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Evaluation of bisacrylate terminated epoxy resins as coatings

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Abstract

The paper describes the effect of backbone flexibility on the coating performance of vinyl ester resin. For this purpose four resins of varying flexibility were prepared. Bisacrylate terminated epoxy resin (D) was prepared by reacting 2 mol of acrylic acid with 1 mol of diglycidyl ester of hexahydrophthalic anhydride. The flexibility of the backbone was increased by chain extension of mono acryloxy derivative of diglycidyl ester of hexahydrophthalic anhydride with sebacic acid (resin G′). Partial cross-linking of resin D containing pendant hydroxyl group was also done by reacting with small amounts of isophorone diisocyanate (D_2I_{10}, D_2I_4).

Fifteen resin formulations were used to evaluate the coating performance in terms of hardness, scratch, adhesion, abrasion resistance and weatherability. Nanosilica and nano-ZnO were used as additives in few formulations for stabilizing transparent coated metallic substrates. The flexibility of the resin backbone (G′) improved adhesion performance of coatings. The increase in the cross-linking improved thermal stability (D_2I_{10} and D_2I_4) of the resin. Weatherability was only marginally affected by the backbone structure.

Keywords: Vinyl ester resins; UV cured; Weathering; Coatings; Thermosetting resin

1. Introduction

The surface properties of materials, particularly their resistance to weathering in exterior applications, can be substantially improved by protective coatings. Such coatings are usually based on highly cross-linked polymers, which show superior weathering performance than their linear counterparts, because chain scissions have less dramatic effects on the polymer durability [1,2]. The commonly used methods for cross-linking of coatings on the surface of a substrate are thermal or photochemical. Out of these techniques UV curing (photochemical) appears to be a valuable alternative to the conventional thermal curing of solvent based clear coats due to: (a) high speed process, (b) low energy consumption because the operation is carried out at room temperature and (c) environmental friendly with nonvolatile evolution. UV curable systems have been used as clear top coatings for providing a good surface protection of materials like metals, wood, paper, plastics and optical fibers.

Several low molecular weight prepolymers such as urethane acrylates, epoxy acrylates, polyester acrylates, polyether acrylates and acrylated oils have been used in UV curing formulations. Acrylated urethane oligomers have a potential to combine the high abrasion resistance, toughness, tear strength and good low temperature properties of polyurethanes with the superior optical properties and weatherability of polyacrylates [3,4]. Recently a series of dendritic polyesters based on poly (amide ester) and poly (amine ester)s having aromatic backbone and modified with (meth)acrylate endgroups have been used as coatings. Studies on phosphorus containing methacrylate based difunctional cross-linking agent having fire resistant property for UV curable formulations have also been reported [5].

The epoxy acrylate resins have the merits of: (a) high reactivity (b) possibility of structural variation in backbone (e.g. bisphenol A or epoxy novolacs) [6–8] which provides good coating properties after curing and (c) excellent adhesion performance (due to the presence of pendant hydroxyl groups). However, the UV cured films based on epoxy diacrylates as oligomers are very brittle and the relative elongation at break is very low [9–11]. A series of epoxy diacrylates synthesized from acrylic acid, diglycidyl ether of bisphenol A and saturated long chain dibasic acid have been recently reported for increasing the flexibility of the backbone [12]. These modified epoxy diacrylates because of their backbone flexibility may be used as oligomers in UV cured coatings of papers and plastics instead of urethane acrylates. There is a need to carry out systematic

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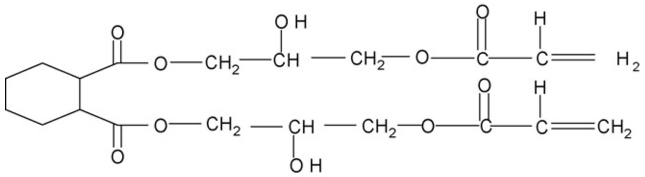


Scheme 1. Bis acrylate terminated cycloaliphatic epoxy resin (resin D).

work for evaluating the effect of flexibility of epoxy acrylate backbone on coating performance.

So far no studies have been reported on the cycloaliphatic epoxy based thermoset resins in UV coating formulations. Such resins are expected to have better weathering characteristics due to the absence of aromatic groups in the backbone. Therefore it was considered of interest to synthesize bisacrylate terminated cycloaliphatic epoxy resins having varying extent of flexibilising units in the backbone.

