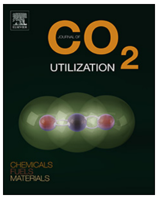
Journal of CO_2 Utilization 26 (2018) 302–313

Contents lists available at ScienceDirect

Journal of CO_2 Utilization

journal homepage: www.elsevier.com/locate/jcou



Critical transition of epoxy resin from brittleness to toughness by incorporating CO_2-sourced cyclic carbonate

Jiexi Ke[a,b], Xiaoyun Li[a,b], Shuai Jiang[a,b], Junwei Wang[a,*], Maoqing Kang[a], Qifeng Li[a], Yuhua Zhao[a]

[a] *Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, 030001, China*
[b] *University of Chinese Academy of Sciences, Beijing, 100049, China*

ARTICLE INFO

Keywords:
CO_2-sourced monomer
Cyclic carbonate
Epoxy resin
Toughness
Hydrogen bonding
Urethane linkage

ABSTRACT

A five-membered cyclic carbonate as CO_2-sourced monomer was prepared from ethylene glycol diglycidyl ether (EGDE) with CO_2 by cycloaddition reaction, abbreviated as 5CC-EGDE, at 130 °C under 10 bar CO_2 pressure in the presence of quaternary ammonium salt modified amberlyst (D296) for 20 h. The complete conversion and 98.6% selectivity were obtained, respectively. The incorporation of 5CC-EGDE into epoxy resin could reduce the viscosity during preparation process and improve the toughness effectively. It was ascribed to the ring-opening reaction of 5CC-EGDE with curing agent, and hydrogen bonding, formed between urethane groups and other polar groups. Besides, the low crosslinking density and unreacted carbonate groups remaining in epoxy network were beneficial to the movement of molecular chains and dissipation of energy during deformation process. In addition, effects of hydrogen-bonding interactions and crosslinking density on mechanical performances were also investigated by varying EGDE conversion and amount of added curing agent, respectively. The results indicated that mechanical performances of epoxy resin were promoted by combined effects of urethane linkage, hydrogen bonding, low crosslinking density and unreacted carbonate groups.

1. Introduction

Carbon dioxide (CO_2) is widely regarded as one of the main greenhouse gas, which is notorious for global warming. The chemical fixation of CO_2 has been drawing a huge amount of attention as a result of the fact that it's an important C1 feedstock in industry as it is abundant, easily available, non-toxic and inexpensive [1], and it quite fits well the concepts of "green chemistry" and "sustainable society" [2]. Employing CO_2 as a raw material to prepare chemicals may create a positive pathway for utilization of CO_2. One of the promising routes is the synthesis of cyclic carbonate *via* cycloaddition reaction of CO_2 with epoxides [3]. Since cyclic carbonate has special properties, it is widely used as green polar solvents, electrolytes in lithium batteries as well as intermediates for organic synthesis [4].

Epoxy resin, one of the most important thermosetting polymers, is widely used as adhesives [5], coatings [6] and structural materials for high-performance composites [7] due to its outstanding performances. As thermosetting materials, epoxy resin exhibits a high degree of crosslinking density, which endows it with useful properties. However, the highly cross-linked structure also causes epoxy inherently brittle and vulnerable to cracks, thus limiting their advanced applications. Therefore, it is of great interest to improve the toughness of epoxy resin. Numerous attempts have been adopted in this field. The toughening strategies mainly include three categories: (1) reduce of crosslinking density [8], (2) use particles/fillers as a second phase [9], and (3) introduce plasticizers to increase plastic deformation [10]. Among these methods, incorporation of polyurethane linkage is beneficial for the formation of chemical bonding and physical entanglements such as urethane and hydrogen-bonding interactions, which can increase intra- and inter- molecular forces in epoxy network [11].

