Green antimicrobial coating based on quaternised chitosan/organic montmorillonite/Ag NPs nanocomposites

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ABSTRACT
This work is aimed at developing a green antimicrobial coating. First, a green antimicrobial agent, quaternised chitosan (QCS)/organic montmorillonite (OMMT)/silver nanoparticles (Ag NPs) (QOMA) nanocomposite was fabricated through an environmental-friendly one-step approach. Morphological and structural characteristics of QOMA were investigated, and good antimicrobial activity was proved. QOMA was then incorporated into powder coating formulations to form a homogeneous coating on steel plates, which was studied by scanning electron images. Besides, the physical and mechanical properties as well as the antimicrobial performances of the coatings were discussed. The results showed that the addition of QOMA imparted good antimicrobial capacity to the powder coating, but did not affect its physical and mechanical properties. The coatings were able to effectively inactivate Gram-negative bacteria (Escherichia coli), Gram-positive bacteria (Staphylococcus aureus) and fungi (Aspergillus niger, Penicillium funiculosum, Chaetomium globasum, Paecilomyces varioti, Asp. terreus and Aureobasidium pullulans). Our findings demonstrate the possibilities of green antimicrobial coating containing QOMA for practical applications in medical devices, domestic appliances and other solid surfaces concerning bacterial infection and contamination.

1. Introduction
Due to the increasingly environmental concerns, the coating industry is suffering from stricter environmental regulations. Liquid coating, which is most widely used, involves toxic organic solvent, long processing time and high energy consumption [1]. In comparison with liquid coating, powder coating with no emission of volatile organic compounds and energy saving merits is a green coating technique, aiming to meet the market demands [2,3]. And the utilisation of environmental-friendly resources in powder coating technology would offer a ‘green + green’ solution to the current coating industry [4–6]. Powder coatings employed in medical and consumer products including medical devices, food packages, household appliances, building materials and so forth require sterile,
therefore the addition of innoxious antimicrobial agent with excellent antibacterial activity is much in demand [7–9].

Our group has lately reported a green antimicrobial agent, exfoliated silver nanoparticles (Ag NPs)-loaded quaternised chitosan (QCS)/clay nanocomposites [10]. In this nanocomposite, QCS, chitosan derivative, modified product of chitosan extracted from crab or shrimp shells [11,12], is used as a green reducing and stabilising agent to reduce Ag NPs, and meanwhile QCS intercalated into the montmorillonite layers leading to the layers peeled. The preparation process of this nanocomposite is green and environmentally-friendly, and all of the components, QCS, Ag NPs and organic montmorillonite (OMMT), possess outstanding antimicrobial property and high safety. We therefore propose using QCS/OMMT/Ag NPs (QOMA) nanocomposites as green antimicrobial agents for powder coating.

In this study, we report the characterisation and antibacterial activity of QOMA nanocomposites. QOMA was then formulated into powder coatings and their properties were discussed in detail. Furthermore, the antimicrobial activities of QOMA coating on steel plates against Gram-positive bacterial, Gram-negative bacterial and fungi were determined to investigate the potential utilisation of an effective biocidal coating material based on QOMA for houseware, medical and environmental applications.

2. Experimental

2.1. Materials and apparatus

Chitosan was provided by Jinan Haidebei Marine Bioengineering Co., Ltd. (Shandong, China). The molecular weight (Mw) of chitosan was 2.0 × 10^5 and the degree of deacetylation was 85%. 2, 3-epoxypropyltrimethyl ammonium chloride (ETA) was obtained from Dongying Guofeng Fine Chemical Co., Ltd. (Shandong, China). Sodium-montmorillonite (Na-MMT) was purchased from JianRong Mineral Refining Plant (Zhejiang, China), and the cation exchange capacity value of Na-MMT is 87 mmol/100 g. Gemini surfactant was supplied by DaoChun Chemical Technology Co., Ltd. (He’nan, China). All other chemicals employed were of analytical grade.

