

Side-Chain Type Benzoxazine-Functional Cellulose via Click Chemistry

Tarek Agag,* Kevin Vietmeier, Andrey Chernykh, Hatsuo Ishida

Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio 44106-7202

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ABSTRACT: A side-chain type benzoxazine-functional cellulose has been developed using click chemistry via the reaction of ethynyl-monofunctional benzoxazine monomer and azide-functional cellulose. The synthesis, crosslinking, and thermal properties of the benzoxazine-functional cellulose are studied by NMR, FTIR, DSC, and TGA. The crosslinking reaction of the benzoxazine side-chain unusually takes place at low-temperatures in comparison to an

ordinary benzoxazine resins. Upon crosslinking, the polymer shows high char yield of 40%, which is a marked improvement from a mere 4% of the unfunctionalized cellulose. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 1346–1351, 2012

Key words: benzoxazine; polybenzoxazine; click chemistry; char yield

INTRODUCTION

As the concern for global warming increases and supply of natural resources decreases, it is essential to seek alternative means to produce materials such as polymers without compromise in properties in comparison to the existing materials. The use of renewable resources for these new materials is a desired approach. Cellulose is the most abundant natural resource on the planet, which makes it particularly appealing. Furthermore, cellulose can be easily bound to other compounds by replacing the hydroxyl groups with a more reactive group such as an azide group.^{1–3} Therefore, it can readily be covalently bonded with those compounds that possess triple bonds through click chemistry.

Small molecular weight benzoxazine chemistry was developed more than 60 years ago by Holly and Cope⁴ and actively studied by Burke and his group during the 1950s and 1960s.^{5–7} Patents were issued to Schreiber for benzoxazine oligomer development^{8,9} and to Higginbottom for use as coating materials.^{10–12} Oligomerization kinetics was studied by Ries et al. in 1985.¹³ In 1994, the synthesis and properties of crosslinked polybenzoxazines and their properties were first reported by Ning and Ishida.¹⁴ Since then, numerous articles have been published on monomeric benzoxazines,^{15–27} main-chain type

polybenzoxazine^{28–39} and side-chain type polybenzoxazines.^{40–45} It is this high molecular weight polybenzoxazine precursors with side-chain type structures that the current article aims at developing because high-molecular weight precursors offer usual thermoplastic properties, such as good film forming ability and solubility in solvent for easy structural analysis. Upon heat treatment, the oxazine group that is on the polymeric chain will ring-open and cationically polymerize to form a cross-linked polymer with the original polymer chain as the backbone. The crosslinked polymer offers typical advantage of thermosetting polymers, such as high-dimensional stability, high thermal, and chemical resistance.

Benzoxazines based on renewable resources have attracted attention in the past few years. Cardanol, components in cashewnut oil, based benzoxazines^{46–48} and chitosan-based benzoxazine have been reported.⁴⁹ The synthesis of benzoxazine compounds that possess triple bonds, such as ethynyl and propargyl groups for click reaction has been reported in the Refs. 18,23,27,34,35,50. Therefore, it is the intent of the current study to develop a cellulose with benzoxazine functionality on the side chain via click chemistry. This will allow addition of advantageous properties of polybenzoxazines to be added to the already useful cellulosic material.

Click chemistry is first proposed by Sharpless in 2001 as efficient and environmental friendly chemical reactions.⁵¹ Those well-known click chemistry are the Huisgen 1,3-dipolar cycloaddition, Diels-Alder reaction, nucleophilic substitution to small strained rings-like epoxy and azilidin, and thiolene reaction among others. While, there are many features that

*On leave from Tanta University, Tanta, Egypt.
Correspondence to: H. Ishida (hxi3@cwru.edu).

need to satisfy the reaction to be called click chemistry, some of the important features of click chemistry include: (i) near quantitative reaction, (ii) specific reaction without side reactions, and (iii) purification possible without environmental unfriendly methods. Click chemistry has been applied to modify cellulose to introduce various side groups.^{52–56}

EXPERIMENTAL

Materials

Avicel® PH-101 cellulose was obtained from Fluka. 3-ethynylaniline, *p*-cresol, and paraformaldehyde were purchased from Aldrich. All compounds were used without further purification.

