



Synthesis and characterization of poly(propylene carbonate) glycol-based waterborne polyurethane with a high solid content

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ABSTRACT

Waterborne polyurethanes (WPU) with high solid contents were synthesized by using poly(propylene carbonate) glycol (PPC) as the soft segment, methylene-bis(4-cyclohexylisocyanate) (HMDI) and 1,4-butanediol (BDO) as the hard segments, 2,2-bis(hydroxymethyl)butyric acid (DMBA) and 2-[(2-aminoethyl) amino]-ethanesulfonic acid monosodium salt (AAS) as the donors of hydrophilic groups. For comparison, polypropylene glycol (PPG) and polytetramethylene ether glycol (PTMG) were also used as soft segments in the synthesis of WPU (PPG-WPU and PTMG-WPU, respectively). The particle size and distribution of the emulsions were measured and analyzed by submicron particle size Zeta-potential analyzer and transmission electron microscopy (TEM). The storage stability, contact angle and viscosity of the emulsions were also tested. The structure, mechanical properties, acid and alkali resistance, water absorption and thermogravimetric analyses (TGA) of WPU films were also characterized. The results showed that the WPU emulsions exhibited narrow particle distributions, small particle dimensions, good appearance and excellent storage stability. The emulsion viscosity increased slowly at low solid contents and then showed an abrupt change when the solid content exceeded 52%. PPC-WPU films showed superior overall properties in terms of tensile properties, rubber hardness and T-peel strength relative to the PPG-WPU films or PTMG-WPU films. The water absorption rate of the PPC-WPU film was slightly lower than that of the PPG-WPU film but higher than that of the PTMG-WPU film. The hydrogen atom on the α -C atom and the special structure of bonds in the poly(propylene carbonate) glycol molecular chain resulted in excellent acid and alkali resistance but poor thermal stability at high temperature. Moreover, the crystallinity of the PPC-WPU film was lower than that of the PTMG-WPU film due to the irregular structure of poly(propylene carbonate) glycol.

1. Introduction

With the rapid development of the polyurethane industry, polyurethane has become one of the most useful polymeric materials in our daily lives. Due to the high volatile organic compounds (VOCs) evaporation of conventional solvent-based polyurethane, waterborne polyurethane (WPU) has attracted increasing attention due to its advantages of environmental friendliness, economic efficiency and low toxicity. WPU is widely used in adhesives, coatings, paper, wood products, and other uses. Compared to solvent-based polyurethane, WPU with a low solid content (20%–40%) shows many disadvantages, such as low production efficiency, high cost of transport and storage, slow drying, and high energy consumption. Therefore, the preparation of WPU with high solid content has been a focus of research in this field.

Normal waterborne polyurethane is stabilized by anionic stabilization carried out after the emulsification process and is mostly sulfonic- or carboxylic-type waterborne polyurethane [1]. Due to its poor

hydrophilicity, the carboxylic group cannot be used as the only hydrophilic group in the synthesis of high-solid-content WPU. By the incorporation of a small amount of sulfonate with carboxylic acid, polyurethane (PU) dispersions with a more stable 'double layer' structure acquired better overall performance characteristics such as acid and alkali resistance, electrolyte resistance, and mechanical stability [2]. Zuo et al. prepared a kind of waterborne polyurethane containing both carboxylic and sulfonic groups, which had good mechanical properties but poor water resistance [3]. Our team has successfully synthesized a series of WPU and PU elastomers by using poly (propylene carbonate) glycol as the soft segment and found that the obtained polyurethane exhibited excellent hydrolytic stability and mechanical properties. The application of poly(propylene carbonate) glycol in the synthesis of polyurethane solved the problem of the fixation of carbon dioxide and provided a novel material for the synthesis of polyurethane [4]. In this study, poly(propylene carbonate) glycol-based waterborne polyurethane with high solid content was synthesized by

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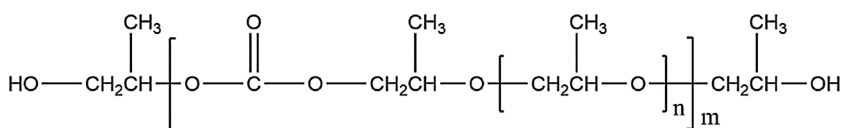


Fig. 1. Molecular structure of poly (propylene carbonate) glycol.

using AAS and DMBA as hydrophilic chain-extenders. The properties of PPC-WPU were compared to those of PPG-WPU and PTMG-WPU.

2. Experimental

2.1. Materials

Poly(propylene carbonate) glycol ($M_n = 3000 \text{ g mol}^{-1}$) was supplied by Guangdong Dazhi Environmental Protection Technology Incorporated Company (China). The structure of poly (propylene carbonate) glycol is illustrated in Fig. 1. Polypropylene glycol (PPG, $M_n = 2000 \text{ g mol}^{-1}$) was purchased from Jiangsu Haian Petrochemical Plant (China). Polytetramethylene ether glycol (PTMG, $M_n = 2000 \text{ g mol}^{-1}$) was obtained from Mitsubishi Chemical Corporation. Methylene-bis(4-cyclohexylisocyanate) (HMDI) was obtained from Wanhua Chemical Group Co., Ltd. (China). Triethylamine (TEA) and acetone (analytically pure) were obtained from Tianjin Damao Chemical Reagent Factory (China). 1,4-Butanediol (BDO) and 4A molecular sieve were supplied by Tianjin Kermel Chemical Reagent Co., Ltd. (China). AAS was supplied by Shanghai Devise Future Industrial Co., Ltd. (China). Stannous octoate (T-9) was purchased from Aladdin Company. DMBA was obtained from Shanghai Baoman Biology Technology Co., Ltd. (China).

