

Bio-based thermo-healable non-isocyanate polyurethane DA network in comparison with its epoxy counterpart



Z. Karami^a, M.J. Zohuriaan-Mehr^{a,b,*}, A. Rostami^c

^a Adhesive and Resin Department, Polymer Processing Faculty, Iran Polymer and Petrochemical Institute, P.O. Box 14965-115, Tehran, Iran

^b Biomass Conversion Science and Technology (BCST) Division, Iran Polymer and Petrochemical Institute, P.O. Box 14965-115, Tehran, Iran

^c Department of Chemistry, Faculty of Science, Shahid Beheshti University, P.O. Box 1983963113, Tehran, Iran

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ABSTRACT

Degradability, reusability or healability of polymer networks have significant importance in features of the environmental, economic and materials application. This study deals with synthesis of a reversible non-isocyanate polyurethane (NIPU) network in comparison with its epoxy counterpart. First, furfuryl cyclocarbonate ether (FCE) was synthesized by a green method of CO₂ fixation (carbonation reaction) on furfuryl glycidyl ether (FGE; a bio-based compound). Afterwards, Diels-Alder (DA) adducts were synthesized by the reaction between a bismaleimide and FGE or FCE. The DA adducts were characterized by ¹H NMR and FTIR. Amine-curing of the adducts produced two different networks. According to dynamic mechanical thermal analysis, the existence of the cyclocarbonate ring resulted in the formation of a more flexible network having less cross-link density in comparison with its epoxy counterpart. Thermal behavior of the DA adducts were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis. The results showed a retro-DA process occurred at ~130 °C. Unlike the epoxy network, molecular disconnection of the NIPU network occurred completely at this temperature after 25 min. Disconnected moieties of both networks were re-casted and DA re-structuring of networks was confirmed by solubility test and DSC. Finally, the NIPU showed superior thermo-healing behavior comparing with its epoxy counterpart.

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1. Introduction

Exposure of polymer networks to environmental stresses including chemical, mechanical and thermal attacks can result in irreversible damages led to loss of the material's physical properties [1]. Due to the insolubility and infusibility of polymer thermosets, recycling and reusing of them is not possible. Since the physico-mechanical properties of damaged thermosets are lost, they are usually annihilated by methods such as incineration, landfilling or degradation using acidic or basic agents [2].

The main reason for utilizing healable materials is preserving the physical properties after quick and complete repair. Common repair methods, such as welding or patching are used to macroscopic mending. However, these repairs are not suitable for inaccessible damages, or in the case of samples which must

have constant dimensions [3]. Numerous methods have been developed for preparation of self-healing materials, for instance, using the materials which are intrinsically healable. Some of these materials needs external stimuli (e.g., temperature, pH, radiation) to be re-mended [1]. In this case, bond breaking-rebuilding process by external stimuli leads to healing. Diels-Alder (DA) reaction, particularly furan-maleimide reaction as a temperature-dependent reversible covalent bond formation process, is an effective click-type approach for achieving intrinsic self-healing polymers [4]. In order to transform the thermosets into remendable or soluble polymers under mild conditions, reversible DA bonds can be embedded into them [5].

Regarding epoxy networks, due to high crosslink density, they are brittle and stiff with a relatively high glass transition temperature (T_g) and low toughness [6]. Therefore, improvement of mechanical properties such as toughening seems to be indispensable. There are two main strategies to achieve this objective: (a) physical modification includes blending of epoxy with ductile fillers and additives such as rubber particles [7,8], and epoxidized plant oils [9] which lead to phase-separated morphologies, and (b) chemical modification includes incorporation of a

* Corresponding author: Biomass Conversion Science and Technology (BCST) Division, Adhesive and Resin Department, Polymer Processing Faculty, Iran Polymer and Petrochemical Institute, P.O. Box 14965-115, Tehran, Iran.

E-mail addresses: mjzohuriaan@yahoo.com, bcst.ippi@gmail.com (M.J. Zohuriaan-Mehr).

flexible chain or group into the epoxy network. The second method results in the formation of a homogeneous structure and improves the epoxy network properties rather than the first one [10].

Carbon dioxide as a byproduct of all combustion processes, is a resource which recently got much attention to be an alternative renewable carbon feedstock for production of a various valuable chemicals [11]. One of the extensively described application, is consumption of CO₂ as a primary material in CO₂ fixation (carbonation reaction) on epoxides leading to production of cyclic carbonates [12,13]. Ghanbaralizadeh et al. [14], prepared a toughened bi-functional epoxy resin through CO₂ fixation method. They showed that the formation of urethane bonds and a large number of hydrogen bonding, as a result of curing with an amine agent, resulted in a significant increase of toughness. Furthermore, unlike the conventional polyurethane production processes, the use of toxic chemicals, particularly isocyanates, is not required in the aforementioned process of carbonation followed by amine reaction [15].

Although the reversibility of non-isocyanate polyurethane (NIPU) has preliminarily been studied as an adhesive [16], to the best of our knowledge, no published study is found on the self-healing ability of these urethanes especially as networks of NIPU. These networks are unquestionably fascinating due to eliminating the use of toxic isocyanate, enabling the healing after defect formation or recycling of materials after usage. Additionally, “greenness” of starting materials and processes are also of significant importance regarding the sustainability (renewability of the material resources), human health, and environmental issues.