Preparation of 3-(3-ethynylphenyl)-6-methyl-2H, 4H-benzo[e]1,3-oxazine

3-Ethynyl-functional benzoxazine, 3-(3-ethynylphenyl)-6-methyl-2H, 4H-benzo[e]1, 3-oxazine, was prepared from the reaction of 8 mmol of 3-ethynylaniline, 8 mmol of *p*-cresol, and 16 mmol of formaldehyde in a 1 : 1 : 2 ratio by applying the solventless method.⁵⁷ The mixture was then stirred at 125°C for 45 min, following benzoxazine formation by ¹H-NMR. The resulting product was dissolved in dioxane and precipitated in 10 mL of methanol. The precipitate was washed several times with methanol, followed by filtration, and dried under vacuum at room temperature to yield pale brown powder.

¹H-NMR (CDCl₃), ppm: δ = 2.18 (s, CH₃), 4.15 (*t*, ≡CH), 4.62 (s, CH₂, oxazine), 5.37 (s, CH₂, oxazine), and 6.8–7.1 (7H, Ar).

Synthesis of azide-functional cellulose

Cellulose solution was prepared by suspending 20.75 g of cellulose in 470 mL of dimethylacetamide (DMA). This slurry was stirred at 160°C. Afterwards, the solution was concentrated by evaporating ~ 40 mL of DMA. Then, 50.0 g of lithium chloride was added at 100°C. The slurry was stirred overnight and cooled to room temperature. The mixture was then combined with a mixture of 60.4 mL of triethylamine and 40.0 mL of DMA. The solution was cooled to no higher than 8°C and a mixture of 60.0 mL DMA and 40.0 g *p*-toluenesulfonyl chloride was added dropwise over a period of 30 min. After stirring for 24 h under 8°C, the solution was slowly poured into 5.0 L of water. This resulted in a white precipitate, which was then filtered and washed with 15 L of water and 1 L of ethanol. The material was suspended in 1 L of acetone for 48 h. The suspension was then precipitated in 2 L of water. The precipitate was washed five times with 500 mL of

ethanol. The resulting material, tosyl-cellulose, was dried overnight at 50°C under vacuum.

Azide-functional cellulose was synthesized according to the following procedure. To a solution of 10.0 g tosyl-cellulose in 200 mL DMF, 10.7 g of sodium azide was added. The reaction mixture was then stirred at 100°C for 24 h. The mixture was precipitated in 700 mL of water and filtered. The solid was then washed five times with 250 mL of water. After this, the solid was washed several times with 250 mL of ethanol and dried under vacuum at 60°C for 24 h.

Synthesis of benzoxazine-functional cellulose

3-Ethynyl-monofunctional benzoxazine in a 4 : 1 molar ratio was added to solution of azidocellulose in dimethyl sulfoxide. To this, copper iodide dissolved in water was added as a click reaction catalyst. Finally, pyridine was added to the solution. The reaction was then allowed to stir at 25°C for 72 h. The solution was filtered through silica gel pad to remove copper salts and then poured into water to precipitate the final benzoxazine-functional cellulose. The precipitate has been repeatedly washed with water and acetone to afford solid fibrous product, which was allowed to dry at room temperature.

Crosslinking of benzoxazine-functional cellulose

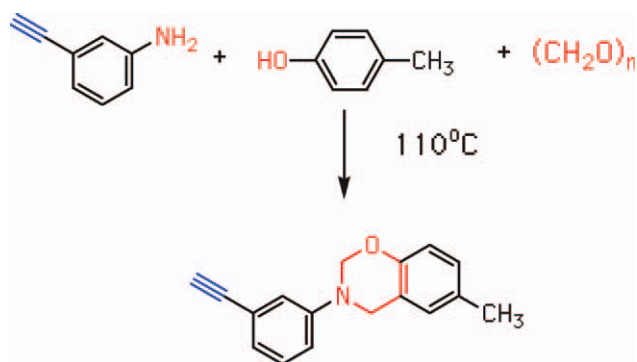
A solution of benzoxazine-functional cellulose was dissolved in DMSO. The solution was cast over a glass plate and step-wise polymerized at 100, 150, and 180°C for 1 h each.

