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Preparation and Properties of Fe_3O_4 Biomimetic Micro-nano Structure Coatings[1]

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Abstract: Nanoparticles filling is one of the most effective methods to build the micro-nano structure. In this paper, the composite coatings containing Fe_3O_4 nanoparticles were prepared from fluorinated silicon polymer by in-situ polymerization. FT-IR was used to characterize the structure of the composite material. SEM and AFM were performed to observe the microstructure of the coatings. The contact angle of water and coatings was tested. The results showed that the biomimetic micro-nano structure of the coatings, which formed on the glass plate, was exactly familiar with that of the surface of lotus leaves.
Keyword: micro-nano structure; Fe_3O_4 nanoparticles; in-situ polymerization; biomimetic

1. INTRODUCTION

The natural lotus leaf surface is one of the most typical examples of the self-cleaning effect as a result of the micro-nano structure. The SEM photographs revealed that the lotus leaf surface was made up of many

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5~9μm papillae which possessed a nano-scale multiple structure. P. Ball (Ball, 1999) explained the mechanism of self-cleaning of lotus leaf surface as follows: there were micro-nano multiple structures on the lotus leaf surface, and the wax in the micro-nano structures was hydrophobic. Imitating the micro-nano structure features and mechanisms of the self-cleaning lotus leaf, super-hydrophobic surface has been cognized and made significant progress in terms of theoretical foundation, building technology and applications. There are two ways to construct the micro-nano structure in the aspect of bionics: one is constructing the micro-nano structure on the low surface energy coatings, the other is forming low surface energy materials on the matrix with micro-nano structures (JIANG, 2005).

Since the self-cleaning mechanism of lotus leaf was discovered, a variety of methods have been tried to obtain the super-hydrophobic coating with micro-nano structures. Representative works are as follows: (1) Chen (Shiu et al., 2004) and his co-workers used nanoparticles etching method to construct double layered polystyrene nanoscale beads array, and then oxygen plasma was used to process to further reduce the size of nanoscale beads to obtain micro-nano structure; (2) Youngblood (Youngblood & McCarthy, 1999) used a radio frequency plasma to etch polypropylene (PP) to prepare the random microstructure in the presence of PTFE, and the surface contact angle with water reached the maximum as 172°; (3) Jiang Lei (LI et al., 2002; LI et al., 2003) used CVD method to prepare aligned carbon nanotube films with a variety of patterns on the structure, such as honeycomb-like, columnar and island, and the contact angle of water on the membrane surface was beyond 160°; (4) Cho (HAN et al., 2004) used sol-gel process to get the super-hydrophobic surface from the silicone supramolecular (supraTES) with a quadruple hydrogen bond. (5) Xu Jian (XIE et al., 2004) used the solvent evaporation process mechanisms of self-aggregation, surface tension and phase separation to construct a similar micro-nano structure of lotus leaves on the polymer surface at room temperature and atmospheric conditions. The common characteristics of the above coating are micro-nano structures, which have been treated with low surface energy compounds. The surface treatment generally require laboratory equipments and strict conditions or special substrate, such as carbon nanotube array, and the preparation process is complicated and expensive, especially, large area films could not be formed, which lead to it is hard to be used widely for the coatings.

In order to solve these problems, in-situ polymerization by dispersing Fe_3O_4 nanoparticles in polymer solution by ultrasonic is used to build micro-nano structure coating only in company with the natural evaporation of the solvent. This method has advantages of low cost, simple process and easy to form large area micro-nano structure, which provides great potential in practical applications (HOU et al., 2006).

2. MATERIALS AND METHODS

2.1 Materials and instruments

Methyl methacrylate (MMA); β hydroxyethyl methacrylate (HEMA); methyl Isobornyl (IBOMA); butyl acrylate (BA); styrene (St); dodecafluroheptyl methacrylate ester; Cetyltrimethylammonium bromide(CTAB); dibutyltin dilaurate (DBTDL); linear two-hydroxy silicone oil; isophorone diisocyanate (IPDI). Above reagents are as chemically pure. Azobis isobutyronitrile (AIBN); butyl acetate; xylene; Fe_3O_4 nanoparticles.

NicoletV70 type FT-IR analyzer; S-4800 type scanning electron microscope SEM; TS-150 type AFM atomic force microscope; JC2000C1 intravenous infusion of contact angle/surface tension measuring instrument.

