



Improved thermal stability of polybenzoxazines by transition metals

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Abstract

The incorporation of various transition metal salts increases the char formation of polybenzoxazines. It is shown that the effect of the transition metal salt is not simply additive and is independent of the amine and phenol structures. While the metal salts have an insignificant effect on the polymerization, their presence in benzoxazine favors the formation of carbonyl functional groups. It is proposed that reduced flammability of polybenzoxazines is achieved through the evolution of CO₂ during thermal degradation.
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1. Introduction

Inorganic–organic hybrid systems have been well established [1]. They have important applications both in the biochemistry and engineering fields. In particular, transition metal complexes with organic functional groups have been extensively explored. The ability of transition metals to possess different oxidation states allows them to complex with various organic functional groups. For example, Schiff bases and amides are well studied ligands that complex with transition metals. These systems are used to probe and mimic the behavior of coordination compounds in proteins. In the area of polymeric materials, transition metal salts are often used as catalysts for polymerization and flame-retardants. Flammability and thermal stability of polymers, such as polystyrene [2], polymethylmethacrylate [3] and polyacrylate [4] were found to improve by incorporating small amount of metal salt (often less than 1% by

weight). Transition metal salts are also known to catalyze the curing of epoxy [5]. Contrary to the polymers mentioned above, incorporating metal salts into epoxy did not improve the thermal stability. It was reported that where copper oxide was added into epoxy to catalyze polymerization, the thermal stability of the resulting epoxy decreased [6].

This paper will explore the effects of metal salts on the thermal stability of polybenzoxazines. Polybenzoxazines are nitrogen-containing phenolic resins. The monomer consists of oxazine rings that thermally polymerize via ring opening polymerization into phenolic structures linked by Mannich bridges. These phenolic resins have shown unique properties that make them a potential candidate for high performance applications. The flexible chemistry of the monomer synthesis offers the opportunity to tailor the properties. One of the most attractive properties shown by these resins is the high thermal stability. A char yield as high as 80% (at 800 °C under nitrogen environment) has been achieved without sacrificing the ease of processing [7].

In a previous study on the thermal degradation of polybenzoxazines, it was reported that Schiff bases and

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secondary amides are present in polybenzoxazines [8]. Although the nature of Schiff bases has not been confirmed, it was proposed that Schiff bases may be present as defect structures or more likely terminal groups in polybenzoxazines. In a different study, oxidation of Mannich base was proposed to result in the formation of secondary amide and imide linkage [9]. It was shown that the flammability of polybenzoxazines was reduced by the presence of these carbonyl groups. Both Schiff base and amide functional groups are known to complex with transition metals.

2. Experimental

The benzoxazine monomers were synthesized from a phenolic derivative, primary amine, and aldehyde. The structures and abbreviations of the benzoxazines used in this study are shown in Scheme 1. All chemicals were purchased from Aldrich Chemical Co. and used as received. The benzoxazine monomers used in this study were synthesized and purified according to previous studies [10,11]. The physical, mechanical and thermal properties have been reported [12,13].

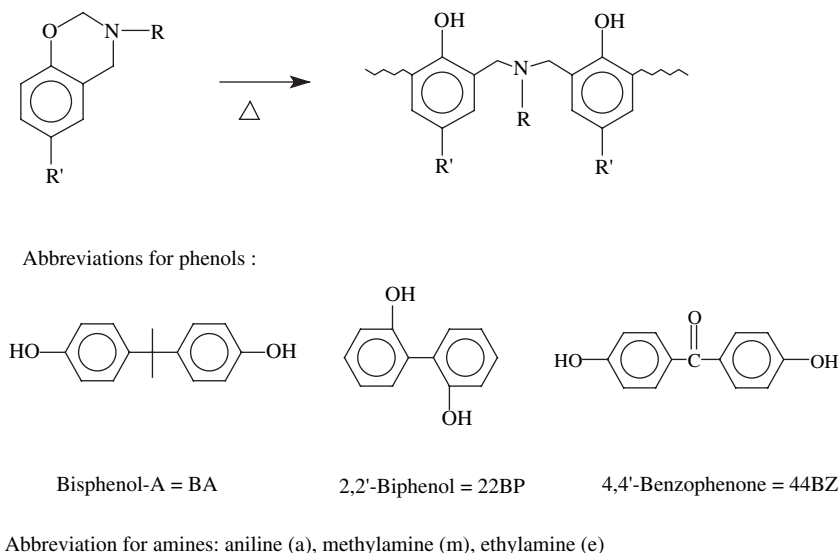
The incorporation of metal salts into benzoxazines was carried out in organic solvents for a period of 12 h at room temperature. Table 1 shows the solvents and the conditions used for the incorporation of metal salt into benzoxazines. Washing with deionized water was performed in order to remove chloride ions and their absence was verified by the lack of white precipitate with AgNO_4 aqueous solution. Benzoxazine monomers were polymerized in a convection oven under the following conditions: 180 °C – 2 h, followed by 200 °C – 3 h. Samples that were washed will be referred to as

benzoxazine:metal, and samples that were not washed will be referred to as benzoxazine:metal salt.

Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA 2950. Thermal degradation experiments were carried out under nitrogen at a flow rate of 90 ml/min and a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) experiments were performed on a TA Instruments DSC 2920. All DSC experiments were carried out under nitrogen purge (60 ml/min) at a heating rate of 10 °C/min.

Fourier transform infrared spectroscopy (FTIR) was performed on a Bio-Rad FTS 60A, which was equipped with a linearized, nitrogen cooled mercury–cadmium–telluride (MCT) detector. Benzoxazine film was cast on a potassium bromide (KBr) plate and polymerized in an oven with the aforementioned polymerization cycle. FTIR experiments were obtained by co-adding 200 scans at a spectral resolution of 2 cm^{-1} . Evolved gas spectra were obtained by interfacing the TGA to the FTIR spectrometer through a heated glass transfer tube. The temperatures of the transfer tube and gas cell were set at 260 °C. A deuterated triglycine sulfide (DTGS) detector was used for these experiments. The spectra were obtained by co-adding 3 scans. The spectral resolution was 4 cm^{-1} with time resolution of 3 s.

Proton nuclear magnetic resonance (^1H NMR) spectra were obtained from a Varian XL-200-H spectrometer at a proton frequency of 200 MHz, and operated at a fixed field of 4.2 T. Samples were dissolved in deuterated chloroform containing 0.05% of tetramethylsilane (TMS) in which TMS served as an internal standard. Atomic absorption (AA) spectroscopy was performed on a Varian GTA 100. The lamp current was 4.0 mA and the monochromator had a wavelength of 327.4 nm and a slit width of 0.5 nm. A solution of 5 ppm of monomer in



Scheme 1. Structures of benzoxazine monomers and polymers. R represents the amine substituent while R' represents the phenolic linkage.

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