Design and synthesis of bactericidal block copolymer for preparing durably antibacterial PA6 fibre

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Polymer fibres are widely used in various materials in contact with the human body. As bacterial contamination may lead to the emergence of disease, it is necessary to provide fibres with durably antibacterial properties. In this work, based on 4-vinyl pyridine, fluorine-containing monomers and acrylic acid monomers, new quaternary ammonium salt polymer containing fluorine (NP) were prepared by solution polymerisation, and then the antibacterial composite fibre was prepared by melt spinning of the NP (9 wt%) and Nylon 6 fibre (PA6). The structure and properties of NP and composite fibres were characterised, respectively. The results indicated that the water contact angle of NP reached 104°, the pyrolysis temperature was 302°C, and the interface interaction between NP and PA6 was good, which could achieve more uniform dispersion in Nylon 6 matrix. In addition, the composite fibre decreased obviously the number of colony-forming units within 24 h (the bactericidal rate was 99.99% against *E. coli* and 99.81% against *S. aureus*) compared with pure PA6 fibre. The composite fibre was a good durably antibacterial material, which could still inactivate over 96% inoculated *E. coli* and *S. aureus* after washing 7 days.

1. Introduction: With the development of the society and the improvement of people's living standard, working and living environment, the health of people, has been improved constantly. Textile is one of the materials that is used for people in their daily life. Naturally, more attention will be paid to its hygiene. Textiles are easy to breed bacteria in the process of taking, storage and transportation, which bring harm to people's health [1–3]. PA6 fibre has shown wide application in textiles because it has many advantages such as high strength, abrasion resistance, lightweight and good elasticity breathable as well as it has easy mass production. Therefore, antimicrobial PA6 composite fibre, a kind of function textiles, has gained the attention of researchers [4, 5]. Antimicrobial PA6 composite fibre can inhibit or even kill bacteria, reducing the growth of bacteria and protecting people's health. To achieve this goal, antibacterial functions are induced to textile materials through physical or chemical incorporation of multifarious functional antibacterial agents onto fibres.

However, the big disadvantage of antibacterial textile is poor stability. The reason is that the antibacterial agents can fall off easily or dissolve in water, which severely blocks their practical applications. For example, Lin *et al.* [6] synthesised a series of antibacterial agents and polymeric quaternary ammonium monomers with different alkyl chain length generate cationic fluorinated polymer emulsions by copolymerising with fluorine-containing and other acrylic monomers, and then it is applied onto cotton fabrics. However, after 20 cycles washing, antibacterial properties dramatically decreased. In addition, many types of research show that antibacterial agents like quaternary ammonium salts (QASs) containing polymers have good antibacterial activities against *E. coli* and *S. aureus*, which have been the subject of many investigations as water in antifouling coatings and commercially available disinfectants [7]. However, many disinfectants are corrosive for skin or mucosa and inflammable. They are not suitable for textile finishing. Therefore, antibacterial fibre is one of the ideal materials to reduce microbial contamination and the occurrence of health risks for people. To achieve durable antimicrobial properties of PA6 fibres, the designed antibacterial agents are insoluble in water and added to the matrix material by melt spinning method.

Recently, the number of antibacterial agents increased dramatically is used to fibre, textile and cloth [8–11]. The antibacterial agents include metals, metal salts, polybiguanides, quaternary ammonium compounds, chitosan, N-halamine and triclosan [12]. Unfortunately, the inorganic antibacterial materials are limited in use, such as Ag^{+}, Cu^{2+}, ZnO and TiO_2. There are two major problems in the treatment of metallic antibacterial agents that are the absorption and durability of metals in textiles, respectively. In addition to the above issues, many heavy metals can damage the environment. In contrast, there are many organic antibacterial agents with excellent performance such as QASs, quaternary phosphonium salts and halogenated amines, etc. Among them, QAS has three major characteristics that are low cost, simple preparation and fast sterilising. The QAS, especially low molecular or soluble ones, has been studied extensively in antibacterial mechanism. Their antibacterial activity is characterised by the ability of bacterial killed in water. However, the quaternary ammonium compounds have some inherent weakness such as leaching from the textiles, dissolving in water, causing secondary pollution and other problems. In addition, the thermal decomposition temperature of low-molecular organic antibacterial agent of QAS is low, which has a great impact on the melting processing temperature of nylon and other materials. These problems limit the application of low-molecular organic antibacterial agent of QASs.

