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Experimental Study, Characterization and Performance Test of Epoxy Cyclohexane-Based Transparent Polyurethane Material

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A novel epoxy cyclohexane-based polyurethane material was synthesized from a self-made epoxy cyclohexane-tetrahydrofuran (CHO-THF) co-polyether. Due to the special rigid six-membered ring skeleton in the polyether molecular chain, the polyurethane materials have excellent mechanical properties, good optical transparency and weather resistance. In this paper, the synthesis process of the epoxy cyclohexane-based polyurethane material was studied and the properties of the material were tested. The results showed that curing parameters R value had effects on the mechanical properties and optical transparency of the material.

Keywords: CHO-THF co-polyether, transparent polyurethane, optical transparency, mechanical properties.

1. INTRODUCTION

Polyurethane is a polymer containing carbamate group (–NHCOO–) in its molecular structure, which is formed in a reaction between monomers that contain at least two hydroxyl (–OH) groups and other monomers that contain at least two isocyanate (–N=C=O) functional groups [1]. Ordinary polyurethane materials suffer from some serious application drawbacks, including low optical transparency, insufficient impact resistance, low resistance to open flames and high temperatures [2, 3]. However, transparent polyurethane has wider applications in several high-tech areas such as laminated windshield glass of aircraft and high-speed rail due to the transparent property and good performance in impact resistance and outstanding low temperature performance, which is a new direction in the development of polyurethane industry in recent years [4].

The factors that influence the transparency of PU materials are composition (e.g., the structure of diisocyanate), the type and molecular weight of the soft segment, crystallinity, and hydrogen bonding (intermolecular interactions) [5]. Polyester polyurethane (PU) is easy to crystallize due to the high polarity of ester group (–C=O–) in its molecular structure, thus light transmittance is lowered [6]. However, the intermolecular chain force of polyether polyurethane is much smaller than that of polyester polyurethane, which is not easy to crystallize and has high transparency [7].

In this paper, epoxy cyclohexane-tetrahydrofuran (CHO-THF) transparent polyurethane material (TPU) was synthesized by means of pre-polymer reaction method using self-made co-polyether of cyclohexane oxide-tetrahydrofuran (CHO-THF). Here, we report a novel synthetic routes and processes to produce PU materials of improved properties, in attempts to strengthen the application performance of transparent PU materials.

2. EXPERIMENTAL SECTION

2.1. Materials and instruments

Isophorone diisocyanate (IPDI), CHO-THF co-polyether and methacrylic acid-β-hydroxyethyl ester (HEMA) were used as raw materials; dibutyltin dilaurate (DBTL) was selected as catalyst and azobisisobutyronitrile (AIBN) was used as curing crosslinking agent. All other reagents were analytical grade provided by Tianjin Kemiou Chemical Reagent Co., Ltd.

The following equipment and instruments were used: Constant Temperature Water Bath, DF-101S, Henan Baize Instrument Co., Ltd.; Analytical Balance, AV Ⅱ -400, Metler-Toledo Instruments Co.; Differential Thermal-DSC-TGA, DTG-60, Shimadzu Corporation, Japan; Shaw hardness tester, LX-A, Shanghai Precision Scientific Instruments Co., Ltd.; Cantilever Beam Notch Impact Testing Machine, XJU-22, Chengde City Testing Machine Factory; Electronic Universal Material Testing Machine, INSTRON 1185; A Fourier infrared spectrometer, FT-IR200, Thermo Corporation of the United States; Nuclear magnetic resonance instrument (NMR), INOVA-400, Bruker Corporation of the United States.

2.2. Preparation

The process is divided into two steps: (1) Self-made CHO-THF co-polyether: The copolymerization of CHO and THF was achieved at 0 °C using $BF_3.OEt_2$ as catalyst and glycerol as chain extender. The molar ratio of THF to CHO was 1:2, that of $BF_3.OEt_2$ to CHO was 0.045:1, and that of glycerol to CHO was 0.01:1. After 5.5 h, a new kind of transparent light-yellow viscous liquid with yield of 98.0 % and number average molecular weight of 4295 was obtained. (2) Preparation of TPU: In this experiment, the molar ratio of IPDI, CHO-THF co-polyether and HEMA

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was set to 3:1:3. IPDI, CHO-THF and DBTL were added under the condition of N_2 protection, stirring constantly at the 80 – 90 °C for 1h, then some HEMA was added with continuous stirring at 70 – 80 °C for 50 min. Finally, TPU was obtained by adding AIBN to at a certain temperature.

