



Fatty acid-based cross-linkable polymethacrylate coatings

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ABSTRACT

In this paper, novel epoxy prepolymers from oleic acid-based monomers were cross-linked to prepare thermosets for coating application. For this purpose, methacrylate moiety was firstly added to oleic acid via Steglich esterification prior to conventional radical polymerization. The resulting oleic acid-based polymer was obtained with a number molecular weight 40,000 g/mol (DP = 110). Then the internal unsaturations of this polymer were epoxidized at different epoxy contents to provide cross-linkable functionalities. Based on a study of the internal epoxy reactivity of a model compound with different nucleophiles, the synthesized oleic-based polymers with epoxy functions hanging off the main chain were successfully cross-linked with succinic anhydride. Dynamic mechanical and thermal analyses, as well as swelling index properties have been studied for all the resulting thermosets. Additionally, the properties of coatings on steel substrates were studied to determine coating hardness, and adhesion. The results of this work provide evidence of the potential of these materials as bio-based coatings and adhesives.

1. Introduction

Since the last few years, epoxy thermosets represent one of the best performing commercially available chemical networks due to their excellent mechanical strength, adhesion as well as chemical, electrical and heat resistance after curing [1]. The oxirane group can react with varying curing agents, such as amines [2,3], acid anhydrides [4], and Lewis acids or bases [5], to afford thermosets by cationic polymerization [6] or by ring opening reactions [7]. The adjustable properties of the cured thermosets depend greatly on the environment of oxirane ring and type of curing agent employed. Hence, this class of thermoset materials has been used extensively in a variety of applications as unique building block for high-performance adhesives [8], paints [9], coating [10], flame retardant [11], or nanocomposites [12] in the last decades.

Currently, most of the epoxy monomers used are derived from petroleum resources and present toxic issues leading to harmful environmental and health effects [13,14]. For instance, the most common epoxy monomers used in industry are synthesized from bisphenol A diglycidyl ether (BADGE), cycloaliphatic epoxies, or epoxy phenol novolac resins [15]. Hence, in most of these cases, the reagent used to add

epoxy functions on these monomers is epichlorohydrin which is a carcinogenic, mutagenic, and reprotoxic (CMR) substance. Hence, *in order to satisfy the industrial need for polymers compatible with the environment, the design of bio-based and less toxic epoxy network has become an important challenge to enhance sustainable development in the last decades [16,17,18].*

Among the most promising renewable resources for the production of eco-friendly epoxy thermosets, vegetable oils (VOs) and their fatty acids (FAs) derivatives appear as an interesting alternative for various reasons including their wide availability, their low glass transition temperature (T_g), their low cost and especially their low toxicity toward human and environment [19]. Additionally, VOs and unsaturated FAs contain reactive sites, particularly the double bond and the carboxylic acid, which can be suitably functionalized to tailor monomers or polymers with cross-linkable functions as epoxy group [20,21,22,23]. Indeed, the internal unsaturations of fatty acids can be easily epoxidized using enzymatic process or even organic pathways where the couple $H_2O_2/HCOOH$ acts efficiently onto various triglycerides [24]. However, epoxy groups resulting from the epoxidation of the triglyceride unsaturations are internal epoxides and generally induce a lower reactivity than terminal moieties of commercial prepolymers and has

Abbreviations: SEC, size exclusion chromatography; DSC, differential scanning calorimetry; TGA, thermogravimetric analysis; DMA, dynamic mechanical analysis; NMR, nuclear magnetic resonance; MAEO, 2-(methacryloyloxy)ethylolate; PMAEO, poly(2-(methacryloyloxy)ethylolate); MEK, methyl ethyl ketone

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only a low content in the vegetable oils backbone [25]. Hence, the use of epoxidized triglyceride are generally limited to a few applications as plasticizers or stabilizers for PolyVinyl Chloride (PVC) synthesis [20]. Innovative polymers from unsaturated fatty acids may be synthesized by free radical polymerization to provide epoxy thermosets with high epoxy content inducing interesting adhesion surface properties after curing. For this purpose, it is necessary to graft polymerizable moieties on the unsaturated fatty acids, such as methacrylate function, to afford reactive monomer through free radical polymerization [26,27,28,29]. Several research groups have used this strategy to solve the drawback of the low reactivity of natural triglycerides internal unsaturations through radical process [30,31,32,33,34]. For instance, Wang et al. have recently designed suitable monomers from soybean oil by using a two-step method of (meth)acrylation [35]. Then, novel sustainable bio-based polymers from soybean oil with cross-linkable functionalities were successfully obtained by using free radical polymerization and subsequent epoxidation [33]. The resulting soybean-oil thermosets have shown better mechanical and thermal properties compared to thermosets resulting from the epoxidized soybean-oil-anhydride which have less cross-linkable functions. Various potential practical applications were proposed but none of them was yet studied in their work. In addition, an alternative to their two-step (meth)acrylation process can be performed because Maiti et al. proposed a one-step strategy to provide methacrylate monomer using Steglich esterification [30]. Then, the internal unsaturations of the resulting polymer can be easily epoxidized to add cross-linkable functionalities [30]. Nevertheless, polymers with high epoxy content may also induce high viscosity which may require high processing temperature at which polymers are sensitive to degradation. Partially epoxidized polymers can be an alternative way to properly regulate the viscosity of such polymers. Several research groups have already reported strategies to partially epoxidized triglycerides by simply regulating the amount of peracids formed *in situ* during the process of epoxidation or by varying the reaction time [36,37]. Such polymers with a low T_g could be used as epoxy prepolymers without the need of hazardous reagents such as epichlorohydrin. These partially epoxy prepolymers could be cross-linked with effective hardeners such as amines and anhydrides which are well-known to react with internal epoxy functions [3,38,39,40].

