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Benzoxazine–bismaleimide blends: Curing and thermal properties

K.S. Santhosh Kumar, C.P. Reghunadhan Nair *, R. Sadhana, K.N. Ninan

Propellant and Special Chemicals Group, Vikram Sarabhai Space Center, Thiruvananthapuram 695 022, India

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Abstract

A blend of bisphenol A based benzoxazine (Bz-A) and a bismaleimide (2,2-bis[4(4-maleimidophenoxy) phenyl] propane (BMI), was thermally polymerised in varying proportions and their cure and thermal characteristics were investigated. The differential scanning calorimetric analysis, supplemented by rheology confirmed a lowering of the cure temperature of BMI in the blend implying catalysis of the maleimide polymerisation by benzoxazine. FTIR studies provided evidences for the H-bonding between carbonyl group of BMI and –OH group of polybenzoxazine in the cured matrix. The cured matrix manifested a dual phase behaviour in SEM and DMTA with the minor phase constituted by polybenzoxazine dispersed in an interpenetrating polymer network (IPN) of polybenzoxazine and cured BMI. The IPN possessed improved thermal stability over the constituent polybenzoxazine. A benzoxazine monomer possessing allyl functional groups, 2,2′-bis(8-allyl-3-phenyl-3,4-dihydro-2*H*-1,3-benzoxazinyl) propane (Bz-allyl) was reactively blended with the same bismaleimide in varying stoichiometric ratios (Bz-allyl/BMI), where the curing involved mainly Alder-ene reaction between allyl- and maleimides groups and ring-opening polymerisation of benzoxazine. The rheological analysis showed the absence of catalytic polymerisation of BMI in this case. The overall processing temperature was lowered in the blend owing to the co-reaction of the two systems to form a single-phase matrix. The cured resins of both Bz-A/BMI and Bz-allyl/BMI blends exhibited better thermal stability than the respective polybenzoxazines. The T_g of the IPN was significantly improved over that of polybenzoxazine (Bz-A). However, the co-reaction resulted in a marginal decrease in the T_g of the system in comparison to the polybenzoxazine (Bz-allyl).

Keywords: Allyl polymers; Polybenzoxazine; Bismaleimide; Alder-ene reactions; IPN

1. Introduction

High temperature resistant polymers are in great demand for high-speed aircraft structures and as structural components of space vehicles. Polybenzoxazine is a novel class of phenolics and it can be used as the matrices of high performance composites because of its superior mechanical

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* Corresponding author. Tel.: +91 471 2564951; fax: +91 471 2706136.
E-mail address: cprnair@gmail.com (C.P. Reghunadhan Nair).

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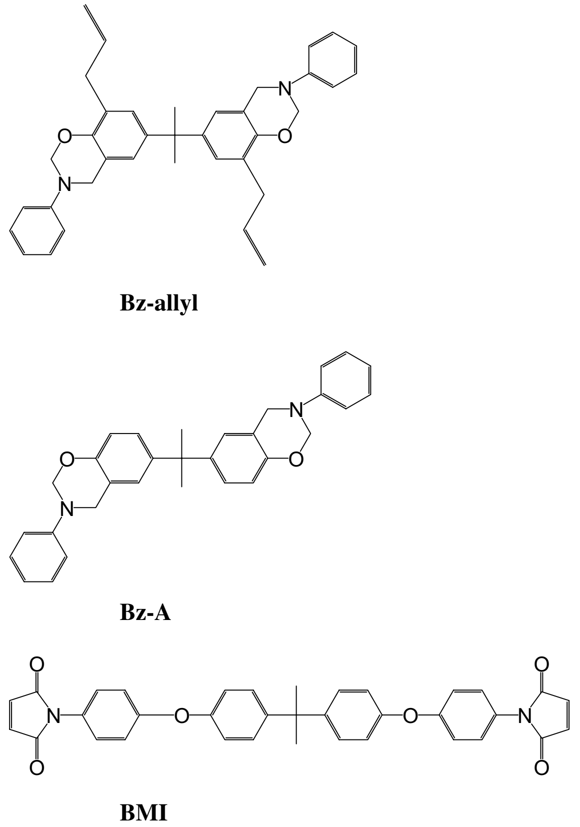
properties and high temperature stability. It possesses excellent processability through a wide range of molecular design flexibility [1–8]. This high performance polymer possesses high T_{g}, low volumetric shrinkage on curing, low moisture absorption, excellent resistance to chemicals and UV light, thermal and dimensional stability and superior electrical properties [9,10]. Although, benzoxazines possess many advantages over other state-of-the-art thermosetting resins, their brittleness, long cure time and higher cure temperature point to the need of modifications on the matrix. The polybenzoxazine properties could be improved or modified via the formation of blends, alloys, copolymers [11–15] and organic–inorganic nanocomposites [16–19]. Blending with an epoxy resin significantly improves the processability of benzoxazines resins, but the resulting binary mixtures require higher curing temperatures than the pure benzoxazine resin [20,21]. Polybenzoxazine containing furan groups showed higher curing temperature (247 °C) [7] and polybenzoxazine–polyimide alloy exhibited a curing temperature of 241 °C [22].

The bismaleimide systems dominate over the other polymer matrices primarily due to their high performance-to-cost ratio and relatively high temperature resistance [23]. They have superior thermal and oxidative stability, low propensity for moisture absorption and good flame retardance. They offer excellent thermomechnical properties and withstand high stress at high temperatures at which typical phenolics and epoxies as well as most high performance plastics are unstable. However, their processability and fracture toughness are not promising. Attempts to reduce brittleness by way of reduction of cross-link density through structural modification, toughening etc. adversely affect the high temperature performance.

Maleimides are known to react with allyl derivatives via Alder-ene reaction. Many studies on allyl-modified bismaleimides have been reported and these materials draw attention in view of ease of processing and good mechanical performance [24–29]. There are a few reports on polybenzoxazine containing imide units as part of the molecule. Preliminary investigations on the co-curing of polybenzoxazine containing BMI as part of the benzoxazine molecule have been reported [13,30–32].

The objective of the present work is to examine the polymerisation and properties of the blends of traditional benzoxazine based on Bisphenol-A – [(6,6′-bis(3-phenyl-3,4-dihydro-2*H*-1,3-benzoxazinyl) isopropane] (Bz-A) and an allyl functionalised benzoxazine [2,2′-bis(8-allyl-3-phenyl-3,4-dihydro-2*H*-1,3-benzoxazinyl) propane] (Bz-allyl) with a bismaleimide (2,2-bis[4(4-maleimidophenoxy) phenyl] propane) (BMI), all possessing closely resembling backbone structures based on bisphenol-A. Bisphenol-A based benzoxazine was blended with the bisphenol-A bismaleimide (Bz-A/BMI) and the curing pattern and thermal properties were studied. Allyl groups were introduced into benzoxazine monomer and then the monomer was reacted with the same bismaleimide. The components of the blends are Bz-A, Bz-allyl and BMI (structures are given in Scheme 1). The structural similarity is expected to facilitate good miscibilisation and thereby to reduce the probability of phase separation in the cured matrix. Apart from this, this bismaleimide is a low melting solid and affords a network with reduced brittleness due to the phenyl ether spacing between the two maleimide groups. The goal of this work also includes the preparation,



Scheme 1. Selected benzoxazines and bismaleimide resins for blending.