2.3. Determination of NCO content and hydroxyl number

Determination of hydroxyl number: 0.5 g sample was got and added in 20 mL toluene, stirring to completely dissolve, then 10 mL of 1 mol/L Dibutylamine-Toluene Mixture was added and mixed at room temperature. Another 50 mL of isopropanol and a few drops of Bromcresol green indicator were added, and titrated with a standard HCl solution, at the same time, a blank test was performed, which was observed that the liquid changed from blue to yellow as the reaction end point. The NCO content can be calculated by the following formula:

$$\mathrm{NCO}\% = \frac{(V_1 - V_2)\times C\times 42.02}{m\times 1000}\times 100\%. \qquad (1)$$

Among them, V_1 is the volume of HCl standard solution required for titration blank test, ml; V_2 is the volume of HCl standard solution consumed by sample, ml; C: HCl standard solution concentration, mol/L; 42.02:-NCO group relative molar mass, g/mol; M is the sample quality, g.

Determination of hydroxyl number [8]: hydroxyl number was determined according to national standard GB/T 12008-1989.

2.4. Performance test

Hardness and tensile properties were tested according to national standard [9] GB/T 2411-2008 and national standard [10] GB/T 1040.1-2006. Impact strength was tested according to national standard [11] GB/T 1843-2008.

Optical performance test: the light transmittance of the material was measured by UV-260 ultraviolet-visible diffuse reflectometer, whose test conditions were as follows: the temperature was 23 ± 2 °C, the sample size was 50 × 50 × 1 mm, and the relative humidity was 50.5 %.

3. RESULTS AND DISCUSSION

3.1. Experimental principle

The reaction process of preparing PUA with CHO-THF and IPDI, HEMA, etc. is shown in Fig. 1.

The epoxy cyclohexyl transparent polyurethane (TPU) with higher molecular weight was obtained by curing and crosslinking PUA at a certain temperature.

3.2. Effect of reaction temperature on NCO content

In this experiment, IPDI, CHO-THF co-polyether, HEMA, etc. were selected as raw materials, whose ratio was set to 3:1:3, while the quality of DBTL is 0.2 % of that of the polyether, and a series of PUAs were prepared at different polymerization temperatures by pre-polymer method, and also the NCO content was measured every 10 minutes during the reaction. Fig. 3 show the effect of reaction temperature on NCO content.

It can be seen from Fig. 3 that, in pre-polymerization stage, the NCO content sharply decreased first and then tended to stability, and also the reduction rate of NCO content at 90 °C was faster than that of 70 °C and 50 °C.

