



Effect of glycidyl methacrylate (GMA) content on thermal and mechanical properties of ternary blend systems based on cardanol-based vinyl ester resin, styrene and glycidyl methacrylate

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ABSTRACT

Cardanol-based vinyl ester resin (CVER) was prepared by reacting indigenously synthesized cardanol-based epoxidized novolac resin (CENR) with methacrylic acid (MA) in the presence of triphenylphosphine as catalyst. Five samples of cardanol-based vinyl ester resin containing styrene and glycidyl methacrylate (GMA), as diluents, in the weight ratios 40:0, 30:10, 20:20, 10:30 and 0:40 were prepared at room temperature. Sharp exotherms were observed in DSC scans in the temperature range of 60–170 °C. The onset temperature (T_{onset}), peak exothermic temperature (T_p) and completion temperature (T_{stop}) decreased with increase in GMA content in the ternary blend systems of CVER/styrene/GMA. A broad exotherm was observed after the initial sharp exotherm that was attributed to the etherification reaction. Cured samples were found to be stable up to 205–235 °C and started losing weight above this temperature. Rapid decomposition was observed in the temperature range of 400–550 °C as evidenced by TGA analysis. Increase of GMA content in ternary blend systems of CVER/styrene/GMA lowered the tensile strength progressively and enhanced the impact strength and elongation-at-break. The cured films of VER containing mixture of styrene and GMA exhibited good gloss and impact resistance. The chemical resistance of cured films of VER containing mixture of styrene and GMA showed good resistance to acids, deionized water, synthetic sea water and mineral turpentine oil.

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1. Introduction

The synthesis of polymer from renewable resources is a preferred research topic nowadays. This is due to the eco-friendly grouping of the related polymers which contribute to environment sustainability and to diminution of global warming by replacement of petroleum-based resins. In this respect, cashew nut shell liquid (CNSL) holds considerable promise as a source of unsaturated hydrocarbon, an excellent monomer for thermosetting polymer production for the “greening” of thermosets. CNSL occurs as an amber-coloured viscous liquid in the soft honeycomb structure of the shell of cashew nut, a plantation product obtained from the cashew tree, *Anacardium occidentale* L., Native to Brazil, the tree grows in the coastal areas of Asia and Africa. CNSL and its distillation product cardanol and CNSL-residue have become very important raw materials because of their versatile uses in surface coatings, plastics, rubbers, synthetic chemicals and drugs, synthetic wood

and other fields. The multisided applications of CNSL are due to the presence of the phenolic group in its structure, combined with an unsaturated long side chain. Cardanol, extracted from CNSL, has been the attraction for many researchers for the production of novolac- or resol-type phenolic resins in the past [1–6]. The cardanol-based novolac-type phenolic resins may be modified by reacting with epichlorohydrin to produce polyepoxy resins having superior performance in various fields [7–10]. The introduction of unsaturation along the epoxy resin backbone by the reaction with acid functional acrylic/methacrylic monomer can produce a hybrid resin system to produce an eco-friendly vinyl ester resin (VER) system.

VERs are the addition product of an epoxide resin and ethylenically unsaturated monocarboxylic acid containing ester groups and carbon-to-carbon double bond linkages at the end of the polymer chain [11–15]. VERs are the widely used thermosetting materials. VERs have terminal unsaturation, a form referred to as ‘structoterminal’, where they are very reactive, causing it to cure rapidly and enable to give a product of desirable properties. Because the viscosity of the neat resin is considerably high, diluents are needed to be used in the resin formulations. These resins can be used

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in the neat form (i.e. no diluent) or they can contain a vinyl-type reactive comonomer (viz., styrene, acrylates, vinyl toluene, trimethylpropane triacrylate, etc.) or a non-reactive diluent (e.g. methyl ethyl ketone or toluene) [11,16,17]. Undiluted VER varies in physical state from semisolid to solid and, therefore, both the reactive and non-reactive diluents can provide the workable viscosity levels. Reactive diluents are preferred because they provide systems with appropriate reactivity, viscosity and coatibility before cure, and desired cross-linked density, strength, percent elongation, hardness, chemical resistance, and surface finish, etc., after cure.

Styrene is the most commonly used reactive diluent because of its low cost, high compatibility, and reactivity. Styrene imparts good mechanical properties and heat distortion resistance to cured resins. The styrene content in these resin formulations ranges from 30 to 60 wt% [12,18]. Substitution of styrene by small quantities of α -methyl styrene in VERs acts as an exotherm peak depressant and increases cure time [19,20]. Other reactive diluents used in the resin formulations are methyl methacrylate (MMA), ethyl methacrylate, vinyl toluene, dicyclopentadiene diacrylate [16], etc.

There has been considerable dearth of literature pertaining to systemic studies on use of functional vinyl monomer such as glycidyl methacrylate (GMA) as a reactive diluent [21]. However, studies on copolymerization of GMA and MMA using free-radical as well as group transfer polymerization have been reported [22]. Copolymerization of GMA and VER through a vinyl double bond yields a repeating unit containing pendant epoxide groups. GMA is a versatile bidentate monomer capable of imparting oxirane functionality to VER containing styrene or other vinyl monomers.

