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Synthesis of novel vinylester from dicyclopentadiene prepolymer

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ABSTRACT

In this paper, for the first time a vinyl ester prepolymer was synthesized from epoxided dicyclopentadiene prepolymer commercialized under the trade name Tactix 756. Indeed this molecule has an interesting chemical structure with aromatic and aliphatic rings, for use in composite materials. Also, it is an industrial compound that presents the advantage to be a non-classified harmful compound. A new synthesis way has been established: the synthesis of the Tactix methacrylated carried out directly in the presence of styrene, which plays both the role of solvent during the methacrylation reaction and the purification, and as reactive diluent for reducing the viscosity and prepare VE materials. This process is very interesting and avoids the use of solvent for the preparation of the VE materials. Three VE materials have been performed with different proportions of styrene. These obtained materials have a good thermal stability, up to 400 °C and have a Tg from 153 to 169 °C, for 61 wt % and 35 wt% of styrene, respectively. These Tg values are high compare to Tg value of standard based on Diglycidyl Ether of Bisphenol A methacrylated.

1. Introduction

Vinylester (VE) resins are one important class of thermosetting resins that combine the chemical, mechanical and thermal properties of epoxy resins with the rapid cure as in the case of unsaturated polyester resins (UP). Thus, VE resins are used for various industrial applications such as surface coatings, adhesives, printed circuit board coatings, radiation curable inks, spherical lens materials and composites [1–6]. From structural point of view, VE prepolymers consist in the addition products between epoxy precursor and (meth)acrylic acid [7–9]. Epoxy precursors most commonly used in the synthesis of VE prepolymers are Diglycidyl Ether of Bisphenol A (DGEBA) and epoxidized novolac. By means of the two terminal reactive double bonds, VE prepolymers can easily form cross-linked network structures by a free-radical polymerization mechanism. Due to the high viscosity of VE prepolymers, it is necessary to add some reactive diluents such as vinyl monomers, viz., styrene, α-methyl styrene, acrylates and methacrylates [10–13]. These reactive diluents take part in the curing reactions and copolymerize with VE prepolymers [11]. Styrene is highly polymerizable with acrylate of methacrylate functions. This high reactivity is stated by their Alfred–Price *Q* and *e* coefficients. The *Q* value is related to the degree of resonance. The higher is *Q*, the more the double bond is stabilized by resonance. The e value represents electro-donating or electro-accepting properties

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of a double bond. A positive value is characteristic of an electron withdrawing double bond [35]. For styrene and methyl methacrylate, Q are close, respectively of 1.0 and 0.8, and e are opposite, respectively of −0.8 and 0.4, which proves their reactivity as comonomers.

The methacrylated Diglycidyl Ether of Bisphenol A is the vinylester prepolymer most commonly used because it allows to obtain materials with a good thermal resistance, and in particular a high glass transition temperature value (Tg) about 140 °C with styrene as reactive diluent. However as we know Diglycidyl Ether of Bisphenol A methacrylated is a derivative of bisphenol A which is a compound classified as Carcinogenic, Mutagenic, Reprotic (CMR). The primary focus in the present article is to substitute the Diglycidyl Ether of Bisphenol A (DGEBA), by a non-CMR product.

Some publications report the use of vegetable oils to synthesize vinylester (VE) prepolymers [14,15], and show that with a high functionality of 8 methacrylic functions, the glass transition temperature value (Tg) reaches 70 °C with styrene as reactive diluent. Moreover, diepoxided cardanol was used for the synthesis of vinylester (VE) prepolymers allowing to reach a glass transition temperature value (Tg) of 80 °C with styrene as reactive diluent [16]. However, oil and cardanol cannot reach glass transition temperature value similar to the ones of materials based on DGEBA (i.e. 150 °C). Therefore the substitution of DGEBA by non-harmful epoxy prepolymer remains a challenge to propose high Tg vinyl ester polymers.

In the present article, we discuss the use of an epoxy novolac resin (Tactix 756), commercialized by Huntsman and based on dicyclopentadiene, for the synthesis and formulation of vinylester materials. Indeed, the Tactix 756 molecule has an interesting chemical structure with aromatic and aliphatic rings that could be advantageously used in composite materials. Furthermore, this is an industrial compound that presents the advantage to be a non-harmful and non-CMR compound. However, the epoxy Tactix 756, which is a solid compound, has never been modified by the addition of methacrylic acid to give a vinylester (VE) prepolymer. Therefore we proposed a route to functionalize Tactix and open its use in vinyl ester as a substituent of DGEBA.

2. Experimental section

2.1. Materials

TACTIX 756 was obtained from Huntsman and used as supplied, the epoxy equivalent weight (EEW) is given by supplier between 245 and 265 g/eq, that is an epoxy value *I* between 3.7 and 4.1 eq/kg. Methacrylic acid (contains 250 ppm MEHQ as inhibitor, 99%), styrene ($\geqslant$99%), triphenylphosphine (TPP) ($\geqslant$98.5%), hydroquinone ($\geqslant$99%) and tetrahydrofuran (THF) (contains 250 ppm BHT as inhibitor, $\geqslant$99.9%) were purchased from Sigma Aldrich and used as received.

2.2. Synthesis of TACTIX-based VE prepolymer in the presence of the reactive diluent: the styrene

TACTIX-based VE prepolymer was synthesized by the reaction between TACTIX 756 and methacrylic acid (MA). VE prepolymer was obtained using the following procedure: TACTIX 756 (10 g, 0.014 mol), methacrylic acid (4.9 g, 0.057 mol), Styrene as a solvent (10 mL), TPP as a catalyst (1% by weight of total weight of Tactix 756 and methacrylic acid) and hydroquinone as inhibitor (0.25% by weight of total weight of Tactix 756 and methacrylic acid) were mixed in a round bottom flask equipped with a mechanical stirrer and a thermometer. The system was heated at 80 °C under stirring for about 20 h.

In order to remove the unreacted MA, the prepared prepolymer was treated with potassium carbonate (K_2CO_3), stirring for 2–3 h at 30 °C. Styrene was added through of the reaction because of the evaporation.

MA in the form of an acid salt was extracted by water. The prepolymer TACTIX methacrylate vinylester (TMAVE) was a viscous brown product.

2.3. Formulation and curing of VE materials: TACTIX-based VE prepolymer/Styrene

TACTIX-based VE prepolymer was already blended with styrene (ST) as reactive diluent to form VE resins. Free radical polymerization was initiated with 2 wt% tert-butyl peroxybenzoate (Trigonox C). The mixture was poured into an aluminum mold and allowed to cure 15 h at 120 °C and 2 h at 150 °C.

2.4. Measurements

2.4.1. Nuclear magnetic resonance spectroscopic analysis

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker AC 400 NMR spectrometer operating at 400 MHz at room temperature with deuterated acetone as solvent. The chemical shifts were reported in ppm relative to tetramethylsilane as internal standard.

2.4.2. Epoxy titration

Epoxy equivalent Weight, EEW, represents amount of grams of resin that contains one molecule of an epoxy group. We start about the epoxy group reaction with acid halide. The epoxy groups are opened with hydrochloric acid in excess in the