2.2 Methods

2.2.1 Preparation of nanoparticles modified organic fluorine - polyacrylate (NP-FPA)

CTAB was added in the solvent of a certain proportion of xylene and butyl acetate, and then Fe_3O_4 nanoparticles was dispersed by ultrasonic in such solvent, which would be added appropriate AIBN later. In the N_2 atmosphere, the above solvent was dropped into the mixture of MMA, St, IBOMA, BA, HEMA and dodecafluroheptyl methacrylate ester. After 6h, NP-FPA was obtainted.

2.2.2 Preparation of silicone modified polyurethane (SPU)

IPDI and DBTDL were added in the solvent of a certain proportion of xylene and butyl acetate. In the N_2 atmosphere, linear two-hydroxy silicone oil was dropped in the above solvent, and SPU was prepared after 6h.

2.2.3 Preparation of nano-composite polymer

A small amount of DBTDL was added in the mixture of NP-FPA and SPU with a certain ratio, and the target product was prepared after 30 min.

2.2.4 Preparation of coatings

Nano-composite polymer solution was diluted with an appropriate amount of mixed solvent, and then clean glass slides were immersed in the solution of uniform depth twice in speed of 5cm/min and dried in the air.

3. RESULTS AND DISCUSSION

3.1 FT-IR analysis

Fig.1 and 2 show the FT-IR spectra of NP-FPA and SPU, respectively.

For 1, characteristic absorption peak of C=C double bond is not observed at 1401cm^{-1} and 1636cm^{-1}, which shows that acrylate monomer polymerization occurred; 1390cm^{-1}, 1150cm^{-1} and 750cm^{-1} are the absorption peak of more fluorinated alkanes. 1731cm^{-1} is the stretching vibration absorption peak of C=O, 1257cm^{-1}, 1176~1160cm^{-1} and 1123~1110cm^{-1} are the stretching vibration absorption peak of C–O–C, 3503cm^{-1} is the characteristic absorption peak of –OH, 2930cm^{-1} is the absorption peak of $–CH_3$ and $–CH_2–$. Above results show that NP-FPA is prepared.

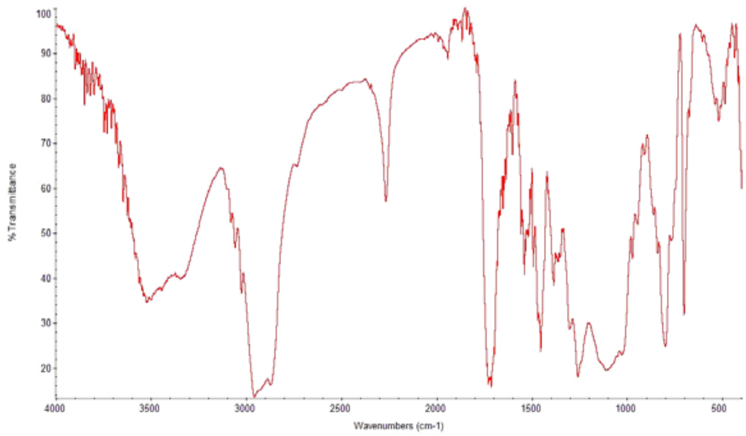

Fig. 1: The FT-IR spectra of NP-FPA

For 2, 2275cm^{-1} is the characteristic absorption peak of –NCO; 3335cm^{-1} is the stretching vibration absorption of $–NH_2$, 1541cm^{-1} is the co-frequency peak of N–H bending vibration absorption and C–N stretching vibration absorption, which show that the reaction of –NCO and –OH occurred. 2963cm^{-1} is the stretching vibration absorption of $–CH_2–$; 1262cm^{-1}, 807cm^{-1} and 1096cm^{-1} are the characteristic absorption peak of siloxane. Above results indicate that the –NCO of IPDI was connected up silicone main chain and the expected product is prepared.

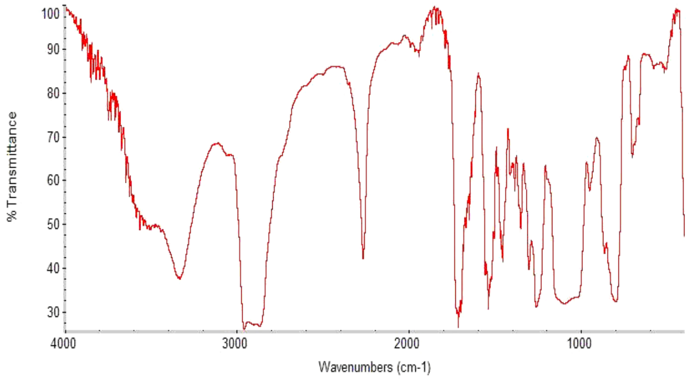

Fig. 2: The FT-IR spectra of SPU

3.2 SEM characterization

Fig.3 showed the SEM photo of the Fe_3O_4 nanoparticles composite polymer coating. Due to the addition of Fe_3O_4 nanoparticles, micro-nano structure, which is similar to the lotus leaf surface, is constructed. Furthermore, the comparison of a single lotus leaf surface papilla (SU & CHEN, 2008) (Figure 4) and an Fe_3O_4 nanoparticles composite polymer coating papilla (Figure 5) indicate that the Fe_3O_4 nanoparticles are wrapped by organic polymers to 5~9μm papilla which possesses a nano-scale Fe_3O_4 secondary structure at high magnification. That structure is very similar to the micro-nano multiple structure of lotus leaf surface in terms of size or scale structure.