In this Letter, the present work aims to develop durably antibacterial composite fibre containing new QAS polymer containing fluorine (NP) that was prepared through the melt spinning process. We synthesised NP by solution polymerisation, mainly using antibacterial QAS monomers and fluorine-containing monomers as materials. Due to the coexistence of QAS and fluorine components, we studied that the NP has both positive charge and hydrophobicity, and its thermal stability is good, it is suitable for melt spinning. Then the NP was added to the PA6 fibre by melt spinning, which has a better antibacterial property and hydrophobicity of PA6 fibres.

2. Experimental section: The PA6 (spinning grade) in the experiment was supplied from Yiwu Huading Nylon Co. Ltd. 4-vinyl pyridine (96%), 2-(perfluorooctyl) ethyl methacrylate (98%), methyl methacrylate (MMA, 99%), 1-bromododecane (98%) and 2,2-azobis-(2-methylpropionitrile) (AIBN, 99%) were purchased from Shanghai Macklin Biochemical Co., Ltd. *Staphylococcus aureus* (ATCC 6538) and *Escherichia coli* (ATCC 8099) were

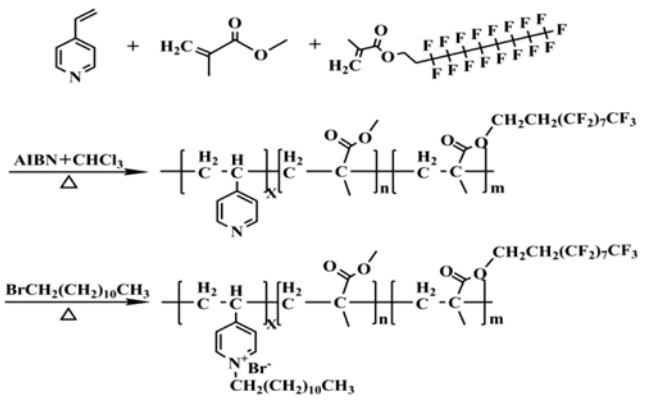

Fig. 1 *Synthetic routine of NP*

purchased from Shanghai Lu Wei Technology Co., Ltd. Nutrient agar (NA) was purchased from Hangzhou Best Biotechnology Co., Ltd.

The synthetic routine of NP was shown in Fig. 1. First, a certain amount of azodiisobutyronitrile initiator (AIBN) was dissolved in trichloromethane and added into a 250 ml flask at 65°C. Four-vinyl pyridine, 2-(perfluorooctyl) ethyl methacrylate and methyl methacrylate were added to flask (a ratio of 1.5:1:1.1), which was stirred under nitrogen for 14 h, and then cooled to room temperature. Finally, the solution was added to petroleum ether, filter the precipitate and dry it at room temperature. Then, the above precipitate and methanol were added to flask (a ratio of 1:6), then an appropriate amount of bromododecane was added to the above solution as quaternary ammonium reagent, and the solution stirred was heated at 65°C for 24 h. After the reaction, the solution is added into n-hexane to precipitate, and then the precipitate is filtered. After washed by boiling water, the precipitate is dried at room temperature.

