Preparation of New Polymer Nanocomposites and Analysis of Their Superhydrophobic Properties

Wei Wang
School of Mechanical and Control Engineering, Shengli College China University of Petroleum, Dongying 257061, China
2015014@slcupc.edu.cn

Abstract. As an important branch of the superhydrophobic research field, polymer/nano composite superhydrophobic materials have broad application prospects in anti-corrosion, self-cleaning and oil-water separation. In this paper, a polymer-based nanocomposite superhydrophobic coating was prepared by a simple method, and its microscopic morphology, wettability and other related properties were characterized and analyzed. The SiO2/PS and SiO2/PVC superhydrophobic nanocomposite coatings were prepared by spin coating. The method is simple, easy to implement, low in cost, and does not require special equipment and harsh conditions. The addition of hydrophobic nano-silica reduces the surface energy of the coating while increasing the surface roughness, without the use of low surface energy substances. The coating exhibits excellent acid and alkali corrosion resistance, and is suitable for a variety of substrates. It can be used as an anticorrosive coating for metal protection and has a good application prospect.

Keywords: Nano-Si02 polymer; superhydrophobic and super lipophilic; friction; reversible conversion.

1. Introduction
Polymer/nanocomposites have attracted people's attention due to their good application prospects in many fields such as optics, chemical engineering and biology [1]. Polymer/nanocomposite superhydrophobic materials are a kind of superhydrophobic composites formed by dispersing and filling inorganic nanoparticles in various forms in a polymer matrix, which is an important branch of superhydrophobic materials research [2].

Nanoparticles refer to various solid ultrafine particles with an average particle size between 1 nm and 100 nm. Due to their unique small size and special structure, nanoparticles have some strange physical and chemical properties that traditional materials do not have. Surface and interface effects: as the particle size decreases, the number of surface atoms of nanoparticles increases rapidly, and their specific surface area, surface energy and surface binding energy also increase rapidly, thus giving nanoparticles high chemical activity [3]. But this also becomes the reason why the nanoparticles are very easy to adsorb and agglomerate, and it is difficult to uniformly disperse. When the size of the nanoparticle is equal to or smaller than the De Broglie wavelength of conducting electrons, its periodic boundary conditions are destroyed, resulting in its macroscopic physical properties (such as special...
magnetic properties, thermal properties, and mechanical properties). This effect opens up many new areas for the practical application of nanoparticles [4]. The ability of microscopic particles to penetrate the barrier is called the tunneling effect. In recent years, it has been discovered that some macroscopic quantities can also change through the barriers of the macroscopic system, so it is called the macroscopic quantum tunneling effect. This special effect, together with the quantum size effect, becomes the basis of future electronic devices.

The combination of nanoparticles and polymers can simultaneously play a synergistic effect between the components, which is also one of the common characteristics of composite materials. In general, in the process of composite modification of polymers, inorganic materials increase their strength while reducing the toughness of the polymer. However, when the nanoparticles are compounded and modified on the polymer, they can strengthen the polymer and at the same time play a toughening effect, and obtain a composite material with excellent performance. Secondly, composite materials with some special properties can be prepared by selecting nanoparticles or polymers with different properties. By simply dispersing nanoparticles in a polymer matrix, new functional materials with special properties such as photoelectric conversion, catalysis or intelligent response can be obtained [5]. Third, by adding a small amount of nanoparticles, the strength and toughness of the polymer material can be significantly improved, which can reduce the use of raw materials and reduce costs. On the basis of these properties, coupled with the superhydrophobic properties of composite materials, greatly expand the scope of application of polymer/nanocomposites, making the materials more meaningful.

In this article, a simple spin coating method is used to prepare silica/polystyrene and silica/polyvinyl chloride superhydrophobic coatings. Since the phase separation between silica and polystyrene is easy to occur, the silica is easy to precipitate from the polystyrene during the volatilization of the solvent. Therefore, we use a silane coupling agent to improve and enhance the compatibility between silica and polymer, and prepare a stable superhydrophobic coating resistant to acid and alkali [6].

2. Preparation of polymer/nanocomposite superhydrophobic materials

2.1. The mechanical stability and durability of superhydrophobic surfaces need to be further studied

For the superhydrophobic surface to move towards the direction of large-scale industrial production, its surface structure must be stable and the bonding force between the coating and the substrate must be good, that is, it has excellent anti-pollution ability and high mechanical strength [7]. However, most of the artificially prepared superhydrophobic coatings are easily damaged and lose superhydrophobicity. Even with very small external forces, this is far from meeting the application requirements.

