Polymer Journal (2016) 48, 259–265

www.nature.com/pj

ORIGINAL ARTICLE

Synthesis, characterization and antibacterial properties of polyurethane material functionalized with quaternary ammonium salt

Chun-Hua Wang, Gui-Ge Hou, Zhen-Zhen Du, Wei Cong, Ju-Feng Sun, Yan-Yan Xu and Wen-Shuai Liu

Novel block antibacterial polyurethane (BAPU) and terminated antibacterial polyurethane (TAPU) with *N*-methyl-*N*-dodecyl-*N*, *N*-bis(2-hydroxyethyl) ammonium bromide (C12QAS) were prepared through pre-polymerization, chain-extending and termination reactions. The physical performances of the antibacterial polyurethane (APU)s, including the film-building effect, differential scanning calorimetry, viscometry, mechanical properties and water absorption rate, were primarily investigated. Their antibacterial properties, tested by the inhibition zone method and the oscillation method, indicate that the APUs display marked mechanical properties, water absorption and improved antibacterial properties against Escherichia *coli*, *Staphylococcus aureus* and *Bacillus subtilis*, with the most potency against *E. coli*. This polyurethane material may have potential applications as an antibacterial material for biomedical devices and implants.
Polymer Journal (2016) **48,** 259–265; doi:10.1038/pj.2015.108; published online 18 November 2015

INTRODUCTION

Polyurethane (PU) is a macromolecular polymeric material that exhibits properties between those of common rubber and rigid plastic, and has excellent properties such as wide rigidity, high intensity, oil resistance, ozone resistance, good vibration absorption ability, radio resistance and air permeability resistance.[1,2] At the same time, it also possesses a high tensile strength, elongation at break, good wear resistance, flexural resistance and solvent resistance. Moreover, it can be easily contour-machined and is performance controllable. It is widely used in food processing, in the packing industry and in healthcare. However, polyurethane and its products can induce the growth and reproduction of bacteria under certain temperature and humidity conditions during usage and storage. Thus, they can be hydrolyzed easily by bacteria, become aged and generate color changes and odors before breaking and may seriously threaten human health.

Antibacterial polyurethane (APU) can not only avoid the damage due to microorganism-induced erosion, but it can also prevent the reproduction and spread of pathogenic bacteria in polyurethane products, thereby reducing diseases.[3] Consequently, research on antibacterial polyurethane has important significance. Studies demonstrate that bacteria grow and adhere to the surface of the material and form a bacterial biofilm together with an extracellular matrix, which is the essential cause resulting in material infection.[4] Antibacterial polyurethane can prevent the formation of bacterial biofilms[5] by inhibiting bacterial adherence[6,7] through the introduction of elements and groups on the surface with the ability to disinfect, such as silver[8–10] and quaternary ammonium salt (QAS).[11–13] The properties of QAS are similar to those of inorganic ammonium salts. They are easily dissolved in water, and the water solution can be electrically conductive.[14] They also possess the characteristics of high efficiency, low toxicity, high bactericidal efficacy and pug-stripping ability and application in a wide pH range. QAS are widely used in water treatment, papermaking, antibacterial textiles, antibacterial ceramics, and antibacterial polyurethanes and can thus effectively prevent the growth and spread of pathogens.[15–17]

In a previous report, we prepared five *N*-methyl-*N*-R-*N*,*N*-bis(2-hydroxyethyl) ammonium bromides (R = -benzyl (chloride, BNQAS), -dodecyl (C12QAS), -tetradecyl (C14QAS), -hexadecyl (C16QAS), -octadecyl (C18QAS)) and the antibacterial-screening results proved that they display good antibacterial abilities against *Escherichia coli*, *Staphylococcus aureus*, *Bacillus subtilis*, especially C12QAS, which had the best antibacterial ability (100% to *E. coli*, 95.7% to *S. aureus* and 91.4% to *B. subtilis*).[18]

In order to investigate whether it will be helpful to improve the bioactivity and performance of it after introducing this clutch of QAS into PU, in this study, block antibacterial polyurethane (BAPU) and terminated antibacterial polyurethane (TAPU) were prepared on the basis of C12QAS (Figure 1). Their antibacterial properties were tested using qualitative (inhibition zone method) and quantitative tests (oscillation method), and the physical performances of the APUs were also investigated.

