

1,3-Bis(benzoxazine) from Cashew Nut Shell Oil and Diaminodiphenyl Methane and Its Composites with Wood Flour

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ABSTRACT: Cashew nut oil-based benzoxazine monomer has been synthesized applying solvent-less method through the Mannich reaction of cashew nut shell oil as phenol, amine, and formaldehyde. A difunctional 1,3-benzoxazine is synthesized using diaminodiphenyl methane as the amine component. ^1H and ^{13}C -nuclear magnetic resonance spectroscopy and Fourier transform infrared spectroscopy are used to characterize the structure of the monomers. Wood flour is used to prepare composites, making both reinforcement and matrix resin the materials derived from renewable resources. Observation of catalytic effects on DSC exothermic temperature and crosslink density by the added wood flour is discussed. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: renewable resources; polybenzoxazine; cashew nut oil; wood flour

Received 20 December 2011; accepted 25 February 2012; published online

DOI: 10.1002/app.37584

INTRODUCTION

Rapid advances in technology and a great amount of nonrenewable natural resources being used in manufacturing have vastly affected the environment. Moreover, as the high cost of limited resources has become an urgent issue to solve, more and more companies are implementing excellent green and sustainable initiatives. Ecofriendly alternatives, which is of great interest to the modern society, could still maintain the beneficial properties and, at the same time, reduce the cost and give less impact on the environment.

Benzoxazines are attractive resins that have recently been developed by the Mannich condensation of a phenol, formaldehyde, and a primary amine. Moreover, a thermally accelerated ring-opening polymerization of the benzoxazine monomers yields high-performance resins, polybenzoxazines.¹ They have not only overcome shortcomings associated with conventional phenolic resins, but also provided more advantages that cannot be seen in traditional phenolic resins. In the polymerization process of the traditional phenolics, strong acids are used as catalysts, and also formaldehyde and phenol are released into the air, which could result in a negative effect to both environment and human health. In addition to the reduced drawbacks, these novel resins maintain interesting aspects, such as near-zero shrinkage upon cure, the great molecular design flexibility, low-water absorption, improved mechanical and thermal properties, and good chemical resistance.^{1–4} Accordingly, the polybenzoxa-

zines are the strong contenders for the replacement of phenolic, epoxy, bismaleimide, and cyanate ester resins as well as some polyimides. Furthermore, unusual properties of benzoxazine resins offer great potential to develop unique materials in areas such as aerospace, electronic, energy, and environmental applications.

With a growing interest in manufacturing more green, sustainable, low-cost, and high-performance materials, cashew nut shell liquid (CNSL) has attracted attention in both academic and industrial research. CNSL, which is the byproduct of the cashew nut extraction, is used in various applications such as phenolic resins, surface coatings, lubricating oil additives, and frictional materials.⁵ Compared to conventional phenolic resins, CNSL-based polymer has improved flexibility due to the internal plasticization of the long chain, which provides a better processability. The side chain imparts a hydrophobic nature to the polymer, making it water resistant.⁶ The main constituents of the CNSL, cardanol, anacardic acid, cardol, and 2-methyl cardol possess phenolic structures with a long unsaturated alkyl side chain as shown in Figure 1.⁷ Each of them has different properties and so is applied to various applications. For instance, despite the fact that it is a pollutant from the cashew nut industry, the cardanol is well known as a renewable and low-cost raw material. The use of cardanol for the synthesis of monofunctional benzoxazine has recently been reported^{8–10} and their thermal properties analyzed.^{9,11} The effect of CNSL on gelation,

