

Preparation, Characterization and Polymerization of Maleimide-Modified Benzoxazine Monomers as a Novel Class of Thermosetting Resin

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[Introduction]

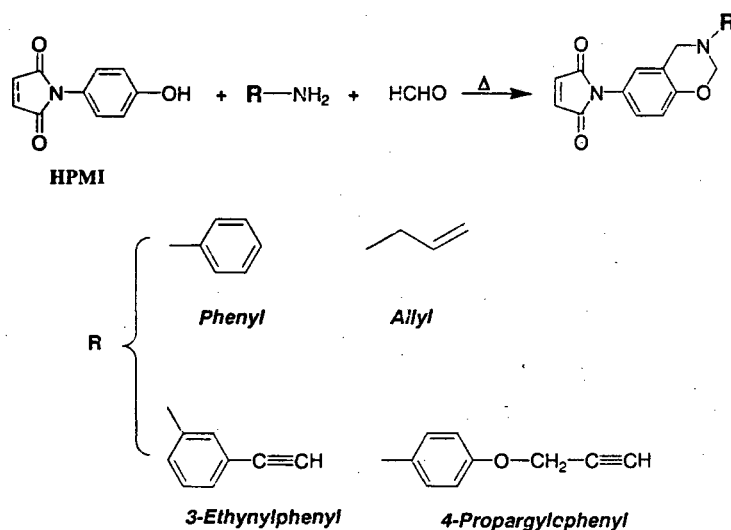
With the recent advancement in technology, a need is becoming more crucial for modern polymers that are easy processable with low cost and capable of surviving in more severe operating environments with a good retention of thermal and mechanical properties.

Polybenzoxazine has been studied as a novel class of phenol resins to overcome the shortcomings of the traditional phenol resins [1]. It can be synthesized from inexpensive raw materials and cured without strong acid as a catalyst and without forming any by-products. Further enhancement on the thermal properties is also strongly needed to meet applications in harsh conditions. We have reported various studies on the preparation of high performance polybenzoxazines by inclusion of clay [2], or alloying with other polymers [3] or by preparing specially designed polymers [4].

Bismaleimides offer excellent thermomechanical properties and withstand high stress at temperature at which typical phenolics and epoxies as well as most high performance plastics are no longer satisfactory [5]. The current study is aimed at preparation of a series of novel hybrid monomers comprising of both benzoxazine and maleimide structures.

[Experimental]

The benzoxazine monomers containing maleimide were prepared from hydroxyphenylmaleimide (HPMI), formalin, and various amines e.g. aniline, allylamine, aminophenyl propargyl ether and ethynylaniline as shown in Scheme 1. In a typical method, the monomers were prepared by the addition of amine in dioxane to



Scheme 1. Preparation of novel monomers

aqueous formalin in dioxane, followed by adding of HPMI. The temperature was raised gradually and the solution was kept stirring at 100°C for 4h. After the removal of dioxane the monomer were purified by recrystallization.

The monomers were processed into film form by dissolving them in dioxane and casting on glass plates followed by solvent evaporation and gradual curing up to 250°C.

[Result and Discussion]

The structure of the novel monomers were confirmed by ¹H-NMR and IR spectra. The DSC cure of the novel monomers, shown in Fig. 1, showed exotherms at different temperature range that correspond the cure of benzoxazine, which occurred firstly, followed by the cure of maleimide along with other crosslink such as allyl, propargyl or ethynyl. The cure of benzoxazine is typically goes through the ring opening of benzoxazine. However, the thermal crosslinking of maleimide goes by the addition polymerization of maleimide double bonds. In case of the presence of another crosslink site like ethynyl (Mal-Bz-Et), propargyl (Mal-Bz-Pg), or allyl (Mal-Bz-Al), the amount of exotherm increased due to further crosslinking.