The PA6 was dried in a vacuum oven at 100°C for 24 h, the mass ratio of PA6 and NP powder was 100/0, 100/9 by micro spinning machine (HAAKE MiniLab II type, Germany Semel Fisher Technology Co. Ltd.) at 250°C melting blend spinning. Then, the fibre was drafted in thermal drafting device (DSM XPLORE, Netherlands, DSM Company) set at 120°C. Under the action of the stretching roller, the fibre is drawn four times. The fibre containing NP was marked PA6/NP.

The structure of the NP was characterised by Fourier transform infrared (FTIR), recorded in KBr disks on a Nicolet 5770 FTIR spectrometer (Nicolet Co., United States) over the range of 4000–400 cm^{-1} and the scanning number was 32. The structure of NP was further characterised by 1H NMR using $CDC1_3$ as a solvent on Avance AV400 MHz spectrometer (Bruker Co., Swiss Confederation). The molecular weight of NP was determined by 1515 gel permeation chromatography (GPC) (Waters Co., USA), using N, N-dimethylformamide (DMF) as solvent, the flow rate of DMF is 1 ml/min and polystyrene as the standard substance at room temperature. The thermal behaviour of PA6/NP was determined by thermogravimetric analysis (TGA). TGA and derivative thermogravimetry (DTG) curves were obtained from 7 to 8 mg of samples on a PYRIS1 TGA (Birkin Elmer Co., USA) heating from the room temperature to 700°C at a rate of 10°C/min under nitrogen atmosphere. The NP powders were weighed and added to equivalent amount of different solvents methylene chloride (MC), ethanol anhydrous (EA), formic acid (FAC), acetone (CP), dimethyl benzene (DMB), tetrahydrofuran (THF), water for 24 h to observe whether there were precipitated in the solvents. The solubility was obtained according to the Hildebrand concentration formula

$$\Delta H_M = V_M \emptyset_1 \emptyset_2 \left[(\omega_1 - \omega_2)^2 + (\Omega_1 - \Omega_2)^2 \right]; \quad \omega^2 = P\delta^2; \quad \Omega^2 = \mathrm{d}\delta^2 \tag{1}$$

P signifies molecular polarity fraction, δ is solubility. The contact angle (CA) analysis of the NP was performed with a JY-82B video contact angle tester (Chengde Ding Sheng Testing Machine Testing Equipment Co. Ltd., China). The surface and section morphology of the sample was observed by Ultra55 Thermal Field Emission Scanning Electron Microscope (Carl Zeiss SMT Pte Ltd, German) with energy dispersive X-ray (EDX) spectroscopy for analysing chemical element composition of the fibre. The mechanical properties of the composite fibres were tested by Instron-3369 Universal Material Testing Machine. The effective clamping distance was 20 mm, and the drawing speed was 20 mm/min.

2.1. Durability test: Washing is an easy way to indicate the durability of the PA6/NP. The process was that a bundle of fibres was, respectively, washed by a stirrer for 0, 1, 3, 5, and 7 days in water at 500 r/min, and then dried at room temperature in order to test the antibacterial activity and surface morphology of fibres.

2.2. Antibacterial property: The antibacterial property of PA6 and PA6/NP was evaluated against *S. aureus* (ATCC 6538) and *E. coli* (ATCC 8099) by the antimicrobial test of textiles (GB/T 20944. 3-2008). The *E. coli* and *S. aureus* cultures were grown in a Luria Bertani (LB) broth at 37°C for 24 h. Then the bacterial cells were diluted to 1.1×10^8 CFU/ml. The PA6 and PA6/NP (including washed and unwashed samples), and sterilise with UV lamp for 20 min. Then put the fibres into asepsis tubes. Subsequently, the *E. coli* and *S. aureus* suspension contain 3 ml (1.1×10^8 CFU/ml) were poured into the asepsis tubes and shaking incubated at 37°C, 130 r/min, for 24 h. Then, a tenfold dilution was made up to 10^{-5} with 900 µl PBS, and each dilution was plated on agar plates. The plates were incubated at 37°C for 24 h, and the bacterial colonies were counted for biocidal efficacy analysis. Afterwards, the number of colonies was carefully counted, and the bacteria reduction rate was calculated based on (2) to evaluate the antibacterial activities of PA6 and PA6/NP fibres

$$\text{Bacteria reduction rate}\,(\%) = \frac{(A-B)}{A} \times 100\% \tag{2}$$

where A and B signify the value (CFU/ml) of viable bacteria concentration in the flask after 18 h of oscillating contact from the PA6 and PA6/NP, respectively. Six repetitions were carried out to obtain an average data for each sample.