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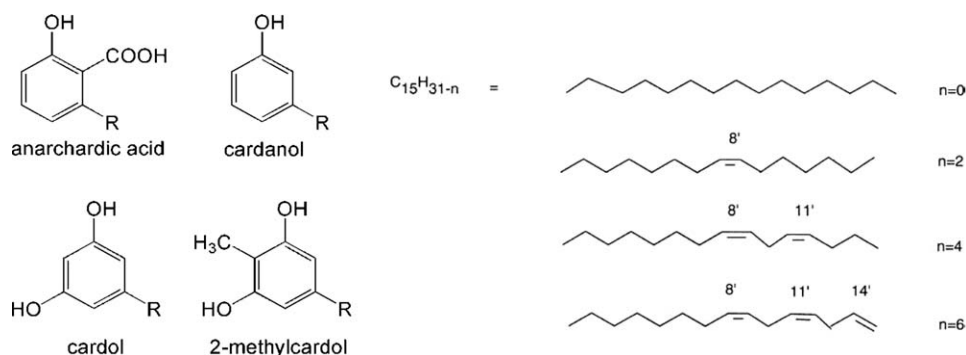


Figure 1. Components of CNSL.

cure kinetics, and thermomechanical properties has also been studied.¹²

However, its use for the synthesis of standard bifunctional benzoxazines using aliphatic or aromatic amine has not been reported. It is known that monofunctional benzoxazines lead only to oligomeric materials upon polymerization, because the thermal dissociation of the monomer is competing with chain propagation reaction. Thus, the development of high-mechanical properties could not be achieved from this approach.¹³ In this study, we report on the synthesis of novel types of benzoxazine monomer using cardanol via a solvent-less process, where an aldehyde, amine, and phenol are physically mixed together and heated above melting point. This method shortens the reaction time, limits the use of potential pollutants or toxins, and reduces the production of byproducts.^{11,14} As the novel benzoxazine emphasizes not only on using the economical, sustainable, and green materials, but also implementing its polymerization process that minimize the environmental impact. In addition, the use of this monomer for making polybenzoxazine composites has been studied. Wood flour was used as a filler material to produce a polybenzoxazine composite. Thus, both the matrix resin and the filler are either naturally produced or derived from the naturally produced material.

EXPERIMENTAL

Materials

4,4'-Diaminodiphenyl methane (DDM) was purchased from TCI America. Paraformaldehyde, ethyl acetate, and anhydrous sodium sulfate were purchased from Fisher Scientific. CNSL, distilled technical grade, was kindly supplied by Cardolite Corporation and used as received without purification. Hard wood flour was kindly supplied by American Wood Fibers.

Synthesis of Cashew Nut Shell Oil-Based Benzoxazine

In a 100-mL beaker, DDM, CNSL, and paraformaldehyde were obtained in 10 : 20 : 40 mmol ratio. The system was magnetically stirred between 80 and 85°C for 4 h. The reaction proceeded as shown in Scheme 1. The reaction yield of crude product via the solvent-less method was around 90%, whereas after the purification as described below, it was between 70 and 75%. To remove the excess carbon chain that had not reacted, purification was followed by base washing. The benzoxazine was dissolved in 500 mL of ethyl acetate, and the mixture was

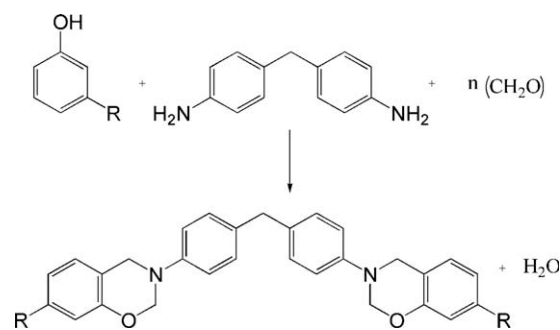
washed with 1 L of 0.5M NaOH solution. Then, it was washed with 200 mL of distilled water twice. With 5 g of anhydrous sodium sulfate, the mixture was magnetically stirred for 20 min and sodium sulfate was filtered. A rotavapor was used for the removal of water, which is formed during the reaction, and the solvent, ethyl acetate. The benzoxazine was purged with dry air overnight.