The Key Laboratory of Traditional Chinese Medicine Prescription Effect and Clinical Evaluation of State Administration of Traditional Chinese Medicine, School of Pharmacy, Binzhou Medical University, Yantai, China
Correspondence: Professor C-H Wang or Professor J-F Sun, The Key Laboratory of Traditional Chinese Medicine Prescription Effect and Clinical Evaluation of State Administration of Traditional Chinese Medicine, School of Pharmacy, Binzhou Medical University, Guanhai Road 346#, Yantai 264003, China.
E-mail: chunhuawang508@126.com or sjf.xzy@163.com
Received 4 April 2015; revised 22 September 2015; accepted 24 September 2015; published online 18 November 2015

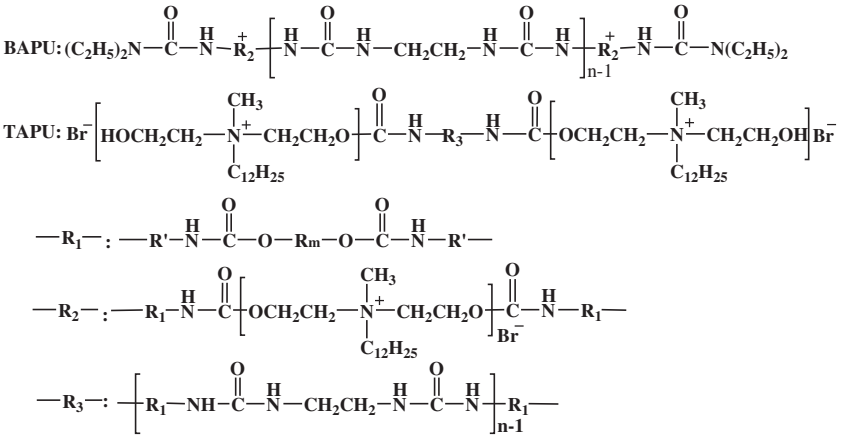

Figure 1 The structures of BAPU and TAPU.

EXPERIMENTAL PROCEDURE

Materials and Methods

C12QAS was synthesized according to the literature.[18] 4,4'-diphenylmethane diisocyanate (HO-R_m-OH) and polyoxytetramethylene glycol (M.W.: 1800, OCN-R'-NCO) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Nutrient agar medium, yeast extract and tryptone were purchased from Sigma-Aldrich Corporation (Shanghai, China). *E. coli*, *S. aureus* and *B. subtilis* were purchased from the American Type Culture Collection (Manassas, VA, USA).

The infrared (IR) samples were prepared as KBr pellets, and the spectra were obtained in the 400–4000 cm^{-1} range using a Nicolet MAGNA-IR 550 FTIR spectrometer.

Preparation of BAPU

Pre-polymerization reaction: BAPU.

Polyoxytetramethylene glycol (M.W.: 1800, 0.10 mol) and 4,4'-diphenylmethane diisocyanate (0.22 mol) were mixed and stirred for 30 min at 65 °C. A certain concentration of C12QAS (2500 p.p.m., 5000 p.p.m. or 10 000 p.p.m.) was then added to the mixture, reacting for 10 min to obtain the pre-polymer. The pre-polymer was diluted to a concentration of 50% with dimethyl formamide, and the chain extender (ethanediamine, 0.08 mol) was added after the temperature reached 70 °C. The terminating agent (diethylamine, 0.02 mol), divided into a few portions, was added when the reacting solution was like glycerin. The solution was then cooled to 50 °C, and the BAPU solution was obtained.

Preparation of TAPU

Termination reaction: TAPU

Polyoxytetramethylene glycol (M.W.: 1800, 0.10 mol) was heated and dehydrated in a vacuum, and then 4,4'-diphenylmethane diisocyanate (0.22 mol) was added. The mixture was stirred for 40 min at 60–70 °C to obtain the pre-polymer, which was then diluted to a concentration of 50% with dimethyl formamide. Next, the chain extender (ethanediamine, 0.08 mol) was added at 70 °C. A certain concentration of C12QAS (2500 p.p.m., 5000 p.p.m. or 10 000 p.p.m.) was added to the mixture when the solution was glycerin-like, and the terminating agent (diethylamine, 0.02 mol) was then added in several increments. The reaction solution was cooled to 50 °C, and a TAPU solution was obtained.

Preparation of film

A certain amount of antibacterial PU solution was smeared on a glass plate, which was put into water or was left to stand in air after being scratched with another glass plate. Then, the colorless and transparent film was prepared once the glass plate was dried in the oven and desiccated in the vacuum oven for 24 h again.

Method of antibacterial-activity testing

Method for qualitative testing: inhibition zone method. First, a 0.1 ml bacterial suspension was put on the solid culture medium, and the membrane samples (1 cm × 1 cm) were tiled on the medium. Next, the culture dishes were turned over and put into a constant temperature incubator at 37 °C. The inhibition zone diameters on the sample films were measured after 24 h. The antibacterial activity of the antibacterial polyurethane was evaluated according to the size of the inhibition zone.

