a lack of rigidity and strength necessary for most thermoset applications.\textsuperscript{11} Even though hemicellulose-derived isosorbide is known to be rigid and nontoxic, epoxy resins as well as thermosetting materials derived from it suffer from low water resistance.\textsuperscript{12} Lignin-derived polyphenols are reputed as promising bio-based resources for preparing thermosets because of inherent aromatic characteristics. However, their applications are severely challenged by effectively converting lignin down to useful chemicals.\textsuperscript{13} Furans are widely considered as important candidates for replacing petroleum-based thermosets due to similar aromatic characteristics.\textsuperscript{14} Furan-based chemicals can be effectively derived from hemicellulose and cellulose. For instance, as the most abundant component in wood, cellulose is able to be chemically and bacterially converted into polyose and transformed into hydroxymethylfurfural (HMF).\textsuperscript{15} Hemicellulose is also able to be converted to furan-based alcohols which are potentially useful as biobased resources.\textsuperscript{2, 8}
Furfuryl glycidyl ether\textsuperscript{16} and furfuryl amine\textsuperscript{17} are two examples of extensively used furan-based chemicals in epoxy thermosetting applications. However, neither of them possess the ability to cross-link when cured with hardeners which greatly limits their utilizations. The reason for this is that furan rings in these two chemicals are serving as pendant groups in the cured network due to the mono-functional epoxy group in their chemical structures. Generally, thermosetting resins with outstanding thermomechanical properties include multifunctional epoxy and amine monomers with aromatic structures that become part of the cured network backbone.\textsuperscript{18} For instance, DGEBA (diglycidyl ether of bisphenol A) has two epoxy groups connected with phenyl rings on its backbone. This characteristic endows DGEBA thermosets with high thermomechanical performance when cured with diamine agents, such as diethyl toluene diamine (EPIKURE W)\textsuperscript{19} and 4,4’-methylene biscyclohexanamine (PACM).\textsuperscript{20}

There is limited work regarding the preparation of difunctional epoxy monomers with furan rings as building blocks. Nor have the properties of networks prepared with such epoxy monomers been studied. To better design furan-based thermosets with the goal of replacing petroleum-based thermosets, we seek to understand structure-property relationships of furan-based epoxies relative to those of phenyl-based epoxies. Jeong et al. recently reported that furanyl photo-polymerizable vinyl ester presented similar surface hardness and bonding strength when compared with a phenyl-based vinyl ster.\textsuperscript{14b} However, to the best of our knowledge, no direct comparisons between furanyl and phenyl-based epoxy resins have been reported. Hu et al. recently reviewed the thermomechanical properties of current bio-based thermosetting materials and summarized that a few factors such as curing condition, extent of reaction, purity, curing agent selection and building blocks have significant impacts on the final properties of prepared thermosets.\textsuperscript{21} In this work, two mimetic epoxy monomers, 2,5-bis[(2-oxiranylmethoxy)methyl]-Furan (BOF) and 2,5-bis[(2-oxiranylmethoxy)methyl]-Benzene (BOB), were prepared according to literature and cured with EPIKURE W and PACM with all the factors mentioned above being taken into account. Their thermomechanical properties were evaluated and conclusions regarding structure-
property relationships between furanyl and phenyl building blocks in thermosetting epoxy resins were drawn.