Polymerization and Compression Molding of the CNSL-Based Benzoxazine

Wood flour was dried under vacuum at 100°C for 2 days. In total of 20 g each sample, the preheated benzoxazine was mixed with 30 (6 g), 50 (10 g), and 70 (14 g)% of wood flour. To make the compound homogenous, each sample was mixed thoroughly with a spatula on a preheated aluminum plate. The materials were filled in a square mold of 50 mm × 50 mm with a thickness of 2 mm and cured at 90°C overnight. At least 7.1 MPa of pressure was applied to each sample by Carver Laboratory Press at 150 and 180°C for 2 h, respectively.

Measurements

¹H-nuclear magnetic resonance (¹H-NMR) spectra of the precursor were recorded on a Varian Gemini 2000 NMR with a proton frequency of 300 MHz, and deuterated chloroform was used as a solvent. Fourier transform infrared (FTIR) spectra were obtained on a Bomem Michelson MB100 FTIR spectrometer, with a deuterated triglycine sulfate detector. Thin films of precursors and polymerized sample composed of 50% wood flour were cast on a KBr plate and purged with dry air. At a spectral resolution of 4 cm⁻¹, spectra of 64 scans of the films were collected.



Scheme 1. Synthesis of CNSL-based benzoxazine

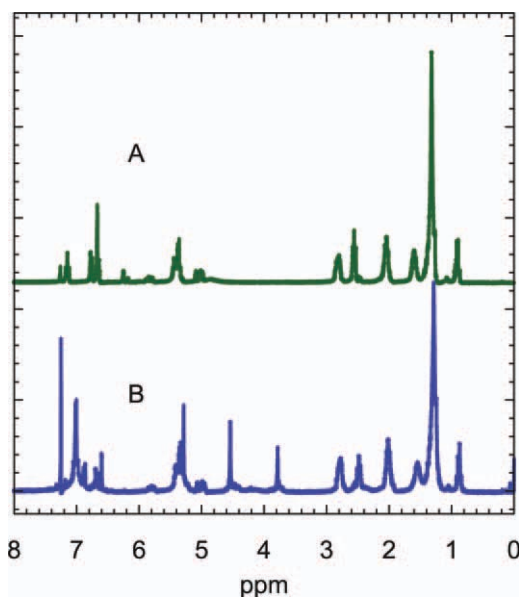


Figure 2. $^1\text{H-NMR}$ spectrum of (A) cashew nut shell oil (CNSL) and (B) CNSL-based benzoxazine. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

To examine the polymerization of the precursor and samples before and after the heating, differential scanning calorimetry, TA Instruments DSC model 2920, was used. Samples, which were enclosed in hermetic aluminum pans with lids, were heated from 25 to 300°C at a heating rate of 10°C/min under nitrogen purge at a constant flow rate of 62 mL/min.

A TA Instruments Q500 Thermogravimetric Analysis (TGA) was used to study the degradation temperatures. Samples were placed in an open platinum crucible and heated from 25 to 850°C at a heating rate of 10°C/min under nitrogen purge at a constant flow rate of 32 mL/min.

Dynamic mechanical analysis (DMA) was conducted on a TA instruments Q800 DMA with a heating rate of 3°C/min from -100 to 100°C at an operating frequency of 1 Hz. The deformation was within the linear viscoelastic limit.

RESULTS AND DISCUSSION

Preparation of CNSL-Based Benzoxazine Monomers

The synthesis of precursor is based on the reaction of cashew nut shell oil (CNSL), diaminodiphenyl methane, and paraformaldehyde at the molar ratio of 1 : 2 : 4. After the mixture was heated at 85°C for 2 h, the brown color of CNSL started to become lighter and white particles began to precipitate due to the formation of perhydrotriazine intermediate structures. Among the main constituents of CNSL, cardanol is widely known and often used in commercial application. However, instead of using only cardanol by purifying CNSL, in this study, CNSL was used as received to reduce excess time and waste during the purification process, thereby focusing on environmental impact and efficiency. The benzoxazine, which is synthesized with a raw material, CNSL, is mixed with another natural source, wood flour, which is composed of cellulose and lignin.

