



Preparation and antimicrobial activity of terpene-based polyurethane coatings with carbamate group-containing quaternary ammonium salts



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ABSTRACT

A series of novel carbamate group-containing quaternary ammonium salts (QASs) have been synthesized, which were subsequently used as antimicrobial agent and incorporated into polyurethane coatings through crosslinking with terpene-based polyol and polyisocyanate. The chemical structures of QASs were characterized by FT-IR, ¹H NMR, and ¹³C NMR. The effects of QASs on the properties of coatings were investigated. The results showed that the resulting coatings exhibited significant antimicrobial activity against both *Staphylococcus aureus* and *Escherichia coli* by introducing QASs into the polyurethane networks. Furthermore, with the increasing of QAS content, the antimicrobial activity and adhesion of the coatings were enhanced, while the pencil hardness, water resistance and thermal stability of the coatings were decreased.

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1. Introduction

The increasing awareness of healthcare has prompted the use of antimicrobial coatings to prevent the growth and accumulation of harmful bacteria. The antimicrobial coatings usually prepared by either addition of antimicrobial additives or chemical modification of coatings with appropriate antimicrobial functional groups [1]. Compared to addition of antimicrobial additives, the latter approach attracted more concerns because of advantages such as non-releasing of antimicrobial agents into the environment, prolonged lifetime of antimicrobial activity, lower toxicity and chemical stability [2,3].

Polyurethanes (PU) are commonly used as biomaterials due to their good biocompatibility, biodegradability, mechanical and physical properties [4]. Various strategies such as incorporation of different bactericidal substances have been proposed to

enhance the antimicrobial activity of PU [5–10]. Especially, quaternary ammonium salts (QASs), which have been widely used as antimicrobial agents due to their robust and broad-spectrum antibacterial activities [11–13], have gained considerable interest in the development of antimicrobial PU coatings [14–19]. However, the widespread use of QASs leading to an increased number of microorganisms which are resistant to the most common QASs. As a result, extensive efforts have been conducted to search for novel and effective QASs.

In this study, the novel terpene-based carbamate group-containing QASs were synthesized as promising antimicrobial agents through the quaternization of terpene-based carbamate with alkyl bromides (Fig. 2). Then, the QASs with reactive hydroxyl groups were mixed with terpene-based polyol, and reacted with polyisocyanate to yield PU coatings with chemically linked QAS groups. The chemical structures of the resulting products were characterized by FT-IR, ¹H NMR, and ¹³C NMR. The antimicrobial activities of the QASs and PU coatings were determined against both *Staphylococcus aureus* and *Escherichia coli*. By introducing the QASs into the PU coatings, the antimicrobial activity of the coatings were expected to be improved.

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2. Experimental

2.1. Materials

The terpene-maleic ester-type epoxy resin with epoxy value of 0.34 mol/100 g was prepared according to the literature [20]. The terpene-based polyol (Fig. 1) was prepared according to the literature [21]. Carbon dioxide (99.99%) was commercially available. The hydrophilically modified hexamethylene diisocyanate (HDI) tripolymer with isocyanate (NCO) group content of 13 wt% was supplied by Shanghai Sisheng Polymer Materials Co., Ltd., China. All other chemical reagents were chemically pure and were supplied by Sinopharm Chemical Reagent Co., Ltd., China.

2.2. Measurements

The NMR measurements were performed on a Bruker DRX 500 spectrometer (Bruker, Switzerland). The IR spectra were recorded on a Nicolet IS10 FT-IR spectrophotometer (Nicolet, Madison, WI, USA). Mechanical properties of PU coatings were evaluated according to standard test methods (impact strength GB/T 1732-93 [22], adhesion GB/T 1720-89 [23], flexibility GB/T 1731-93 [24], pencil hardness GB/T 6739-96 [25]). 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 analysis (TGA) were performed with NETZSCH STA 409 PC/PG thermogravimetric analyzer (Germany) at a heating rate of 10 °C/min under a nitrogen atmosphere.

