



# Synthesis and properties of non-isocyanate polyurethane coatings derived from cyclic carbonate-functionalized polysiloxanes

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## ABSTRACT

A series of novel cyclic carbonate-functionalized polysiloxanes (CC) were successfully prepared by the reaction of epoxy-functionalized polysiloxanes with carbon dioxide. Then the CCs with different carbonate content were reacted with various structural diamines such as isophorondiamine (IPDA), 4,4'-diaminodicyclohexylmethane (PACM), 1,2-propanediamine (PDA) and 1,6-hexamethylenediamine (HMDA) to form non-isocyanate polyurethane (NIPU) coatings, respectively. The properties of the NIPU coatings were determined, and the effects of carbonate content as well as chemical structure of diamine on mechanical and thermal properties of NIPU coatings were investigated. The results showed that the cycloaliphatic amines cured coatings had higher tensile strength, Yong's modulus, water resistance and glass transition temperature compared to the aliphatic amines cured coatings. Furthermore, with the increase of the carbonate content, the tensile strength, Yong's modulus and glass transition temperature of the coatings were increased, while the thermal stability and water resistance of the coatings were decreased.

## 1. Introduction

As one of the most important classes of polymeric materials, polyurethanes (PUs) are widely used in many fields of applications such as thermoplastics, elastomers, foams, adhesives, coatings, sealants and so on [1,2]. PUs are commonly synthesized by reacting polyols with isocyanates, and the main drawback of this chemistry is the use of isocyanates which are known to be toxic and harmful for human health. Recently, numerous efforts have been directed towards the development of innovative synthetic routes for replacing isocyanates in the manufacture of PUs because of health and environmental concerns in sustainable development [3–11]. Especially, the reaction of cyclic carbonates with amines has been identified as an attractive green route to non-isocyanate polyurethanes (NIPUs) [12–26]. Moreover, although many synthetic methods have been used to prepare cyclic carbonates, the most common method is the chemical insertion of carbon dioxide into appropriate epoxide in the presence of catalysts [27–29]. Therefore, the additional benefit of the cyclic carbonate route to NIPUs is the fixation and utilization of carbon dioxide, which is known as a non-toxic, abundant, inexpensive and renewable C1 source. However, in contrast to conventional PUs, the NIPUs have a disadvantage in that the materials exhibit poor water resistance due to the presence of the

hydrophilic primary and secondary hydroxyl groups in the main chain [30–32]. So how to improve their water resistance is an important issue for the wide application of NIPUs.

Polysiloxanes, which have a number of fascinating properties such as high thermal and oxidative stability, low surface energy, resistance to high and low temperature and excellent flexibility, have been extensively researched on optimizing some properties of polymer materials in the last few years [33]. Particularly polysiloxanes were widely used as hydrophobic agents in various coating formulations, and polymers modified with polysiloxane showed good water and chemical resistances [34–36]. In the field of NIPU, it has been reported that the water tolerance, flame retardancy and mechanical strength of NIPUs could be improved obviously by incorporating polysiloxane into the polymeric matrix [37–39].

In this work, a series of cyclic carbonate-functionalized polysiloxanes (CC), which were synthesized from the cycloaddition reaction of epoxy-functionalized polysiloxanes with CO<sub>2</sub>, were reacted with diamines to form NIPU coatings, respectively. The chemical structures of the resulting products were characterized by FT-IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR. As well as, the mechanical and thermal properties of the NIPU coatings were determined. It was expected that the NIPU coatings containing polysiloxane segments could have excellent water resistance

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and mechanical properties.