This combination makes the benzoxazine doubly green and sustainable.

The $^1\text{H-NMR}$ spectrum was measured to examine the structure of the CNSL and the benzoxazine as shown in Figure 2. Naturally occurring CNSL contains mainly four components: cardanol, cardol, anacardic acid, and 2-methyl cardol. However, commercial-grade CNSL contains little anacardic acid, because anacardic acid is converted to cardanol or 2-pentadeca-diethyl phenol during the roasting process.¹⁵ The CNSL is rich in cardanol via decarboxylation reaction and contains smaller amounts of cardol and a trace of residual anacardic acid.^{16–18} Therefore, the structure of cardanol was most visible in Figure 2. The condensation reaction of cardanol hydroxyl groups with DDM and paraformaldehyde resulted in the formation of benzoxazine monomer. The typical resonances of benzoxazine are observed at 5.35 and 4.61 ppm. The theoretical ratio of the methylene protons of oxazine ring for the fully ring-closed structure is 1 : 1, and their characteristic chemical shifts have an equal integrated intensity. The intensities of the peaks found were 1.07 to 1.00. Thus, the content of the ring-closed structure was calculated to be as high as 93.5%.

The FTIR spectrum of the monomer was recorded as shown in Figure 3. The characteristic absorption bands for benzoxazine appeared at 1190 and 1220 cm^{-1} due to the asymmetric stretching modes of C—N—C of an oxazine ring and C—O—C, respectively.¹⁹ Because of both antisymmetric and symmetric stretching bands that arise from the methylene groups of the benzoxazine, strong bands at 2920 and 2850 cm^{-1} appeared in the spectrum. Moreover, another strong band at 1505 cm^{-1} due to the vibration of trisubstituted benzene ring was observed. The characteristic absorption bands^{20,21} of cardanol due to phenolic O—H (3400 cm^{-1}) was absent in crosslinked polybenzoxazine, suggesting a complete conversion of hydroxyl groups of cardanol to ring opening of oxazine.

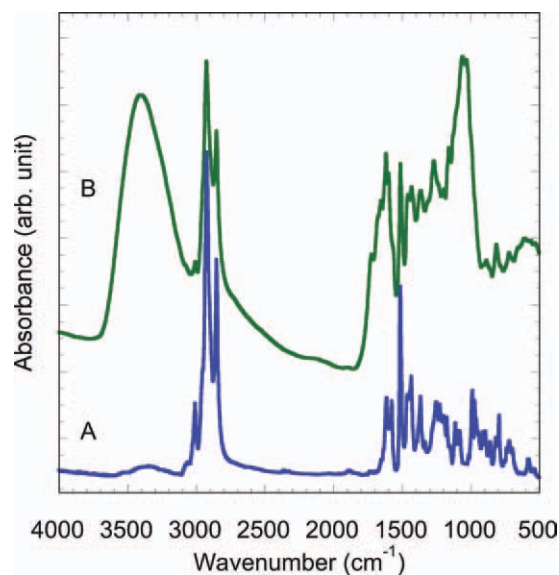


Figure 3. FTIR spectra of (A) the precursor and (B) crosslinked polybenzoxazine composed of 50 wt % wood flour. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

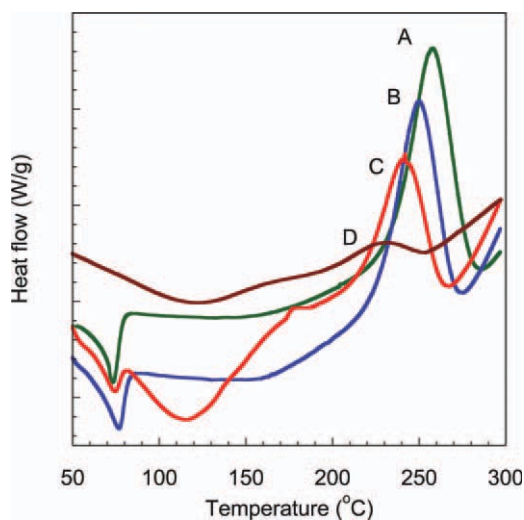


Figure 4. DSC thermograms for polybenzoxazine composites containing: (A) monomer only, (B) 30, (C) 50, and (D) 70 wt % wood flour. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Thermal Properties of the Composites