A XH-100B microwave synthesis system was procured from Beijing XiangHu Sci. Tech. Dept. Co., Ltd. (Beijing, China).

2.2. Preparation of QCS and OMMT

QCS was prepared as previously described [13]. Briefly, chitosan and ETA were reacted at 800 W and 75 °C for 70 min, and the molar ratio of ETA to amino groups of chitosan was 8:1. After the reaction, the product was precipitated by acetone, and then rinsed to neutral pH value. QCS was obtained after dialysis against ultrapure water and lyophilisation at −50 °C.

OMMT was synthesised according to our previous procedure [14]. Briefly, MMT was dispersed in a 50% (v/v) isopropanol and left to stand for 24 h after 30 min vigorous stirring. Gemini surfactant was added into the MMT suspension at 80 °C under stirring.
Next, the product was rinsed by ultrapure water until no chloride anions could be determined. After being lyophilised and ground, OMMT was obtained.

### 2.3. Fabrication of QOMA

First, AgNO₃ was dissolved into ultrapure water to prepare a solution of 1 mmol/mL, and NaOH solution was added into AgNO₃ solution to generate silver oxide, Ag₂O. Ammonium hydroxide was then added dropwise under stirring until the brown precipitate was dissolved. At that time, the solution of [Ag(NH₃)₂]OH was obtained.

After swelling for 24 h, 1% (w/v) OMMT suspension was reacted at 800 W and 85 °C with stirring under microwave irradiation. The fresh [Ag(NH₃)₂]OH solution was added into the QCS aqueous solution, and the mixture was then dropped into the OMMT suspension. After reacting for 70 min under microwave irradiation, the products were purified by dialysis for three days. QOMA samples were finally obtained by lyophilisation at −50 °C.

### 2.4. Preparation of QOMA coatings

The formulation contained a commercial polyester/epoxy-based powder varnish, with different percentages of QOMA and other additives (as listed in Table 1). The mixture was extruded in a screw extruder with thread diameter of 20 mm and speed screw of 200 rpm (Yantai Donghui Powder Processing Equipment Company, Yantai, China). After the processing, the chips were ground in a bench top knife-mill, and sieved (200 mesh). The coatings were applied to the steel plates via electrostatic spray gun (Gema Company, Switzerland). The curing process was conducted in an air circulation oven at 185 °C for 15 min.

### 2.5. Characterisation

The X-ray diffraction (XRD) experiment of QOMA was performed with D8 advance X-ray diffractometer (Bruker, Germany) utilising a Cu-Kα radiation (λ = 0.15418 nm) at 40 kV and 50 mA. The intensity was recorded in the scattering scope of 1°–10° at a scanning rate of 0.5°/min and 5°–90° at a scanning rate of 4°/min.

The microstructure and surface morphology of QOMA were analysed by JEM-2010HR transmission electron microscopy (TEM) (JEOL, Japan) at an accelerating voltage of 200 kV. The nanocomposites with clay were prepared by cutting from the epoxy block (LEICA, Austria) with the embedded nanocomposite sheet at room temperature.

| Ingredient                  | w/w% |
|-----------------------------|------|
| Polyester resin/QOMA       | 37.18|
| Epoxy resin                | 23.53|
| Rutile titanium dioxide    | 19.12|
| Ultrafine barium sulphate  | 17.65|
| Levelling agent            | 0.88 |
| Luster-enhancing agent     | 0.88 |
| Micro wax                  | 0.38 |
| Benzoin                    | 0.38 |
The morphological and structural characteristics of the coatings were evaluated by a SU-70 scanning electron microscope (SEM) (Hitachi, Japan) and an Energy Dispersive X-ray (EDX) Detector (Oxford, UK).