2. Experimental

**Materials.** tetrabutylammonium bromide (98+%), tetrabutylammonium hydrogen sulfate (99+%), hexane (95%), ethyl acetate (99.8%), tetrahydrofuran (THF, 99.9%), furfuryl glycidyl ether (FGE, 96%), epichlorohydrin (99%), silica gel (60 Å, 70-230 mesh), acetic anhydride (99+%), sodium hydroxide (98%), methylene chloride (99.8%), glacial acetic acid (99.7%), crystal violet indicator, 1,4-benzenedimethanol (99%), potassium acid phthalate (99.9%) and perchloric acid (0.1 N solution in glacial acetic acid) were supplied by Sigma Aldrich, USA; 2,5-bis(hydroxymethyl) furan (b-HMF, 98+) was supplied by Pennakem, LLC, USA; 1,4-Bis(glycidyloxy)benzene (DGEPP, 97+) was supplied by Alfa Aesar, USA; EPON 828 composed of diglycidyl ether of bisphenol A (DGEBA) and low molecular weight oligomers of DGEBA and EPIKURE W composed of isomers of diethyl toluene diamine were supplied by Miller-Stephenson chemical company, USA; 4, 4′-methylene biscoyclohexanamine (PACM, 99+) was supplied by Air Products, USA. All chemicals were used as received.

The chemical structures of the materials used in this work are summarized in Figure 1. A and B are two analogous epoxy monomers that were prepared according to literature. A is the furan-based epoxy monomer, while B is the phenyl-based epoxy monomer. C, D and E are commercial epoxy materials employed in this work. F and G are amine hardeners used for preparing thermosets.
Synthesis of 1, 4-bis[(2-oxiranylmethoxy)methyl]-Benzene (BOB). A 500 mL three-necked round-bottom flask was equipped with a constant-pressure dropping funnel, an inlet for dry nitrogen, a magnetic stirring bar and a thermometer. Moisture and oxygen in the system was replaced with dry nitrogen. Tetrabutylammonium bromide was used as the catalyst. 1, 4-benzenedimethanol (6.9 g, 50 mmol), TBAB (1.61 g, 5 mmol) and 40% w/w sodium hydroxide solution (125 mL) were stirred in the flask at 50 °C for 1 h. The flask was then put into an ice batch for 0.5 h before epichlorohydrin (36.8 g, 0.4 mol) was added dropwise through the constant-pressure dropping funnel within 0.5 h. The reaction was allowed to continue for another 21 h at RT. Then, the mixture was poured into 65 mL ice/water and extracted several times with ethyl acetate. Deionized water was utilized to wash the combined organic layer to neutral, and then the organic layer was dried using anhydrous MgSO₄ and evaporated with vacuum. The crude product was purified using silica gel chromatography to yield BOB (11.25 g) with an overall yield of 90% and 99% purity by ¹H-NMR.
Synthesis of 2, 5-bis[(2-oxiranylmethoxy)methyl]-Furan (BOF).\textsuperscript{14b} A 500 mL four-necked round-bottom flask was equipped with a condenser, a constant-pressure dropping funnel, inlet for dry nitrogen, a magnetic stirring bar and a thermometer. Moisture and oxygen in the system were replaced with dry nitrogen. Tetrabutylammonium hydrogen sulfate was utilized as the catalyst.\textsuperscript{23} Tetrabutylammonium hydrogen sulfate (2.04 g, 6 mmol) and epichlorohydrin (101.2 g, 1.1 mol) were charged into the flask at 65 °C. 2,5-bis(hydroxymethyl) furan (b-HMF, 64 g, 0.5 mol) was added into the flask after being melted (T\text{m} = 68 °C). The mixture was kept stirring at 65 °C for 4 h, and cooled down to 50 °C. 160 mL of 50% w/w sodium hydroxide solution was added into the flask dropwise. After 2h, the mixture was poured into ice/water and extracted with ethyl acetate several times. Deionized water was utilized to wash the combined organic layer to neutral and dried with anhydrous MgSO\textsubscript{4}. Solvent was removed using a rotary evaporator, and crude product was purified with silica gel chromatography with hexane/ethyl acetate (2 to 1 by volume) as elution solution. An overall yield of 60% was achieved (72 g) with a purity of 99% by \textsuperscript{1}H-NMR.

Characterization of BOF and BOB. BOF and BOB were characterized using several techniques such as gel permeation chromatography (GPC), epoxy titration (ASTM D 1652-90), \textsuperscript{1}H-NMR, \textsuperscript{13}C-NMR (nuclear magnetic resonance), Fourier transform infrared spectroscopy (FT-IR), mass spectrometry (MS) and rheometry.