Both endothermic and exothermic peaks were observed in the monomer and polybenzoxazine composites containing different amounts of wood flour as shown in Figure 4. The melting temperature of the monomer is 74 °C, and its exothermic peak is at 258 °C with a total enthalpy of 83.23 J/g. This small heat of polymerization is due to the dilution effect of the long alkyl chain of cardanol. Wood flour was dried to remove any water. However, because of the high affinity of the wood flour to water, the monomer still maintained some water content. Therefore, there are downward peaks in composites containing

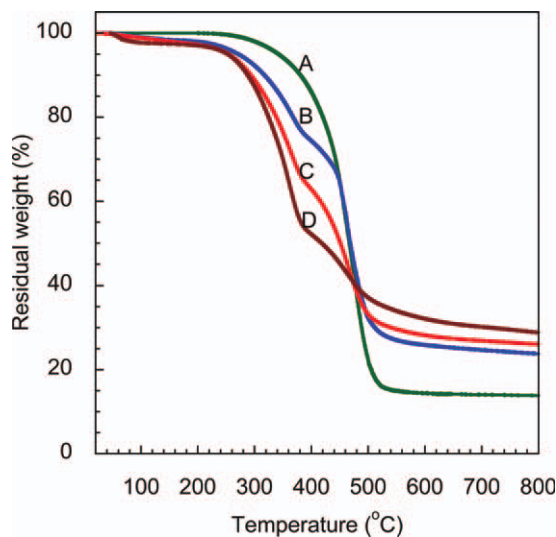


Figure 5. TGA thermograms for crosslinked composites containing: (A): 0 wt %; (B): 30 wt %; (C) 50 wt %; and (D) 70 wt % wood flour. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

50 and 70 wt % wood flour other than the melting temperature (T_m) peaks. The melting points of the composites containing 30, 50, and 70 wt % were found to be 77, 75, and 70 °C, respectively. The exotherms due to the ring-opening peak at 250, 239, and 228 °C for the respective composite with 30, 50, and 70 wt % wood flour are observed. As the content of the wood flour in the composites increases, the exotherms corresponding to benzoxazine ring opening as well as melting point decrease. This lowering of the heat of polymerization is due to catalysis of the oxazine ring-opening polymerization by phenolic groups.²² The composites consisting of 30 and 50 wt % wood flour have total enthalpies of 54.0 and 42.7 J/g, respectively. There was no peak present for the composite composed of 70 wt % wood flour.

Thermal stability of the composites was examined by TGA as shown in Figure 5. The 5 and 10% weight loss temperatures (T_{d5} and T_{d10}) for the polymerized composites containing 30, 50, and 70 wt % wood flour decrease as the wood flour content increases and are 271 and 317 °C; 254 and 294 °C; and 252 and 288 °C, respectively. On the other hand, the char yield at 800 °C increases as the content of wood flour increases; the char yield for the composites containing 30, 50, and 70 wt % wood flour are 24.0, 26.1, and 28.8%, indicating that the majority of the char originates from wood flour rather than polybenzoxazine. The composite containing higher content of wood flour degrades at lower temperature than that of composites with lower content. These results suggest that there is certain content that wood flour can be added without significant damage in thermal stability.²³

Dynamic Mechanical Analysis

The results of dynamic mechanical analysis of the monomer and composites containing 30 and 50% wt wood flour are shown in Figure 6 for the storage modulus and $\tan \delta$. The DMA spectra of the 70% by weight wood flour sample could