Generally, there are three types of preparation methods of polymer/inorganic nanocomposites. One is the blending method. It refers to the method of blending nanoparticles and polymers (solution blending/emulsion blending/melting blending/mechanical blending), so that the nanoparticles are uniformly dispersed in the polymer matrix to prepare the polymer/nano composite material. This method is simple and easy to implement, but the disadvantage is that the nanoparticles are very easy to agglomerate and it is difficult to achieve uniform dispersion. Therefore, the key to this method is how to ensure uniform dispersion. The second is the sol-gel method. The process of dissolving the precursor in a pre-formed polymer solution, hydrolyzing and condensing into a sol, and converting the sol into a gel through post-treatment. The experimental conditions of this method are mild and the two phases are evenly dispersed. However, there are disadvantages: the precursor is expensive and toxic. The volatilization of solvents and small molecules during the gel drying process can easily cause the material to shrink and brittle, which is difficult to prepare in a large area. Using nano-layered inorganic substances (graphite, metal oxide, etc.) as the host, inserting the polymer as a guest between the layers of the host, a nanocomposite material with mechanical, electrical and optical properties is obtained. The intercalation method has a simple process, cheap and readily available raw materials, and is easy for industrial production.
2.2. The multifunctionalization and application of superhydrophobic materials need more in-depth research

At present, artificially prepared superhydrophobic surfaces generally have a short service life. This is because when exposed to an open environment, the superhydrophobic surface will not only be exposed to a single pollutant, but also organic pollutants, dust, and acid rain in the outdoor environment [8]. Superhydrophobic materials lose their superhydrophobic properties due to pollution, corrosion or dust adsorption. Therefore, research on multifunctional superhydrophobic materials is more conducive to practical applications. In recent years, there have been more and more researches on some superoleophobic, transparent, anti-corrosion super-hydrophobic materials, but there are few reports on how to make super-hydrophobic materials have multiple functions that are beneficial to applications.

On this basis, the researchers combined with various other preparation methods related to superhydrophobic surfaces, and successfully prepared a variety of polymer/nanocomposite superhydrophobic materials. Raghav G R et al. [9] nano SiO$_2$ was dispersed in polystyrene tetrahydrofuran solution, and a superhydrophobic film was prepared on a glass substrate. The surface contact angle was controlled by controlling the drying temperature of the film. Under ultraviolet light and heating conditions, the reversible conversion from super-hydrophilic to super-hydrophobic can be realized. Ali M et al. [10] prepared a carbon nanotube-polytetrafluoroethylene bulk material at 39°C under hot pressing conditions. The block has excellent overall super-hydrophobic and super-lipophilic properties, and it maintains super-hydrophobic properties under various conditions such as repeated rubbing, as shown in Figure 1.

![Figure 1. Preparation of polymer/nanocomposite superhydrophobic material](image)

In recent years, polymer/nanocomposite superhydrophobic materials, as a branch of the research field of superhydrophobic materials, have broad application prospects in anti-corrosion, self-cleaning, and oil-water separation. It is a very simple and common method to prepare superhydrophobic materials by filling nanoparticles in polymers. Commonly used filler particles are: silicon, titanium oxide, polytetrafluoroethylene, metal oxide and so on [11]. The intervention of filler particles not only increases the strength of the material, but also increases the roughness of the material and improves the hydrophobicity. The polymer phase and the nanophase show a good synergy: on the one hand, the filling and effective dispersion of nanomaterials can improve the mechanical properties of the polymer matrix; on the other hand, the polymer phase can pass through the coating, steric effect or change the surface properties of the particles, improve their dispersion and compatibility in different media, and give full play to the peculiar synergistic effect of nanoparticles. Nano-silica (SiO$_2$) has special properties such as
small particle size, large specific surface area, strong surface adsorption and large surface energy, as well as its excellent stability, reinforcement, thickening and thixotropy[12]. One of the important new high-tech ultrafine inorganic materials, it has an irreplaceable role in many disciplines and fields, and is widely used in various fields such as chemical engineering, medicine, environmental protection, etc. The surface is rich in hydrophobic nano-materials with long-chain organic modifiers. Silica, in many organic media, has a polymer/nanocomposite method to prepare superhydrophobic surfaces. There are many reports. At present, the preparation of superhydrophobic materials is moving in the direction of simplicity, efficiency and large-scale production. Development. Regarding the research on superhydrophobic surfaces, rich research results have been obtained in terms of theoretical basis, preparation and application. However, there are still many problems to be solved if superhydrophobic surfaces are truly widely used in actual production and life.

