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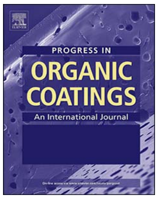

# Synthesis and properties of ambient-curable non-isocyanate polyurethanes

Zhijun Wu[a], Wang Cai[a], Ronghua Chen[b], Jinqing Qu[a,*]

[a] School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, Guangdong, 510641, People's Republic of China
[b] Carpoly Chemical Group Co., Ltd., Jiangmen, Guangdong, 529085, People's Republic of China

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## ABSTRACT

The cyclic carbonate polymer (EC-51) was synthesized with diglycidylether of bisphenol A (E-51) and $CO_2$ under 0.6 MPa at 130 °C for 6 h. The EC-51 prepolymers (EC-51-P) carrying cyclic carbonate groups were prepared by EC-51 reacted with isophorone diamine (IPDA), and then NIPU coatings were prepared by EC-51-P cured with PEI at room temperature. The structures and molecular weights of EC-51-P and NIPU coatings were characterized with FTIR and GPC. The GPC results revealed that molecular weights of EC-51-P were ranged from 2000 to 3800 with 1.30-1.55 of the PDI. The influence of IPDA additions on the properties of EC-51-P and NIPUs were investigated and the results showed that EC-51-P could be cured at room temperature, and their NIPU films hardness increased with the increasing of carbonate/IPDA molar ratios accompanying with the glass transition temperatures increasing. The cured films of NIPU displayed high hardness, excellent impact strength, adhesion and flexibility. They also exhibited excellent solvent resistance to toluene, alkali, xylene and alcohol. Meanwhile, cured films had good thermal stabilities with the temperatures of 5% weight loss ($T_{5\%}$) were in the range of 260–292 °C.

## 1. Introduction

Polyurethane is extensively used in coatings, adhesives, foam, textile and packaging industry due to it providing excellent surface protection, abrasion resistance, weather and chemical resistance [1–7]. Despite of its good properties, it is harmful to environment and human health due to the toxicity of isocyanate compounds [8,9]. Non-isocyanate polyurethanes (NIPUs), which were mainly obtained from the ring-opening reaction of cyclic carbonates and amines, have gained an increasing interest for their environmental synthetic routes [10]. The NIPUs contain a part of primary alcohols and secondary hydroxyl groups to form hydrogen bonding with the urethane group which results in excellent mechanical properties accompanied by marked resistance to solvents and chemicals. Recently, more and more researchers have explored the applications of NIPUs in the fields of sealants and adhesives foams [11–17]. However, their application is still greatly limited in coating industry due to the low reactivity of cyclic carbonates with polyamines (e.g., butanediamine, 1,6-hexanediamine, polyether amine average Mn-230, IPDA, decyl diamine and aromatic amine) at room temperature [10,18–24].

To develop ambient-curable NIPUs coatings, various catalysts have been prepared to decrease the curing temperature and curing times of NIPUs in the past few years. The catalysts include 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD), thiourea, LiCl, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), triethylamine (TEA) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), and so on [25–27]. Lambeth et al. [25] reported the reaction of model compounds 4-phenyl-1,3-dioxolan-2-one (5CC1) and hexahydrobenzo[d][1,3]dioxol-2-one (5CC2) with hexyl amine at room temperature by using TEA, LiCl, thiourea, DBU and TBD as catalysts. They found that TBD had high catalytic efficiency and enable to converse 100% of 5CC1 after 2.5 h, while that was 80% by TEA after 12 h. Blain et al. [26] studied a large number of catalysts and also found the TBD was a promising catalyst, which the conversion of carbonate of model carbonate reaction with N-butyl amine for 1 h at 25 °C were high up to 92% of the conversion. However, TBD was employed for small molecule model compounds and there are few employed macromolecular cyclic carbonates or polycarbonate. Moreover, TBD is also too expensive to use in preparing NIPU coatings. In order to synthesis NIPU at room temperature without any catalysts, Yuen et al. [28] used 5-membered, 6-membered and 8-membered cyclic carbonate reaction with amines, the results showed that the N-substituted 8-membered cyclic carbonates have highly reactive activity with hexamethylene diamine to achieve NIPU at room temperature without any catalysts. However, NIPU were recently prepared by reaction of activated 5-membered cyclic carbonates with amines at room temperature without any catalysts [29].