### 2.6. Evaluation of antibacterial activity

*Staphylococcus aureus* (ATCC 6538), *Bacillus subtilis* (ATCC 6633), *Escherichia coli* (ATCC 25922), *Pseudomonas aeruginosa* (ATCC 9027) and *Aspergillus niger* (ATCC 16404) were utilised as model micro-organisms. They are all received from Microbial Culture Collection Center of Guangdong Institute of Microbiology (Guangzhou, China). The minimal inhibition concentration (MIC) against the tested bacteria was determined as the concentration of QOMA causing the complete inhibition of bacterial growth [15].

The MIC test was conducted based on various concentrations of QOMA in batch cultures. The bacteria suspension was adjusted to $10^5$–$10^6$ cell/mL by sterile distilled water. A loop of bacteria suspension was inoculated on the agar plate. The microbes were incubated at $37 \pm 0.5 ^\circ C$ for $24$ h. The concentration of QOMA inducing a sterilised effect was recorded based on the absence of colonies on the agar plate.

Antimicrobial activities of the coatings were assessed using Gram-negative bacterial (*E. coli*), Gram-positive bacteria (*S. aureus*) and fungi (*Aspergillus niger* ATCC 16404, *Penicillium funiculosum* ATCC 36839, *Chaetomium globasum* ATCC 6205, *Paecilomyces variotii* CICC 4024, *Asp. terreus* CICC 40377 and *Aureobasidium pullulans* CICC 40329) according to HG/T 3950-2007 (trade standards of chemical industry in China).

### 2.7. Test of physical and mechanical properties

Thickness was measured using a Qnix 1500 thickness gauge. Adhesion test was performed according to ISO 2409-1992. Pencil hardness was measured following ASTM D 3363. And gloss was determined by a Gloss Checker JKG gloss meter (Tianjin Jingke Material Testing Co., China) according to ASTM D 523.

### 3. Results and discussion

#### 3.1. Structure and morphology of QOMA

XRD technique was used to characterise the basal spacing of MMT in polymer/MMT hybrids, verifying the morphology of the nanocomposites [16,17]. Figure 1 displays the XRD patterns of OMMT, QCS and QOMA. As shown in Figure 1(a), a peak of OMMT can be observed at $2 \theta = 4.03$, indicating the interlayer distance is 2.2 nm calculated by the Bragg equation: $n\lambda = 2d\sin\theta$ [18]. However, the $d_{001}$ diffraction peaks of OMMT disappeared in QOMA, suggesting the formation of exfoliated QOMA nanocomposites [19,20]. In Figure 1(b), obviously, there are five diffraction peaks at 38.35°, 44.48°, 64.56°, 77.54° and 81.72°, respectively, which are assigned to diffraction from the (111), (200), (220), (311) and (222) planes of face-centred cubic silver [21]. This result demonstrates the formation of Ag NPs in the nanocomposites.

The surface morphology of QOMA and the dispersion of Ag NPs in QOMA were investigated by TEM. The TEM micrograph of OMMT was presented as comparison. We can
effortlessly observe from Figure 2(a) that OMMT has ordered clay layers, which provides possibility for the intercalation. The micrograph shown in Figure 2(b) reveals that the dark sphere-like particles are related to Ag NPs, the gray entities around the particles associate with QCS and the layered matrix correlates with OMMT. It is clearly observed from Figure 2(b) that spherical Ag NPs are well distributed throughout the matrix with an average size of 26 nm. The nucleation and growth of Ag NPs may be attributed to the interaction of $[\text{Ag(NH}_3\text{)}_2]^+$ with quaternary ammonium groups on QCS chains. Meanwhile, the OMMT was exfoliated, thus it can be inferred that the large driving force for intercalation was obtained to peel the OMMT layers when QCS was reduced to generate Ag NPs [10].