Therefore, the purpose of this work is to synthesize bio-based epoxy networks from oleic acid, without the use of CMR reagents, with promising mechanical, thermal and adhesive properties after curing with a suitable hardener. Firstly, oleic acid was functionalized with the 2-hydroxyethyl methacrylate (HEMA) by Steglich esterification and the resulting monomer was involved in radical process. Then, functionalization via epoxidation was performed on internal unsaturations of oleic acid-based methacrylate polymer with different epoxy contents without the use of epichlorohydrin. In order to investigate the reactivity of these internal epoxy functions, benzylamine and succinic anhydride were used as nucleophiles on a model compound resulting from the epoxidation of the methyl oleate. Then, the epoxy polymers were cross-linked with the most performing curing agent to afford bio-based thermosets with low T_g . Finally, the most interesting thermosets have been studied through DSC, TGA, DMA analyses and used as well as coatings. Hence, this work proposes a strategy to design new biobased epoxy cross-linkable materials. Bulk thermosets and coatings have been synthesized from partially epoxidized polymethacrylate and characterized in order to open up new kind of applications.

2. Materials and methods

2.1. Materials

Oleic acid (OA) was purchased from Fisher Scientific and used as received. Dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), 2-hydroxyethyl methacrylate (HEMA), hydrogen peroxide solution 30% in H_2O (H_2O_2), *p*-toluenesulfonic acid monohydrate (*p*-

TSOH), benzoyl peroxide (BPO), imidazole, benzylamine, benzophenone and succinic anhydride were purchased from Sigma-Aldrich and used without any further purification. Deuterated solvent $CDCl_3$ was obtained from Sigma Aldrich for NMR study. Tetrahydrofuran (THF), toluene, methanol (MeOH), ethyl acetate (EtOAc) and cyclohexane were purchased from Sigma-Aldrich. Formic acid solution 60% in H_2O was purchased from ICKOWICZ manufacturer. All materials were used as received.

2.2. Methods

2.2.1. NMR analyses

Proton and carbon nuclear magnetic resonance (1H and ^{13}C NMR) analyses were performed in deuterated chloroform ($CDCl_3$) using a Bruker Avance 400 MHz NMR spectrometer at a temperature of 25 °C. NMR samples were prepared as follows: 10 mg of product for 1H experiment in around 0.4 mL of $CDCl_3$. The chemical shifts were reported in part per million relative to tetramethylsilane. Spin multiplicity is shown by s = singlet, d = doublet, t = triplet, m = multiplet.

Thermogravimetric analyses (TGA) were performed using a TG 209F1 (Netzsch) at a heating rate of 20 °C/min. Approximately 10 mg of sample was placed in an aluminum crucible and heated from room temperature to 600 °C under nitrogen atmosphere (20 mL.min⁻¹).

Differential scanning calorimetry (DSC) analyses were carried out using a NETZSCH DSC200F3 calorimeter. Constant calibration was performed using indium, *n*-octadecane and *n*-octane standards. Nitrogen was used as the purge gas. Approximately 10 mg of sample was placed in pierced aluminum pans and the thermal properties were recorded between -150 °C and 150 °C at 20 °C.min⁻¹ to observe the glass transition temperature. The T_g values were measured on the second heating ramp to free from over the thermal history of the polymer. All the reported temperatures are middle values.

2.2.2. Size exclusion chromatography (SEC)

Molar mass and molar mass distribution (dispersity, \mathcal{D}) of polymers were determined by size exclusion chromatography using a GPC 50 Varian equipped with an RI refractive index detector. The system used two PLgel 5 μ m Mixed D columns with THF as eluent with a flow rate of 1 mL.min⁻¹. Poly(methyl methacrylate) (PMMA) standards were used for the calibration. The typical sample concentration was 5 mg.mL⁻¹.

Dynamic Mechanical Analyses (DMA) were carried out on Metravib DMA 25 with Dynatest 6.8 software. Uniaxial stretching of samples was performed while heating at a rate of 3 °C.min⁻¹ from -120 °C to 80 °C, keeping frequency at 1 Hz with a fixed strain (10⁻⁵ m). A variable stress has been firstly applied to the material at fixed temperature ($> T_g + 30$ °C) to determined its elastic domain. The dynamical strain applied on the second test has been chosen on this elastic domain.

2.2.3. Titration of the epoxy equivalent weight by 1H NMR

The Epoxy Equivalent Weight (EEW) is the amount of product needed for one equivalent of reactive epoxy. It was determined by 1H NMR using an internal standard (benzophenone). A known weight of epoxy and benzophenone was poured into an NMR tube and 500 μ L of $CDCl_3$ were added. It was determined using the Equation 1 by comparing the integral of the protons of the benzophenone and the integral of the protons of the epoxy function.

$$EEW = \frac{\int_{PhCOPh} * H_{epoxy} * m_{epoxy}}{\int_{epoxy} * H_{PhCOPh} * m_{PhCOPh}} * M_{PhCOPh} \quad (1)$$

\int_{PhCOPh} : integration of the benzophenone protons; \int_{epoxy} : integration of the protons of the epoxy functions; H_{epoxy} : number of protons of the epoxy functions; H_{PhCOPh} : number of protons of the benzophenone; m_{epoxy} : weight of the epoxy product; m_{PhCOPh} : weight of the benzophenone; M_{PhCOPh} : molecular weight of the benzophenone.

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