On the other hand, some properties of NIPU coatings are not so good including water-absorption and films hardness attributed to the

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* Corresponding author.
*E-mail address:* cejqqu@scut.edu.cn (J. Qu).

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existence of hydroxyl groups and long aliphatic chains in the molecular structures [30]. In order to improve these properties, some inorganic and rigid moieties were introduced into the NIPU coatings, including ZnO particles, POSS, cycloaliphatic and aromatic compounds [17,30–32]. Kong et al. [31] used POSS units to modify rosin-based NIPU coatings to enhance the films hardness from 2H to 3H with addtion of 20% POSS in NIPU. They also used the POSS units to modify gallic acid-based and terpene-based NIPU coatings [32,33] and found the hardness of films were enhanced from 1H to 3H with 16–20% contents of POSS units at 150 °C for 1 h.

The epoxy resin E-51 possesses aromatic ring structures to provide high hardness, good chemical resistance and thermal stability in the NIPU coating system. In this work, the NIPU coatings cured at room temperature with good mechanical and chemical properties were firstly reported. The cyclic carbonate polymer (EC-51) was prepared with E-51 and $CO_2$, and then reacted with diamines to synthesize prepolymers (EC-51-P) carrying cyclic carbonate groups with different molecular weights. The ambient-curable NIPU wood coatings were prepared from EC-51-P with hyperbranched polyamines (PEI) at room temperature. The structures of EC-51 and EC-51-P were characterized by $^1$H NMR and FTIR spectrum. The properties of NIPU coatings were investigated by DSC and TGA. The influence of the amine types and the molar ratio of EC-51/amine on the properties of NIPU coatings were also studied and found that the NIPU coatings displayed excellent solvent resistance, high hardness and impact strength, good thermal stabilities and adhesion.

## 2. Experimental

### 2.1. Materials

Diglycidylether of bisphenol A (E-51) with epoxy value of 0.518 mol/100 g, tetrabutyl ammonium bromide (TBAB), acetone, tetrahydrofuran (THF), sodium hydroxide (NaOH) and hydrochloric acid (HCl) were procured from Sinopharm Chemical Reagent Co., Ltd. Isophorone diamine (IPDA), ethylene imine polymer (PEI-400, PEI-1000, PEI-2000, PEI-3000 and PEI-4000, containing 6.71, 13.60, 21.50, 43.0 and 51.48 mol primary amine groups, respectively), the ratios of primary/secondary/tertiary amine groups in the different PEIs are PEI-400:43/34/23, PEI-1000:34/35/31, PEI-200033/35/32:, PEI-3000:35/33/32, PEI-4000:33/34/33, carbon dioxide (99.999%) and dimethylformamide (DMF) were commercially available. All the chemical reagents were used as received without further purification.

### 2.2. Synthesis of EC-51

EC-51 was prepared as follows: E-51 (800 g, 2.04 mol) and TBAB (12 g, 1.5 wt% of E-51) were added into a 2 L high pressure stainless steel reactor. The autoclave atmosphere with carbon dioxide was maintained at 0.4–1.0 MPa and stirred at 130 °C for 2–8 h, then the autoclave reactor was cooled to 60 °C and degassed $CO_2$, and then obtained the viscous liquid of target product, catalyst of TBAB was completely removed by dissolving in dichlormethane followed by extraction with water. A white solid of EC-51 was obtained after drying by vacuum.

### 2.3. Preparation of EC-51-P

The sample of EC-51 was dissolved in DMF, and variable proportion of IPDA were added, which the molar ratios of carbonate/primary amine were ranged from 10:1 to 10:6. The mixture was stirred at 150 °C for 3 h and then obtained the cyclic carbonate-terminated prepolymers EC-51-P.

