A simple method to prepare superhydrophobic and regenerable antibacterial films

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Keywords: N-halamine, antimicrobial, self-adhesive silicone rubber, superhydrophobic, chlorination and re-chlorination

Abstract
Macromolecules incorporating N-halamines have shown significant antibacterial properties and can be regenerated by chlorination. In this work, a new type of regenerable material made of nano-sized latex particles having N-H groups was prepared via the emulsion polymerization of methacylamide and dodecafluorohexyl methacrylate with divinylbenzene as a crosslinker. The N-H moieties in this polymer were subsequently transformed into N-Cl groups by chlorination with an aqueous sodium hypochlorite solution, and films were prepared by casting on substrates previously coated with a self-adhesive silicone rubber. The nanoparticles and the films were characterized by Fourier transform infrared (FTIR) spectroscopy, x-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), contact angle measurements, scanning electron microscopy (SEM) and microbiological tests. The results showed that F and Cl were successfully incorporated in the nanoparticles, that the films were thermally stable and hydrophobic (with a contact angle of 152°), and that these materials exhibited antimicrobial properties. The N-Cl groups killed bacteria by releasing active chlorine as they transitioned to N-H groups, and could be re-chlorinated with a methanol solution of isocyanuric chloride. FTIR and XPS analyses confirmed this regeneration, while SEM image showed that the morphology of the original microspheres was maintained after re-chlorination. The re-chlorinated films also maintained superhydrophobic and bactericidal characteristics.

1. Introduction
Bacteria, some of which are harmful, are ubiquitous in all environments [1]. As such, various antimicrobial agents have been developed, such as triclosan, polypeptides, chitosan, essential oils and silver nanoparticles [2–7]. However, these materials are typically non-renewable, unsustainably sourced and difficult to manufacture in a controlled manner, and may induce resistance in various microbes. In contrast, several polymers have exhibited excellent antibacterial activity while avoiding these disadvantages. Such antimicrobial polymeric films should ideally be fabricated such that they are sterile and renewable, while not degrading the durability or reusability of the polymer [8–10]. N-halamines are a class of antimicrobial compounds with the advantages of high antimicrobial activity, long-term stability, good durability, easy regeneration, low toxicity and minimal environmental impact [11–15]. These compounds function by releasing active chlorine as N-Cl functional groups are converted to N-H [16–19]. As an example, Cerkez et al reported that textiles based on N-halamines exhibited excellent bactericidal properties [20]. One important aspect of such materials incorporating N-halamines is renewability [21]. That is, after bacteria have been inhibited or inactivated by the
conversion of N–Cl groups to N–H, the substance can be regenerated via a chlorination reaction, avoiding the one-time use of the material such that the entire process is more environmentally-friendly.

Bacteria are known to adhere to the surfaces of various materials to generate so-called biofilms, and this is a very important stage in the bacterial infection process [22]. Bacteria can also survive for long time spans on the surfaces of medical devices, which can result in the spread of contamination in hospital settings [23–25]. Of interest in this regard is the concept of a superhydrophobic surface, which is defined as having a low surface energy that is not readily wetted by water. When water droplets form on such surfaces, they will rapidly roll off in the case that there is any incline, removing various surface contaminants in a process known as a self-cleaning effect [26, 27]. Hydrophobicity is related to the roughness of the material surface as well as to other factors. Thus, while a high level of surface roughness promotes the adhesion of bacteria [28], many studies have established that superhydrophobicity will greatly weaken the adhesion of bacteria to a surface [29–33]. Even so, a standard superhydrophobic surface will not kill bacteria but rather simply hinders bacterial adhesion and expansion [34]. Consequently, at present, there is significant interest in preparing materials with both antimicrobial and superhydrophobic properties, as such characteristics would both detach and kill bacteria [35, 36].