Poly(propylene carbonate) glycol and BDO were dehydrated under vacuum at 110°C for 2 h prior to use. DMBA was dehydrated at 130°C for 5 h prior to use. TEA and acetone were dehydrated by molecular sieve prior to use.

2.2. Preparation of waterborne polyurethanes

Poly(propylene carbonate) glycol, DMBA and HMDI were charged into a 500 ml, 4-neck flask equipped with IKA EUROSTAR 20 digital stirrer for mixing for approximately 10 min at 500 rpm. T-9 (0.2 wt% of PPC glycol) was added into the mixture, and then the mixture was heated up to 80°C to react until the NCO content reached a certain value (after approximately 3.5 h of reaction). The NCO terminated prepolymer was cooled to 70°C , and then BDO was added, followed by the reaction for another 1 h. Then, the mixture was cooled to $25\text{--}30^\circ\text{C}$, and AAS was introduced into the reaction mixture to react for 15 min. Stoichiometric TEA as the neutralizing agent was added into the mixture to react for 5 min. After the neutralization, the mixture was poured into cold deionized water (approximately 5°C) and stirred vigorously at approximately 3000 rpm for 15 min. Then, the post polymerization was carried out for 1 h at 80°C to obtain WPU emulsions with a high solid content. The reactant proportion is listed in Table 1. The reaction scheme for the synthesis of WPUs is illustrated in Fig. 2.

Table 1
Reactant proportion of waterborne polyurethane.

Sample	Compositions (g)	Hard segment (%)
PPC-WPUs	PPC/HMDI/DMBA/BDO/AAS/TEA (60/31.5/3.0/1.0/2.0/2.0)	38.4
PPG-WPUs	PPG/HMDI/DMBA/BDO/AAS/TEA (60/31.5/3.0/1.0/2.0/2.0)	38.4
PTMG-WPUs	PTMG/HMDI/DMBA/BDO/AAS/TEA (60/31.5/3.0/1.0/2.0/2.0)	38.4

Note: As the main factor affecting the properties of WPUs, the content of hard segment was kept as the same value.

The obtained WPU emulsions were coated onto a polystyrene plate stored for 24 h at room temperature, and the coatings were then dried at 80°C for 24 h until a constant weight was obtained. Then, the WPU films were obtained.

The hard segment content was calculated according to the following equation:

$$\text{Hard segment content (\%)} = \frac{W_1 + W_2}{W_1 + W_2 + W_3} \times 100\%$$

W_1 : weight of isocyanate

W_2 : weight of chain extender

W_3 : weight of polyols

2.3. Characterization

The emulsion appearance (including transparency, blue light and impurity) of WPUs were observed by visual measurements.

Emulsion viscosity of WPUs was measured at 25°C using a Brookfield viscometer with DV-II + Pro and UL adapter spindle. The average of three experimental measurements was taken as the viscosity [5].

Solid content was tested in a drying oven (DHG-9076A, Shanghai Jinghong macro laboratory equipment co., LTD, China). Approximately 1 g emulsion was placed on a glass-surface vessel and weighted (m_1). The weight of the glass-surface vessel was m_2 . The sample was dried at 120°C to a constant weight (m_3). The test was performed three times and the average was taken as the final value [6]. The solid content (X) was calculated according to:

$$X (\%) = \frac{m_3 - m_2}{m_1 - m_2} \times 100\%$$

Particle size and distribution were measured by a submicron particle size and Zeta potential analyzer (Delsa Nano C, Brookhaven Counter, Inc) at room temperature. The solid content of the sample emulsion was controlled to be 0.5% by diluting with deionized water. Morphology and size of emulsion particles were also observed by transmission electron microscopy (TEM, JEM-2100, Japan Electron Optics Laboratory Co., Ltd). The acceleration voltage was kept at 100 kV. Prior to the observation, WPU emulsions were first diluted to 0.5% by deionized water and dyed for 1 min using phosphotungstic acid (the pH was regulated to 7 by sodium hydroxide prior to use); the volume ratio of emulsion to phosphotungstic acid was 1:1. Then, the mixed solution was dropped onto a copper grid coat [6]. The sample was dried at 60°C for 12 h prior to observation.

The composition analyses of WPUs were performed using a Nicolet 6700 Fourier Transform Infrared (FT-IR) Spectrometer at the range from 500 cm^{-1} to 4000 cm^{-1} .

The thermal properties of the WPU films were characterized by thermal gravimetric analysis (TGA) (STA 409 PC, NETZSCH-Gerätebau GmbH, Germany) under nitrogen atmosphere (flow rate: 50 ml/min) at the heating range from room temperature to 600°C . The heating rate was $10^\circ\text{C}/\text{min}$ [7].

The tensile properties of WPU films were tested by an electro-mechanical universal testing machine (CMT4204, MTS SYSTEMCO., Ltd.) at the rate of 200 mm/min according to ASTM D 412-1998-2002. The dumbbell-shaped samples with a gauge section with a length and width of 25 mm and 4 mm, respectively, were cut from films with the thickness of 0.5 mm.

Water absorption testing was performed at room temperature. The WPU films were cut into squares of $2 \text{ cm} \times 2 \text{ cm}$ and weighted (m_1).

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