3. Results and discussion: According to the FTIR spectra in Fig. 2, the strong peaks at 2922 and 2849 cm^{-1} were assigned to C–H stretching in the $–CH_3$ and $–CH_2$ groups of the quaternary ammonium polymers. The sharp, strong peak at 1732 cm^{-1} was assigned to C = O stretching of esters in polyacrylate. The absorption peaks at 1636 cm^{-1} were attributed to the stretching vibration of C = N in the

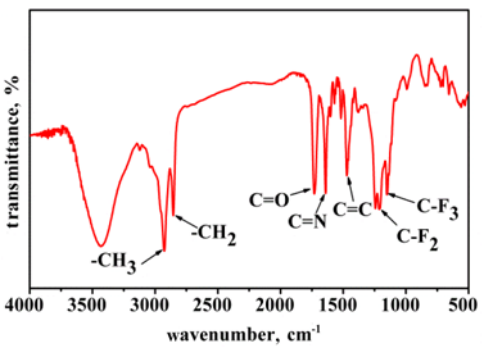

Fig. 2 *FTIR spectra of NP*

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pyridine ring, this indicates that the quaternary ammonium reaction has occurred on the pyridine ring to form the QAS. The absorption peak at about 1459 cm^{-1} was assigned to the stretching vibration of the C = C bond. The absorption peaks at 1201 and 1146 cm^{-1} were assigned to the stretching vibrations of C–F_2 and C–F_3 in the fluorinated polymers.

In order to further confirm the fabrication of NP, we performed ^{1}H NMR spectroscopic analysis. The ^{1}H NMR spectrum was shown in Fig. 3, the peak at 1.24 ppm was the –CH_2– of the main chain. The broad peak at 2.49 ppm that was due to the formed –CH–CH_2– single bonds on the polymer backbone, the peaks at 8.11 and 9.09 ppm were the H of the benzene ring. The –CH_2– near the benzene ring of peaks at 2.0 and 1.24 ppm, respectively, and the –CH_3– near the benzene ring and on the side chain at about 0.90 ppm. The peaks at 3.58 ppm belonged to the –CH_3–, that near the ester group in MAA segment, and the –CH_2– exists of the –CF_2– near. There was an obvious NMR vibration peak at 4.78 PPM, which belonged to the –CH_2– in Fluoride segment. Their structures demonstrated that NP was successfully synthesised [13].

Can be seen from Fig. 4, the synthesis of NP number average molecular weight (Mn) was 33,160 g/mol, weight average molecular weight (Mw) was 51,086 g/mol, dispersion coefficient was 1.54, the molecular weight distribution was narrow, the result showed that the synthesis of NP has a high molecular weight, the NP was successfully obtained. Compared with organic small molecule antibacterial agents, high molecular antibacterial agents were easy to store and had stable chemical properties. Due to the dense antibacterial functional groups, the antibacterial performance of the NP is excellent [14].