GPC was utilized to measure the purities of BOF and BOB. A Waters 515 GPC was equipped with two 5 \textmu m (poly)styrene-divinyl benzene columns (PLgel 5 \textmu m Mixed-C column and PLgel 5 \textmu m 50 Å column) with 30 cm length and 7.5 mm diameter in series. Columns were operating at 45 °C with THF as elution solvent at a flow rate of 1 mL/min. The effluent was monitored with two detectors at 25 °C: a Waters 2410 refractive index detector and a Waters 2487 dual absorbance detector with wavelength at 254 and 280 nm. GPC samples were prepared by dissolving samples into THF with a 2 mg/mL concentration and filtered before being injected into GPC with 25 minutes as the total monitoring duration. Epoxy titration was conducted by following ASTM D 1652-90, procedure B,\textsuperscript{24} to measure EEW of BOF and BOB. For instance, a solution of BOF (0.4 g), tetraethylammonium bromide solution (10 mL, 0.25 g/mL), methylene chloride (10
mL) and 8 drops of 0.1% solution of crystal violet indicator in glacial acetic acid was prepared, and titration was performed with 0.1 N perchloric acid agent. The solution displayed a sharp color change from blue to green, and the used perchloric acid agent volume was recorded. Multiple trails were performed and the average was reported. $^1$H-NMR and $^{13}$C-NMR measurements were employed to investigate chemical structures of BOF and BOB. They were both conducted using a Varian Unity Inova NMR (500 MHz) instrument with ± 2000 Hz spectral window at 293 K and 90° pulse width. 32 scans were used for $^1$H-NMR and 5000 scans for $^{13}$C-NMR measurement. A Thermo Nicolet Nexus 870 FT-IR spectrometer in absorbance mode was employed to identify functional groups of BOF and BOB. FT-IR spectra were recorded at an 8 cm$^{-1}$ resolution at RT with a deuterated tryglycine sulfate (DTGS) detector with 32 scans in 4000 to 8000 cm$^{-1}$ range for near-infrared (N-IR) and 650 to 4000 cm$^{-1}$ for mid-infrared (M-IR) spectra. MS was performed using a Water AutoSpec-Ultima tripe sector high resolution mass spectrometer with chemical ionization having methane as the ionizing gas in positive ion mode. Viscosities of BOF and BOB were measured with a TA AR2000 ex Rheometer using 40 mm flat plate configuration with a shear rate ranging from 0.01 to 1000 s$^{-1}$ at 25 °C. Shear stress was recorded every 2 s at each shear rate, and viscosity was assigned as the average of three measurements at 1000 s$^{-1}$ shear rate.

**Preparation of BOF and BOB thermosetting polymers.** EPIKURE W and PACM were employed as amine hardeners. BOF thermosetting polymers were prepared by curing BOF with varying weight ratios to DGEBA and hardeners at stoichiometry. $W_{BOF}$ ranging from 0 to 1 were used to indicate the weight fraction of BOF in the whole epoxy resin of the matrix. BOB thermosetting polymers were similarly prepared.

BOF and BOB samples were poured into rubber molds (10 × 40 × 5 mm$^3$) and cured. Curing temperatures and curing durations were established using differential scanning calorimetry (DSC, TA Instruments Q2000) and N-IR studies. Thermosetting polymers were processed into uniform dimensions (9 × 38× 4.5 mm$^3$) for dynamic mechanical analysis (DMA, TA Instruments 2980) after they were post cured. Full conversion of epoxy and amine functional groups in these samples was investigated with N-IR. Spectra
of post cured samples were measured following the same procedure as that used to characterize BOF and BOB.

**Thermosetting polymer properties.** Thermomechanical properties of BOF and BOB thermosetting polymers were investigated by DMA which was conducted with a TA Instruments 2980 in single cantilever geometry. Polymer samples were tested at 1 Hz frequency from RT to a particular temperature (approximately 60 °C higher than glass transition temperature of the sample) with a 2 °C ramp rate and amplitude of 15 μm. Each sample was tested twice and the second run was utilized to report $T_g$ and storage modulus. $T_g$ was reported as the peak temperature of loss modulus curve.