In the present study, furfuryl alcohol (FA) and glycerol are used as two starting materials which both are bio-based compounds produced industrially from lignocellulosic bio-resources and plant oils, respectively. As shown in Scheme 1, 2-[(Oxiran-2-ylmethoxy)methyl]furan (furfuryl glycidyl ether, FGE) as a bio-based compound [17], was synthesized by the reaction of FA and a glycerol-based epichlorohydrin (ECH). FA, a well-established industrial commodity, is produced from furfural (an industrial

product for many decades which has been obtained quite readily and economically from a vast array of agricultural or forestry wastes) [18]. Recently, glycerol as a byproduct of the manufacture of biodiesel, particularly in Europe, has been used in the manufacture of chemicals, such as ECH [19]. So, both of the ECH and FA used in this investigation are from renewable feedstocks.

In our study, a thermo-reversible NIPU network was prepared via DA reaction and its properties was compared to its epoxy counterpart. The reversible epoxy network containing both reversible DA linkages and irreversible epoxy bonds has been investigated in a few studies [5,20,21], however, thermo-reversible NIPU is rarely reported and synthetic aspect is mainly emphasized [22]. Indeed, our central purpose was replacement of epoxy groups with cyclocarbonate groups through CO₂ fixation and converting an epoxy network to a NIPU network and investigation of this replacement effect on physical and mechanical properties.

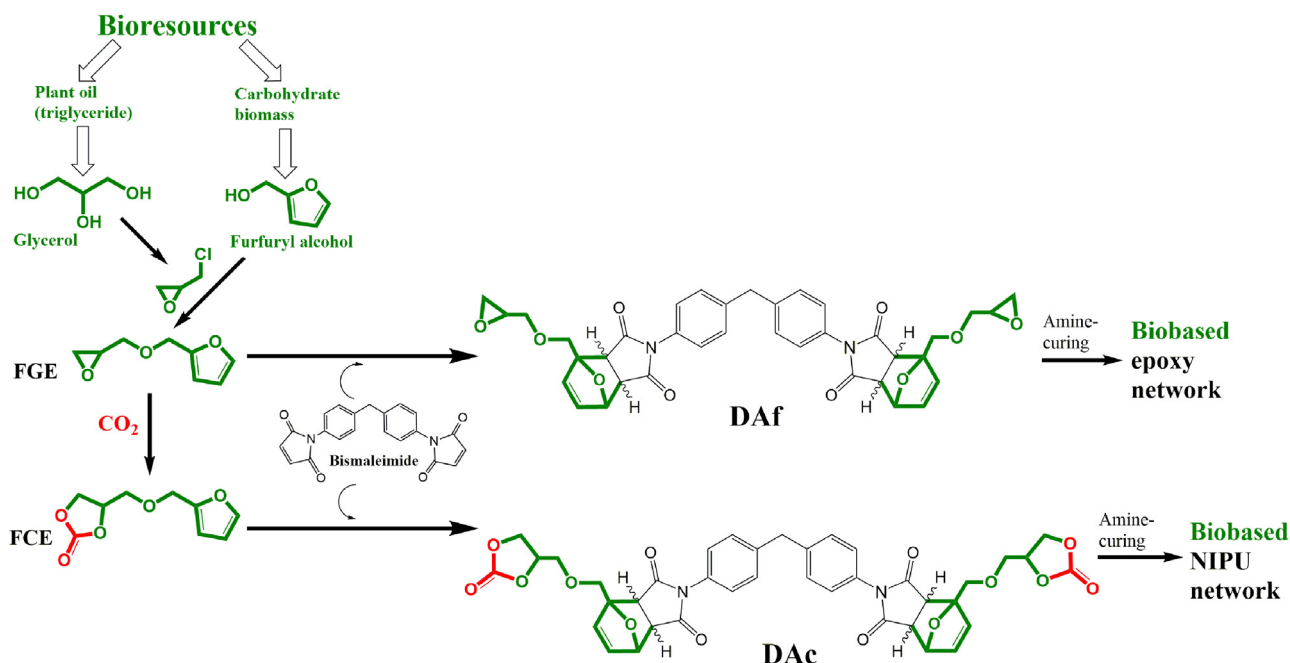
2. Experimental

2.1. Materials

Furfuryl alcohol (FA, 99%), diethylene triamine, (DETA, 99%) and epichlorohydrin were purchased from Daejung Chemicals Co (Korea). 1,1'-(Methylenedi-4,1-phenylene) bismaleimide (BMI) (98%) was provided by Shenzhen Nexconn Pharmatechs, Ltd. (China). Tetrabutylammonium bromide (TBAB, 98%), NaOH and solvents were supplied by Merck (Germany) and used as received.

2.2. Characterization

Nuclear magnetic resonance (¹H NMR) spectra were recorded on a Bruker Avance 300 spectrometer (300 MHz) spectrometer at room temperature using tetramethylsilane (TMS) as an internal standard. Fourier transform infrared (FTIR) spectra of samples (as KBr pellet) were obtained by a Bruker instrument, model IFS48 spectrophotometer.



Scheme 1. The path of synthesis of the bio-based adducts and networks.

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