2.3. Synthesis of terpene-based cyclic carbonate 1

The terpene-based cyclic carbonate was prepared according to the literatures [26,27]. Terpene-maleic ester-type epoxy resin (100 g, 0.34 mol), LiBr (1.0 g, 0.01 mol), ethylene glycol (0.5 g, 0.008 mol), and N-methylpyrrolidone (50 mL) were placed in an autoclave equipped with a magnetic stirrer. The atmosphere was replaced with carbon dioxide, the mixture was heated to 110 °C, and the pressure was maintained at 2 MPa. The reaction was completed in about 7 h. The catalyst and N-methylpyrrolidone were completely removed by washing with water. A brown solid of compound **1** was obtained after drying by vacuum.

Compound 1: $^1\text{H NMR}$ (500 MHz, CDCl_3 , δ): 5.96–6.23 (CH=CH); 4.73–5.06 (CO–O–CH–CH₂); 4.46–4.58 (CO–O–CH₂–CH); 3.98–4.36 (CO–O–CH₂); 2.92–3.01, 3.19–3.31 (CH–C=O); 1.98–2.22 (CH–CH₃); 0.86–1.86 (CH₂, CH₃). $^{13}\text{C NMR}$ (500 MHz, CDCl_3 , δ): 171.0–171.9 (C=O); 154.5 (C=O); 134.4–137.9 (CH=CH); 73.7 (CO–O–CH–CH₂); 65.7, 65.8 (O–CH₂); 63.2 (CO–O–CH₂–CH). IR (cm^{-1}): 2956, 2873 (CH₃, CH₂); 1792 (C=O); 1731 (C=O); 1455, 1388 (CH₂, CH₃); 1161, 1051 cm^{-1} (C–O–C).

2.4. Synthesis of terpene-based carbamate 2

The terpene-based cyclic carbonate **1** (20 g, 0.068 mol) was dissolved in ethanol (20 mL), *N,N*-dimethylaminopropylamine (6.94 g, 0.068 mol) was added dropwise into the solution and the mixture was stirred at 75 °C. The reaction progress was monitored by IR spectroscopy. While the absorbance band due to cyclic carbonate

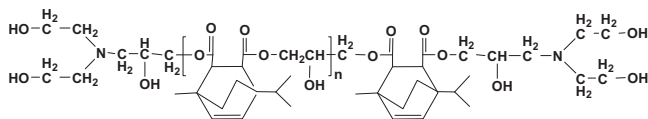


Fig. 1. Chemical structure of terpene-based polyol.

moieties at 1792 cm^{-1} diminished and finally disappeared, the reaction was terminated. After removal of the solvent, the product was obtained as a yellow solid. Purification was accomplished by recrystallization with ethanol and ethyl acetate to give compound **2**.

Compound 2: $^1\text{H NMR}$ (500 MHz, CDCl_3 , δ): 6.03–6.15 (CH=CH); 3.96–4.30 (CO–O–CH₂); 3.57–3.75 (HO–CH₂); 2.93–3.02, 3.16–3.31 (CH–C=O); 2.31–2.45 (N–CH₂); 2.21 (N–CH₃); 2.04–2.16 (CH–CH₃); 0.86–1.85 (CH₂, CH₃). $^{13}\text{C NMR}$ (500 MHz, CDCl_3 , δ): 171.8–173.4 (C=O); 156.6 (NH–CO); 135.0–136.0 (CH=CH); 62.7–72.3 (O–CH₂, CH–OH, CH₂–OH); 57.1, 57.7 (N–CH₂–); 45.0 (N–CH₃). IR (cm^{-1}): 3304 (OH); 2952, 2871 (CH₃, CH₂); 1719 (C=O); 1531 (N–H); 1461, 1372 (CH₃, CH₂); 1248 (N–C); 1172, 1037 (C–O–C).

2.5. Synthesis of terpene-based carbamate group-containing QASs 3 (a–d)

Compound **2** (15 g, 0.034 mol) was dissolved in ethanol (20 mL), alkyl bromide (0.17 mol) was added to the solution. The mixture was stirred for 18 h at 70 °C. After removal of the solvent, the product was obtained as a brown solid. Purification was accomplished by recrystallization with ethanol and ethyl acetate to give compound **3 (a–d)**.