RESULTS AND DISCUSSION

Ethynyl monofunctional benzoxazine as a novel benzoxazine monomer has been synthesized following Scheme 1. The monomer was prepared from the reaction of 3-ethynyl aniline, *p*-cresol, and paraformaldehyde applying the solventless method.⁵⁷ The structure of the monomer has been confirmed by ¹H-NMR. NMR spectrum shown in Figure 1(A) indicates the presence of singlet at 4.18 ppm confirming the presence of ethynyl group. In addition, benzoxazine bands were observed at 4.51 and 5.25 ppm.

Click reaction was applied to functionalize cellulose with benzoxazine structure as shown in Scheme 2.

The structure of the polymer has been confirmed by ¹H-NMR to investigate the presence of benzoxazine structure. Figure 1 shows the characteristic oxazine peaks located at 4.55 and 5.34 ppm for the 3-ethynyl benzoxazine are now shifted to 5.1 and 5.8 ppm, respectively, showing the effect from the nearby oxygens in the cellulose structure. These



Scheme 1 Preparation of 3-ethynyl monofunctional benzoxazine monomer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

frequencies are the most downshifted of all the benzoxazine groups reported in the literature as the majority of benzoxazines fall into the range 3.8–4.8 ppm for the $-\text{Ar}-\text{N}-\text{CH}_2-$ group and 4.7–5.7 ppm for the $-\text{O}-\text{CH}_2-\text{N}-$ group, respectively. The multiplets in the range of 7–8 ppm are because of the aromatic structure in the benzoxazine side-chain, further providing additional evidence of successful modification.

Additional support for successful benzoxazine modification of cellulose comes from the FTIR study shown in Figure 2. The tosylated cellulose, which is shown in spectrum B exhibits new, intense bands at 1193 and 1178 cm^{-1} that can be assigned to the S=O stretching modes of the tosyl group. The bands near 825 cm^{-1} are due to the para-substituted benzene ring, also coming from the tosyl group. Upon modification with sodium azide, these bands arising from

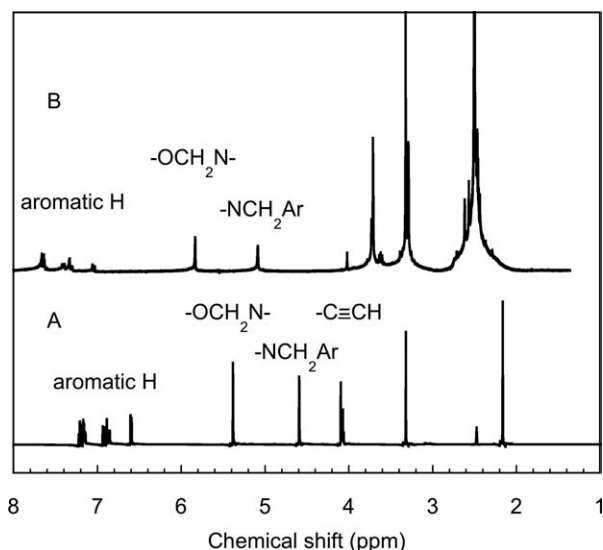
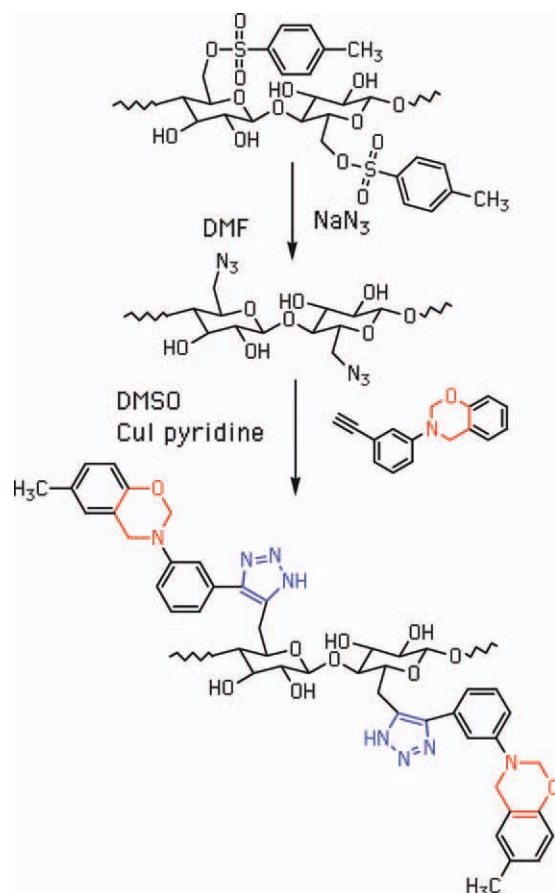


Figure 1 ^1H NMR spectra of (A) 3-ethynyl monofunctional benzoxazine monomer and (B) benzoxazine-functional cellulose.