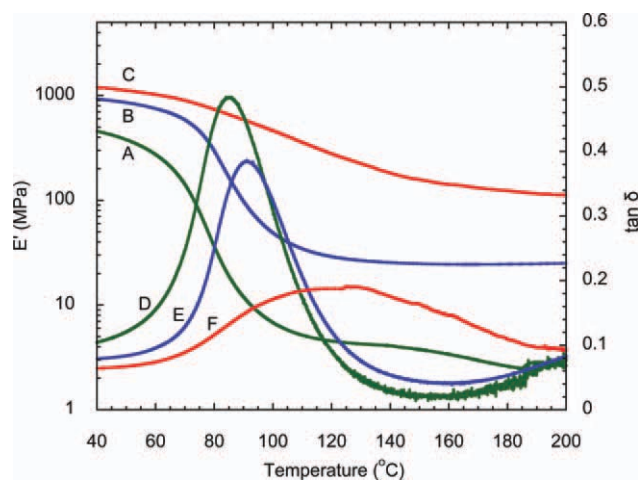


Figure 6. Dynamic mechanical analysis results of polybenzoxazine derived from CNSL and DDM-based benzoxazine monomer (A: E' ; D: $\tan \delta$); 30% wood flour-filled polybenzoxazine (B: E' ; E: $\tan \delta$); and 50% wood flour filled polybenzoxazine (C: E' ; F: $\tan \delta$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

not be obtained due to the brittleness. Expectedly, this rather flexible polybenzoxazine after crosslinking reaction showed the T_g of 85°C without wood flour as defined by the peak position of the $\tan \delta$ spectrum. Ideally, G' peak should be used for determining the T_g . However, this material showed rather ill-defined G' peak, and the determination of the T_g lacks accuracy. Thus, $\tan \delta$ spectrum was used, instead. Upon filling the polymer with 30% by weight of wood flour increased the T_g to 91°C with slight broadening in the $\tan \delta$ peak. Further significant increase in T_g to 124°C as well as the breadth of the $\tan \delta$ peak was noted for 50% by weight wood flour-filled composite. Quite unexpectedly, the rubbery plateau moduli of the composite drastically increased, indicating the enhanced degree of crosslinking. In comparison with the homopolymer that shows slight decrease in rubbery modulus as a function of temperature, the two composites show well-known flat rubbery plateau moduli as a function of temperature, reflecting extensive cross-linked network formation. The molecular origin of this enhancement is quite likely due to the presence of phenolic structure of lignin on the surface of wood flour, which acts as a ring-opening polymerization initiator of the benzoxazine. The E' of the homopolymer is rather low around 0.44 GPa at room temperature in comparison with ordinary crosslinked polybenzoxazines, which show around 2–6 GPa.²⁴ Upon wood flour filling to 50% by weights, E' increased to above 1 GPa. This composite can be readily cut by a thaw. With a broad-damping curve, it might have vibration damping characteristics and could potentially be considered artificial wood replacement material with superb chemical resistance as well as better flame retardance property than wood itself.

CONCLUSIONS

The novel polybenzoxazine composites has been prepared using the solvent-less method and cashew nut shell oil as green starting material. We emphasize here not only on using the economical, sustainable, and green materials, but also implementing its polymerization process that minimize the environmental negative impact. The structure of CNSL-based benzoxazine monomer was confirmed by FTIR and ¹H-NMR. Moreover, the monomer was mixed with a natural material, wood flour as a filler to produce composites. The composite-containing 30 wt % of wood flour showed the better thermal and mechanical properties compared to other composites. Addition of wood flour catalyzed polymerization reaction, shifting the DSC exotherm maximum from 258°C of the neat monomer to 228°C of 50 wt % wood flour composite. Reflecting this accelerated polymerization rate, the wood flour composite showed dramatic increase in crosslink density, which corresponded to the increased rubbery plateau modulus (E') from 4 to 120 MPa. The 50% wood flour composite exhibited extremely broad glass transition, reflecting the broad structural variation and ability to absorb energy in a wide temperature range.

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