The monomers were cured up to 250°C. The completeness of the curing was monitored by DSC and IR. Fig. 2 shows the DSC of aniline-based monomer (Mal-Bz) as an example after thermal cure at various temperatures, which indicates the disappearance of the exotherms by the end of 250°C cure. The structure of the proposed network of

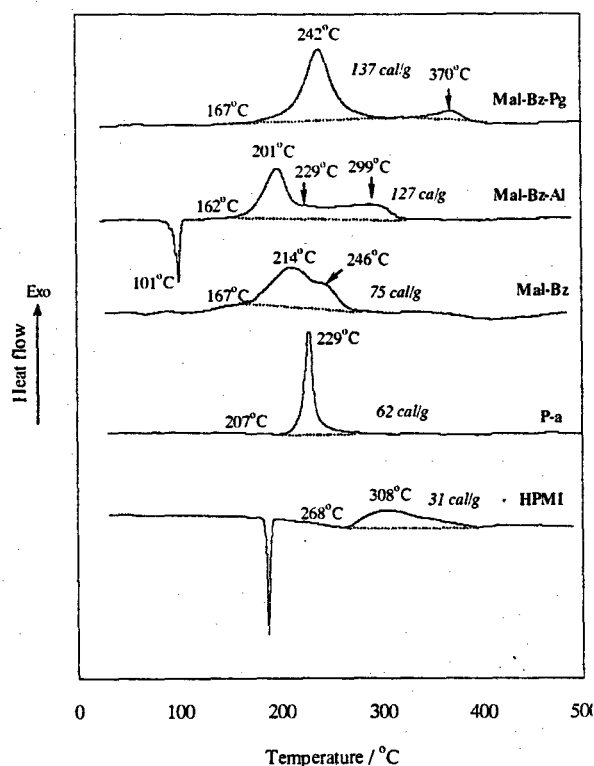


Fig. 1 DSC cure of maleimidobenzoxazine monomers

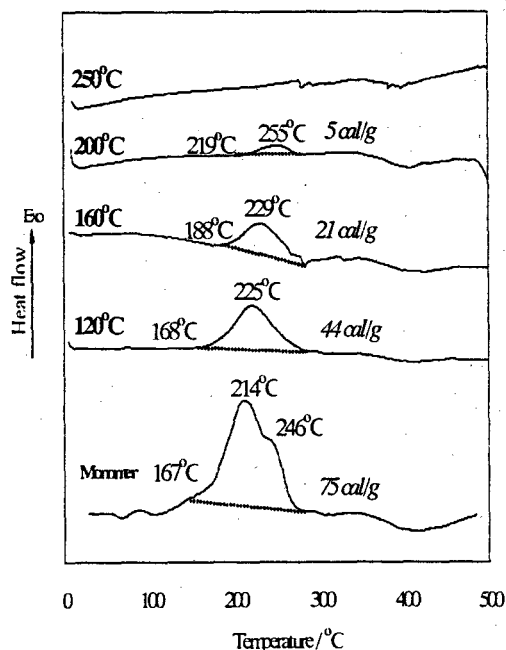
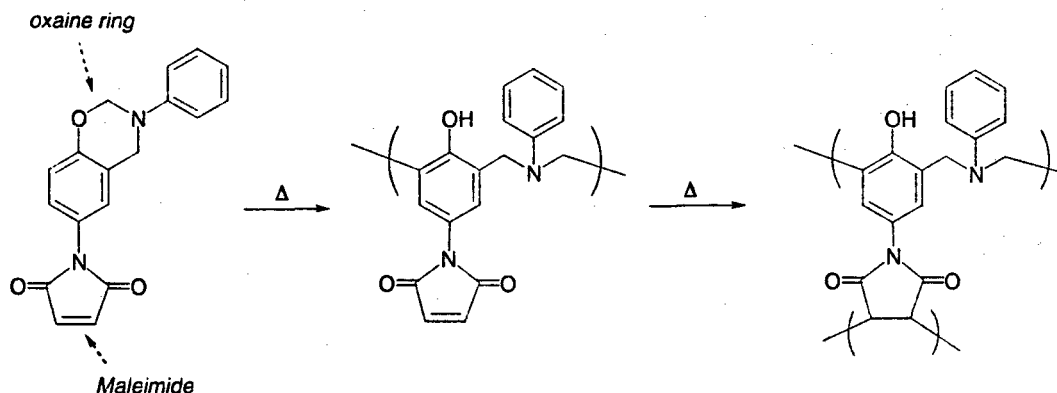


