Synthesis and properties of Non-isocyanate polyurethane Based on Aromatic amine

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Abstract. Non-isocyanate polyurethane (NIPU) was synthesized via cyclic carbonate(DiCC), which was synthesized through the thiol-ene click reaction that has high selectivity and orientation, and aromatic diamine, which is one alternative for preparing conventional polyurethane without isocyanate, which as the promising materials in green and sustainable chemistry. It will replace the traditional polyurethane in the future chemical industry. A simple non-isocyanate route of synthesizing aromatic polyurethane has been studied in this paper. The chemical structures of DiCC and NIPU were characterized by fourier transform infrared spectrometer (FT-IR), 1H nuclear magnetic resonance spectra (1H NMR). The Mn and Mw of NIPU were measured up to 2964 g·mol⁻¹ and 11528 g·mol⁻¹ through gel permeation chromatography (GPC). Moreover, the initial decomposition temperature showing over 225°C and the shear strength reaching 2.38 MPa.

1. Introduction
In the field of polymer, polyurethane has become one of the most widely used materials due to its excellent performance.¹,² Meanwhile, isocyanate, the basic constituent of conventional polyurethane, which own some disadvantages such as moisture sensitivity, water decomposition and emit carbon dioxide. It is easy to produce bubbles and product quality is impacted in polyurethane production process. In addition, the characteristics of the isocyanate include the high toxicity, miraculous volatilization, and the toxicity of the phosgene for synthesizing isocyanate will turn greater, which would cause even more damage to human health and environment in production process.³-⁵ In order to overcome the disadvantages of traditional polyurethane in production process, more and more attention is applied to the research and development of non-isocyanate polyurethane in recent years. Non isocyanate polyurethane generally refers to a kind of new environment-friendly polyurethane, which is synthesized by cyclic carbonate compound reacted with a polyamine.⁶ NIPU has many advantages when compare with the conventional isocyanate based-polyurethane. Firstly, the absence of isocyanate in process of synthesis and use of NIPU, the harm to the body and environment is eliminated.⁷ Besides, the cyclic carbonate as its raw materials can be synthesized through biological epoxy derivatives and CO₂.⁸-¹¹ SO the synthetic route of the polyurethane can not only ease the problem of oil resources shortage, but also reduce the greenhouse effect. It conforms to the trend of environmental protection. Moreover, hydrogen bonding has a stable seven membered ring structure between the hydroxyl groups and carbonyl...
group of urethanes, which leads to the higher water absorption, the ability to resist the organic solvents improved, and increase Young’s modulus as well as higher tensile strength.12-14

In this paper, a simple non-isocyanate route synthesizing aromatic polyurethane was reported. Firstly, difunctional cyclic carbonate (DiCC) was synthesized via Thiol-ene “clickreaction” which had rapid reaction rates, mild reaction conditions, and high yields.15, 16 Then, NIPU was prepared via reaction the obtained DiCC and aromatic diamine, which is alternative for obtaining the conventional polyurethane without isocyanate. In the structure of polymer, the methylene two benzene rings can be used as curing point. Besides, it has a guiding significance for its application in rubber. The chemical structures, molar masses, thermal stability and dynamic mechanical properties of NIPU were investigated by Fourier transform infrared spectrometer (FT-IR), 1H nuclear magnetic resonance spectra (1H NMR), gel permeation chromatography (GPC), thermogravimetric analysis (TGA), and dynamic thermomechanical analysis (DMA), respectively. A detailed study of adhesive properties of NIPU was carried out.

DiCC was prepared by adding vinyl-1, 3-dioxolan-2-one (0.1 mol), 1,6-hexanedithiol (0.1 mol) and Benzoin dimethyl ether (2 wt% relative to VEC) in a glass dish and the reactant was irradiated for 2 hours by UV curing lamp (365 nm). As shown in Fig. 1a, light yellow transparent viscous liquid product, which as the difunctional cyclic carbonate (DiCC), was obtained. The collected product was analyzed by FTIR spectroscopy to confirm functional group conversion. The schematic representation of the reaction as shown in Fig. 1(1)

NIPU was prepared by adding Bis(cyclic carbonate)s (0.1 mol), 4,4'-diaminodiphenylmethane (0.08 mol/0.1 mol/0.15 mol), Lithium bromide anhydrous (10 mmol% relative to VEC) and N,N-dimethyl formamide (25 mL) were charged into a 250 mL four-necked round bottom flask, which was equipped with a mechanical stirrer, a gas inlet, and a temperature controller. The temperature was maintained at 120°C for 24 h. solvent and volatile residuals were removed in vacuo resulting in a dark brown non-isocyanate polyurethane. The three samples were named as NIPU-1, NIPU-2, NIPU-3 respectively. The conversion was quantitative as confirmed using 1H NMR spectroscopy, FTIR spectroscopy, GPC, TGA, and DMA. The non-isocyanate polyurethane was synthesized via the second step reaction as illustrated in Fig. 1(2).