3. Preparation and performance study of nano-silica/polymer composite coating

3.1. Preparation of superhydrophobic SiO$_2$/PS composite coating

The hydrophobic nano-silica (DNS-2) particles and 0.4 g of polystyrene (PS) were ultrasonically dispersed in 12 mL of the solution, and 0.25 g of mercaptopropyltrimethoxysilane was added, and stirring was continued for 1 h. Use a spin coater (2000 rpm, 30 s) to coat the mixed solution on the glass substrate and dry it for 2 min at room temperature. Table 1 shows the concentration of each component PS, SiO$_2$ and siloxane.

| PS(wt%) | SiO$_2$(wt%) | Mercaptopropyltrimethoxy silane (wt%) |
|--------|--------------|--------------------------------------|
| 60.0   | 14.3         | 30.5                                 |
| 50.0   | 22.9         | 27.0                                 |
| 45.0   | 26.4         | 27.4                                 |
| 40.0   | 30.4         | 26.0                                 |
| 35.0   | 35.2         | 24.9                                 |
| 30.0   | 37.9         | 22.5                                 |

Disperse hydrophobic nano-silica (DNS-2) particles and 0.4 g of polyvinyl chloride in 12 mL of tetrahydrofuran solution ultrasonically, and add 0.25 g of mercaptopropyltrimethoxysilane. Continue to stir for 1h. Use a spin coater (2000 rpm, 30 s) to coat the mixed solution on a glass substrate and dry it at room temperature for 2 min. Table 2 shows the concentration of each component PVC, SiO$_2$ and siloxane.

| PVC(wt%) | SiO$_2$(wt%) | Mercaptopropyltrimethoxy silane (wt%) |
|---------|--------------|--------------------------------------|
| 60.0    | 143          | 30.5                                 |
| 50.0    | 22.9         | 27.0                                 |
| 45.0    | 26.4         | 27.4                                 |
| 40.0    | 30.4         | 26.0                                 |
| 35.0    | 35.2         | 24.9                                 |
| 30.0    | 37.9         | 22.5                                 |

3.2. Analysis of coating surface morphology and wettability

Figure 2 shows that there are many irregular cluster-like structures scattered on the surface of the composite coating. These clusters form the roughness of the micro-structure, which happens to form a micro-nano layered structure with the nanoparticles on the clusters. It is this rough structure that makes the coating obtain super-hydrophobic properties. We investigated the influence of different proportions
of nano-silica on the wettability of the coating, as shown in Figure 2. It can be seen from the figure that the content of silica has a significant effect on the wettability of the coating. For the SiO2/PS composite coating, when the concentration of silica increases from 18.7 wt% to 27.8 wt%, the corresponding contact angle increases from 112° to 152°. The SiO2/PVC composite coating also has a similar rule. The concentration of silicon dioxide is 31.6 wt%, and the contact angle reaches 162°. It is well known that surface roughness and chemical composition are the decisive factors for the wettability of a solid surface. Theoretically, the contact angle \( \theta \) of a rough surface is the contact angle of a smooth surface. The relationship between \( \theta \) can be described by the Cassie-Baxter equation (1):

\[
\sin \theta = a_1 \sin \theta - a_2
\]

where \( a_1 \) and \( a_2 \) are the contact area coefficients of liquid and solid surface and air respectively. When the gate is larger, the macro contact angle is larger. In other words, a larger air contact area will help improve the superhydrophobicity of the coating surface. The surface of the three-phase contact line (gas-liquid-solid) is curved and discontinuous. It can trap air to prevent moisture from entering the solid space, resulting in a larger contact angle. The addition of hydrophobic nano-silica particles increases the surface roughness while reducing the surface energy of the coating, so we obtain a super-hydrophobic surface.

![Figure 2. Different content of SiO2 influence on coating contact angle](image)

3.3. Analysis of the corrosion resistance of the coating

The study found that the SiO2/PS and SiO2/PVC nanocomposite coatings prepared by us not only have superhydrophobicity to distilled water, but also have superhydrophobic properties under the acidic and alkaline conditions of corrosive liquids. In the pH range of 1-14, the contact angle of the coating is maintained at 150°. The fact that superhydrophobic coatings can still exist stably under corrosive conditions will be of great significance in practical applications. Taking the SiO2/PS composite coating as an example, it can be clearly seen in Figure 3 that under the continuous contact of the pH=1 droplets, the composite coating changes from the initial 163° in 0-20 min. It is gradually reduced to 152°, but still maintains superhydrophobicity, which indicates the strong acid corrosion resistance of the composite coating. Similarly, the coating has a similar situation under strong alkaline droplets. It can be seen from Figure 3 that when the alkaline droplets (pH=14) are on the coating surface within 0-20 min, the coating remains. When the corrosion time reaches 20 min, the contact angle is reduced to 149°. Although the superhydrophobicity is lost, it is still in a hydrophobic state. The corrosion resistance of the SiO2/polymer composite coating will have a good application prospect in actual production, especially in engineering applications.
Basic solution  
(pH 14)