Method for quantitative testing: oscillation culture method. First, 10 ml of phosphate buffer was put into an Erlenmeyer flask, and an autoclaving device was prepared. Subsequently, the blank film, the sample film and 10^{-3} ml bacteria were put into the Erlenmeyer flask, which was then fixed on an oscillation table. After the flask was oscillated for 3 h, 0.05 ml was added to a sterile culture dish, and 18 ml agar culture medium was also added. The dish was shaken carefully to blend the mixture and was then put on the table. After the agar culture medium solidified, the culture dishes were inverted and placed in a constant temperature incubator at 37 °C. The colony counts of the bacteria (the residual number of living bacterium) were observed after 18 h. The clump counts of the bacteria after culturing were compared with those of the control sample to calculate the antibacterial ratio.

RESULTS AND DISCUSSION

Structural analysis

The APU synthesis procedure was divided into the pre-polymerization reaction, the chain-extending reaction and the termination reaction. BAPU was synthesized by adding C12QAS during the pre-polymerization reaction, and TAPU was synthesized by adding C12QAS during the termination reaction. As shown in the FTIR spectrum of the APU, a distinct peak at 722 cm^{-1} belongs to the stretching vibration peak of linear paraffin (Figure 2), which is identical to that of C12QAS,[18] but there is no 722 cm^{-1} peak in the polyurethane material. The results show that the QAS bonded with the polyurethane chain. In addition, the FTIR spectrum of the APU was basically identical to that of the polyurethane material, including the peak shape and intensity. This result proves that the polyurethane chain basically maintains its overall performance despite the introduction of the QAS. Therefore, these functionalized polyurethane systems can provide an excellent advantage for studying interesting antibacterial activities.

The measurement of molecular weights of APU

High-performance gel permeation chromatography was used to determine the molecular weights of the APUs. The molecular weights of the APUs synthesized were ~30 000, which could guarantee that

there was no influence on the antibacterial activity of the end QAS, shown in Table 1.

Film-building effect analysis of QAS-PUs

Scanning electron microscope photos were taken to identify the film-building effects of different films. As shown in Figure 3 a and b, the surface of the polyurethane film that was made in water was irregular, and this was caused by the CO_2 generated from the reaction between diphenyl-4,4-methane diisocyanate and water. However, the surface of the polyurethane film that was built in air was smooth, with no bubbles observed under the 5000× scanning electron microscope. Thus, the best film-building condition is the film formation in air, drying at 60 °C in a drying oven and then drying at 60 °C in a vacuum drying oven for 24 h.

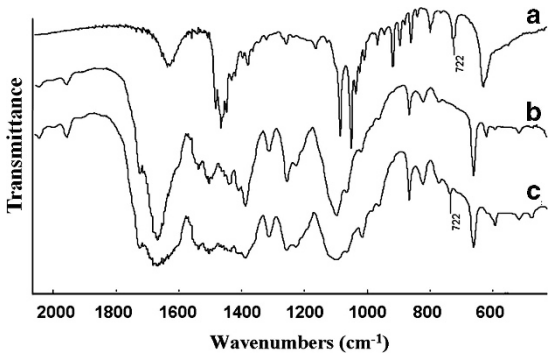

Figure 2 FTIR spectra of C12QAS and PUs (a-C12QAS, b-common PU, c-antibacterial PU).

Table 1 The molecular weights of APUs

Name	*Number-average molecular weight (Mn× 10^4)*	*Weight-average molecular weight (Mw× 10^4)*	*Polydispersity (PDI)*
BAPU	3.06	5.17	1.69
TAPU	2.72	4.19	1.54

Abbreviations: BAPU, block antibacterial polyurethane; TAPU, terminated antibacterial polyurethane.

Differential scanning calorimetry (DSC) of APUs

DSC is a thermoanalytical technology that measures the energy variation with temperature between the test material and a reference material under the control of programmed temperature conditions. The curves obtained during this process are called differential scanning curves or DSC, and this is an effective method for confirming the thermal transition of a polymer. The temperature that leads to a change in the intrinsic heat is the transition temperature, and the most obvious transition occurs at the glass transition temperature (GTT), which reflects the flexibility of a molecular chain. The greater the flexibility of the main chain, the lower the GTT is.[19,20]

The GTT of the APUs (BAPU: −82.4 ~ −61.7 °C; TAPU: −78.6 ~ −62.6 °C) was lower than that of other common PUs (−70.6 ~ −62.1 °C), demonstrating that the flexibility of the APU main chains are slightly superior to those of common PUs, as shown in Figure 3c, d and e and Table 2. The increasing molecular weight of the polyether resulting from the bond with the QAS improved the flexibility of the chain. In addition, because only a small amount of the QAS bonded to the PUs, the GTT of the APUs changed only slightly. Therefore, QASs bonded to the PUs did not influence the GTT of the matrix PU. In other words, the thermal properties of the APUs were essentially unaffected.