DiCC was obtained using 4-vinyl-1,3-dioxolan-2-one (VEC) and 1,6-hexanedithiol (HDT) in the presence of a photo initiator via thiol – ene “Click” Chemistry. The reaction between Thiol and double bonds in the thiol – ene addition reaction was monitored quantitatively through IR spectroscopy and 1H-NMR spectroscopy. The FTIR spectra of 4-vinyl-1,3-dioxolan-2-one (VEC), 1,6-hexanedithiol (HDT) and DiCC as shown in Fig. 2. In the VEC FTIR spectra, the absorption peaks at 3095 cm-1 and 991 cm-1 are the stretching vibration peak and bending vibration peak of C=C, respectively. In the HDT FTIR

![Fig. 1 Isocyanate free strategy from cyclic carbonate to non-isocyanate polyurethane](image-url)
spectra, the absorption peak at 2556 cm\(^{-1}\) is the stretching vibration peak of S-H. In addition, the disappearance of 3095 cm\(^{-1}\), 991 cm\(^{-1}\) and 2556 cm\(^{-1}\), which were the characteristic absorptions of VEC and HDT. The phenomenon indicates that the thiol-ene reaction was completed.

Further the structure of difunctional cyclic carbonate (DiCC) was also confirmed by 1H NMR spectroscopy as shown in Fig. 3: 1H NMR (500 MHz, DMSO-d\(_6\), \(\delta\)) 4.92 – 4.82 (m, O-CH, 2H), 4.57 (t, \(J = 8.1\) Hz, O-CH\(_2\), 2H), 4.21 – 4.13 (m, O-CH\(_2\), 2H), 3.32 (s, H2O), 2.66 – 2.42 (m, S-CH\(_2\), 8H), 2.06 – 1.82 (m, CH\(_2\), 4H), 1.50 (d, \(J = 6.5\) Hz, CH\(_2\), 4H), 1.35 (d, \(J = 6.5\) Hz, CH\(_2\), 4H). These observations discussed above confirmed the structure of DiCC product.

![Fig. 2 IR spectra of DiCC prepared by VEC and HDT via UV curing.](image)

![Fig. 3 1H-NMR (500 MHz, DMSO-d6) spectra of DiCC](image)

NIPU was prepared by reacting difunctional cyclic carbonate (DiCC) with 4,4’-DiaminodiphenylMethane(MDA) in the presence of inorganic Lewis acid catalyst (Fig. 1). The five membered cyclic carbonate ring in the amino group of MDA is opened to afford linear NIPU. In order to examine the reactivity of DiCC, the model reaction of MDA with DiCC was investigated at different hours. Fig. 4 displays the IR spectra of DiCC before and after NIPU. The carbonyl IR absorption at 1790 cm\(^{-1}\) decreases as a function of time at 120°C as given in Fig. 4. Compared with DiCC FTIR spectra, new absorption peak appear in the FTIR spectra of NIPU. In addition to the carbonate carbonyl band at 1790 cm\(^{-1}\) changes, new signals appear at 1731, 1578, and 3361 cm\(^{-1}\), which are typical for the carbonyl IR absorption of the urethane groups, N-H deformation of the urethane group, respectively.
It was possible to measure the reaction of DiCC and MDA by using 1H-NMR spectroscopy. Fig. 5 illustrates an example of the conversion of DiCC to NIPU at 120°C for 24 h and LiBr as catalyst. As shown in Fig. 5, the hydroxyl group, was acquired through the ring opening reaction, which can be confirmed by the signal obtained at 1.96 ppm. Further protons from urethane linkage could be assigned to the peak obtained at 7.96 ppm.17 the signals between 6.40 ppm and 7.00 ppm are ascribed to the proton in the aromatic ring between two urethane linkage. The 1H-NMR spectra confirmed that the ring opening reaction of the cyclic carbonate moiety with aromatic amine was successfully achieved. Moreover, the protons from the long aliphatic chain of NIPU was assigned as shown in Fig. 5.

The molecular weight of NIPU at 120°C for 24 h and LiBr as catalyst is displayed in Table 1. As shown in Table 1, GPC analysis showed that the Mn and Mw of the obtained NIPU were 2964 g·mol⁻¹ and 11528 g·mol⁻¹, which were remarkable under solvent and catalyst conditions. Moreover, the polydispersity index (PDI) was relatively extensive 3.89. When the molar ratio of DiCC and MDA is not 1:1, the low activity between DiCC and MDA leads to the difficulties in molecular chain growth. In addition, when excess amine was added and the temperature exceed 100°C, aminolysis of the ester groups occurred, thus the chain growth was limited.18
Table 1. GPC data of the NIPU

| Sample   | Mn(g·mol⁻¹) | Mw(g·mol⁻¹) | PDIa |
|----------|-------------|-------------|------|
| NIPU-1   | 1808        | 11132       | 6.16 |
| NIPU-2   | 2964        | 11528       | 3.89 |
| NIPU-3   | 1010        | 5717        | 5.66 |

* Determined via GPC.

