Journal of CO_2 Utilization 16 (2016) 474–485

Contents lists available at ScienceDirect

Journal of CO_2 Utilization

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

The hybrid polyhydroxyurethane materials synthesized by a prepolymerization method from CO_2-sourced monomer and epoxy

Jiexi Ke[a,b], Xiaoyun Li[a,b], Feng Wang[a], Maoqing Kang[a], Yuelan Feng[a], Yuhua Zhao[a], Junwei Wang[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

Article history:
Received 27 September 2016
Accepted 2 November 2016
Available online xxx

Keywords:
CO_2-sourced monomer
Pre-polymer
Amine
Epoxy
Polyhydroxyurethane

ABSTRACT

A series of hybrid polyhydroxyurethane (PHU) materials were prepared from CO_2, polypropylene glycol diglycidyl ether, amines, and bisphenol-A diglycidyl ether (BADGE). Firstly, the five-membered cyclocarbonate (5CC) as the CO_2-sourced monomer was synthesized by a cycloaddition reaction from CO_2 and polypropylene glycol diglycidyl ether at 120 °C under 10 bar CO_2 pressure in the presence of an amberlyst catalyst. The selectivity of 5CC was confirmed through an analog computation method based on the results of ^{1}H NMR. Then, 5CC was reacted with excessive amines to produce the $-NH_2$ terminated pre-polymers. Finally, the pre-polymers reacted with BADGE to produce hybrid PHU materials. The effect of amine type and BADGE content on the properties of PHUs was studied by means of Fourier transform infrared spectra, dynamic mechanical thermal analysis, and thermogravimetric analysis and solvent swelling test. The results indicated that introducing BADGE as a chain extender not only enhances the gelation rate of PHU, but also improve the mechanical and thermal properties of PHU materials.

1. Introduction

In the past years, CO_2 has got social attention. The source of CO_2 mainly derives from the combustion of fossil fuels [1,2]. But in recent years, the release of a lot of CO_2 causes various environment problems, therefore CO_2 utilization could help alleviate environmental problems to a certain extent. CO_2 as a renewable resource can be used in the four categories: (I) solar fuel, (II) mineralization, (III) polymer synthesis, (IV) biological utilization [3]. The CO_2 is an attractive building block in as it is abundant, inexpensive, nontoxic and nonflammable. One of the most promising methodologies of CO_2 utilization is the synthesis of five-membered cyclocarbonate through the CO_2 fixation reaction with epoxy groups. And this chemical fixation reaction has attracted wide attention of researchers [4–7]. Cyclocarbonates have physical and chemical properties which have been widely used as polar aprotic solvents, intermediates for organic and polymeric synthesis, and ingredients for chemicals in biomedical applications [8,9].

One of cyclocarbonate utilization is to be used as monomer to produce polyurethane has attracted considerable attention in recent years (the so-called NIPU: non-isocyanate polyurethane). However, the traditional PU materials are usually prepared from polyol, isocyanate and chain extender [10]. The synthesis and use of isocyanates can cause environmental pollution and increase cancer risk [11,12]. Common isocyanates, for instance methane diphenyl 4,4′-diisocyanate and toluene diisocyanates, are reported to be harmful to human health, especially the exposure to them when the polyurethanes are synthesized [13,14].

To minimize environmental pollution and the harm to workers during the processing of PU, the manufacture of polyurethanes without isocyanate has attracted considerable attention in recent years. Among the reported NIPUs, polyhydroxyurethanes (PHUs), synthesized by the reaction between multiple cyclocarbonate and primary amine, are expected to replace the traditional PU materials [10]. Compared with the traditional PUs containing urethane group in the main chains, PHUs contain also hydroxyl groups throughout the macromolecular chain. The hydrogen atom of the hydroxyl group can form intermolecular hydrogen bond with the carbonyl oxygen atom of urethane group, thereby constituting a stable seven membered ring structure. Due to the formation of tautomerism inside the ring, the structure of the ring is very stable [15–17]. This improves the mechanical properties and hydrolytic stability of the material, and makes up the weak bond structure of the traditional PUs from the point of molecular

---

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

http://dx.doi.org/10.1016/j.jcou.2016.11.001
2212-9820/© 2016 Published by Elsevier Ltd.

structure [10]. Unfortunately, due to the low reactive activity between cyclocarbonate and secondary amine or amide, it is difficult to form the cross-linkage among the main chain as traditional PU. Therefore, the low cross-linkage of PHU is one of the main reasons for its poor mechanical properties [18]. Besides, another main drawback of PHU is its low molecular weight, which affects the mechanical properties greatly. The low molecular weight is mainly caused by lower reactivity between cyclocarbonate and amines due to the steric hindrance and ring strain of cyclocarbonate [19–23].

To resolve these questions, scientists put in efforts either on the development of catalysts to improve the reaction activity of cyclic carbonate with primary amines, or on the design of molecular structure. Several groups [24–27] have devoted to the research on 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) which is a costly compound but the best catalyst for promoting aminolysis reaction conversion. Endo et al. [23,28–36] have been tremendously studied on the relationship between the properties and structure of this material as well as various types of catalyst for the reaction. Moreover, Figovsky and coworkers [37,38] reported the synthesis of PHU hybrid coating from several aliphatic and aromatic cyclocarbonates and bisphenol resins via a prepolymerization method. Although various methods were attempted to learn structure of PHU and modify the properties of PHU, the overall performances of PHU are still far from satisfactory.