Fig. 2 DSC cure of aniline-based maleimidobenzoxazine monomer after various cure cycle



Scheme 2. Proposed structure of the thermoset obtained from the cure of aniline-based maleimidobenzoxazine

poly(benzoxazine-maleimide) obtained from the cure of (Mal-Bz) is shown in Scheme 2.

The viscoelastic properties of the novel thermosets were investigated by dynamic mechanical analysis. Fig. 3 shows the temperature dependence of the storage modulus (E') of the thermosets after 250°C cure. The DMA showed that the storage moduli of the novel thermosets maintained constant up to high temperature in comparison with the typical PP-a. The glass transition temperatures were as high as 241~335°C.

The thermal stability of the thermosets was studied by TGA. Fig. 4 shows the TGA profiles of the thermosets obtained by the thermal cure of the monomers at 250°C. TGA revealed that the thermoset did not show any weight loss up to 300°C with char yield ranging from 62~70% at 800°C. This reflects the outstanding thermal stability of these novel thermosets.

[Conclusions]

We have prepared new series of benzoxazine monomers containing maleimide structure. The monomers were easily soluble in all common solvent. The novel monomers crosslinked

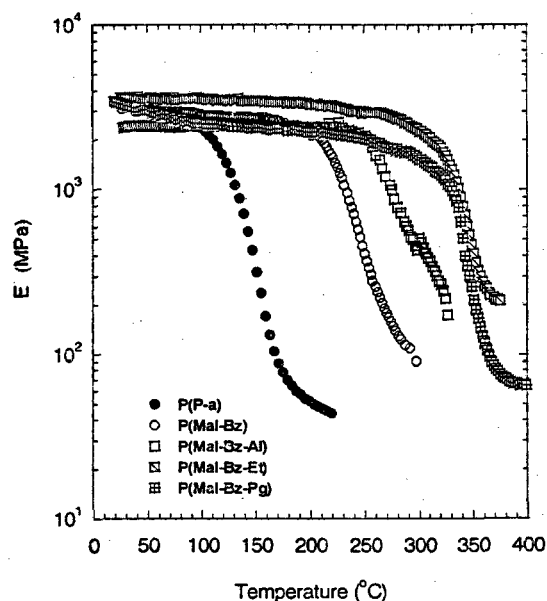


Fig. 3. Viscoelastic properties of thermosets

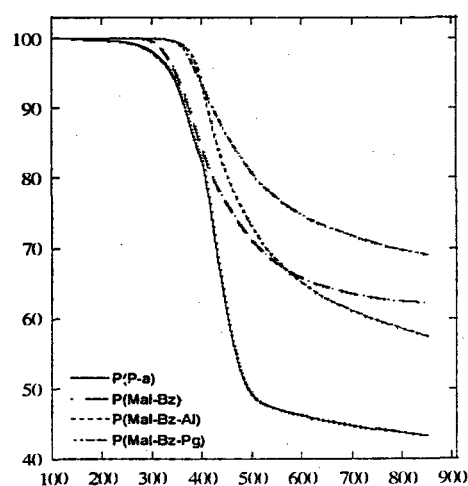


Fig.4 TGA Of thermosets

through the ring-opening polymerization of benzoxazine and addition polymerization of maleimide double bonds along with other crosslink, if any. The thermal cure of the monomers gave novel thermosets with high T_g s and decomposition temperatures. The presence of maleimide as a reactive group towards vinyl monomers offers an opportunity to incorporate benzoxazine structure into vinyl-based polymers via copolymerization which will be addressed in our future studies, which is going to widen the fields of applications of benzoxazines.

[References]

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