TGA was used to Letter the decomposition of NP. Fig. 5 shows the TGA curves of NP. The NP had three thermal decomposition processes. The first weight loss was about 5% at 302–336°C, and which were corresponded to the thermal decomposition of C–N

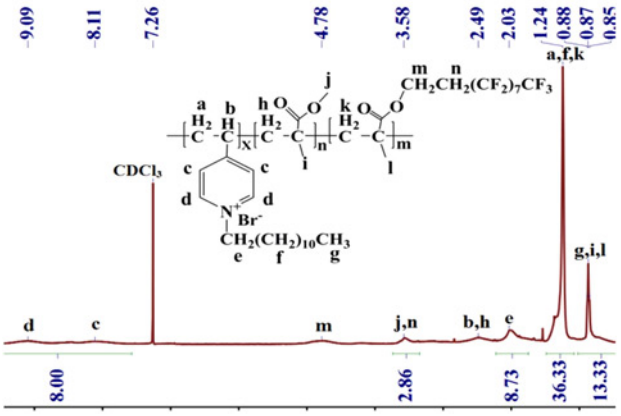

Fig. 3 *^{1}H NMR spectra of NP*

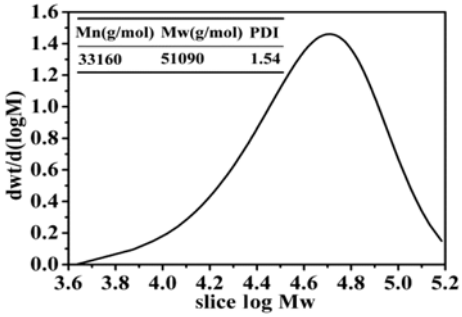

Fig. 4 *Molecular weight and molecular weight distribution of NP*

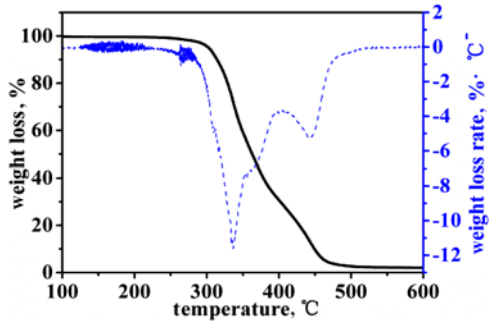

Fig. 5 *TGA curves of NP*

and QAS ions. The second weight loss of NP occurred at 336–443°C, which was caused by the thermal decomposition of ester groups and C–F on polymers. The third weight loss occurred at 443–524°C, which was corresponded to the thermal decomposition of C–C on polymer chains. Importantly, since the melting temperature of PA6 fibre was 250°C, the initial decomposition temperature of the added antimicrobial agent must exceed 250°C to ensure that the antimicrobial agent will not decompose during the processing [15]. The experimental results of TG not only showed that the initial decomposition temperature of the NP macromolecule antimicrobial agent with excellent heat resistance was over 250°C but proved that the antimicrobial PA6 fibre could be prepared.

The antibacterial agent is mainly used in textiles. Therefore, the hydrophilicity and hydrophobicity of the NP are one of the important factors affecting its antibacterial properties. As shown in Fig. 6*a*, the NP can be dissolved in MC, EA and other organic solvents and showed transparent colour. It was slightly soluble in organic solvents such as CP, DMB and THF. According to (1), for the solubility of polar polymers, it is required not only to be close to the non-polar part of the solvent concentration parameter, but also to be close to the polar part. The polarity fraction of CP ($\delta = 10.0$, $P = 0.695$) was too high and the polarity fraction of DMB ($\delta = 9.0$, $P = 0.001$) and THF ($\delta = 9.9$, $P = 0$) were too small. According to the solubility, the antimicrobial solution is coated on the surface of textiles without affecting their colour and lustre. When the solvent is water, the NP is insoluble. The reason is that the fluorocarbon chain in the NP can screen the hydrophilic groups and improve the water-resistance of the NP. Further, its water contact angle reached 104° as shown in Fig. 6*b*. Therefore, when applied to fibres, clothing and fabrics, it can meet the requirements of durably antibacterial resistance.