Scheme 2 Preparation of benzoxazine-functional cellulose. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the tosyl groups all disappeared as shown in spectrum C. Instead, a very broad and intense band centered at 2112 cm^{-1} , which is assigned to the azide group, has been observed, indicating successful

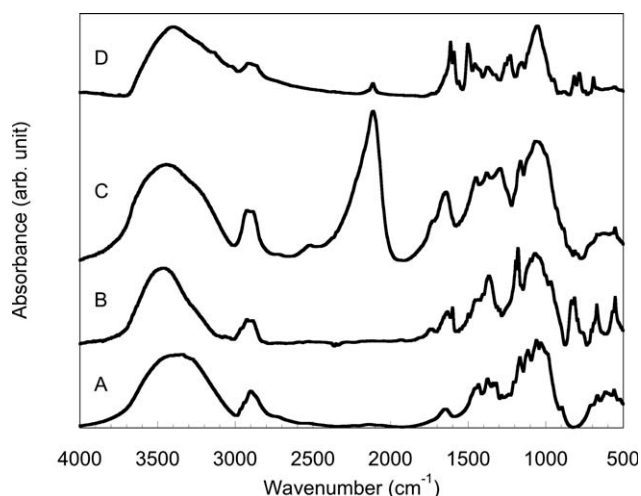


Figure 2 FTIR spectra of (A) cellulose, (B) tosylated cellulose, (C) azide-functional cellulose, and (D) benzoxazine-functional cellulose.

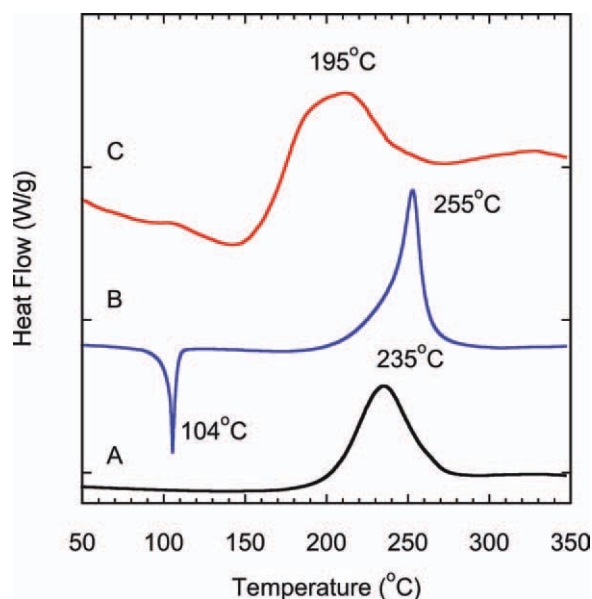


Figure 3 DSC thermograms of (A) 3-ethynyl benzoxazine, (B) azide-functional cellulose, and (C) benzoxazine-functional cellulose. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

azide functionalization. Azide-functional cellulose was reacted with 3-ethynyl benzoxazine in dimethyl sulfoxide (DMSO) using copper (II) iodide/pyridine as a catalyst. The ratio of benzoxazine monomer to azide-functional cellulose was 1 : 4, at which point the azide peak was almost eliminated, reflecting more than 98% conversion. The benzoxazine-functional cellulose shown in spectrum D exhibits a characteristic benzoxazine band at 950 cm^{-1} and the disubstituted benzene ring around 800 cm^{-1} , indicating successful benzoxazine functionalization.