### 2.4. Preparation of NIPU coatings

The prepolymers and PEI were mixed according to the molar ratio of carbonate/primary amine as 1.0. After stirred for 3–10 min, the films were casted on tin or glass plate with a 50 μm applicator and cured at room temperature, then tested the tack-free time and the actual drying time, the other film properties were tested after 5 days at room temperature.

### 2.5. Characterization of EC-51, EC-51-P and NIPU coatings

$^1$H NMR spectrum of EC-51 was recorded on a Bruker AVANCE III400 (400 MHz) nuclear magnetic resonance spectrometer. EC-51 was dissolved in deuterated dimethyl sulfoxide (DMSO-$d_6$). The Fourier transform infrared spectra (FTIR) of samples were performed on a PerkinElmer spectrum 2000 spectrometer. All samples were casted on the tinplate and scanned from 4000 to 400 $cm^{-1}$ at a resolution of 2 $cm^{-1}$. The viscosities of EC-51-P were surveyed at 25 °C by Brookfield LVT rotational viscometer. Thermogravimetric (TG) of NIPU films were recorded on a TA Instruments SDT Q600 thermalgravimetric-differential thermal analyzer and the NIPU sample (5–10 mg) was heated from 30 to 600 °C at a heating rate of 10 °C $min^{-1}$ under nitrogen flow rate of 100 mL $min^{-1}$. The molecular weights and polydispersity index (PDI) of EC-51-P were obtained using a gel permeation chromatography (GPC) equipped with Shodex RI-201H differential refractive index detector and Shodex KF-805 column system, using THF as a eluant at a flow rate of 1 mL $min^{-1}$. The glass transition temperature ($T_g$) of NIPU films were measurements by NETZSCH DSC 204 F1 differential scanning calorimetry (DSC). All the NIPU coatings were heated from −20 to 120 °C at a heating rate of 10 °C $min^{-1}$ under nitrogen atmosphere.

Pendulum hardness and pencil hardness were measured according to ISO 1522:2006 and ISO 15184:2012, respectively. Adhesion was tested by cross cut according to ISO 2409:2013. The films gloss was measured by incidence angle of 60° according to ISO 2813:2014. Flexibility was tested according to ISO 1519:2011. Impact resistance was measured on the impact tester with maximum height of 100 cm and load of 1 kg according to ISO 6272-2:2011. The chemical resistance (e.g., acid, alkali, alcohol, toluene, xylene, acetone, and water resistance) were evaluated by immersion method according to ISO 2812-1:1993. Tack-free time of NIPUs was evaluated according to the standard EN ISO 9117-3. The actual drying time of NIPUs was evaluated according to Chinese Standard GB/T 1728–1979(1989). The gel time of NIPUs was evaluated by referring the ISO 2535:2001. The pot life of NIPUs/PEI coating systems were tested by viscosity date tested with NK-2 cup, and the times of viscosity increased twice is defined as pot life.

The water- and toluene-absorption of NIPU coating films were determined as follows: Films casted on PTFE plates were weighed $W_0$ firstly before immersed in water or toluene for 24 h at room temperature, followed by wiping surficial water or toluene immediately with a piece of filter paper and weighed $W_1$. Water- and toluene-absorption ($W$ %) was calculated as shown in formula:

$$W\,(\%) = \frac{W_1 - W_0}{W_0} \times 100$$

## 3. Results and discussion

### 3.1. Synthesis and characterization of EC-51

EC-51 was prepared via the reaction of E-51 epoxy resin with $CO_2$ in the presence of TBAB at 130 °C, 0.6 MPa for 6 h without organic solvents according to Scheme 1. Fig. 1 shows that the peak of epoxy groups at 913 $cm^{-1}$ was gradually disappeared and a new peak at 1802 $cm^{-1}$ attributed to cyclic carbonate groups appeared with the $CO_2$ pressure increase from 0.4 to 0.6 MPa. Fig. 2 also shows that the intensity of the

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