Furthermore, the element mapping images and spectrum of NP were shown in Fig. 7. Two new elements N and F appearing in the NP were observed in Fig. 7, suggesting that the NP obtained by solution polymerisation. Based on the SEM-EDS technique, the weight percentage of N and F was detected as ∼3.4 and 18%, respectively. The above results indicated the NP mainly including 4-vinyl pyridine and 2-(perfluorooctyl) ethyl methacrylate have successfully synthesised.

Figs. 8*a* and *b* show the fracture section morphology of PA6 and PA6/NP, respectively. It is apparent that the fracture section of pure

Fig. 6 *Physical properties of NP*
a Solubility of NP in different reagents
b Water contact image and numerical contact angle value of NP

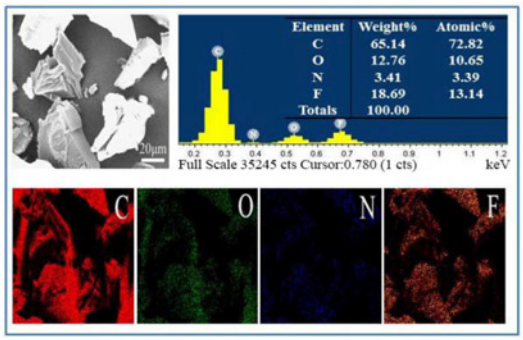

Fig. 7 *SEM result (including elements mapping) of NP*

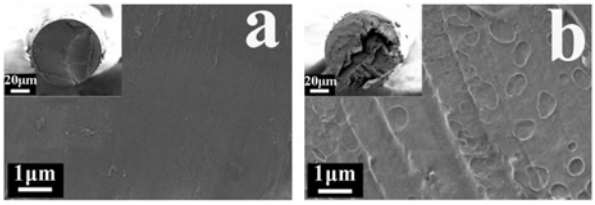

Fig. 8 *Section morphology of fibre*
a PA6 fibre
b PA6/NP fibre

PA6 was smooth, while the PA6/NP had a rough section due to the strong interfacial interactions between the NP and PA6. The rough section was also an indication of more energy absorption during fracture. Moreover, the NP had a uniform distribution in the PA6 matrix.

The mechanical properties of the PA6 and PA6/NP were shown in Fig. 9. Compared with PA6 fibre, the addition of antibacterial agent NP did increase the tensile strength. The elongation at break of PA6/NP was lower than that of pure PA6 fibre. This phenomenon might be due to the fluorine atoms on the fluorocarbon chain in the NP were highly electronegative, which was easily introduced into PA6 to form weak hydrogen bonds with the N–H groups in PA6, forming a more compact structure. On the other hand, this interaction restricted the movement of molecular segments, resulting in a reduction in elongation. The strength of PA6/NP had not gone down due to the improvement of interfacial adhesion between the two phases.

In Fig. 10*f*, the surface morphology of PA6/NP was smooth due to the uniform dispersion of NP in PA6 matrix. Moreover, the surface morphology of PA6/NP in Figs. 10*g–j* was smooth after washing for 1, 3, 5, 7 days, respectively. Combined with Fig. 6, it showed that the NP in the PA6/NP was insoluble in water after washing and not cause damage to the fibre structure.

Durably antibacterial PA6/NP was assessed by determining the change of the bacteria reduction rate after the washing durability