The crosslinking of benzoxazine functional cellulose has been studied by DSC and FTIR. Figure 3 shows the DSC thermograms of azide-functional cellulose, 2-ethynyl benzoxazine, and benzoxazine-functional cellulose. In the middle curve, there is an exotherm at $\sim 250^\circ\text{C}$, which corresponds to the polymerization of benzoxazine. Typically, a DSC thermogram of benzoxazine polymerization of a pure compound is symmetric centered around 250°C for an ordinary benzoxazine monomer. The asymmetric line shape observed in this thermogram does not originate from impure sample as the melting endotherm is sharp and strong around 103°C , reflecting rather high purity compound. The most likely cause for this asymmetric line shape is the polymerization reaction of the ethynyl group as it can polymerize in the range of $170\text{--}200^\circ\text{C}$.³⁸ A most striking feature of the DSC thermogram of the benzoxazine-functional cellulose is its low-exotherm peak position showing broad peaks around 195°C with onset temperature as low as 145°C . Only very select benzoxazines have

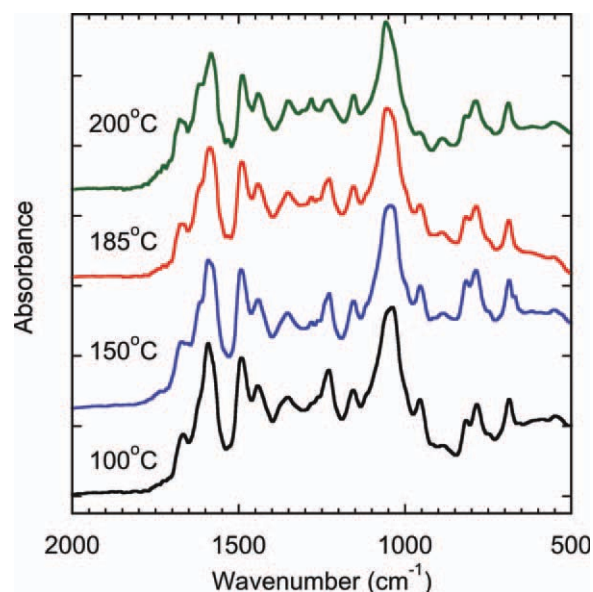


Figure 4 FTIR spectra of benzoxazine-functional cellulose heated at various temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

been reported to show such phenomena.^{36,59,60} At the present time, its molecular origin is unknown.

FTIR spectra and DSC thermograms were taken at various temperatures of polymerization and can be found in Figures 4 and 5, respectively. It is seen in Figure 4 that the peak at 950 cm^{-1} decrease as the temperature is raised. This peak, which is indicative of the benzoxazine monomer, is reduced as the monomer is polymerized. While this peak can disappear upon ring opening only without polymerization, when there is no complication with hydrolysis

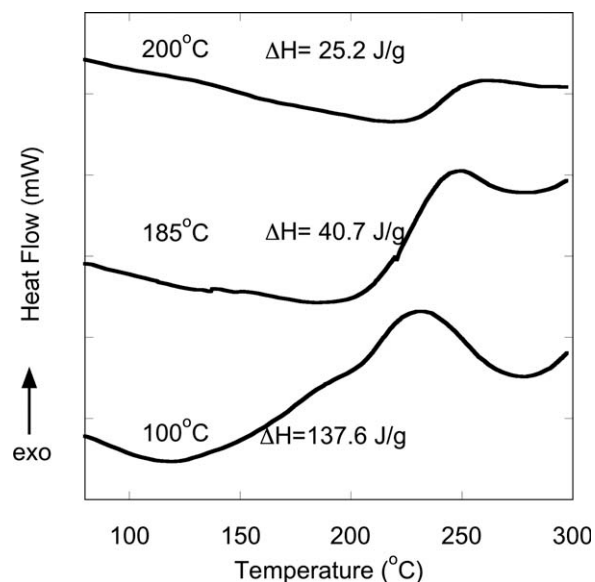


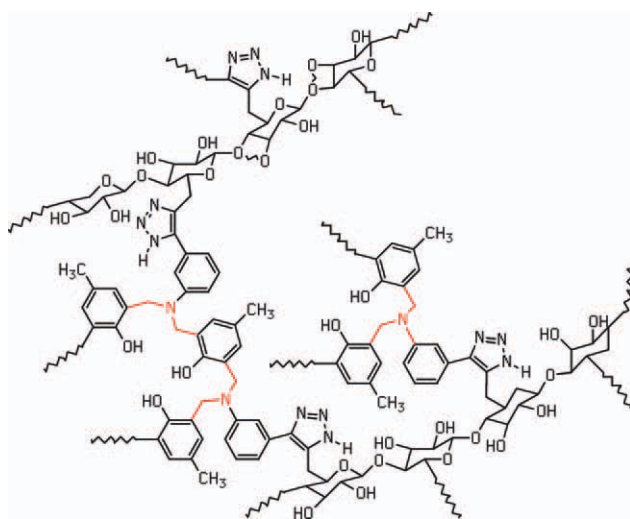
Figure 5 DSC thermograms of step polymerization for the samples treated at 100, 185, and 200°C .

of the oxazine group, intensity reduction can be related to polymerization process.