Zhang et al prepared superhydrophobic surfaces containing Cu/Ag (both of which exhibit antimicrobial activity) by electroplating and hot oxidation [37]. Wu et al deposited poly(ethyleneamine), silver nanoparticles and fluorinated decyl polyhedral oligomeric silsesquioxane on the surfaces of cotton fabrics using a solution-dipping method to impart antimicrobial and superhydrophobic properties [38]. These prior studies combined antimicrobial properties with superhydrophobic characteristics by incorporating antimicrobial agents into specific substrates [39]. However, the disadvantage of these materials is the limited release time of the antimicrobial agents due to wear and other factors. Therefore, it would be beneficial to prepare environmentally-friendly superhydrophobic materials that also exhibit long-term effectiveness. Several studies have shown that N-halogenated amines can react with amines or amides to form membranes containing these compounds, although these materials show rapid declines in antimicrobial activity over time due to wear [40–42]. Consequently, many adhesives have been studied as means of enhancing the surface stability and wear resistance of superhydrophobic materials. Men et al used poly (furfuryl alcohol) to bond carbon nanotubes and polytetrafluoroethylene to form a stable superhydrophobic interface [43], while Hou et al employed a phenolic resin as a binder for silica nanoparticles [44]. Self-adhesive silicone rubber is a biocompatible, environmentally benign adhesive, and could potentially improve the overall wear resistance of superhydrophobic materials by promoting the adhesion of nanoparticles to a base material.

Superhydrophobic nanoparticles can be prepared via solution, suspension, controlled radical and emulsion polymerizations [45–51]. Among these, emulsion polymerization avoids the use of toxic organic solvents, represents a highly stable process, is suitable for large-scale industrial production, has a low environmental impact and is efficient [52, 53]. The polymeric nanoparticles resulting from this process can be used to prepare superhydrophobic materials by casting, which is a very simple and economical method [54, 55].

To the best of our knowledge, few studies have been conducted on the preparation and characterizations of superhydrophobic, durable and regenerable antibacterial films based on macromolecules incorporating N-halamines. In the present work, divinylbenzene, dodecafluoroheptyl methacrylate and N-halamine were copolymerized to form nano-scale polymeric microspheres. These spheres were subsequently suspended in ethanol solutions of a chlorine-based oxidant such that the N–H bonds in the polymer were oxidized to N–Cl groups so as to synthesize nanoscale microspheres with antimicrobial properties. Substrates were uniformly coated with a silicone adhesive, after which these polymeric nanoparticles were spin-coated by casting to prepare superhydrophobic anti-bacterial films. After use, during which the N–Cl bonds in the material were converted to N–H bonds while inhibiting or inactivating bacteria, an ethanol solution containing the chlorine-based oxidant was applied to the film surface to regenerate the N–Cl groups. The ethanol was found to rapidly volatilize in air, which made it unnecessary to introduce a solvent extraction step. This method is both simple and environmentally-friendly, and is believed to be suitable for large-scale production.

2. Experimental

2.1. Materials and methods

2.1.1. Materials

Sodium dodecyl sulfonate (SDS), hexadecanol (HD), methanol, methacrylamide, sodium hypochlorite (NaClO) and isocyanuric chloride were used as-received without further purification. Dodecafluoroheptyl methacrylate, styrene and divinylbenzene (DVB) were distilled under reduced pressure. Potassium persulfate (KPS) was recrystallized from water. All reagents were purchased from the Aladdin Chemistry Co., Ltd.
2.1.2. Preparation of nanoparticles
In each trial, 0.25 g SDS, 0.835 g HD and 85 ml deionized water were added to a 250 ml flask fitted with a condensing tube and stirred magnetically at 70 °C under nitrogen for 30 min. The mixture was then cooled to room temperature and 13 g DVB was added, after which the flask was immersed in an ice water bath for 30 min. An aqueous 0.05 g ml⁻¹ potassium persulfate solution was subsequently added to the solution slowly in a dropwise manner at 20 °C over 20 min. Finally, the solution was heated at 70 °C for 8 h to generate Product A.

Subsequent to the above, 20 ml deionized water, 0.35 g SDS, 1 g styrene, 3 g dodecafluoroheptyl methacrylate and 4 g methacrylamide were added to a 50 ml flask and stirred for 30 min. Following this, two constant pressure dropping funnels were placed in different necks of the flask and a solution of the initiator (0.45 g KPS in 15 ml water) and a solution of Product A were simultaneously added dropwise (one through each funnel). This addition took place over 30 min, during which time nitrogen gas constantly flowed through the flask and the mixture was heated to 80 °C. The solution was allowed to react under these conditions for 2 h, after which the mixture was cooled to room temperature and an equal volume of a 10% NaClO solution was added. This new combination of reagents was allowed to react for 3 h, at which point the product was recovered by centrifugation at 3000 rpm for 10 min and then redispersed in ethanol.