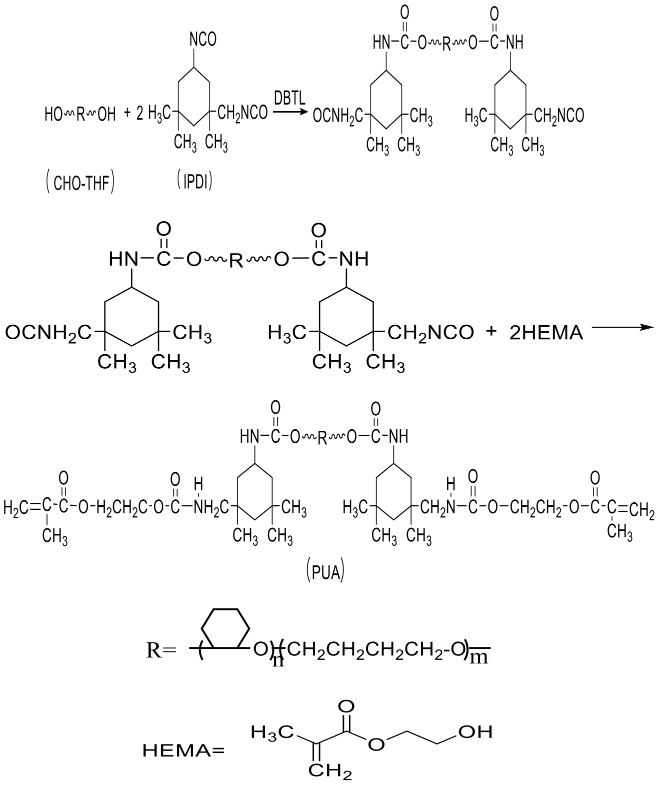


Fig. 1. Synthesis of epoxy cyclohexane-based macro-monomer

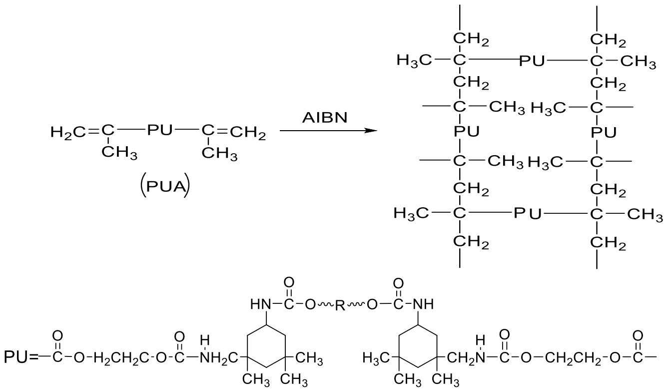


Fig. 2. Preparation of TPU

As can be seen from Fig. 4, in chain extension stage the reduction, rate of NCO content was lower than that in the pre-polymerization stage. NCO content was basically stable after about 50 minutes in the pre-polymerization process, however, which was stable after about 40 minutes at 75 °C and 60 minutes at 50 °C in the polymerization process. Because of the fact that the reactivity of two NCO groups in IPDI is different, NCO group attached to the six-membered ring is more active, so NCO content is rapidly stabilized in the pre-polymerization stage, while the activity of another NCO group is reduced due to substituent group steric hindrance effect, which takes longer for NCO content to fall to stability compared with the former.

Although raising the reaction temperature is conducive to accelerating rate of polymerization， if the temperature is too high， the heat released in reaction is much faster and hard to remove, which leads to explosive polymerization and color of polymer deepened. Therefore, considering the rate of polymerization and the transparency of the polyurethane material, the reaction temperature in the pre-polymerization stage was selected to be 90 °C, while the optimum temperature in the chain extension stage was 75 °C.

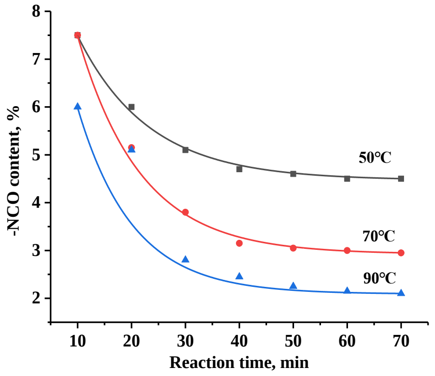


Fig. 3. Change of –NCO content in pre-polymerization stage

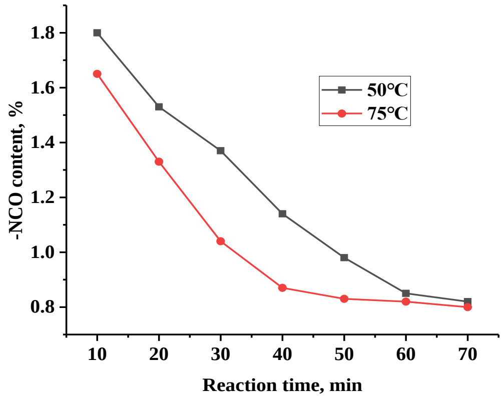
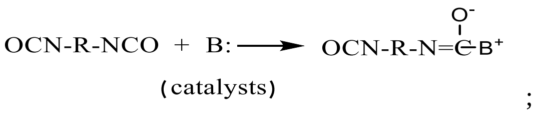