3. **Results and discussion**

**Characterization of BOF and BOB.** BOF and BOB were characterized with multiple techniques. As shown by Figure 2 which illustrates GPC results of BOF and BOB before and after purification, impurities were successfully removed after purification with silica gel chromatography and the characteristic peaks for BOF and BOB were at 15.6 and 15.5 minute, respectively.

![Figure 2. GPC results of crude, purified BOF and BOB, and epichlorohydrin.](image-url)
EEW for purified BOF and BOB were measured as described above and the results were 123 and 126 g/eq, respectively. Both results matched well with their stoichiometric values which were 120 and 125 g/eq. Figure 3 shows the $^1$H-NMR (500 MHz, CDCl$_3$) spectra of purified BOF and BOB whose peaks were attributed to their chemical structures and labeled therein. Additionally, the integration of the area under peaks matched well with the ratio of proton numbers at different positions in both BOF and BOB. Their purities were calculated according to the integration of the area under peaks as well which were both higher than 99%.

![Figure 3. $^1$H-NMR spectra of BOF and BOB.]

$^{13}$C-NMR Spectra of BOF and BOB are plotted in Figure 4, and the peaks were attributed according to chemical structures of BOF and BOB and labeled therein. MS was employed to characterize BOF with CIMS (m/z (%)): 240.1 [$M^+$]. Calcd for C$_{12}$H$_{16}$O$_5$: 240.1. Found: 240.09. MS was also used for BOB with CIMS (m/z(%)): 250.1 [$M^+$]. Calcd for C$_{14}$H$_{18}$O$_4$: 250.1. Found: 250.15. Therefore, BOF and BOB were verified as expected. Viscosity of both BOF and BOB was measured as 0.05 Pa.s at 25 °C. Both M-
IR and N-IR spectra were conducted to confirm functional groups of BOF and BOB without being plotted here.

![Chemical structures of BOF and BOB](image)

**Figure 4.** $^{13}$C-NMR spectra of BOF and BOB.$^{21}$

**Property comparison of BOF and BOB thermosetting polymers.** N-IR was employed to confirm full conversion of epoxy and amine functional groups in BOF and BOB thermosetting polymers. For example, N-IR spectra of a BOF/PACM thermosetting sample are plotted in Figure 5. The red and blue curves represent the first scan at 60 °C and the last scan at 60 °C after 9 h, and the black scan represents the last scan at 160 °C after another 9 h. As shown from the black and red curves, epoxy groups (4530 cm$^{-1}$) started reacting with amine groups (primary amine at 4935 cm$^{-1}$ and primary/secondary amine at 6500 cm$^{-1}$) at 60 °C, and hydroxyl groups (at 6990 cm$^{-1}$) were formed from the epoxy ring opening reaction. The comparison between the last scans at 60 °C and 160 °C (the red and blue curves, respectively) indicates that primary amine groups fully reacted during 9 h at 60 °C, while secondary amine groups did not which is reflected by the presence of primary/secondary amine peak in the red curve. This observation matches well with the known cure behavior of epoxy and amine groups, as secondary amine groups are less reactive than primary ones. After 9 h post cure at 160 °C, epoxy, primary
and secondary amine peaks were no longer present, meaning within the limits of IR measurements, epoxy and amine functional groups were fully converted after the cure process was finished. This investigation was a representative of all compositions that were studied in this work.