Compound 3a: $^1\text{H NMR}$ (500 MHz, CD_3OD , δ): 6.16–6.28 (CH=CH); 3.97–4.42 (CO–O–CH₂); 3.71–3.82 (HO–CH₂); 3.38–3.57 (N⁺–CH₂); 3.28 (N⁺–CH₃); 3.04–3.11, 3.14–3.22 (CH–C=O); 2.04–2.18 (CH–CH₃); 0.96–1.96 (CH₂, CH₃). $^{13}\text{C NMR}$ (500 MHz, CD_3OD , δ): 172.5–174.2 (C=O); 157.2 (NH–CO); 134.9–135.9 (CH=CH); 62.6–72.8 (O–CH₂, CH–OH, CH₂–OH); 61.8 (N⁺–CH₂); 50.1 (N⁺–CH₃). IR (cm^{-1}): 3288 (OH); 2955, 2873 (CH₃, CH₂); 1719 (C=O); 1530 (N–H); 1460, 1371 (CH₃, CH₂); 1243 (N–C); 1173, 1038 (C–O–C); 1162 (N⁺–C).

Compound 3b: $^1\text{H NMR}$ (500 MHz, CD_3OD , δ): 6.18–6.27 (CH=CH); 4.10–4.42 (CO–O–CH₂); 3.70–3.82 (HO–CH₂); 3.39–3.55 (N⁺–CH₂); 3.27 (N⁺–CH₃); 3.00–3.06, 3.15–3.17 (CH–C=O); 2.04–2.15 (CH–CH₃); 0.96–1.93 (CH₂, CH₃). $^{13}\text{C NMR}$ (500 MHz, CD_3OD , δ): 172.1–173.8 (C=O); 157.2 (NH–CO); 134.8–135.9 (CH=CH); 62.7–72.8 (O–CH₂, CH–OH, CH₂–OH); 61.7 (N⁺–CH₂); 50.0 (N⁺–CH₃). IR (cm^{-1}): 3298 (OH); 2954, 2871 (CH₃, CH₂); 1720 (C=O); 1528 (N–H); 1461, 1372 (CH₃, CH₂); 1242 (N–C); 1173, 1037 (C–O–C); 1153 (N⁺–C).

Compound 3c: $^1\text{H NMR}$ (500 MHz, CD_3OD , δ): 6.14–6.24 (CH=CH); 4.07–4.39 (CO–O–CH₂); 3.66–3.78 (HO–CH₂); 3.35–3.50 (N⁺–CH₂); 3.23 (N⁺–CH₃); 3.04–3.11, 3.14–3.21 (CH–C=O); 2.01–2.18 (CH–CH₃); 0.99–1.99 (–CH₂, –CH₃). $^{13}\text{C NMR}$ (500 MHz, CD_3OD , δ): 171.8–174.2 (C=O); 157.2 (NH–CO); 134.8–135.6 (CH=CH); 62.7–72.9 (O–CH₂, CH–OH, CH₂–OH); 61.7 (N⁺–CH₂); 50.0 (N⁺–CH₃). IR (cm^{-1}): 3287 (OH); 2924, 2854 (CH₃, CH₂); 1716 (C=O); 1526 (N–H); 1463, 1372 (CH₃, CH₂); 1242 (N–C); 1175, 1037 (C–O–C); 1152 (N⁺–C).

Compound 3d: $^1\text{H NMR}$ (500 MHz, CD_3OD , δ): 6.15–6.24 (CH=CH); 4.07–4.39 (CO–O–CH₂); 3.66–3.79 (HO–CH₂); 3.36–3.51 (N⁺–CH₂); 3.23 (N⁺–CH₃); 3.00–3.06, 3.15–3.21 (CH–C=O); 1.98–2.22 (CH–CH₃); 1.00–1.97 (CH₂, CH₃). $^{13}\text{C NMR}$ (500 MHz, CD_3OD , δ): 172.4–173.9 (C=O); 157.2 (NH–CO); 134.9–135.7 (CH=CH); 62.7–72.8 (O–CH₂, CH–OH, CH₂–OH); 61.7 (N⁺–CH₂); 50.0 (N⁺–CH₃). IR (cm^{-1}): 3301 (OH); 2922, 2852 (CH₃, CH₂); 1717 (C=O); 1528 (N–H); 1464, 1372 (CH₃, CH₂); 1245 (N–C); 1176, 1038 (C–O–C); 1154 (N⁺–C).

2.6. Preparation of terpene-based polyurethane coatings

Polyurethane coatings were prepared from a mixture of terpene-based polyol, various QASs, and the hydrophilically

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