2.1.3. Film preparation and regeneration
The above ethanol dispersion was directly spin-coated onto a clean glass sheet that was then dried at room temperature under vacuum for 1 h. The chloride regeneration step was performed by dropping a 5 wt% ethanol solution of isocyanuric chloride onto the surface of the film, followed by drying under vacuum at room temperature for 1 h.

2.2. Characterization
The film surfaces were analyzed by x-ray photoelectron spectroscopy (XPS) using an ESCA 5600 spectrometer with a Mg Ka x-ray source (1253.6 eV), employing a take-off angle of 0°. Fourier transform infrared (FTIR) spectra of the films were obtained with a Nicolet 20XB spectrophotometer, while TGA was performed with a NETZSCH TG 209 thermal analyzer. Scanning electron microscopy (SEM) observations were carried out with an FEI NOVA Nano-SEM 450 instrument to assess the surface morphologies of the films. Dynamic light scattering (DLS) analyses of the polymeric nanoparticles were performed using a Malvern Zetasizer Nano-ZS90 instrument. The water contact angles on the films were measured with a contact angle goniometer (China, Suolun) at room temperature after placing 4 μl droplets on four or five different sites on each film surface, and average values are reported. The experimental error associated with the contact angle data was less than 2 °.

The antimicrobial properties of the films were examined using E. coli purchased from the China General Microbiological Culture Collection Center (CGMCC) and stored at −80 °C in glycerol. Solid agar was purchased from the Wenzhou BIO—KONT Biotechnology Co., Ltd. The E. coli was cultured at 37 °C for 24 h in 10 ml of liquid Lennox broth (10 g l⁻¹ tryptone, 5 g l⁻¹ yeast extract, 5 g l⁻¹ NaCl). After culturing, the bacterial solution was diluted to a concentration of 1 × 10⁸ colony forming units (CFU)/mL with sterile phosphate-buffered saline (PBS) solution. A 1 × 1 cm film specimen was irradiated with ultraviolet light for disinfection, after which it was fixed on a glass slide and 10 μl of the diluted bacterial solution was added dropwise to its surface. The film was subsequently covered with another identical film sample. After the surfaces of the films were thoroughly covered with the bacterial solution, the slide was cultured in an incubator at 37 °C for 4 h, after which the films were placed in a test tube filled with 30 ml of PBS solution and agitated for 10 min. A 100 μl aliquot of the PBS solution in the test tube was removed and evenly applied to a solid medium that was placed in the incubator at 37 °C for 24 h. Finally, the number of bacterial colonies on the medium was counted and recorded. Control trials were also performed using sterile glass sheets. All specimens were tested in triplicate. Following each experiment, the film was washed several times with a 75% ethanol solution, followed by three washes with ultra-pure water and drying in an oven. After rechlorination of each sample, the specimen was used for a repeat antimicrobial activity experiment.

The ability of each film to prevent the adhesion of E. coli was also assessed, using glass slides without nanoparticles as controls. In these trials, sterile film specimens were cultured in 10 ml of the 1 × 10⁸ CFU/ml E. coli suspension at 37 °C for 24 h. Following this, each film was gently washed with PBS several times to rinse away any non-adherent E. coli and the samples were ultrasonicated in 10 ml of the same PBS solution at 37 °C to remove bacteria. Following this procedure, the number of bacteria was determined using the plate count method.
3. Results and discussion

Divinylbenzene, dodecafluoroheptyl methacrylate and methacrylamide were co-polymerized using a two-step emulsion polymerization method to obtain the polymeric nanoparticles, after which the nanoparticle emulsion was added to an aqueous solution of sodium hypochlorite. In this manner, the N–H groups were converted to N–Cl units so that chlorinated polymeric nanoparticles were obtained. Following this, films of these nanoparticles were prepared by casting. The N–Cl groups were able to kill bacteria by releasing active chlorine, upon which they reverted to N–H groups. A facile means of replenishing the nanoparticle films was established, involving the application of an ethanol solution of a chlorine-based oxidant. In this manner, the film could be re-chlorinated to regain the N–Cl groups. The detailed reaction process is shown in figure 1.