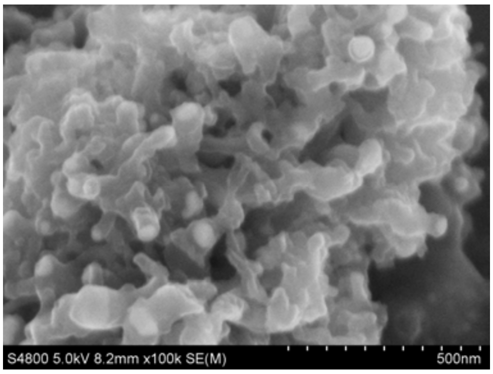

Fig. 3: The SEM photo of the Fe_3O_4 nanoparticles composite polymer coating.

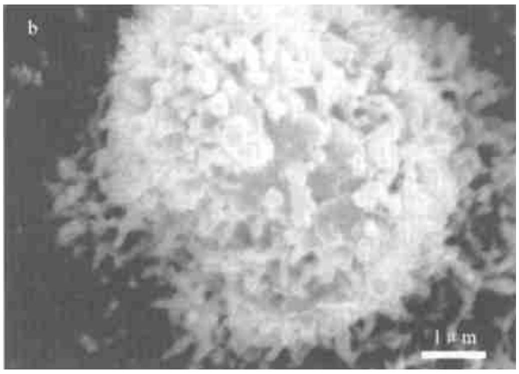

Fig. 4: The papilla SEM photo of lotus leaf surface

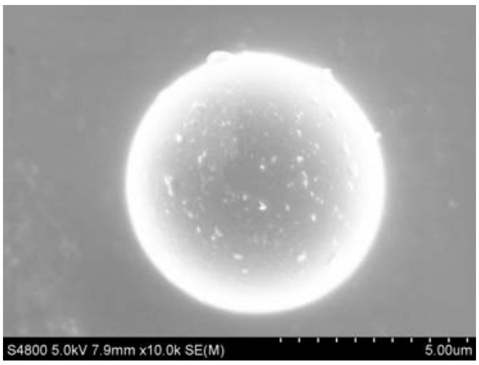

Fig. 5: The papilla SEM photo of the Fe_3O_4 nanoparticles composite polymer coating

3.3 AFM characterization

Fig.6 and 7 show the AFM photos of the polymer coating without Fe_3O_4 nanoparticles and the Fe_3O_4 nanoparticles composite polymer coating, respectively. The surface of the coating without Fe_3O_4 nanoparticles is smooth and the fluctuation was only about 5nm. Nevertheless, the surface fluctuation of the Fe_3O_4 nanoparticles composite polymer coating increases significantly and reached to 500nm, in addition to the tall peaks, there are a large number of low peaks, which together constituted the micro-nano structure. It demonstrates that the use of nanoparticles filling to construct the micro-nano structure was feasible.