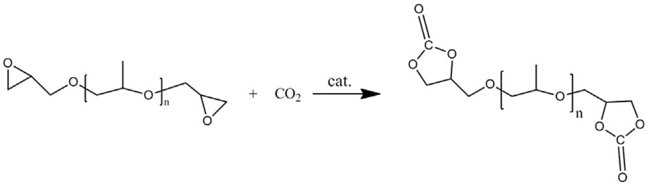
The epoxy group, especially, the group adjacent to aryl ring, could react with amines rapidly, which encourage us preparing PHU by a prepolymer method to accelerate the chain extending reaction and increase the cross-linkage of PHU.

In this process, the five-membered cyclocarbonate (5CC) as the CO_2-sourced monomer was synthesized by a cycloaddition reaction from CO_2 and polypropylene glycol diglycidyl ether (PPGDGE) in the presence of an amberlyst catalyst. Then, the $-NH_2$ terminated pre-polymers were obtained by reacting 5CC with excessive amines. Finally, the pre-polymer was reacted with the chain extender bisphenol-A diglycidyl ether (BADGE) to yield a series of cross-linked hybrid PHU materials. The influence of amine type, equivalent ratio and BADGE content on properties of PHUs was studied by FTIR, DMA, TG, ect. It was found that the introduced BADGE could increase cross linkage density and acted as rigid segments in PHU, which accelerated the curing process of PHU significantly.

2. Experimental

2.1. Materials

Polypropylene glycol diglycidyl ether (PPGDGE) was kindly supplied by Wuhan Yuanchen technology Co., China. The quaternary ammonium salt modified amberlyst (D296) was purchased from Tianjin Resin Technology Co., China. CO_2 was supplied by Shanxi Institute of Coal Chemistry, Chinese Academy of Sciences. 1, 2-ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylene pentamine (TEPA), and triethylenediamine (TEDA) were obtained from Sinopharm Chemical Reagent Beijing Co., Ltd. Bisphenol-A diglycidyl ether (BADGE), 5.34 meq/g of epoxy equivalent weight (EEW), was purchased from Zhejiang Bangfeng Plastic Co., China. All the raw materials were used as received without further purification.



Scheme 1. The scheme of 5CC synthesis through CO_2 fixation reaction with PPGDGE.

2.2. Synthesis

2.2.1. Reaction of PPGDGE with CO_2

The poly(propylene oxide) bis-cyclocarbonate, hereafter this cyclocarbonate being abbreviated as 5CC, were synthesized by coupling PPGDGE (100 g) with CO_2 in a 500 mL autoclave at 120 °C under 10 bar CO_2 pressure in the presence of 10 wt% of catalyst compared to the PPGDGE (Scheme 1). In order to obtain 5CC with different cyclic carbonate contents for quantitative analysis, reaction time of 10 h, 20 h, 25 h, and 30 h was adopted, respectively. The corresponding 5CC was abbreviated as 5CC–10 h, 5CC–20 h, 5CC–25 h, 5CC–30 h, respectively. Cyclic carbonate equivalent weight (CEW) and epoxy equivalent weight (EEW) was confirmed by ^1H Nuclear Magnetic Resonance (^1H NMR) spectroscopy with Eq. (1). Meanwhile, the selectivity of the cyclic carbonate was calculated through mathematical simulation from the results of ^1H NMR spectra of 5CC with different PPGDGE conversions. Besides, further characterization of the cyclic carbonates was carried out by Fourier Transform Infrared Spectra (FTIR), Gel Germeation chromatography (GPC), and viscosity measurement.

2.2.2. Synthesis of PHU pre-polymer

The 5CC of 100% conversion (60 g, 72 mmol), amine (according to the formula) and TEDA (0.3 g, 5 mmol) were mixed at 90 °C for 4 h as shown in Scheme 2. The content and active hydrogen number of amine for 5CC–30 h or BADGE was summarized in Table 1, and the amount of amine is calculated according to Eq. (3). Due to the limited reactivity of cyclocarbonate towards secondary amine of the organic amines, the number of active site in amine was fixed to 2 for 5CC. For obtaining $-NH_2$ terminated pre-polymer, the excessive amine was necessary. Therefore the mixed pre-polymer products were composed of PHU pre-polymer and excessive amine. The excessive amine was left in the reaction system to increase the reaction activity of BADGE and improve the cross-linkage of final product when the BADGE was introduced. One EDA derived pre-polymer was selected as model system to learn the opening ratio of 5CC after the aminolysis reaction. Further analysis of the PHU pre-polymers was conducted by ^1H NMR, FTIR, and differential scanning calorimetry (DSC).

The resultant pre-polymers from EDA were noted as pre-polymer-0–4, respectively, which were decided by formulation.

Table 1
Characterization of the various types of amines.

	Molecular weight(g/eq)	Amine content(meq/g)	Number of active site for 5CC or BADGE	
			For 5CC	For BADGE
EDA	60	16.67	2	4
DETA	103	9.71	2	5
TETA	146	6.85	2	6
TEPA	189	5.29	2	7