Figure 2 presents the FTIR spectra of the original nanoparticles and of a chlorinated and re-chlorinated film. The presence of dodecafluoroheptyl methacrylate generated a characteristic peak at 1235 cm$^{-1}$, assigned to the vibration of $-\text{CF}_2$ groups. In addition, the peak at 1738 cm$^{-1}$ is assigned to the stretching vibration of C=O groups in the methacrylamide and dodecafluoroheptyl methacrylate. The DVB was responsible for the peak at 1600 cm$^{-1}$, which is attributed to benzene rings. In the spectrum generated by the nanoparticles, the peak at 3208 cm$^{-1}$ is attributable to the N-H stretching vibration and this peak disappears after both chlorination and
re-chlorination. The spectra of the two films also show stronger and broader absorption in the range of 500 to 670 cm$^{-1}$ related to the complex vibrations of C–H and N–Cl bonds. With chlorination, the C–H groups were unchanged while the N–H groups were converted to N–Cl, which is reflected in the spectra.

The dynamic light scattering (DLS) curves (figure 3(a)) show that the obtained nanoparticles have quite narrow monomodal distribution and the z-average diameter is 75.82 nm. Moreover, the obtained nanoparticles by TEM were spherical and uniform (figure 3(b)) and the size was consistent with the DLS data.

The chlorination and re-chlorination reactions were also confirmed by XPS analysis. As shown in figure 4, characteristic C1s (284.9 eV), O1s (532.5 eV), N1s (401.9 eV), F1s (689.2 eV), Cl2s (271.1 eV) and Cl2p3 (200.1 eV) signals appeared. The F1s peak at 689.2 eV generated by all three samples is ascribed to the fluorinated segments of the nanoparticles. However, the spectra of the chlorinated and re-chlorinated films display intense chlorine peaks at 271.1 and 200.1 eV, suggesting the existence of N–Cl groups on the surfaces of these samples. These FTIR and XPS results serve to confirm that the polymeric nanoparticles were chlorinated by the sodium hypochlorite and that the films prepared from this material could be regenerated using an isocyanuric chloride solution.

The TGA curves are provided in figure 5, and demonstrate that the nanoparticles exhibited high thermal stability because of the presence of the cross-linking agent DVB and the fluorine-based functional groups. These nanoparticles and chlorinated and re-chlorinated film samples showed 5% mass loss at temperatures of 162, 180 and 175 °C, respectively. However, the chlorinated and re-chlorinated films demonstrated greater mass losses.
compared to the unchlorinated material above 208 °C. This difference occurred because N-Cl bonds are less stable than N-H bonds and thus more likely to decompose at high temperatures. Above 279 °C, the rechlorinated film showed less thermal stability than the chlorinated film. This discrepancy is attributed to the additional prior treatment of the former material, which was dried at an elevated temperature for a prolonged time period during sample preparation. Despite the presence of fluorine components, this treatment induced some thermal aging in the specimen. The film may be further processed to make medical equipment and the processing parameters, in particular temperature and time should be optimized to avoid the degradation of the film [56]. What’s more, the antimicrobial film always needs the high-temperature sterilization process before recycling. Thus, the antimicrobial film should withstand high temperature.

As discussed, superhydrophobic films are vulnerable to mechanical damage because of poor adhesion between the nanoparticles and substrate surface. To obtain more abrasion-resistant superhydrophobic thin films, silicone rubber was used as an environmentally-friendly adhesive. The advantage of this approach was that the self-adhesive silicone rubber did not react with the polymeric nanoparticles but promoted adhesion between the nanoparticles, which further increased the bonding between the substrate material and nanoparticles. In addition, the surface roughness and superhydrophobicity of the film were maintained.

During the experimental work, the self-adhesive silicone rubber was uniformly coated on the substrate, after which freeze-dried polymeric nanoparticles were cast to prepare a film. SEM images of the resulting film after chlorination and re-chlorination are presented in figure 6. These images demonstrate that the surface of the film...

Figure 4. XPS data acquired from (a) the polymeric nanoparticles, (b) a chlorinated film and (c) a re-chlorinated film.

Figure 5. TGA data obtained from (a) the polymeric nanoparticles, (b) a chlorinated film and (c) a re-chlorinated film.
maintained a microsphere morphology even after re-chlorination. These results confirm that the adhesive was effective and was able to firmly hold the nanoparticles. At the same time, the adhesive showed good stability, as it was able to maintain suitable adhesion and the original surface morphology of the film during the antimicrobial experiment as well as the application of the oxidant.