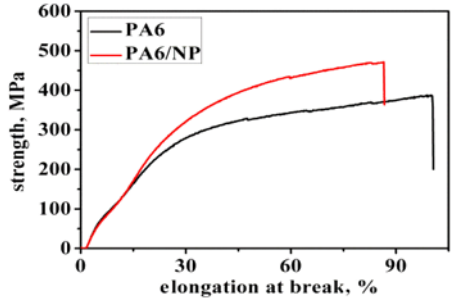

Fig. 9 *Mechanical properties of the PA6 and PA6/NP*

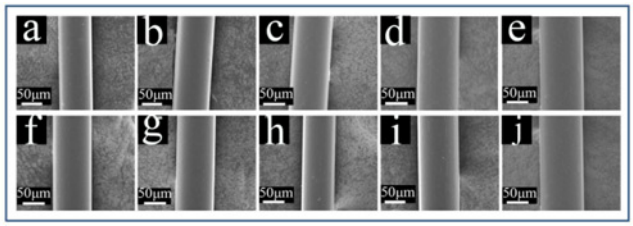

Fig. 10 *Surface morphology of PA6*
a–e PA6 fibre that after washing in water for 0, 1, 3, 5, 7 days respectively and PA6/NP fibre
f–j PA6/NP fibre that after washing in water for 0, 1, 3, 5, 7 days, respectively

test. Fig. 11 shows the typical photographs after dilution culture at the concentration of 1.1×10^8 CFU/ml of the *E. coli* and *S. aureus* bacterial colonies after treatment with PA6 and PA6/NP. From Fig. 11*A* and *B*, with the washing cycles, increase from 0 to 7 days, it was found that the bacteria reduction rate of the PA6/NP against *E. coli* and *S. aureus* had decreased, respectively, from 99.99 and 99.81% to 98.82 and 96.36%. The slight decrease in antibacterial rate is because the NP on the surface of the PA6/NP fibre fell off slightly under the long-term mechanical stirring. In addition, the PA6/NP against *E. coli* had a better than *S. aureus*, so the antibacterial property of PA6/NP against *E. coli* was good. Because the cell wall of both bacteria structure might account for this difference. As far as we have known, most bacteria are negatively charged in nature, the positive ions of quaternary ammonium was firstly come into contact with bacteria through electrostatic interactions, and then the alkyl chains extend into the cell wall and cell membrane, disturbing the normal metabolism of the bacteria and killing them to death.

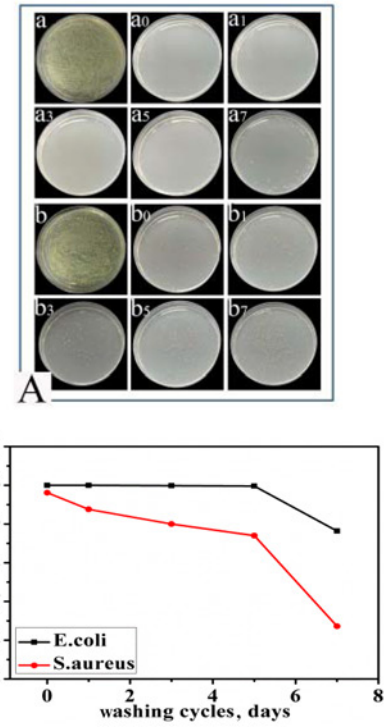

Fig. 11 *Antibacterial properties of NP*
A Optical images of antibacterial behaviour against *E. coli*: (a) pure PA6, (a_0, a_1, a_3, a_5, a_7) PA6/NP during 0, 1, 3, 5, 7 days washing cycles, respectively, and *S. aureus:* (b) pure PA6, (b_0, b_1, b_3, b_5, b_7) during 0, 1, 3, 5, 7 days washing cycles, respectively
B Bacteria reduction rate against *E. coli* and *S. aureus* of the PA6/NP fibres during 0, 1, 3, 5, 7 days washing cycles, respectively

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4. Conclusion: In summary, the NP was synthesised successfully and met the processing requirements of melt spinning. The results showed that the tensile strength of PA6/NP increased and the elongation at break of PA6/NP decreased compared with the PA6 fibre. More importantly, the bacteria reduction rate against *E. coli* and *S. aureus* of the PA6/NP fibre was 99.99 and 99.81%. When the PA6/NP fibre was washed for 7 days, the bacteria reduction rate against *E. coli* and *S. aureus* of the PA6/NP fibre was 98.82 and 96.36%. Therefore, the PA6 composite fibre with excellent durably antibacterial property could be used to the field of textile or cloth.

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