Viscometric analysis of APUs

As shown in Table 3, the viscosity of the APUs increased with an increase in the QAS content. The interaction between the pre-polymer and the chain extender (ethanediamine) produced active macromolecules, bearing the structures of a carbamic acid ester and urea with

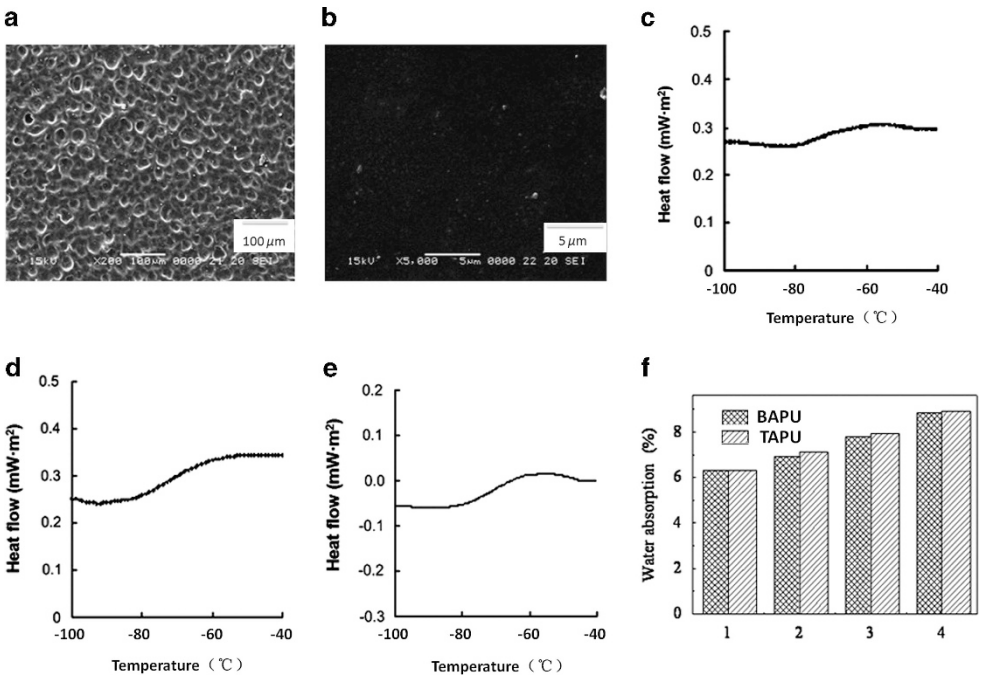

Figure 3 SEM photos of C12QAS-PU membranes in water (**a**) and air (**b**); DSC of common PUs (**c**), BAPU (**d**) and TAPU (**e**); Water absorption of PUs (1–4: 0, 2500 p.p.m., 5000 p.p.m., 10 000 p.p.m.) (**f**). A full color version of this figure is available at *Polymer Journal* online.

Table 2 The experimental results of the GTT for the PUs files

	GTT (°C)			
PUs	*Start point*	*Middle point*	*Inflection point*	*End point*
PU	−76.6	−68.3	−70.6	−62.1
BAPU	−82.4	−72.8	−73.63	−61.7
TAPU	−78.64	−70.3	−67.8	−62.6

Abbreviations: BAPU, block antibacterial polyurethane; PU, polyurethane; TAPU, terminated antibacterial polyurethane.

Table 3 The effect of QAS concentrations on the viscosity of PUs

	Viscosity (Pa·S)	
Concentration of QAS (p.p.m.)	*BAPU*	*TAPU*
0	316	316
2500	327	319
5000	388	354
10 000	402	391

Abbreviations: BAPU, block antibacterial polyurethane; QAS, quaternary ammonium salt; TAPU, terminated antibacterial polyurethane

an –NCO group on both ends, and the chain length can be increased to form a higher molecular weight product, resulting in a higher viscosity for polyurethane. Consequently, the higher the QAS content bonded to the polyurethane and the longer the molecule chain that forms, the greater the molecular weight and the higher the viscosity of the antibacterial polyurethane that is synthesized.

Mechanics property analysis of APUs

The main chain of polyurethane consists of alternating soft-chain segments and rigid-chain segments, and the thermodynamic incompatibility between them leads to microphase separation. This results in the excellent mechanical properties of polyurethane. Thus, the mechanical properties of polyurethane depend on whether the microphase is separate, the degree of separation and the proportion of soft-chain to rigid-chain segments. The rigid-chain segments aggregate due to hydrogen bonding in the polyurethane structure, which leads to microphase separation.[21,22]

From the data indicated in Table 4, we found that both the force for a given elongation and the breaking force increased, and the breaking elongation ratio decreased with an increase in the QAS content in the antibacterial polyurethane molecules, indicating that the mechanical properties improved. The reaction increased between -OH and -NCO because of the addition of QAS, resulting in an increase in the number of rigid groups such as carbamic acid ester and urea. Aggregation was easier with the enhancement of the hydrogen bond-forming ability of the rigid-chain segments, and the microphase separation effect and mechanical properties were both enhanced.