In general, the traditional polyurethane linkage is incorporated into epoxy system by reacting isocyanates or isocyanate-terminated polyurethane oligomers with hydroxyl groups in epoxy resin [12]. However, the repetitive exposure to isocyanate can lead to serious health issues [13]. In addition, the synthesis of isocyanates, for instance methane diphenyl 4,4′-diisocyanate and toluene diisocyanates, requires toxic phosgene [14]. Therefore, in recent years, polyurethane prepared from non-isocyanate methods has attracted considerable attention [15,16]. One of the most attractive ways for synthesis of non-isocyanate polyurethane is that five-membered cyclic carbonate (5CC) is first synthesized from epoxide substrates and CO_2, then reacts with amine. By using this "green chemistry" route, the use of toxic and expensive

---

* Corresponding author.
E-mail address: wangjw@sxicc.ac.cn (J. Wang).

https://doi.org/10.1016/j.jcou.2018.05.020
Received 23 December 2017; Received in revised form 3 May 2018; Accepted 20 May 2018
2212-9820/

isocyanates can be avoided. The 5CC-modified epoxy resin can be obtained either by adding cyclic carbonate [17] or by replacing only part of epoxy groups by reacting it with CO_2 [18]. In previous reports, only several research groups have concentrated on 5CC-modified epoxy by incorporating cyclic carbonate. Khoshkish and co-workers have investigated the effect of CO_2 fixing process producing cyclic carbonate on dynamic viscosity and kinetics of epoxy resin [19]. Rokicki et al. [17] have tremendously studied on the gel time, mechanical properties and curing kinetics of 5CC-modified epoxy resin. However, little attention has been paid to the toughening mechanism of 5CC to epoxy resin. Until recently, Ghanbaralizadeh [20] investigates the toughening mechanism by analyzing activation energy of β relaxation of chain segments. However, epoxy diluent which is adopted during the CO_2 fixation into epoxy also reacts with CO_2. The mixtures achieve high cyclic carbonate content which could increase viscosity causing heterogeneous dispersion. Meanwhile, the report neglects the effect of urethane linkage provided by 5CC-modified diluent on mechanical performances and toughening mechanism of epoxy resin.

In this work, the epoxy resin was toughened by incorporating 5CC-modified diluent. And the toughening mechanism was further investigated. The 5CC was synthesized from CO_2 and bifunctional reactive diluent, ethylene glycol diglycidyl ether (EGDE), which could be obtained from renewable glycerol that was a by-product from the preparation process of biodiesel [21–23]. Therefore, the relationship between mechanical performances and structure of modified epoxy was investigated. The influence of 5CC content on properties of epoxy composites was studied by rheology, fourier transform infrared spectra (FTIR), dynamic mechanical properties (DMA), scanning electron microscopy (SEM), etc. To study the toughening mechanism, effects of urethane linkage, hydrogen bonding, unreacted cyclic carbonate groups and crosslinking density on mechanical properties of epoxy composites were studied.

2. Experimental section

2.1. Materials

Ethylene glycol diglycidyl ether (EGDE) (number-average molar mass = 190 g/mol) was supplied by Wuhan Yuanchen Technology Co., Ltd. Commercially available grade of Bisphenol-A diglycidyl ether (BADGE) with 5.34 mmol/g epoxy equivalent weight (EEW) was purchased from Nantong Xingchen Synthetic Materials Co., Ltd. Quaternary ammonium salt modified amberlyst (D296) was purchased from Tianjin Resin Technology Co., Ltd. Triethylenediamine (TEDA) as catalyst and diethylenetriamine (DETA) as curing agent were purchased from Sinopharm Chemical Reagent Co., Ltd. CO_2 (99.99%) was kindly supplied by Shanxi Institute of Coal Chemistry, Chinese Academy of Sciences. All the raw materials were used as received without further purification.

2.2. Synthesis of five-membered cyclic carbonate-based EGDE

EGDE with complete conversion into five-membered cyclic carbonate, hereafter abbreviated as 5CC-EGDE, was synthesized by coupling EGDE (100 g) with CO_2 (10 bar) at 130 °C in the presence of catalyst (10 wt% compared to EGDE) for 20 h (see Scheme 1). Detailed preparation process of 5CC-EGDE was reported in our previous report [24]. The EGDE with different conversion was also prepared by varying reaction time for 0, 6 and 15 h.