Fig. 4. Variation of –NCO content in chain extension stage

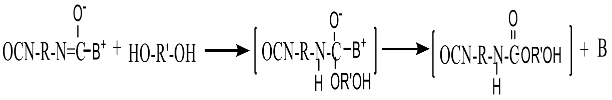
3.3. Effect of catalyst dosage on NCO content

Catalyst can reduce the activation energy, accelerate the reaction rate, shorten the reaction time and control the side reaction. In general, organometallic catalysts have high catalytic selectivity and catalytic efficiency for the reaction of isocyanates with hydroxyl groups (so-called gelation reaction) [12]. Therefore, DBTL was selected as catalyst of polymerization in this experiment. The recognized catalytic mechanism is based on the attack of nucleophilic agents on isocyanates to form intermediate complexes and then react with hydroxyl compounds according to Eq. 2 and Eq. 3 [13].



$$\underset{\text{(catalysts)}}{\mathrm{OCN{-}R{-}NCO} + \mathrm{B}:} \longrightarrow \mathrm{OCN{-}R{-}N{=}\overset{O^-}{\overset{|}{C}}{-}B^+} \quad ;$$

(1)



$$\mathrm{OCN{-}R{-}N{=}\overset{O^-}{\overset{|}{C}}{-}B^+ + HO{-}R'{-}OH} \longrightarrow \left[\mathrm{OCN{-}R{-}\underset{H}{N}{-}\underset{OR'OH}{\overset{O^-}{C}}{-}B^+}\right] \longrightarrow \left[\mathrm{OCN{-}R{-}\underset{H}{N}{-}\overset{O}{\overset{\|}{C}}OR'OH}\right] + \mathrm{B}$$

(2)

In this experiment, the effect of catalyst dosage on the NCO content in the polymerization was studied. The experimental results were shown in Table 1, which showed that the more DBTL was added, the less NCO content was left in the reaction mixture. When catalyst dosage reached 0.2 %, the reaction between –NCO and –OH was almost completed. Therefore, the optimum addition of DBTL was selected to be 0.2 % of quality of polyether.

Table 1. Effect of catalyst dosage on NCO content

Sample	1	2	3
Catalyst dosage	0.1	0.15	0.2
NCO content	1.25	0.78	0.35

3.4. Effect of curing parameter *R* on oroperties of polyurethane materials

Curing parameter *R* refers to the molar ratio of –NCO in isocyanate to –OH in polyether, that is, the relative content of soft and hard segments of polyurethane [14, 15]. In this paper, the ratio of HEMA to IPDI is fixed at 1:1, and the effect of curing parameter *R* on transparency and mechanical properties of TPU is analysed. It can be seen from Fig. 5 that the polyurethanes prepared by different *R* values have good light transmittance, and the change of *R* value has little effect on transparency of materials, which is because the CHO-THF co-polyether is a flexible chain segment, whose molecular structure is disordered, which is hard to crystallize. At the same time, the cross-linked network structure inside the polyurethane material prevents the micro-phase separation between the soft and hard segments to a certain extent, which destroys the crystal structure of the molecules, thereby enhancing the light transmittance.