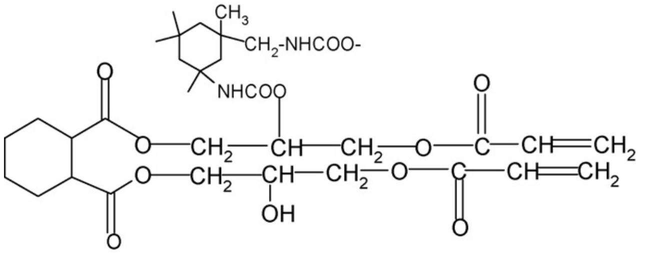
Bisacrylate terminated epoxy resin (D) was prepared by reacting 2 mol of acrylic acid with 1 mol of epoxy resin (Scheme 1). The flexibility of the backbone was increased by incorporating 8-methylene units in the backbone by chain extension of mono acryloxy derivative of diglycidyl ester of hexahydrophthalic anhydride with sebacic acid (resin G′) (Scheme 2). Partial cross-linking of resin D containing pendant hydroxyl group was also done by reacting with small amounts of isophorone diisocyanate (D_2I_{10}, D_2I_4) (Scheme 3). The performance of these resins as coatings on metal, wood, board and glass substrates was evaluated after UV curing.

2. Experimental

2.1. Materials

The epoxy resin (diglycidyl ester of hexahydrophthalic anhydride) was procured from Atul limited, Vadodara, Gujarat, India under the trade name of XR-34. The bisacrylate terminated epoxy resin (resin D) was obtained by reacting epoxy resin and acrylic acid (molar ratio 1:2) in the presence of imidazole as a catalyst at a temperature of 90 ± 5 °C. The reaction was carried out in a four-necked reaction kettle equipped with a mechanical stirrer, oxygen inlet, water condenser, thermometer and was stopped when the acid number reached a value <10 [13].

Chain extension reaction of mono acrylate terminated resin obtained by using 1:1 molar ratios of epoxy resin and acrylic acid was done by reacting with sebacic acid in a molar ratio of 2:1 to yield bis acrylate terminated vinyl ester resin (resin G′) [13].



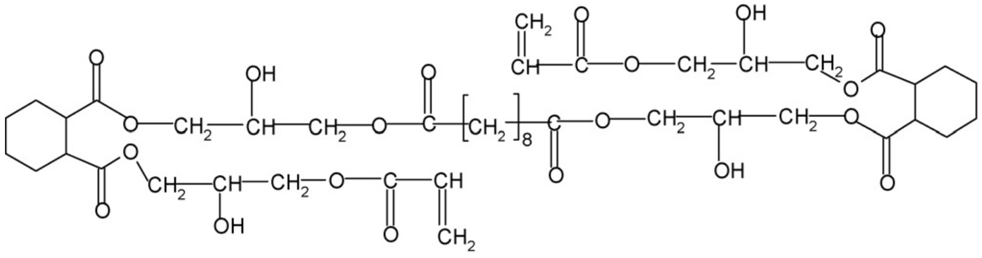
Scheme 3. IPDI modified bisacrylate terminated epoxy resin (resin D_2I_{10} and D_2I_4).

The resin D contains two hydroxyl group/mol which can be reacted with isocyanate to yield urethane linkage. The bisacrylate (sample D) was therefore modified by reacting with varying mole fraction of isophorone diisocyanate. Sample D was reacted with IPDI in molar ratio of 10:1 or 4:1 using methyl methacrylate as a reactive diluent (20 phr on basis of resin D) and the samples have been designated as D_2I_{10} and D_2I_4, respectively [13,14].

The other ingredients used in coating formulations were multifunctional monomers i.e. {tripropane glycol diacrylate (TPGDA) (Fluka) and/or trimethylol propane triacrylate (TMPTA) (Fluka)}, monofunctional monomer {cyclic trimethylol propane formal monoacrylate (CTF) (Actilane 411) (Akzo Novel) and photoinitiators 2-hydroxy 2-methyl phenyl propane 1-one (Darocure1173) (Ciba), 1-hydroxyl-1-cyclohexylphenyl ketone (Irgacure 184) (Ciba). Solvent used was isopropanol (Qualigens). The additives such as silicone (BYK-UV-3500; BYK-Chemie GmbH), dry film stabilizer (Lowlite®92), nanosilica (KADESIT 40–100), nano-ZnO (Zinc Corporation of America) were of commercial grade and used as received. NC filler (surface sealer), anchor coat both procured from Jubiliant Organosys were used as such.

2.2. Coating formulations

Fifteen resin formulations were used to evaluate the coating performance. For this purpose bisacrylate resins D or G′ 37 g, TPGDA 37 g, CTF 21 g, photoinitiator (Darocure 1173) 4 g, silicone additive 0.5 g and dry film stabilizer 0.2–0.5 g were thoroughly mixed. The D_2I_{10} and D_2I_4 coating formulations comprised of resin 35 g, TPGDA 40 g, TMPTA 21 g, photoinitiator (Irgacure 184 in isopropanol) (2:1 ratio, 3 g). All



Scheme 2. Sebacic acid modified bisacrylate terminated epoxy resin (resin G′).