Acidic solution  
(pH1)

10 min
0 min
20 min

0 min
20 min
10 min

Figure 3. Contact angle of the SiO2/PS composite coating changes with time

4. Conclusion
In this paper, we use a simple spin coating method to prepare silica/polystyrene and silica/polyvinyl chloride superhydrophobic coatings. Since the phase separation between silica and polystyrene is easy to occur, the silica is easy to precipitate from the polystyrene during the volatilization of the solvent. Therefore, we use a silane coupling agent to improve and enhance the compatibility between silica and polymer, and prepare a stable superhydrophobic coating resistant to acid and alkali. The SiO2/polymer super-hydrophobic composite coating was successfully prepared by the spin coating method. This method is simple and time-saving, and does not require special equipment and harsh conditions. The addition of hydrophobic nano-silica not only improves the surface roughness but also reduces the surface energy of the coating, without the need to use low surface energy substances for modification. In addition, the coating exhibits excellent corrosion resistance in a wide pH range and is expected to be used as an anti-corrosion coating for metal protection.

References
[1] Zha J , Batisse N, Claves D , et al. A universal fluorous technology toward superhydrophobic coatings[J]. Journal of Colloid and Interface Science, 2019, 55(3):778-787.
[2] Yousefi S Z , Tabatabaei-Panah P S , Seyfi J . Emphasizing the role of surface chemistry on hydrophobicity and cell adhesion behavior of polydimethylsiloxane/TiO2 nanocomposite films[J]. Colloids & Surfaces B Biointerfaces, 2018, 16(7):492-493.
[3] Shaowei Q, Dan W , Jie-Xin W, et al. Polyhedral oligomeric silsesquioxane-coated nanodiamonds for multifunctional applications[J]. Journal of Materials Science, 2018, 5(3):15915-15926.
[4] Park M S , Lim T H , Jeon Y M , et al. Preparation of New Polyelectrolyte/ Silver Nanocomposites and Their Humidity-Sensitive Properties[J]. Macromolecular Research, 2018, 16(4):308-313.
[5] Nguyen Q T , Baird D G . Preparation of polymer - clay nanocomposites and their properties[J]. 2016, 25(4):270-285.
[6] Zhang H , Gu D , Ma C , et al. Surface wettability and superhydrophobic characteristics of Ni-based nanocomposites fabricated by selective laser melting[J]. Applied Surface Science, 2019, 476(5):151-160.
[7] Selim M S , El-Safty S A , Shenashen M A , et al. Progress in biomimetic leverages for marine ant fouling by nanocomposite coatings[J]. Journal of Materials Chemistry B, 2020, 8(15).
[8] Hu D , Ma W , Zhang Z , et al. Dual Bio-Inspired Design of Highly Thermally Conductive and Superhydrophobic Nanocellulose Composite Films[J]. ACS Applied Materials & Interfaces, 2020, 12(9):11115-11125.
[9] Raghav G R , Balaji A N , Muthukrishnan D , et al. Preparation of Co-Gr Nanocomposites and Analysis of Their Tribological and Corrosion Characteristics[J]. Metallofizika i noveishie tehnologii, 2018, 40(7):979-992.
[10] Ali M N, Goud S C, Roy A S. A facile and large-area fabrication method of superhydrophobic self-cleaning polysiloxane/TiO2 nanocomposite films and its dielectric properties [J]. Journal
[11] Akhavan M, Hejazi I, Seyfi J, et al. investigating the effect of surface composition and morphology on oil/water separation efficiency of sponges coated with polymer nanocomposites. Polymer Composites, 2019, 40(1), 3-4.

[12] Beshkar F, Salavati-Niasari M, Amiri O. Superhydrophobic – superoleophilic copper – graphite/styrene – butadiene – styrene based cotton filter for efficient separation of oil derivatives from aqueous mixtures. Cellulose, 2020, 27(6), 1-4.

[13] Fan C, Luo Y. Polyethylene film waste-derived porous nanocomposites with superior mechanical robustness and excellent UV resistance as supported substrates for the development of multifunctional materials. Journal of Materials ence, 2020, 55(24), 10942-10952.