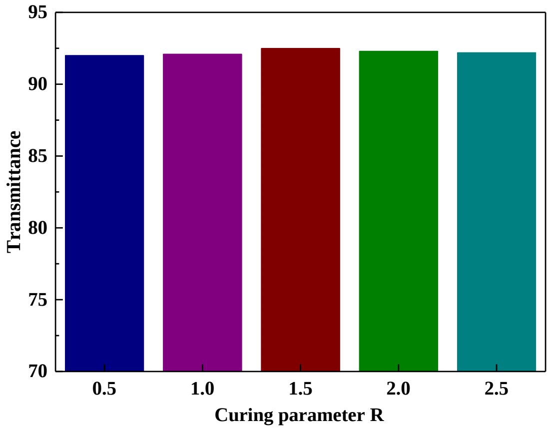


Fig. 5. Effect of curing parameter *R* on transparency of polyurethane materials

The effect of curing parameter *R* value on the mechanical properties of polyurethane materials is shown in Table. 2. It can be seen from the graph that, in a certain range, the shore hardness and tensile strength of TPU increase in different degrees with the increase of curing parameter *R*, while the impact resistance decreases continuously. This is mainly because the increase of the *R* value will increase the hard segment content of the polymer, the hydrogen bonding effect is strengthened and the physical crosslinking point is increased, thereby increasing the tensile properties and the shore hardness. Theoretically, when $R = 1$, the molecular weight is the largest, and the comprehensive properties of the material are the best. Table 2 shows that when $R = 1.5$, the comprehensive properties of the material are the best. When $R > 1.5$, excessive NCO will further react with carbamate or active hydrogen in substituted urea to form cross-linking bonds such as urea carbamate or biuret. The formation of a small amount of cross-linking bonds has a great contribution to improving the strength and other properties of polyurethane materials, but too much isocyanate will produce too much chemical cross-linking, which is not conducive to the mechanical properties of polyurethane materials.

Table 2. Effect of curing parameter *R* on mechanical properties of polyurethane materials

R value	Shore hardness, A	Tensile strength, MPa	Impact strength, kJ/m^2
0.5	49	0.19	1.13
1	60	1.62	2.93
1.5	67	4.56	2.70
2	70	1.70	2.29
2.5	56	1.08	2.08

3.5. FTIR analysis

FTIR spectra of the CHO–THF co-polyether is showed in Fig. 6. As can be seen from the figure that the characteristic absorption peaks of ether bond (C–O–C) are at 1088 cm^{-1}, while the vibration absorption peaks of hydroxyl (–OH) are at 3438 cm^{-1}, and the C–H stretching vibration peaks of methylene (–CH$_2$) and methylene (–CH) are at 2929 cm^{-1} and 2855 cm^{-1} respectively and the deformation vibration of C–H is at 1448 cm^{-1}, which proves that the ring-opening polymerization of CHO and THF is realized and hydroxyl-terminated co-polyether is formed.

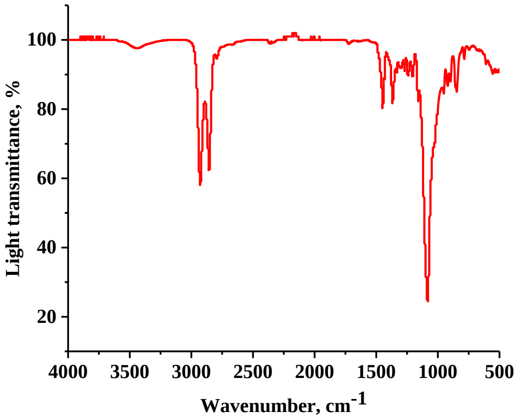


Fig. 6. FTIR spectra of CHO-THF co-polyether

It can be seen from Fig. 7 that, compared with Fig. 6, curve (1) does not exhibit a vibrational absorption peak of –NCO at 2254 cm^{-1}, indicating that –NCO has reacted with CHO–THF copolymer ether and –OH in HEMA completely. In curve (1), bending vibration absorption kurtosis of secondary amide (–NH) is observed at 1532 cm^{-1}, and the characteristic absorption peak of carbonyl group (C=O) of carbamate is observed at 1518 cm^{-1}, which indicates that synthetic PUA contains –N–C=0, which is an important characteristic of judging polyurethane. Curve (1) exhibited a characteristic absorption peak of –C=C– at 1718 cm^{-1}, whereas curve (2) exhibited a significant decrease in peak strength, indicating that –C=C– in PUA did undergo curing and crosslinking to obtain TPU with larger molecular weight.

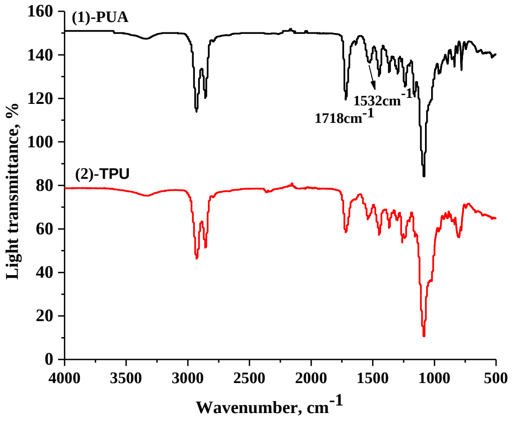


Fig. 7. FTIR spectra of PUA (1) and TPU (2)