3.2. Antimicrobial activity of QOMA

To evaluate the antimicrobial activity of QOMA, the antibacterial assays using Gram-positive bacteria, Gram-negative bacteria and fungi were performed. Table 2 presents that the
MIC of QOMA against *S. aureus*, *B. subtilis*, *E. coli*, *P. aeruginosa* and *A. niger* were 62.5, 62.5, 31.25, 62.5 and 2500 μg/mL, respectively. As widely reported, the MIC ranges from parts per million to parts per thousand concentration levels [22,23]. And the antibacterial activity is generally more pronounced than the antifungal activity [24,25]. In this study, it is presented that the MIC of QOMA against *A. niger* was 2500 μg/mL. Although it was much higher than that against bacteria, it reveals that QOMA with certain concentration showed antifungal capacity. This observation is attributed to the distinction of cellular structure between bacteria and fungus [26,27]. The possible reason for this excellent antibacterial performance of QOMA is that QCS, OMMT and Ag NPs all possess antimicrobial activity. With large specific surface area, OMMT is capable of adsorbing and fixing microbes. Additionally, the hydrophobic interaction between hydrophobic alkyl chains of OMMT and lipophilic components of microbial cell walls may contribute to the adsorption [28]. Moreover, OMMT contains quaternary ammonium groups, which are the well-known disinfectants. The biocidal action is implemented through increasing cell permeability and disrupting cell membranes [29–31]. Analogously, QCS could adsorb and immobilise bacteria via electrostatic and hydrophobic interactions. And the long chain alkyls with hydrophobicity in QCS can penetrate into the cell membrane [10,32]. Ag NPs are a new generation of antimicrobials while silver has been in antimicrobial use for centuries. It is reported that Ag NPs with large surface area could easily attach to the cell membrane, penetrate inside the bacteria and then release silver ions, finally leading to cell death [33–36]. Therefore, contributing to the synergistic effect of these three kinds of antimicrobial materials, quaternised chitosan/ organic montmorillonite/Ag NPs nanocomposites (QCMA) has an exceptional antibacterial and antifungal capacity. In brief, it is the short-distance nano-mechanical contact between QCMA and micro-organisms that provides subsequent local interaction of antimicrobial agent with cell components causing damage to the microbes [37,38].

### 3.3. Microstructure of QOMA coatings

The morphological characteristic and homogeneity of QOMA coatings were analysed by SEM. SEM images presenting the surface of QOMA coatings are shown in Figure 3(a–c). As we can see, a relatively smooth surface morphology of QOMA coatings was obtained, without any cracks or discontinuities (Figure 3(a)). It is reasonable to deduce that QOMA can be directly incorporated into powder coating formulations and that homogeneous coatings are obtained [39]. Note that in the high-resolution SEM micrographs (Figure 3(b,c)) QOMA were evident on the coating surface. We infer that QOMA is primarily blended with the polyester and epoxy matrix, and possibly oriented parallel to the coating surface, similar to the previous studies [40–42]. Additionally, the EDX pattern (Figure 3(d)) provides evidence for the existence of QOMA in the coatings.

### Table 2. MIC evaluation of QOMA nanocomposites (μg/mL).

| Sample  | Gram-positive bacteria | Gram-negative bacteria | Fungus |
|---------|------------------------|------------------------|--------|
|         | *S. aureus* | *B. subtilis* | *E. coli* | *P. aeruginosa* | *A. niger* |
| Blank   | — | — | — | — | — |
| QOMA    | 62.5 | 62.5 | 31.25 | 62.5 | 2500 |

*a*No antimicrobial activity.
3.4. Antimicrobial activity of QOMA coatings

In order to comprehensively assess the antimicrobial performance of QOMA coatings, the antibacterial tests and antifungal tests were conducted, respectively. As shown in Table 3, the QOMA coatings exhibited a bacterial inactivation rate of 99.99% for *E. coli*, relative to the control experiment. However, a lower inactivation rate of 99.83% was achieved against *S. aureus*. As reported previously, *S. aureus* owns a thicker peptidoglycan layer of the cell wall preventing the penetration of Ag NPs inside its cytoplasm [43,44], corresponding to less intense antibacterial activity. Besides, it can be interpreted by considering the nanomechanical contact effect discussed in the above section. Briefly, this result is in agreement with the antimicrobial performance of QOMA.