It is widely accepted that the chemical composition of the surface of a polymer film has a significant effect on wettability. As such, the introduction of fluorine monomers into polymers can effectively increase the hydrophobicity of the surface. The wetting behaviors of the present films were investigated by static contact angle measurements, and the results are shown in figure 7. The contact angle of water on the chlorinated film surface was 152°, indicating a superhydrophobic surface. After carrying out the anti-bacterial trial and re-chlorination of the film, the angle was essentially unchanged at 151°. This outcome indicated that the surface of the material maintained its superhydrophobic nature. Combined with the SEM images, it has been demonstrated that the self-adhesive silicone rubber can effectively improve the adhesion between the nanoparticles and the substrate material, and can maintain the original surface morphology so that the material can be reused many times.

The antibacterial properties of the films were evaluated using the plate count method with E. coli as a model bacteria. As shown in figure 8(b), the film samples exhibited excellent antimicrobial activity, with a bactericidal rate greater than 99.99%. Figure 8(c) demonstrates that the efficiency of the re-chlorinated film was also 99.99%, which indicates that the treatment with isocyanuric chloride was effective. These films thus maintained their original high-efficiency antimicrobial properties after recycling.

The anti-adhesion properties of the films in the presence of E. coli were assessed, as shown in figure 9. The E. coli count on the surface of the control film was \(4.9 \times 10^8\) CFU, while the level on the chlorinated film was less than the detection limit of 10 CFU. These results clearly establish that the superhydrophobic surface of the chlorinated film inhibited bacterial adhesion on the surface. During immersion of this film, the majority of the surface was covered with minute bubbles. As a result of surface tension effects, the bacteria were not readily able...
to cross the air-water interface, such that these small bubbles significantly reduced the contact between the bacteria and the surface. This effectively prevented bacterial attachment and delayed the formation of a biofilm. Moreover, due to the release of active chlorine on the surface of the film, the remaining adherent bacteria were killed. The anti-adhesion activity of the re-chlorinated film was also evaluated, and the results are included in figure 8. The E. coli level on the surface of the re-chlorinated film was also below 10 CFU, while the value for the control group was $5.3 \times 10^8$ CFU.

The stability of active chlorines (N–Cl) in the films was studied in the dry storage conditions. The antibacterial properties of the films stored for different length of time, were evaluated by using the plate count method with E. coli. The experiment results are provided in figure 10 and demonstrate that the viabilities of bacterial on the films. The bacterial viability remained 0% after 14 days. However, the bacterial viability increased to 0.2% on the 16th day and 1.1% on the 20th day. It is demonstrated from the experiment results that the antimicrobial activity against the bacterial was unchanged for at least 14 days storage and remained a relatively high level even after 14 days, indicating that the antimicrobial ability was really stable.

4. Conclusion

Nanoparticles with N-halamine groups were prepared by the emulsion polymerization of methacrylamide, dodecafluoroheptyl methacrylate and divinylbenzene followed by chlorination with sodium hypochlorite. Substrates were first coated with self-adhesive silicone rubber after which these chlorinated nanoparticles were applied as films. The resulting materials exhibited superhydrophobicity, high thermal stability, and antibacterial and anti-adhesion properties. These films were able to kill bacteria through releasing active chlorine by the conversion of N-Cl bonds to N-H groups. The original N-Cl groups could be regenerated by applying an oxidant to the surface. SEM observations showed that the re-chlorinated films maintained good adhesion to the
substrate together with their original surface morphology. Contact angle and bacterial growth tests indicated that the surfaces also retained superhydrophobicity, bactericidal and anti-adhesion characteristics. Some studies show that the traditional antibacterial film can achieve antibacterial effect by sterilization [57] and anti-adhesion [58]. Superhydrophobic antibacterial film can combine the functions of sterilization and anti-adhesion [59]. However, few studies on the regenerable superhydrophobic antibacterial films have been reported. The result of this study demonstrates that the films are not only superhydrophobic, but also have stable and regenerable antibacterial property. Moreover, the process demonstrated herein represents a simple and effective method suitable for large-scale production. The process demonstrated herein represents a simple and effective method suitable for large-scale production.

**Acknowledgments**

This research was financially supported by National Natural Science Foundation of China (31500850), the Medicine and Health Science and Technology Plan Projects of Zhejiang Province (2019KY802) and the Science and Technology Research Projects of Lishui Sci Techn Bureau (2019GYX02, 2016GYX02, 2019GYX21 and 2017GYX17).

**Data availability**

The raw/processed data required to reproduce these findings can’t be shared at this time as the data also forms part of an ongoing study.

**Conflicts of interest**

The authors declare no competing financial interest.

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