



Preparation and characterization of novel vinyl ester formulations derived from cardanol



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ABSTRACT

In this study, two commercially available epoxidized cardanol resins, NC 514 with approximately two epoxies per molecule and LITE 2513HP with approximately one epoxy per molecule were methacrylated and the methacrylated NC-514 resin (NC514VE) was used as the cross-linker unit and the mono-functional methacrylated LITE monomer (LITEVE) was used as the reactive diluent in both conventional DGEBA vinyl ester resin (DGEBAVE) and in NC514VE resin at changing concentrations. Resin formulations of NC514VE using styrene as the reactive diluent were also prepared. The methacrylated products were characterized via spectroscopic techniques like FT-IR and ¹H NMR spectroscopy. The viscosities of the liquid resin mixtures at 30 °C were examined and the curing behavior was analyzed via Differential Scanning Calorimetry (DSC). After the cure, the thermo-mechanical properties of the resins were determined via Dynamic Mechanical Analysis (DMA) and mechanical properties were determined via tensile tests. According to thermal gravimetric analysis (TGA) data, at 30 wt% co-monomer content, the temperature of 5% degradation were in 270–300 °C temperature region meaning that the samples were stable until this temperature range. The effect of the diluent content and the structures of the different monomers on both liquid resin and cured resin properties were also evaluated.

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1. Introduction

Polymers which have become indispensable materials of our modern lives are mainly produced from petroleum derived raw materials. Replacing the petroleum based raw materials used in the production of polymeric materials with renewable plant-based ones would contribute to global sustainability without the depletion of scarce petroleum resources and would also offer both environmental and economical advantages due to the renewable nature, potential biodegradability, world wide availability, relatively low price, and rich application possibilities of these plant-based raw materials. In this context, there is a growing commercial and academic interest in developing polymers from plant based resources which are renewable.

A thermoset resin is defined as a plastic material which is initially a liquid monomer or oligomers or a pre-polymer, that is cured by either application of heat or catalyst to become an infusible and insoluble material. Typical examples of thermosetting liquid molding resins are phenolic resins, amino resins, unsaturated polyester resins, vinyl ester resins and epoxy resins [1]. Vinyl ester resins (VEs) are thermoset resins which are unique in that they combine the chemical,

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mechanical and thermal properties of epoxy resins with the rapid cure of unsaturated polyester resins (UPEs), thus they are used in a variety of industrial applications such as surface coatings, adhesives and composites. The general-purpose vinyl ester is prepared by the reaction of diglycidyl ether of bisphenol A (DGEBA) epoxy resin with methacrylic acid. Due to the high viscosity of VEs, the VE polymer is dissolved in a reactive diluent which is a vinyl monomer such as styrene, α -methyl styrene, acrylates and methacrylates to achieve the desired low viscosity of a liquid molding resin [2]. These vinyl monomers participate in the cross-linking reactions by creating a link between adjacent vinyl ester molecules.

So far many renewable resources have been used to produce thermosetting polymers such as plant oils [3–12], cashew nut shell liquid (CNSL) [2,13,3,8,14–28] as well as lignin [3,8], carbohydrates [8,29,30] and soy protein [3]. Styrene and other common reactive diluents used with unsaturated polyesters (UPEs) and VEs, are hazardous air pollutants (HAPs) and volatile organic compounds (VOCs) so there has been an effort to replace these monomers (eg. styrene) with less volatile alternative monomers. In this context, methacrylated fatty acid based monomers were used in VE resins as styrene replacements giving properties comparable to those of commercial VE formulations with significantly reduced VOC emissions, when ternary blends of the VE, methacrylated fatty acid based monomers and styrene were used [31]. The brominated derivative of the methacrylated stearic acid was similarly used in Bisphenol A type and Novalac type VE resins to introduce fire retardance to these systems and decrease the VOC emissions [32]. These fatty acid based monomers were also used in triglyceride based thermosetting polymers such as acrylated epoxidized soybean oil, maleinated soybean oil monoglyceride and maleinated castor oil monoglyceride as the reactive diluent, however viscosities required for composites industry were only established when the plant-oil based cross-linker is used with a mixture of the fatty acid based monomer and styrene [33,34]. Lignin based single aromatic compounds, such as guaiacol and eugenol were also methacrylated and used as the reactive diluent in VE resins and it was demonstrated that these lignin based monomers can completely replace styrene in liquid molding resins without sacrificing cured resin thermal performance [35].