## 2. Experimental

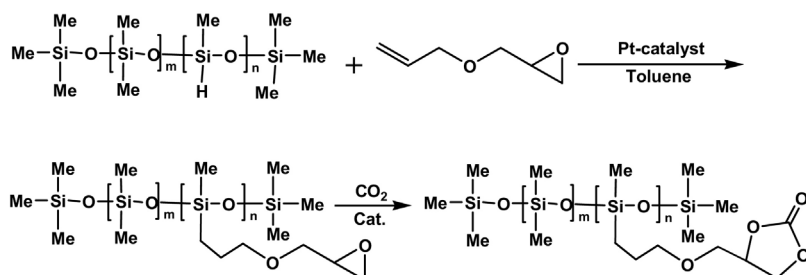
### 2.1. Materials

Allyl glycidyl ether (AGE) was purchased from Anhui Xinyuan Chemical Co., Ltd., three kinds of polymethylhydrosiloxane (PMHS: 1.60, 0.80 and 0.50 mol reactive hydrogen per 100 g PMHS, respectively) were obtained from Shanghai Guiyou New Material Technology Co., Ltd. Carbon dioxide (99.99%) was commercially available. Trimethylbenzenemethanaminium chloride and (TEBA), ethylene glycol (EG), isophorondiamine (IPDA), 4,4'-diaminodicyclohexylmethane (PACM), 1,2-propanediamine (PDA), 1,6-hexamethylenediamine (HMDA) and all other chemical reagents were chemically pure and were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

### 2.2. Measurements

The IR spectra were recorded on a Nicolet IS10 FT-IR spectrophotometer (Nicolet, Madison, WI, USA). The NMR measurements were performed on a Bruker DRX 300 spectrometer (Bruker, Switzerland). Chemical shifts were given with respect to  $\text{CHCl}_3/\text{CDCl}_3$  ( $\delta$   $^1\text{H} = 7.27$ ,  $\delta$   $^{13}\text{C} = 77.0$  ppm). The Viscosities were measured using a Brookfield DV-S rotational viscometer at 25 °C. Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) equipped with a Waters 1515 pump and Waters 2414 (Milford, Massachusetts) differential refractive index detector using THF as eluent after calibration with polystyrene standards. Differential scanning calorimetry (DSC) thermograms were recorded with PerkinElmer Diamond differential scanning calorimeter (USA) at a heating rate of 20 °C/min under a nitrogen gas flow at 20 mL/min. Thermogravimetric analyses (TGA) were performed with NETZSCH STA 409 PC/PG thermogravimetric analyzer (Germany) at a heating rate of 10 °C/min under a nitrogen atmosphere. Dynamic mechanical analyses (DMA) were carried out on a Q800 dynamic mechanical analyzer (TA instrument, USA) at a frequency of 1 Hz, temperature from -20 °C to 120 °C, and heating rate of 3 K/min. The size of the specimens cut from the films was 30 mm × 6.5 mm × 0.5 mm. A universal testing machine (CMT4304, Shenzhen SANS, China) was used to measure the tensile properties of the films at loading rate of 100 mm/min according to the standard ASTM D412 at room temperature. The epoxy content ( $C_{\text{epoxy}}$ ) was determined by hydrochloric acid-acetone method [40]. The carbonate content ( $C_{\text{carbonate}}$ ) was calculated directly from the determined epoxy content; assuming 100% epoxy converted into cyclic carbonate, the  $C_{\text{carbonate}}$  was calculated as the following Eq. (1):

$$C_{\text{carbonate}} = \frac{C_{\text{epoxy}}}{1 + \frac{C_{\text{epoxy}}}{1000} \times 44.01} \quad (1)$$



### 2.3. General procedure of the synthesis of epoxy-functionalized polysiloxanes (EP)

Pt-catalyst (2 wt% isopropyl solution of  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ) was added into the solution of AGE in toluene under nitrogen atmosphere and stirred for 30 min at 60 °C, and then the selected PMHS was added dropwise. The reaction mixture was stirred for 6 h at 90 °C. After the completion of reaction, the activated charcoal was added into the reaction mixture and filtered through celite, the filtrate was concentrated under reduced pressure to afford a colorless product.

Synthesis of epoxy-functionalized polysiloxane 1 (EP-1): Following the general procedure using AGE (1.20 equiv. of initial Si-H, 175.4 g, 1.53 mol), toluene (50 mL), Pt-catalyst (0.8 mL) and PMHS-1 (1.60 mol reactive hydrogen per 100 g, 80 g) to give EP-1.

