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Epoxy-modified, unsaturated polyester hybrid networks

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Abstract

Hybrid polymer networks (HPNs) based on unsaturated polyester resin (UPR) and epoxy resins were synthesized by reactive blending. The epoxy resins used were epoxidised phenolic novolac (EPN), epoxidised cresol novolac (ECN) and diglycidyl ether of bisphenol A (DGEBA). Epoxy novolacs were prepared by glycidylation of the novolacs using epichlorohydrin. The physical, mechanical, and thermal properties of the cured blends were compared with those of the control resin. Epoxy resins show good miscibility and compatibility with the UPR resin on blending and the co-cured resin showed substantial improvement in the toughness and impact resistance. Considerable enhancement of tensile strength and toughness are noticed at very low loading of EPN. Thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) were employed to study the thermal properties of the toughened resin. The EPN/UPR blends showed substantial improvement in thermal stability as evident from TGA and damping data. The fracture behaviour was corroborated by scanning electron microscopy (SEM). The performance of EPN is found to be superior to other epoxy resins.

Keywords: Epoxidised phenolic novolac resins; Epoxidised cresol novolac resins; Hybrid polymer networks; Impact resistance; Toughness; Unsaturated polyester resin

1. Introduction

Unsaturated polyester resins (UPR) are one of the important thermosetting materials used for the fabrication of glass-reinforced plastics and polymeric composites. The widespread use of these resins is due to their relatively low cost, ease of processing, excellent wetting properties with reinforcements, good balance of properties and the wide variety of grades available. UPR are solutions of unsaturated polyester with an unsaturated co-reactant diluent like styrene. Carothers was the first to prepare UPR with well-defined polymeric structures. The general purpose (GP) grade UPR is a blend of styrene with the condensation product of 1,2 propylene glycol with a mixture of maleic acid (MA) and phthalic acid in the form of the anhydride. When cross-linking is initiated with the help of a catalyst and an accelerator, styrene forms polystyrene chains, which cross-link the polyester chains at the sites of unsaturation. The highly

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cross-linked three-dimensional molecular structure of the cured resin gives high stiffness, strength, enhanced glass transition temperature and good heat and solvent resistance. However, they suffer from a major drawback namely, brittleness and poor resistance to crack propagation [1]. Although failure in fibre reinforced plastic (FRP) is often limited to the resin-reinforcement interface [2], areas with relatively low amount of fibres are prone to damage when the product is in use or during demoulding.

UPR are blended with several substances to improve their impact strength and fracture properties. These additives should be miscible in the uncured resin, and get phase separated during curing. The degree of toughening is strongly dependent on the phase-separated morphology [3]. It also depends on the type and proportion of the two components, shape, connectivity and size of the domains [4]. A fine dispersion of elastomer in the UPR matrix and strong adhesion between the matrix and dispersion is desirable. The miscibility and interfacial properties of the additive/resin blends play important roles in the toughening process [5]. The modification of resin, using elastomer additive leads to a randomly dispersed rubbery phase in the material, and helps to dissipate energy for imparting impact resistance. Modification by blending with thermoplastic low profile additives [6] is another possibility. The solubilised or finely dispersed thermoplastics are precipitated into the interstitial spaces within the cross-linking network as styrene is depleted from the solution during cross-linking.

Recently, block copolymers that contain UPR with polyurethanes, polyureas, polysiloxanes, poly- imides, polyoxazolines, or polyglycols have been reported [5]. Another approach is the copolymerisation of hydroxyl or carboxyl terminated liquid rubbers or polyethylene glycols with UPR monomer units [7]. This results in polyesters containing rubber or polyethylene glycol segments in the main chain. Modification of UPR with dicyclopentadiene [8] and bismaleimide [9] has also been reported recently. Reactive blending of UPR with other thermosets is another possibility.

Reactive blending with thermoset resins can lead to deactivating the end groups of UPR chains. In recent years, chemical modification by reactive blending of UPR and other thermosets via semi interpenetrating polymer networks (IPNs) and hybrid polymer networks (HPNs) has been reported. Blending of epoxy resin and polyesters resulting in IPNs [10–13] has been extensively studied. An intercrosslinked network of unsaturated polyester-bismaleimide modified epoxy matrix systems was developed [14]. Interpenetrating networks of varying percentages of bismaleimide in vinyl ester oligomer modified unsaturated polyester matrixes have been developed [15]. Hybrid polymer networks of polyurethane prepolymers and unsaturated polyester are also studied [16–21]. Similarly, chemical bonding between elastomer and UPR using methacrylate end-capped nitrile rubber or epoxy-terminated nitrile rubber (ETBN) or isocyanate end-capped polybutadiene is an attractive route [22]. The mechanical properties of resins and laminates are improved by this technique.

The main objective of this investigation is to study the modifying effect of epoxidised novolac resins on UPR. In the present study, HPNs based on unsaturated polyester and epoxidised novolac resins have been prepared by reactive blending. Epoxidised novolac resins used are epoxy phenol novolac resins (EPNs) and epoxy cresol novolac resins (ECNs). The blends of epoxidised novolac resin with UPR are highly compatible and have a shelf life of at least 6 months. For comparison purposes similar blends of commercial epoxy resin (DGEBA) with UPR are also prepared and properties evaluated. The impact of matrix modification on mechanical, thermal and fracture properties has been examined. To our knowledge, no such a technique has been used for polyester toughening.

2. Experimental

2.1. Materials

General purpose grade UPR (Bakelite Hylam, Hyderabad, India, HSR 8113 M), commercial DGEBA (Athul Polymers India Ltd., Gujarat, India, 103 grade, weight per epoxy [wpe] = 188), methyl ethyl ketone peroxide (catalyst) and cobalt napthenate (accelerator) were supplied by Sharon Engineering Enterprises, Cochin, India. Phenol, *p*-cresol, sodium hydroxide, formaldehyde and epichlorohydrin were supplied by E. Merck India Ltd, Mumbai, India. EPN 1138 (Araldite, wpe = 178) was obtained from Vantico Performance Polymers Pvt. Ltd., Mumbai, India.