The idealized structure of the part of crosslinked networks is shown in Scheme 3 as a guide. It should be understood that there are many possible structures of the polymerized chain as the polymerization of benzoxazine groups are complex. Only the most common chemical repeat units are shown in the figure.

Also, the DSC curves in Figure 5 support the FTIR observation. The 100°C sample experienced this temperature for several hours in order to dry the sample. However, during the drying period at 100°C, no significant polymerization is expected. The 185 and 200°C treatment took place for 1 h. Here, the exothermic peak due to the polymerization of the ethynyl and benzoxazine groups is mostly eliminated by thermal treatment at 200°C for 1 h. It can then be assumed that the polymerization reaches near completion at this temperature with slightly longer heat treatment than 1 h. Significantly, above this temperature will result in degradation because of the thermal instability of cellulose, which is reflected on the up-shift of the baseline near 280°C.

Thermogravimetric analysis thermograms were also obtained of the benzoxazine-functional cellulose, which was synthesized at the 1 : 4 ratio as shown in Figure 6. This thermogram shows a remarkably high 44% residual weight at 800°C under an inert atmosphere, which is defined here as the char yield, considering that the unmodified cellulose shows a mere 4% char yield. Undoubtedly, the benzoxazine side chain that then contributed to crosslinking is responsible for this dramatic increase in the char yield. There are numerous articles published in the litera-



Scheme 3 Idealized structure of the part of crosslinked network of the benzoxazine-functional cellulose formed upon thermal treatment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

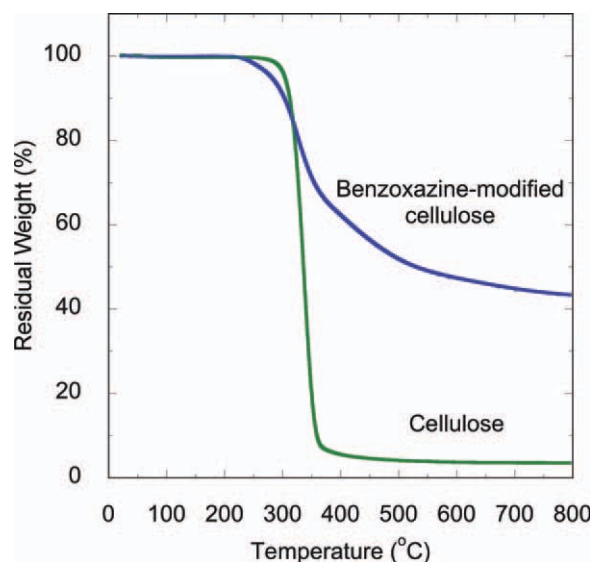


Figure 6 TGA thermograms of benzoxazine-modified cellulose and unmodified cellulose. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ture where polybenzoxazines exhibit one of the highest char yields among processable materials.^{61–68}

CONCLUSION

Combining cellulose with benzoxazine could possibly create a more environmental-friendly material than benzoxazine synthesized by traditional method using petroleum-derived raw materials only. It also produces more flame resistant material than pure cellulose fiber. The benzoxazine-modified cellulose has been successfully synthesized and its property characterized. The char yield of the modified cellulose showed drastic increase in comparison to the unmodified cellulose. The unmodified cellulose abruptly degraded around 320–360°C with the char yield of 4% at 800°C. This very narrow temperature range of degradation and nearly negligible char yield are two properties that relate to high flammability. In comparison, the benzoxazine-modified cellulose showed broader decomposition temperature range from 270 to 500°C with the high char yield of 44%. Polymerization reaction of benzoxazine moiety proceeded at much lower temperatures than the traditional benzoxazine groups, possibly due to the effect of the surrounding hydroxyl groups.

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