Moreover, the force at a given elongation, the breaking force and the breaking elongation ratio of antibacterial polyurethane were not significantly different from those of common polyurethane. Hence, the mechanical properties of polyurethane, to which a small amount of QAS bonded, were not significantly influenced, and it still exhibited the same excellent physicochemical properties as polyurethane.

Table 4 The mechanical properties of PUs (the unit of force, cN)

Concentration of QAS (p.p.m.)		*100 force at a given elongation*	*200 force at a given elongation*	*300 force at a given elongation*	*Breaking force*	*Breaking elongation rate (%)*
0	PU	2.68	5.03	9.02	50.97	625.15
2500	BAPU	2.95	5.75	10.27	50.99	602.71
	TAPU	2.69	5.06	9.21	50.01	624.55
5000	BAPU	3.29	6.60	12.57	59.24	567.31
	TAPU	2.71	5.13	9.19	53.00	629.03
10 000	BAPU	3.54	7.33	14.96	63.74	576.54
	TAPU	2.86	5.66	10.70	59.04	606.95

Abbreviations: BAPU, block antibacterial polyurethane; PU, polyurethane; TAPU, terminated antibacterial polyurethane.

Table 5 The diameters of the inhibition zone of APUs

	BAPU (mm)			TAPU (mm)		
QAS content of samples (p.p.m.)	*S. aureus*	*B.subtilis*	*E. coli*	*S. aureus*	*B.subtilis*	*E. coli*
0	0	0	0	0	0	0
2500	11.2	10.7	11.6	11.5	10.8	12.1
5000	16.7	14.9	18.1	17.1	14.2	19.4
10 000	21.1	18.2	24.8	23.2	19.1	26.3

Abbreviations: BAPU, block antibacterial polyurethane; TAPU, terminated antibacterial polyurethane.

Water absorption rate of APUs

Figure 3 f shows that the water absorption rate of the APUs increased with an increase in the QAS content after bonding with the QAS. The polyurethane cation was obtained when polyurethane bonded with QAS, which made its water-combining ability rise. This result is similar to those observed for polyurethane anions and polyurethane zwitterions.[23] The film swelled after water absorption, which increased the motion of the water chains in the film; this was helpful for the entrance and diffusion of water. At the same time, the water absorption rate did not significantly increase because only a small amount of QAS was bonded to the polyurethane, and the hydrophilicity of the polyurethane matrix was not significantly affected.

Antibacterial activities of APUs

In this study, the antibacterial activities of the APUs were detected using qualitative and quantitative tests. In the qualitative test, the diameters of the inhibition zone for BAPU and TAPU were obtained, as shown in Table 5. The inhibition zone could be found when both types of antibacterial polyurethane with different QAS content were evaluated against *S. aureus*, *B. subtilis* and *E. coli*. The diameter of the inhibition zone was enlarged as the QAS content increased, and the diameter of *E. coli* was larger than those of *S. aureus* and *B. subtilis*. These results demonstrate that both types of antibacterial polyurethane possessed antibacterial effects and that the antibacterial activity against *E. coli* was the most potent of the three strains.

In a quantitative test, BAPU and TAPU with different QAS contents were put into a mixture of phosphate buffer and bacterial suspension at 37 °C and vibrated for 4 h; the obtained curves are indicated in Figure 4 a and b. The data demonstrate that the antibacterial ratios of the two types of antibacterial polyurethane increased with an increase