3.6. ^{1}H NMR analysis

The ^{1}H NMR spectrum of CHO-THF co-polyether is presented in Fig. 8. It can be seen from Fig. 8 that the absorption peaks between δ1.0 and δ2.0 are proton peaks on the carbon not adjacent to oxygen in the residual cyclohexane oxide and those on the carbon not connected to oxygen in the THF segment ($-OCH_2CH_2CH_2CH_2O-$); the absorption peaks between δ3.0 and δ4.0 are proton peaks on the carbon linked to oxygen in the monomer residue; the proton peak at δ3.1 is hydroxyl-terminated, and the strength of the peak is very weak due to the small number of hydroxyl-terminated proton peaks; the solvent peak at δ7.26.

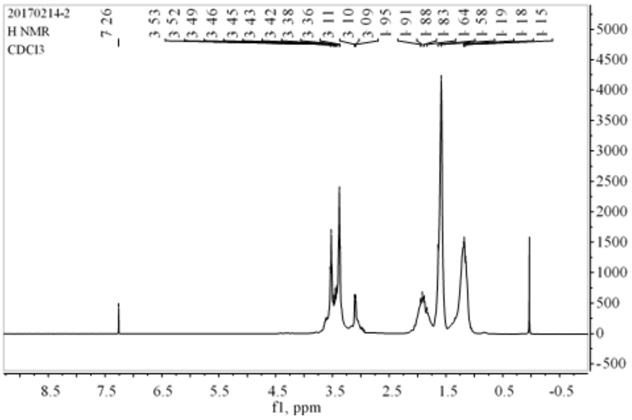


Fig. 8. ^{1}H NMR spectrum of CHO–THF co-polyether

3.7. Thermal analysis of polyurethane material

It can be concluded from Fig. 9 that the epoxy cyclohexane-based transparent polyurethane material has almost no thermal decomposition before 330 °C, indicating that the thermal properties are relatively stable. When the temperature continues to increase, there are two peaks of weightlessness, the first is between 330 °C and 380 °C, and the second is between 380 °C and 413 °C. This is mainly because the thermal decomposition process of epoxy cyclohexane-based transparent polyurethane material is divided into two stages, the first stage is the thermal decomposition of hard segment in polyurethane, and the second stage is the thermal decomposition of soft segment co-polyether. It can be seen that the epoxy cyclohexane-based transparent polyurethane material has a high thermal decomposition temperature and good heat resistance stability.

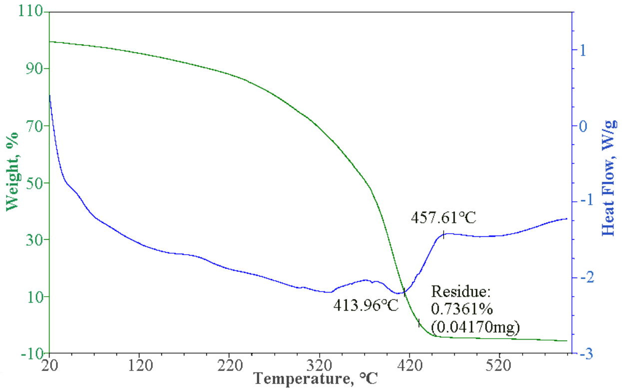


Fig. 9. DSC–TGA curve of epoxy cyclohexane-based transparent polyurethane material

4. CONCLUSIONS

PUA was synthesized from CHO–THF co-polyether. The following conclusions were drawn: The synthesis conditions are as follows: the amount of catalyst (DBTL) is 0.2 % of the mass of polyether; the reaction temperature in the pre-polymerization stage is 90 °C and the reaction time is 50 min; the reaction temperature in the chain extension stage is 75 °C and the reaction time is 40 min. With the increase of the R value of the curing parameter, the Shore hardness and tensile strength of the TPU material are continuously enhanced, the impact resistance is continuously reduced and the light transmittance is basically unchanged.

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