EP-1:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 3.16–3.60 (m, O-CH<sub>2</sub>); 2.87–3.02 (m, methine hydrogens of epoxy group); 2.52–2.66 (m, methylene hydrogens of epoxy group); 2.34–2.46 (m, methylene hydrogens of epoxy group); 1.46 (m, -CH<sub>2</sub>); 0.38 (m, Si-CH<sub>2</sub>); -0.07 (s, Si-CH<sub>3</sub>).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 73.5 (O-CH<sub>2</sub>); 71.0 (O-CH<sub>2</sub>); 50.4 (methine carbons of epoxy group); 43.6 (methylene carbons of epoxy group); 22.7 (-CH<sub>2</sub>); 13.0 (Si-CH<sub>2</sub>); -0.85 (Si-CH<sub>3</sub>).

Synthesis of epoxy-functionalized polysiloxane 2 (EP-2): Following the general procedure using AGE (1.20 equiv. of initial Si-H, 109.6 g, 0.96 mol), toluene (70 mL), Pt-catalyst (0.6 mL) and PMHS-2 (0.80 mol reactive hydrogen per 100 g, 100 g) to give EP-2.

EP-2:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 3.34–3.68 (m, O-CH<sub>2</sub>); 3.06–3.15 (m, methine hydrogens of epoxy group); 2.72–2.80 (m, methylene hydrogens of epoxy group); 2.53–2.61 (m, methylene hydrogens of epoxy group); 1.57 (m, -CH<sub>2</sub>); 0.46 (m, Si-CH<sub>2</sub>); 0.05 (s, Si-CH<sub>3</sub>).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 74.0 (O-CH<sub>2</sub>); 71.3 (O-CH<sub>2</sub>); 50.7 (methine carbons of epoxy group); 44.1 (methylene carbons of epoxy group); 23.1 (-CH<sub>2</sub>); 13.3 (Si-CH<sub>2</sub>); 1.1 (Si-CH<sub>3</sub>).

Synthesis of epoxy-functionalized polysiloxane 3 (EP-3): Following the general procedure using AGE (1.20 equiv. of initial Si-H, 61.6 g, 0.54 mol), toluene (70 mL), Pt-catalyst (0.5 mL) and PMHS-3 (0.50 mol reactive hydrogen per 100 g, 90 g) to give EP-3.

EP-3:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 3.32–3.74 (m, O-CH<sub>2</sub>); 3.09–3.18 (m, methine hydrogens of epoxy group); 2.75–2.81 (m, methylene hydrogens of epoxy group); 2.55–2.64 (m, methylene hydrogens of epoxy group); 1.61 (m, -CH<sub>2</sub>); 0.51 (m, Si-CH<sub>2</sub>); 0.07 (s, Si-CH<sub>3</sub>).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 74.1 (O-CH<sub>2</sub>); 71.4 (O-CH<sub>2</sub>); 50.8 (methine carbons of epoxy group); 44.2 (methylene carbons of epoxy group); 23.1 (-CH<sub>2</sub>); 13.4 (Si-CH<sub>2</sub>); 1.1 (Si-CH<sub>3</sub>).

### 2.4. General procedure of the synthesis of cyclic carbonate-functionalized polysiloxanes (CC)

The cyclic carbonate-functionalized polysiloxanes were prepared as shown in Fig. 1. Epoxy-functionalized polysiloxane (100 g), benzyltriethylammonium chloride (TEBA, 1.0 g) and ethylene glycol (0.5 g) were charged into the reactor without solvent. The atmosphere inside the reactor was then replaced with  $\text{CO}_2$  ( $P = 2$  MPa), and the reaction mixture was stirred at 100 °C. The course of the reaction was monitored with IR spectroscopy by focusing on the disappearance of the

Fig. 1. The synthesis of epoxy and cyclic carbonate-functionalized polysiloxanes.

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