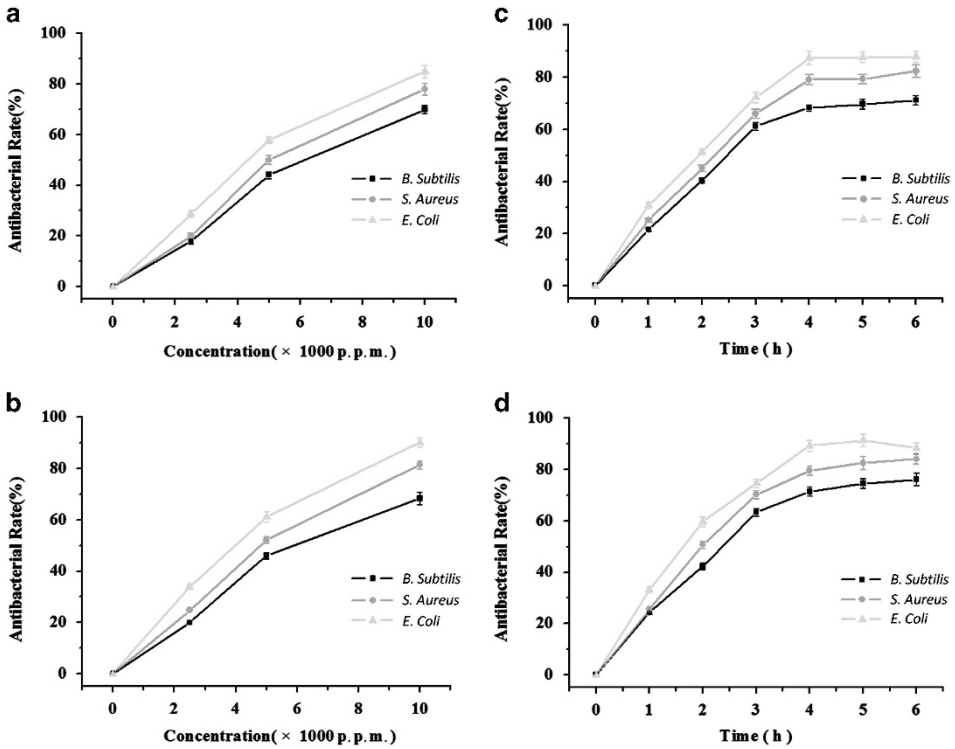

Figure 4 (**a**) Antimicrobial activity of BAPU at different QAS concentrations. (**b**) Antimicrobial activity of TAPU at different QAS concentrations. (**c**) Antimicrobial activity of BAPU at different contact times. (**d**) Antimicrobial activity of TAPU at different contact times. A full color version of this figure is available at *Polymer Journal* online.

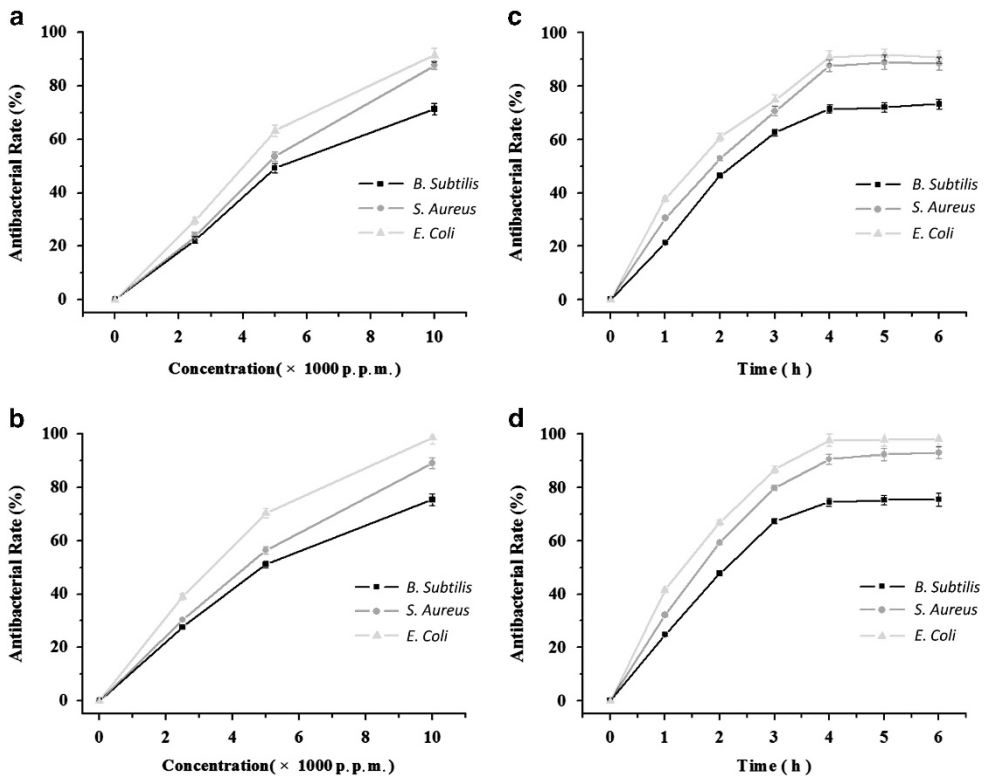

Figure 5 (**a**) Antimicrobial activity of block QAS-spandex fibers at different QAS concentrations. (**b**) Antimicrobial activity of terminated QAS-spandex fibers at different QAS concentrations. (**c**) Antimicrobial activity of block QAS-spandex fibers at different contact times. (**d**) Antimicrobial activity of terminated QAS-spandex fibers at different contact times. A full color version of this figure is available at *Polymer Journal* online.

in the QAS content. The antibacterial ratio against *E. coli* was greater than those against *S. aureus* and *B. subtilis* with the same QAS content. When the content was 10 000 p.p.m., the antibacterial ratios of BAPU against *E. coli*, *S. aureus* and *B. subtilis* were 86.0%, 78.3% and 70.4%, respectively, and the antibacterial ratios of TAPU against *E. coli*, *S. aureus* and *B. subtilis* were 89.7%, 81.2% and 72.1%, respectively, showing that both types of polyurethane possessed antibacterial activity and that the antibacterial effect against *E. coli* was the greatest of the three strains.

In addition, from the antimicrobial activity curves of both types of polyurethane at different contact times shown in Figure 4 c and d, we could observe that the antibacterial ratios increased rapidly over the short-term (1–3 h). However, the ratios reached a maximum after 4 h, showing that both types of polyurethane had enhanced antibacterial abilities.