![N-IR spectra of a W\textsubscript{BOF} = 1 sample cured and post-cured with PACM at 60°C and 160°C.](image)

**Figure 5.** N-IR spectra of a W\textsubscript{BOF} = 1 sample cured and post-cured with PACM at 60°C and 160°C.\textsuperscript{21}

DMA was employed to measure T\textsubscript{g} and storage modulus of thermosetting samples of BOF and BOB cured with PACM and EPIKURE W, and the thermograms are plotted in **Figure 6a** (PACM as the hardener) and **Figure 6b** (EPIKURE W as the hardener). Each of the four compositions present sharp single loss modulus peaks, and T\textsubscript{g}s are assigned as the temperature corresponding to loss modulus curve peak. As shown in **Figure 6a**, BOF possesses a higher T\textsubscript{g} compared to BOB when cured with PACM, and a higher storage modulus all the way from RT to the glass transition region is also observed from BOF/PACM curve. A similar result is found in EPIKURE W case from **Figure 6b**. These results indicate that when cured with aromatic and cycloaliphatic amine agents, BOF with a furanyl building block presents higher temperature resistance and stiffness properties compared to its analog BOB with a phenyl building block. In other words, a furan ring improves thermomechanical properties relative to a benzene ring in an epoxy resin system.
Figure 6. DMA thermograms of cured samples of BOF and BOB with PACM and EPIKURE W at stoichiometry, respectively.

One of the potential explanations for this phenomenon is that hydrogen bonding between the oxygen atoms on furan rings of BOF and generated hydroxyl groups in the epoxy/amine network during cure help to improve the thermomechanical properties of BOF compared to BOB due to the BOF system’s relatively higher crosslinking density. In order to investigate this hypothesis, M-IR was utilized to evaluate hydrogen bonding in a BOF monomer, BOF/PACM and BOF/EPIKURE W thermoset samples, as suggested in literature. The formation of hydrogen bonding slightly impacts bond lengths, electron density distribution and energies of involved chemical bonds, and these changes are generally around two or more orders of magnitude smaller compared to the typical chemical changes. M-IR spectroscopy is sensitive enough to detect the formation of hydrogen bond in this case. M-IR spectra of BOF monomer, BOF/PACM and BOF/EPIKURE W samples are plotted together in Figure 7. As shown in BOF/PACM and BOF/EPIKURE W cases, a broad peak was present in the region of 3200 and 3500 cm$^{-1}$ representing generated hydroxyl groups in epoxy/amine network; no hydroxyl groups were present in BOF monomer. The peak at 1078 cm$^{-1}$ corresponding to the stretching of C-O-C on furan ring in BOF shifted to a low frequency by 9 cm$^{-1}$ after forming thermosets with amine hardeners. It is suggested that the shift of a stretch
vibration of a corresponding functional group to a lower frequency (red shift) could result from hydrogen bonding on this functional group, and the intensity of this red shift is correlated with the strength of formed hydrogen bond.\textsuperscript{26-27} Therefore, hydrogen bonding on furan rings of BOF could be a reason for the improved thermomechanical properties relative to BOB; however, more investigation is needed to evaluate the significance of hydrogen bonding in this improvement.

![Figure 7. M-IR spectra of BOF and cured BOF polymer samples with PACM and EPIKURE W, respectively. (b) is magnification of (a).\textsuperscript{21}](image)

Another hypothesis of this property improvement regarding furan and benzene rings as building blocks arises from structural considerations. Furan rings can not generate rotation around the aromatic unit in BOF, while benzene rings can spin along the para bonding in BOB. This rotation of the benzene ring is a relaxation that could allow larger scale motions of the chains in the network to take place at a low temperature.

**Comparison of BOF and BOB thermosetting polymers blended with DGEBA.** In order to further explore the difference in properties associating with an epoxy network prepared with furanyl and phenyl building blocks, and to evaluate the feasibility of utilizing furan based epoxy resins in conjunction with commercial resins such as DGEBA, thermosetting polymers were prepared by blending with DGEBA at different
concentrations. Four series of BOF and BOB polymers cured with PACM and EPIURE W at stoichiometry were prepared which contained DGEBA with its weight fraction varying from 0 to 1 (0, 0.3, 0.5, 0.7 and 1). They included: (1) BOF/DGEBA/PACM; (2) BOB/DGEBA/PACM; (3) BOF/DGEBA/EPIKURE W; and (4) BOB/DGEBA/EPIKURE W. N-IR was employed as described previously to ensure full conversion of epoxy and amine groups within the limits of IR technique.