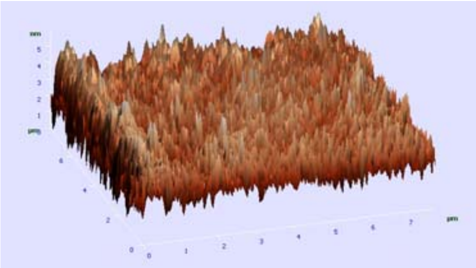

Fig. 6: The AFM photo of the polymer coating without Fe_3O_4 nanoparticles

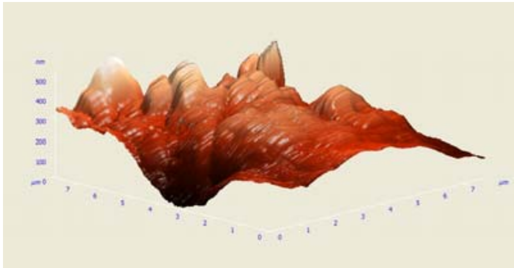

Fig.7: The AFM photo of the Fe_3O_4 nanoparticles composite polymer coating

3.4 Contact angle analysis

Fig. 8 shows the contact angle analysis photos of the composite polymer coatings with different ratios of Fe_3O_4 nanoparticles. Fig. 9 is the variation of contact angles of water droplet with ratios of Fe_3O_4 nanoparticles. When nanoparticles content is very low, the coating surface contact angle was small. With the content of nanoparticles increasing, the coating surface contact angle of water droplet increases first and then decreased. When the nanoparticles content is about 5%, the contact angle reached the maximum. This is dued to the addition of nanoparticles in the coating surface gradually formed micro-nano multiple structure, when the water drops onto the coating surface, the nano-pores are closed and the air film is formed between the coating surface and the water layer, which makes the water droplets and the coatings could not completely contact. It plays a role of hydrophobic because that the water droplets shrinks in the condition of the surface tension effect (GAO et al., 2009). With the continuous increasing content of nanoparticles, due to the process of the agglomeration of nanoparticles causing by the solvent evaporation of the coating, the micro-nano structure of the coating surface is damaged and the contact angle decreased.

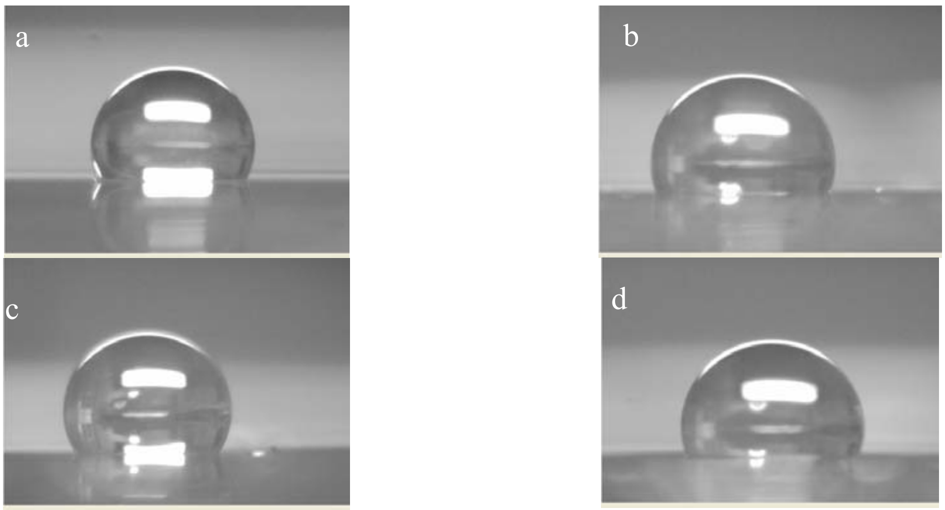

Fig. 8: The contact angle analysis photo of the composite polymer coatings with ratios of Fe_3O_4 nanoparticles (a : 1%, b : 3%, c : 5%, d : 7%)

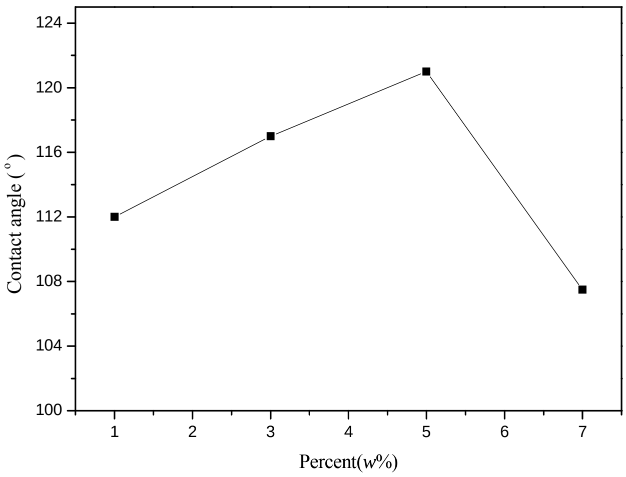

Fig. 9: The variation of contact angles of water droplet with ratios of Fe_3O_4 nanoparticles

4 CONCLUSION

(1) The biomimetic micro-nano structure-coatings were prepared by in-situ polymerization with Fe_3O_4 nanoparticles added in special condition.
(2) The SEM and AFM photos of the coatings show that the micro-nano multiple structure which is similar to the lotus leaf surface is constructed due to the addition of Fe_3O_4 nanoparticles which changes the morphology and surface properties of the coating.
(3) The contact angle of the coating surface increases first and then decreases with the content of nanoparticles increasing, which closely related to the nanoparticles dispersion in the coating systems and the micro-nano structure of the coating surface.

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ILLUSTRATIONS LIST