Among the renewable resources that can be used to prepare thermosetting polymers the Cashew nut shell liquid (CNSL) is an important one due to its composition of phenolic compounds that offer many routes for chemical modification. Cashew nut shell liquid constitutes nearly one-third of the total nut weight; thus, a large amount of CNSL is formed as a by-product of the mechanical processes used to render the cashew kernel edible and its total production approaches one million tons annually. The main component of thermally treated CNSL is cardanol which is a phenol derivative mainly having a meta substituent of a C15 unsaturated hydrocarbon chain with one to three double bonds [36]. This thermally treated CNSL has various potential industrial utilizations, such as resins, friction lining materials, and surface coatings; however, only a small part of the CNSL that is produced is used in the industrial field [13].

Thus cardanol has taken serious attention by researchers and there are a number of reviews that analyzes the various polymers and useful products that can be obtained from cardanol [3,23,26,37,38]. The cardanol based polymers can be classified into four different groups; cardanol based phenolic resins, epoxy resins, their acrylates (or methacrylates) and vinyl ester resins. There are a number of studies in literature on the use of CNSL and cardanol in phenol formaldehyde condensation polymers and the synthesis and characterization of cardanol based Novalac or Resoles type phenolic resins [26,39,40].

In a group of studies on cardanol based epoxies, the addition of cardanol epoxidized through its phenol hydroxyls [36] and cardanol-based epoxidized Novalac resins [14] to Bisphenol A type epoxy resins resulted in considerable improvement in elongation-at-break [36] and a higher energy absorption at break [14] upon curing by a polyamine hardener. In another study on cardanol based epoxies, polycardanols epoxidized through the unsaturation sites of the alkyl chains were enzymatically synthesized and cured with amine hardener, phenalkamine thermally at 150 °C to yield transparent polymeric films with a high gloss surface within 3 h [15]. In a recent study, a bio-based thermoset resin system consisting of benzoxazine and epoxy pre-polymers were synthesized from cardanol and a new curing system has been developed by varying the proportion of these cardanol based monomers in the copolymer mixture. These bio based liquid monomers were suggested to be good candidates for improving the processibility and flexibility of conventional epoxy and benzoxazine thermoset polymer matrices for electronic packaging materials [22].

For the preparation of cardanol based monomers that are reactive in radical polymerization, first attempts were made by introducing acrylate or methacrylate functionality to the phenol hydroxyl of cardanol. In a representative study, the radical solution polymerization of the cardanyl acrylate monomer obtained through the reaction of cardanol with acryloyl chloride, in toluene in the presence of azobis-iso butyronitrile initiator yielded a linear polymer which upon removal of solvent underwent crosslinking on exposure to air (or UV light) to give an insoluble transparent film. In bulk and suspension polymerization, the polymer was reported to undergo *in situ* crosslinking in the absence of any crosslinking agent [17]. In a similar manner the suspension co-polymerization of cardanyl acrylate or methacrylate with methyl methacrylate, styrene and acrylonitrile yielded cross-linked beads with a uniform size distribution [18]. In another related study the thermal behavior and stability of copolymer beads obtained through the suspension copolymerization of cardanyl acrylate with vinyl monomers such as methyl-, ethyl- and butyl-acrylate has been investigated [19]. The curing kinetics of cardanyl acrylate and styrene monomer under isothermal conditions has also been investigated via Differential Scanning Calorimetry method [20].

For the production of vinyl ester resins from cardanol, in a series of articles, Sultania et al. studied the synthesis and curing of cardanol based epoxidized novolac vinyl ester resin [2,13,24,25]. For this purpose the cardanol-based epoxidized novolac vinyl ester resin (CNEVER) was prepared by reacting the synthesized cardanol-based epoxidized novolac (CNE) resin and methacrylic acid (MA) in a CNE:MA molar ratio of 1:0.9, in presence of triphenylphosphine as catalyst at 90 °C. The CNEVER resin was cured with changing amounts of styrene in the presence of benzoyl peroxide at 120 °C and differential scanning calorimetric (DSC) technique was used to investigate the curing behavior. Thermal stability of the vinyl ester sample

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