Figure 8. DMA thermograms of thermosetting samples of BOF and BOB blended with DGEBA (EPON 828) at different concentrations in PACM system.\textsuperscript{21}
Figure 8 summarizes the storage and loss modulus curves of BOF/DGEBA/PACM and BOB/DGEBA/PACM, and Figure 9 summarizes all those curves of EPIKURE W case. As shown in Figure 8, BOF based samples consistently present higher storage moduli and $T_g$ compared to BOB samples when blended with DGEBA. At RT, BOF samples present significantly higher storage moduli relative to BOB, and the storage moduli of these BOF samples increase with BOF content; however, a similar trend is not observed from BOB samples. This result indicates that the furan building block consistently improves glassy modulus of thermosets when blended with DGEBA compared to the phenyl building block with PACM as a hardener. Meanwhile, all BOF and BOB samples display a single sharp loss modulus peak as shown in Figure 8c and 8d, suggesting that no phase separation occurs in formed networks. $T_g$s, as assigned as the temperature of the loss modulus peaks, of BOF and BOB thermosetting samples shifted to higher positions with increasing DGEBA content. Also, the height of loss modulus peaks and the area under the loss modulus-temperature curves in the vicinity of $T_g$ decreased with increasing DGEBA content, indicating DGEBA is more rigid and stiff than BOF and BOB.
As shown in Figure 9a and 9b, at RT, the storage moduli of BOF/DGEBA/EPIKURE W samples did not follow the trend that observed in PACM case. The loss modulus curves of BOF/DGEBA/EPIKURE W and BOB/DGEBA/EPIKURE W samples plotted in Figure 9c and 9d show that BOF and BOB samples cured with EPIKURE W behave similarly to those cured with PACM, whereas single sharp loss modulus peaks indicate no phase separation occurrence. $T_g$s of BOF and BOB samples cured with EPIKURE W
also increased with elevated DGEBA content; the height of the loss modulus peaks as well as the area under the loss modulus-temperature curves decreased with increasing DGEBA content similarly.

Table 1. T$_g$ data of BOF/BOB-DGEBA cured with PACM/EPIKURE W at stoichiometry$^{21}$

<table>
<thead>
<tr>
<th>Weight ratio of epoxy monomers (BOF/BOB:DGEBA)</th>
<th>T$_g$(°C) by DMA$^a$</th>
<th>PACM</th>
<th>BOF-DGEBA</th>
<th>BOB-DGEBA</th>
<th>BOF-DGEBA</th>
<th>BOB-DGEBA</th>
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$^a$T$_g$ assigned as the temperature at the peak position of loss modulus curves from DMA.

T$_g$s of these four series of BOF/BOB samples were obtained from loss modulus peak positions in Figure 8 and 9, and are summarized in Table 1 above. Since all samples display a single T$_g$ which is frequently considered an indication of miscibility on an order of 20-40 nm,$^{28}$ it is concluded that BOF and BOB are well miscible with DGEBA. As shown in Table 1, BOF samples consistently possess higher T$_g$s than the phenyl analog when cured with aromatic and cycloaliphatic amine hardeners. As discussed previously, this is possibly because, compared to benzene rings in BOB, furan rings in BOF are asymmetrical and able to form hydrogen bonding which prevents the ring rotation in cured networks. Polymer samples with EPIKURE W generally possess higher T$_g$s than those with PACM in both BOF and BOB cases, which is mainly because the aromatic ring structures are more rigid thermally than PACM with cycloaliphatic ring structures.$^{29}$ Furthermore, the difference of T$_g$s between BOF and BOB samples in analogous compositions was found to increase with increasing BOF/BOB contents which supports these hypotheses.