Antibacterial activities of QAS-spandex fibers

The antibacterial quantitative test was also conducted for both block and terminated QAS-spandex fibers. The results are indicated in Figure 5. The antibacterial ratios of both types of QAS-spandex fibers increased with an increase in the QAS content (Figure 5 a and b). The ratio against *E. coli* was greater than those against *S. aureus* and *B. subtilis* for the same QAS concentration; the ratios against *E. coli*, *S. aureus* and *B. subtilis* for block and terminated QAS-spandex fibers were 91.8%, 87.4%, 74.6; 98.0%, 90.8% and 78.5%, respectively, when the content of QAS was 10 000 p.p.m..

Moreover, from the antibacterial curves of both the block and terminated QAS-spandex fibers at different contact times at the 10 000 p.p.m. concentration (Figure 5 c and d), we could see that the antibacterial ratios increased rapidly over a short time (1–3 h) but reached a maximum after 4 h, demonstrating that both the block and terminated QAS-spandex fibers had marked antibacterial ability.

In addition, the physical performance of QAS-PUs may have a definite correlation with antibacterial activity. First, the molecular weight can affect the antibacterial activity. It can be seen from Table 1 and Figure 4 a and b that the molecular weight of BAPU (3.06×10^4) is higher than that of TAPU (2.72×10^4), whereas the antibacterial activity of TAPU is greater than that of BAPU. Similarly, it also can be shown from Table 1 and Figure 5 a and b that the antibacterial activity of the terminated QAS-spandex fibers with lower molecular weight is greater than that of the block QAS-spandex fibers with higher molecular weight. The main possible reason is that the TAPU may penetrate into the bacterial cells more easily because of its lower molecular weight. Second, with an increase in the QAS content from 2500–5000–10 000 p.p.m., the antibacterial activity of both the APUs and the QAS-spandex fibers ascended. Because the QAS content increased, the hydrophilicity of the APU increased, and the density of the QAS positive charge rose, making the electrostatic interaction and absorption between the APUs and the bacteria strengthen and resulting in the enhancement of the antibacterial activity.[24]

CONCLUSION

In summary, we synthesized BAPU and TAPU with different content of C12QAS. Their structures were characterized using FTIR and DSC. The viscosity, mechanical properties and water absorption for both APUs were evaluated. The results demonstrated that the best film-building condition was drying at 60 °C in air and drying for another 24 h at 60 °C in a vacuum. The higher the content of QAS in the APUs, the greater the viscosity. The polyurethanes also showed remarkable mechanical performance and good hydrophilicity. The antibacterial properties of the QAS-polyurethanes and QAS-spandex fibers were investigated by qualitative and quantitative testing. Both the polyurethanes and spandex displayed excellent antibacterial activities against *E. coli, S. aureus* and *B. subtilis,* with the most potent activity against *E. coli*. The antibacterial ratios against *E. coli* were 86.0%, 89.7%, 91.8% and 98.0% for the BAPU, TAPU, block QAS-spandex and terminated QAS-spandex fibers, respectively.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

ACKNOWLEDGEMENTS

We are grateful for the financial support from the National Natural Science Foundation of China (No. 21402010), the Foundation of Shandong province (Nos. ZR2014BL008, ZR2013BM022, 2015GGX102013, J11LF27) and the Foundation of Yantai (No. 2013ZH095, 2011076).