2.3. Curing reaction of BADGE/5CC-EGDE mixtures

BADGE was mixed with 5 wt% 5CC-EGDE and 0.1 wt% TEDA as catalyst (compared to total weight of 5CC-EGDE and BADGE) for 10 min using a mechanical stirrer. In order to avoid bubbling, the mixture was degassed in heated oven at 75 °C for 20 min. Then, calculated amount curing agent, DETA, was added. After mixing, an ultrasonic bath was used to eliminate the bubbles during mixing process of the resulting mixtures. Finally, the compositions were poured into polytetrafluoroethylene mold and kept at 75 °C for 24 h, followed by cured at 100 °C for 2 h and further placed at room temperature for one week. An analogous procedure was used to prepare BADGE/5CC-EGDE composites containing 0, 10, 15, 20, 25 and 30 wt% 5CC-EGDE.

There is a large gap between the reactivity of cyclic carbonate and epoxy groups with curing agent DETA. DETA is a linear molecule with two primary amines located on the chain ends and one secondary amine in the backbone. The epoxy groups of BADGE can react with primary and secondary amine. The primary amine and secondary amine has two active hydrogen atoms and one hydrogen atom, respectively, which can react with epoxy groups. Hence, the number of reactive group of DETA towards BADGE is 5. However, primary amine reacts with cyclic carbonates more efficiently than internal secondary amine [25]. It was assumed that only some of the secondary amine would react with cyclic carbonate group. Here, the effective functionality of DETA was taken to be 2.5. And the DETA amount was calculated by following Eq. (1):

$$m_{DETA} = \left(\frac{CEW_{5CC-EGDE} \times m_{5CC-EGDE}}{n_{number\ of\ functional\ groups\ for\ 5CC-EGDE}} + \frac{EEW_{BADGE} \times m_{BADGE}}{n_{number\ of\ functional\ groups\ for\ BADGE}}\right) \times M_{DETA}$$

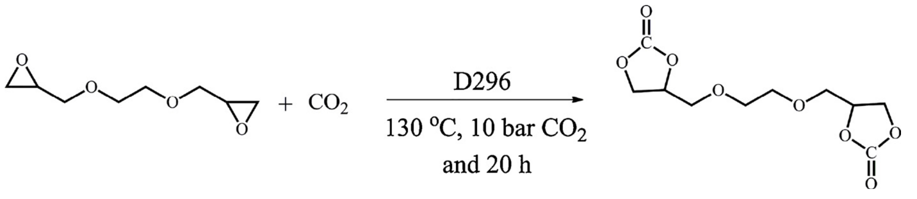
where $CEW_{5CC\text{-}EGDE}$, $m_{5CC\text{-}EGDE}$ represent carbonate equivalent weight (CEW) and mass of 5CC-EGDE, EEW_{BADGE} and m_{BADGE} represent the epoxy equivalent weight (EEW) and mass of BADGE, and n represents the functional groups of DETA for 5CC-EGDE or BADGE. M_{DETA} and m_{DETA} represent the number-average molar mass and desired mass of DETA.

2.4. Characterization methods

Fourier Transform Infrared Spectra (FTIR) of cyclic carbonate and epoxy/5CC-EGDE composites were acquired at 25 °C on a NICOLET-380 Fourier transform infrared instrument (Thermo Electron Co., Ltd. USA). Spectra were recorded in the range between 4000 and 500 cm^{-1}, with 32 scans and resolution of 4 cm^{-1}. The ring-opening conversion of 5CC-EGDE and BADGE with curing agent was determined by FTIR and calculated by following Eq. (2):

$$Intensity\ (\%) = 1 - \frac{\left(I_{functional\ group}/I_{standard}\right)_{after\ reaction}}{\left(I_{functional\ group}/I_{standard}\right)_{before\ reaction}} \tag{2}$$

in the case of BADGE, $I_{functional\ group}$ and $I_{standard}$ represent the intensity of C—O at 911 cm^{-1} and benzene group at 1605 cm^{-1}, respectively. For 5CC-EGDE, $I_{functional\ group}$ and $I_{standard}$ represent the intensity of C=O at



Scheme 1. The scheme of synthesis of 5CC-EGDE.