In the present article, we have reported the results of the effects of the structural variation of cardanol-based vinyl ester resin (CVER) in the presence of mixture of styrene and GMA (40%, w/w) as reactive diluents, on curing characteristics, thermal behaviour and mechanical properties of cured resins.

2. Experimental

2.1. Materials

Cardanol (M/s Dheer Gramodyog Ltd., Kanpur), formaldehyde (40% solution from M/s Qualikem Industries, New Delhi), methanol (M/s S. D. Fine Chemicals Ltd., Mumbai), epichlorohydrin (M/s Ranbaxy Laboratories Ltd., Punjab) and methacrylic acid (M/s CDH Pvt. Ltd., New Delhi) were used for the synthesis of resin. The catalysts used were *p*-toluene sulphonic acid ((PTSA) – E. Merck, New Delhi), sodium hydroxide and triphenylphosphine (M/s CDH Pvt. Ltd., New Delhi). Benzoyl peroxide and hydroquinone (E. Merck, New Delhi) were used as initiators. The diluents used were glycidyl methacrylate (GMA – density 1.074, boiling point 195 °C) and styrene (density 0.906, boiling point 145 °C).

2.2. Methods

2.2.1. Synthesis of cardanol-based vinyl ester resin (CVER)

CVER was synthesized using cardanol by employing a similar procedure as mentioned in our previous publication [14]. The novolac resin synthesized using cardanol (C) and formaldehyde (F) (C:F = 1:0.8) using PTSA as catalyst (0.5% based on cardanol), was reacted with molar excess of epichlorohydrin and 40% solution of sodium hydroxide at 120 °C to form cardanol-based epoxidized novolac resin. This epoxy resin was reacted with methacrylic acid using 1:0.9 mole ratio catalysed by triphenylphosphine (TPP) as catalyst (1% by weight of the resin) and hydroquinone (200 ppm as inhibitor) at 90 °C in nitrogen atmosphere for about 5 h to obtain a product with acid value <10 [23].

Table 1
Sample designation.

S. no.	Vinyl ester	Styrene	GMA	Sample designation
1	100	40	0	CVER _{8G04}
2	100	30	10	CVER _{8G13}
3	100	20	20	CVER _{8G22}
4	100	10	30	CVER _{8G31}
5	100	0	40	CVER _{8G40}

2.2.2. Curing of CVER

Styrene and GMA were used as reactive diluents for curing of CVER (100:40 (w/w), i.e. 100 g of CVER and 40 g of mixture of both the diluent). Five samples of cardanol-based vinyl ester resin containing styrene and GMA, as diluents, in the weight ratios 40:0, 30:10, 20:20, 10:30 and 0:40 were prepared by physical mixing using benzoyl peroxide (2 wt%) at room temperature (refer Table 1). Half of the mixture of reactive diluents was mixed with half the resin and to the other half of the resin benzoyl peroxide was added in two separate flasks. Both the flasks were sealed and kept under refrigeration to avoid premature polymerization prior to use. Equal amounts of the solution were then taken and stirred vigorously with a glass rod at room temperature in a glass vial. Finally, the mixture was poured in an iron-mould preheated in a hot-air oven.

2.2.3. Preparation of films

The films of blend systems of CVERs were applied to the mild steel panels for evaluation of the mechanical properties and on the glass panels for the evaluation of the resistance to water, acid, alkalis and solvents. The panels were prepared by applying the films using the Bird film applicator (Sheen Instrument Ltd., UK). A dry film thickness of about 100 μ m was maintained on all the panels. These films were then cured as per the curing schedule obtained from DSC. These coated glass panels were sealed from three sides of the width of 10 mm using molten paraffin wax. Then, these panels were immersed in different acids, alkalies and solvent solutions for 6 months. Observations were noted at one-month intervals. The coated glass panels were half dipped in the chemicals and rest of the portion was left unexposed to compare the film properties.

2.3. Characterization of the prepared samples

2.3.1. FTIR spectroscopic analysis

The purified resin was subjected to Fourier-transform infra-red (FTIR) spectroscopic analysis, to monitor the appearance and disappearance of various functional groups in the wavelength range of 400–4000 cm^{-1} by Perkin Elmer FTIR, RX-1 spectrophotometer.

2.3.2. ¹H NMR and ¹³C NMR spectroscopic analysis

¹H NMR and ¹³C NMR (nuclear magnetic resonance) analysis of the purified resin was recorded on Bruker 400 MHz FT-NMR spectrophotometer in the temperature range of –90 to 80 °C. About 20 mg of the sample, in 10 mm diameter sample tube, was dissolved in about 5 ml of chloroform-*d*₁ (CDCl₃), which was used as a solvent, along with tetramethylsilane (TMS) as internal standard.

2.3.3. Gel permeation chromatographic (GPC) analysis

Gel permeation chromatograph was recorded with E. Merck A.G., Darmstadt Germany, GPC (E. Merck column oven injection Model L-7350, E Merck Lachrome-7490 R.I. Detector) to determine the number average molecular weight of the synthesized resins. The column (E. Merck) used for GPC calibration was of cross linked polystyrene. THF was used both as mobile and stationary phase for the experiment. Polystyrene standards of different molecular weights viz. 580, 950, 2050, 5100, 11,600 and 30,300 g mol^{-1} were

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