Extended Abstract

Properties of Polymer Alloys of High Molecular Weight Benzoxazine and Bismaleimide

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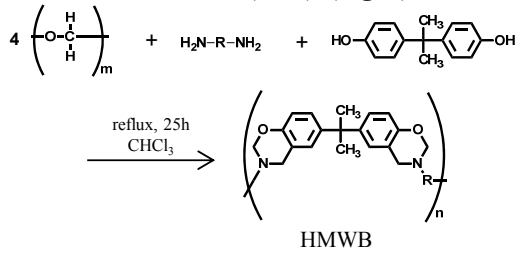
1. Introduction

Polybenzoxazines have been developed as a novel type of phenolic resins that can be afforded by the ring-opening polymerization of benzoxazine monomers. They have unique characteristics such as molecular design flexibility, low moisture absorption, and low dielectric constant. However, there are some shortcomings for polybenzoxazine. Relatively high temperature is needed for the ring-opening polymerization. Also, the cured polymers are brittle.

Recently, we reported preparations of high molecular weight benzoxazines (HMWBs) [1]. As shown in **Scheme 1**, they were synthesized from aromatic or aliphatic diamine and bisphenol A with paraformaldehyde. The toughness of the cured films from HMWBs was greatly enhanced compared with the cured films from the low molecular weight monomers. Additionally, the polybenzoxazines from HMWBs showed excellent thermal properties.

We also reported that polymer alloys of benzoxazine and bismaleimide have much higher glass transition temperatures (T_gs) than those of each homopolymer [2]. The thermal stability also increased with the increase of bismaleimide content.

In this study, we report preparation and properties of novel polymer alloys of polybenzoxazines derived from HMWBs and bismaleimide (BMI). (**Fig. 1**)



Scheme 1. Synthesis of HMWB

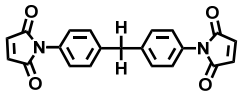


Fig. 1. Chemical structure of BMI

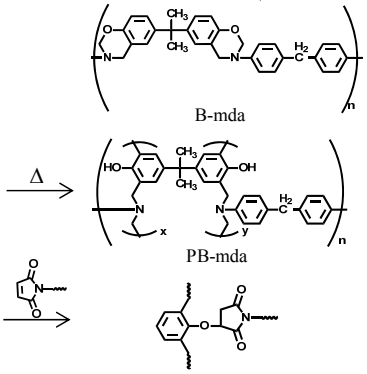
2. Experimental

As shown in **Scheme 1**, we synthesized B-mda from bisphenol A, methylenediamine and paraformaldehyde as pale yellow solid in a 77% yield. B-mda and bismaleimide were mixed at various weight ratios in *N*-methylpyrrolidone. The blend solutions were cast onto glass plates which were pre-treated with dichlorodimetylsilane, dried at 60 ºC for 1 h, and then thermally treated at 100 ºC for 1 h, 160 ºC and 200 ºC for 2 h, at 240 ºC for 3 h each to obtain reddish brown transparent alloy films.

3. Results and Discussion

3.1 Reaction analysis of B-mda/BMI blends

The curing reaction was investigated by FT-IR. It is noteworthy that the absorption at 1200 cm^{-1} assignable to ether bond (C-O-C) increased with the progress of cure. From the IR and DSC results, we considered that the alloys composed of ether linkages between phenolic hydroxyl group formed from ring-opening polymerization of B-mda and double bond of BMI (**Scheme 2**).



Scheme 2. Possible cross linking reaction between PB-mda and BMI

3.2 Thermal properties of alloy films

The viscoelastic properties of B-mda/BMI alloys were studied using DMA. The glass transition temperatures (T_gs) of the alloy films are shifted to higher temperatures with the increase of BMI contents.

The thermal stability of the polymer alloy films was also investigated by TGA. The 5 and 10 % weight loss temperatures are gradually shifted to higher temperatures with the increase of BMI content.

References

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[2] T. Takeichi, Y. Saito, T. Agag, H. Muto, T. Kawauchi, "High Performance Polymer Alloys of Polybenzoxazine and Bismaleimide" *Polymer,* pp. 1173-1179, March 2008.