The TGA and DTG curves of three polyurethane films, whose synthesis temperature is 120°C under nitrogen were shown in Fig. 6 and Fig. 7. The molar ratios of DiCC and MDA of NIPU-1, NIPU-2 and NIPU-3 were 1:0.8, 1:1 and 1:1.5, respectively. As shown in Table 2, the initial thermal decomposition temperatures (Td) of the compound, which have 5% mass loss occurred at 232°C, 225°C, 216°C for NIPU-1, NIPU-2, NIPU-3, respectively.

The three cage compounds display the different mass loss curves, which is ascribed to different decomposition process. However, all of them can be divided into three stages as shown in Fig.6 and Fig.7. In stage I, an insignificant weight loss from room temperature to 210°C was thought to be mainly due to the loss of solvent in samples. Stage II, which occurred at approximately 216°C to 232°C and close peak temperatures from 350°C to 372°C. It may correspond to the thermal degradation of the urethane linkages, ester bonds of alkyl chains, the formation of primary amines, and secondary amines take place in this stage, which as reported in a previous literature. Stage III showed that the onset temperatures from 383°C to 396°C and exhibited peak temperatures from 437°C to 446°C for sample. Thermal degradation of the C–C and C–O bonds of the main polymeric chain may be broken in this stage.

![Fig. 6 TGA curves of NIPU-1, NIPU-2 and NIPU-3 in N2 atmosphere](image)

The dynamic mechanical property of each NIPU film was characterized by using DMA as shown in Fig. 8 and Fig. 9. The Storage modulus (E’) and loss factor (tan δ) of all samples were investigated. The E’ and tan δ values were recorded over a wide temperature range.

The values of the glass transition temperature (Tg) of NIPU-1, NIPU-2 and NIPU-3were reported in Table 2. The highest value of Tg in NIPU-2 that the molar ratio is 1:1. As the molecular chain length increases, molecular motions of polymer chains become more restricted, and the amount of energy that can be dissipated throughout the polymers decreases dramatically. Therefore, the tan δ peak shifts to a higher temperature and the (tan δ) max decreases.
Fig. 7 DTG curves of NIPU-1, NIPU-2 and NIPU-3 in N2 atmosphere

Fig. 8 Storage modulus versus temperature of NIPU-1, NIPU-2 and NIPU-3

Fig. 9 Tan delta versus temperature of NIPU-1, NIPU-2 and NIPU-3
Table 2. Thermal decomposition temperature and glass transition temperature of NIPU samples

| Sample | Td5%(°C)a | Td10%(°C)b | E'(MPa)c | Tg(°C)c |
|--------|-----------|------------|----------|---------|
| NIPU-1 | 232       | 268        | 24       | 17.5    |
| NIPU-2 | 225       | 272        | 35       | 22.6    |
| NIPU-3 | 216       | 265        | 43       | 16.2    |

a 5% weight loss temperature determined by TGA (heating rate: 10 oC·min⁻¹, N2).
b 10% weight loss temperature determined by TGA (heating rate: 10 oC·min⁻¹, N2).
c Determined by DMA (scanning rate: 3 oC·min⁻¹, N2).

Tensile strength, elongation at break, hardness and shear strength of NIPU films were summarized in Table 3. The elongation at break of all NIPUs ranged from 280 % to 560%. The tensile strength and Hardness of all NIPUs showed a huge difference. When the molar ratio of DiCC and MDA was 1:1, the tensile strength and Hardness reached 3.51 MPa and 86 A. For stainless steel sheet, the shear strength of the adhesive showed a huge difference among the samples. When the molar ratio of DiCC and MDA was 1:1, the shear strength reached the maximum 2.38 MPa. The reasons might be ascribed to the stronger mechanical properties of NIPU-2. The poor adhesion of NIPU-1 and NIPU-3 to steel may be because of their cohesive failures.

Table 3. Mechanical properties and adhesion properties of NIPU samples

| Sample  | Tensile strengtha (MPa) | Elongation at breaka (%) | Hardnessb (Shore A) | Shear strengtha (MPa) |
|---------|-------------------------|--------------------------|---------------------|----------------------|
| NIPU-1  | 0.82                    | 418                      | 54                  | 0.53                 |
| NIPU-2  | 2.88                    | 280                      | 86                  | 2.38                 |
| NIPU-3  | 0.62                    | 562                      | 58                  | 0.63                 |

a Determined via electronic universal testing machine.
b Determined via shore hardness test instrument.

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