The antifungal tests were performed with *A. niger*, *P. funiculosum*, *C. globasum*, *P. varioti*, *A. terreus* and *A. pullulans*. The results show that no fungus could be examined under a microscope at up to 50 times magnification (shown in Table 3). It can be concluded that the QOMA coatings exhibit antiseptic activity either bacteriostatic or bactericidal against

### Table 3. Antimicrobial activity of QOMA coatings containing 0.05% of QOMA.

| Bacteria | Fungi                                      |
|----------|--------------------------------------------|
| *E. coli* | *A. niger*, *P. funiculosum*, *C. globasum*, *P. varioti*, *A. terreus* and *A. pullulans* |
| *S. aureus* | Zero-levela          |

| Antimicrobial efficiency | 99.99% | 99.83% | Zero-levela |

*a* It could not be observed under a microscope at up to 50 times magnification.
fungi. In Table 3, the QOMA coating formulation involves 0.05% of QOMA. We use the QOMA coatings containing 0.05% of QOMA, which is the lowest content among three samples, to conduct the antimicrobial experiments. It is believed that if the QOMA coatings containing 0.05% of QOMA present high antibacterial efficiency, it is convincing that the other two coatings with more amount of QOMA also have antimicrobial activities.

SEM analysis was conducted to test the bacteria adhesion on the QOMA coating. Noteworthily, the SEM micrographs were attained before the 24 h incubation, which provided possibilities for observing the active microbes and their affinity with the QOMA coating. As shown in Figure 4, the microbes, *E. coli*, *S. aureus* and *A. niger* all possessed intact shape and tightly attached on the QOMA coating facilitating the subsequent antimicrobial behaviour. And during the incubation, such micro-organisms were likely to be killed or their growths were badly inhibited by the adjacent QOMA coating, which explains the intense bacterial inactivation rate and antifungal efficiency that exhibited in Table 3.

3.5. Physical and mechanical properties of QOMA coatings

Table 4 shows the physical and mechanical properties of QOMA coatings, while Figure 5 provides a naked-eye observation of the exterior. From the digital image (Figure 5), we could not easily discern the coatings with different content of QOMA. The gloss values
were almost the same, about 86° (shown in Table 4), indicating that a few amount of QOMA do not alter the pigment volume concentration [45]. The thickness of the coatings ranged from 65 to 100 μm, increasing with the increase of QOMA content. This variation arises from the addition of QOMA, which has less regular shape compared to the polyester resin. All the coatings showed good pencil hardness (1H) and excellent adhesion to steel plates. It has been demonstrated that the presence of hydroxyl groups has beneficial effects on adhesion [45,46]. Therefore, it is the hydroxyl groups in QOMA that bring about great adhesion, promoting a stable coordination bond with other additives and/or steel plates. In summary, the addition of QOMA barely affected the physical properties of the coating surface.

**4. Conclusions**

This work investigates the possibility of QOMA to develop a green coating material for antimicrobial applications with powder coating technology. SEM data analysis reveals that QOMA blended with powder coating formulations was homogeneously coated on steel plates, forming a stable and uniform microstructure and a relatively smooth surface morphology. The physical and mechanical tests demonstrate that the addition of QOMA does not apparently affect physical properties of the coating surface. Nevertheless, the hydroxyl groups in QOMA produce good adhesion, facilitating a stable coordination bond with other additives and/or steel plates. The irreversible binding of powder coating contained QOMA to steel plate imparted outstanding antimicrobial activity to this coating.
material. And the antimicrobial effect of the coatings on *E. coli* is more intense than that on *S. aureus*, which is associated with the nano-mechanical contact effect as well as the less rigid membrane structure of *E. coli*. These results strongly suggest the application of a green antimicrobial coating based on QOMA nanocomposites to sterilize solid surfaces.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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