T$_g$ increases dramatically with decreasing BOF/BOB contents in PACM and EPIKURE W systems. For instance, T$_g$ difference between BOB/EPIKURE W (80 °C) and DGEBA/EPIKURE W (185 °C), as well as BOB/PACM (55 °C) and DGEBA/PACM (167 °C) is greater than 100 °C. By investigating chemical structures between BOF/BOB
and DGEBA (Figure 1), an obvious difference is that BOF/BOB possess methylene groups between glycidyloxy and central building blocks which do not exist in DGEBA, and it is suspected that these methylene linkages decrease T_g of BOF/BOB thermosetting polymers since furanyl and phenyl segments are thus less constrained. In order to verify this hypothesis, DGEPP (Figure 1) was cured using EPIKURE W at stoichiometry as a control since it is analogous to BOB but without the methylene groups. DGEPP was mixed with EPKURE W at 110 °C (T_m of DGEPP), poured into same silicone molds, and cured at 140 °C and 240 °C for both 9 h. The thermomechanical properties were investigated similarly using DMA with a ramp rate of 2 °C/min from RT to 320 °C, and the result was plotted together with DGEBA/EPIKURE W for comparison in Figure 10. A T_g of 193 °C which is slightly higher than that of DGEBA/EPIKURE W was obtained for DGEPP/EPIKURE W sample, and it is 113 °C higher than that of BOB/EPIKURE W. So it is concluded that these methylene linkages are responsible for the dramatically lower T_g's of BOF/BOB systems compared to DGEBA.

Figure 10. DMA thermograms of cured samples of DGEPP/EPIKURE W and DGEBA/EPIKURE W.²¹
Fox Equation (Equ. 1) was utilized to fix experimental T_g data of these four series of thermosetting polymers, which served the purpose of describing T_g of multicomponent networks as a function of relative epoxy content.

\[
\frac{1}{T_g} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}}
\]  

(1)

In this equation \(w_1\) and \(w_2\) represent weight fractions of components 1 and 2, \(T_{g,1}\) and \(T_{g,2}\) are T_g's of polymer samples only containing components 1 and 2, respectively. For instance, in BOF/DGEBA/PACM case, component 1 is BOF/PACM and component 2 is DGEBA/PACM.

![Figure 11](image)

**Figure 11.** Relationship between \(1/T_g\) and \(W_{BOF}\) or \(W_{BOB}\)^{21}

**Figure 11** plots \(W_{BOF}\) or \(W_{BOB}\) versus the reciprocal of \(T_g\) for these four series of polymers being discussed. Also plotted in **Figure 11** are the best-fit lines corresponding to the Fox Equation for each set of data. All four series of polymer samples show excellent agreement (\(R^2 > 0.997\)) which further indicates that BOF and BOB both possess good miscibility with DGEBA implying the polymer networks are homogeneous.\(^{25,30}\)
4. Conclusion

1, 4-bis[(2-oxiranylmethoxy)methyl]-Furan (BOF) and its benzene analog, 1, 4-bis[(2-oxiranylmethoxy)methyl]-Benzene (BOB), were successfully prepared. BOF and BOB are both liquid with low viscosity and good processability. When cured with standard cycloaliphatic (PACM) and aromatic (EPIKURE W) hardeners, BOF polymers were found to possess higher $T_g$s and storage moduli than BOB ones. Possible hypotheses for this phenomenon are structural advantages of less free rotation of furan rings, and enhanced hydrogen bonding between oxygen atoms on furan rings and new-formed hydroxyl groups in cured networks. Furthermore, the methylene linkages between the aromatic and glycidyloxy groups in BOF and BOB were found to be responsible for the significant $T_g$ drop compared to DGEBA and DGEPP. BOF presents excellent miscibility with DGEBA resulting in the formation of homogenous network following Fox Equation with a high fidelity. These results indicate that furanyl derivations with high biobased availabilities are a promising substitute for incumbent petroleum-based thermosetting materials with improved thermomechanical properties.

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References