1 Wang, H. H. & Lin, M. S. Biocidal polyurethane and its antibacterial properties. *J. Polym. Res.* **5**, 177–186 (1998).
2 Sakagami, Y., Horiguchi, K., Narita, Y., Sirithep, W., Morita, K. & Nagase, Y. Syntheses of a novel diol monomer and polyurethane elastomers containing phospholipid moieties. *Polym. J.* **45**, 1159–1166 (2013).
3 Luo, J., Deng, Y. & Sun, Y. Y. Antimicrobial activity and biocompatibility of polyurethane-iodine complexes. *J. Bioact. Compat. Pol.* **25**, 185–206 (2010).
4 Nagel, J. A., Dickinson, R. B. & Cooper, S. L. Bacterial adhesion to polyurethane surfaces in the presence of pre-adsorbed high molecular weight kininogen. *J. Biomater. Sci. Polym. Ed.* **7**, 769–780 (1996).
5 Bakhshi, H., Yeganeh, H. & Mehdipour-Ataei, S. Synthesis and evaluation of antibacterial polyurethane coatings made from soybean oil functionalized with dimethylphenylammonium iodide and hydroxyl groups. *J. Biomed. Mater. Res. A.* **101**, 1599–1611 (2013).
6 Nandakumar, V., Chittaranjan, S., Kurian, V. M. & Doble, M. Characteristics of bacterial biofilm associated with implant material in clinical practice. *Polym. J.* **45**, 137–152 (2013).
7 Yung, L. Y., Colman, R. W. & Cooper, S. L. Neutrophil adhesion on polyurethanes preadsorbed with high molecular weight kininogen. *Blood* **94**, 2716–2724 (1999).
8 Jain, P. & Pradeep, T. Potential of silver nanoparticle-coated polyurethane foam as an antibacterial water filter. *Biotechnol. Bioeng.* **90**, 59–63 (2005).
9 Phong, N. T. P., Thanh, N. V. K & Phuong, P. H. Fabrication of antibacterial water filter by coating silver nanoparticles on flexible polyurethane foams. *J .Phys. Conf. Ser.* **187**, 012079–012088 (2009).
10 Paladini, F., Cooper, I. R. & Pollini, M. Development of antibacterial and antifungal silver-coated polyurethane foams as air filtration units for the prevention of respiratory diseases. *J. Appl. Microbiol.* **116**, 710–717 (2014).
11 Bakhshi, H., Yeganeh, H., Mehdipour-Ataei, S., Shokrgozar, M. A., Yari, A. & Saeedi-slami, S. N. Synthesis and characterization of antibacterial polyurethane coatings from quaternary ammonium salts functionalized soybean oil based polyols. *Mater. Sci. Eng: C* **33**, 153–164 (2013).
12 Ma, T., Pradel, G., Ohlsen, K. & Holzgrabe, U. Quaternary ammonium salts and their antibacterial potential: targets or nonspecific interactions? *Chem. Med. Chem.* **7**, 22–31 (2012).
13 Badawy, H. T., Pasetto, P., Mouget, J. L., Pilard, J. F., Cutright, T. J. & Milsted, A. Bacterial adhesion and growth reduction by novel rubber-derived oligomers. *Biochem. Biophy. Res. Commun.* **438**, 691–696 (2013).
14 Shelton, R. S., Campen, M. G., Tilford, C. H., Lang, H. C., Nisonger, L., Bandelin, F. J. & Rubenkoenig, H. L. Quaternary ammonium salts as germicides. I. non-acylated quaternary ammonium salts derived from aliphatic amines. *J. Am. Chem. Soc.* **68**, 753–755 (1946).
15 McDonnell, G. & Russell, A. D. *Clin.* Antiseptics and disinfectants: activity, action, and resistance. *Microbiol. Rev.* **12**, 147–179 (1999).
16 Ma, S., Izutani, N., Imazato, S., Chen, J., Kiba, W., Yoshikawa, R., Takeda, K., Kitagawa, H. & Ebisu, S. Assessment of bactericidal effects of quaternary ammonium-based antibacterial monomers in combination with colloidal platinum nanoparticles. *Dent. Mater. J.* **31**, 150–156 (2012).
17 Makino, M., Ohta, S. & Zenda, H. Effect of alkyl chain length of N-alkyl-N-(2-hydroxy-3-phenoxy)propyl-N,N-dimethyl ammonium butyl phosphate on the antibacterial activity. *Yakugaku zasshi: J. Pharma. Soc. Japan* **114**, 73–79 (1994).
18 Liu, W. S., Wang, C. H., Sun, J. F., Hou, G. G., Wang, Y. P. & Qu, R. J. Synthesis, characterization and antibacterial properties of dihydroxy quaternary ammonium salts with long chain alkyl bromides. *Chem. Biol. Drug. Des.* **85**, 91–97 (2015).
19 Besancon, B. M., Soles, C. L. & Green, P.F. Glass transition of miscible binary polymer-polymer thin films. *Phys. Rev. Lett.* **97** (5), 057801 (2006).
20 Hartmann, L, Gorbatschow, W, Hauwede, J & Kremer, F. Molecular dynamics in thin films of isotactic poly(methyl methacrylate). *Eur. Phys. J. E.* **8**, 145–154 (2002).

21 Velankar, S. & Cooper, S. L. Microphase separation and rheological properties of polyurethane melts. 1. effect of block length, macromolecules. *Macromolecules* **31**, 9181–9192 (1998).
22 Lcl, X. & Siedlecki, C. A. Microphase separation structure influences protein interactions with poly(urethane urea) surfaces. *J Biomed. Mater. Res. A.* **92**, 126–136 (2010).
23 Nagel-Baumgartner, J., Yang, C. Z. & Cooper, S. L. Physcial property analysis and bacterial adhesion on a series of phosphonated polyurethanes. *Biomaterials* **18**, 831–837 (1997).
24 Ye, S. J., Majumdar, P., Chisholm, B., Stafslien, S. & Chen, Z. Antifouling and Antimicrobial mechanism of tethered quaternary qmmonium qalts in a cross-linked poly(dimethylsiloxane) matrix studied using sum frequency generation vibrational spectroscopy. *Langmuir* **26**, 16455–16462 (2010).