Application of copolymerization in preparation of superhydrophobic surfaces

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Abstract. Superhydrophobicity refers to a wetting phenomenon in which the contact angle with water is greater than 150° and the sliding angle is less than 10°. Superhydrophobic surfaces have been extensively studied due to its self-cleaning, corrosion resistance, anti-icing, oil-water separation and other characteristics. Among the studies, copolymerization is one of the important methods in the preparation of superhydrophobic surfaces. In this paper, the mechanism of superhydrophobicity and the models are introduced. Then, in view of the three ways to obtain superhydrophobic surfaces through copolymerization - modification, directly synthesis of superhydrophobic Copolymer, preparation of superhydrophobic coatings or coatings - the methods are summarized, and the related applications are briefly described. Finally, possible future researching directions are summarized and prospected to provide reference for the application of copolymerization in preparation of superhydrophobic surfaces.

1. Introduction

Wettability is an important characteristic which is commonly described with hydrophobic and hydrophilic surface [1]. The hydrophobicity is often measured by the numerical values of the contact angle (CA) and sliding angle (SA) between the surface and water. Superhydrophobicity is a special surface wetting phenomenon whose contact angle is greater than 150° and sliding angle is less than 10° with water [2, 3]. This kind of surface is considered to have a wide application prospect due to its self-cleaning, corrosion resistance, anti-icing, oil-water separation [3-5] and other characteristics. The construction of superhydrophobic surfaces often requires two conditions: first, to reduce the free energy of the material surfaces; second, to construct a rough microstructure on the material surfaces [1, 6, 7]. The following summarizes the wettability models of superhydrophobicity surfaces and introduces the development of superhydrophobic theories.

1.1. Young’s equation - ideal surface

The Young's equation is mainly applicable to the calculation of the contact angle of water droplets dripping on an ideal homogeneous smooth surface [8], in which the contact angle is expressed by $\theta_y$:

$$\cos \theta_y = \frac{y_{st} - y_{stl}}{y_{stl}}$$

in (1), $y_{st}$, $y_{stl}$, $y_{stl}$ are the interfacial tensions of solid-gas, solid-liquid, and liquid-gas interfaces, respectively. It can be found that he surface is hydrophilic when the contact angle is less than 90°, and hydrophobic when the contact angle is greater than 90°.
1.2. Wenzel model and Cassie-Baxter model - rough surface

For real material surfaces, roughness is inevitable. Therefore, it is necessary to introduce the concept of sliding angle, or contact angle lag \[5, 9\].

The sliding angle refers to the tilt angle of the droplet when it happens to roll on an inclined solid surface, which is numerically equal to the difference between the forward angle \( \theta_f \) and the retreat angle \( \theta_r \). The forward angle refers to the contact angle at the moment when the solid-liquid contact area is about to increase, while the retreat angle refers to that at the moment when it is about to decrease \[6\]. The smaller the sliding angle, the smaller the viscous force of the droplet to the surface, and otherwise, the easier it is to adhere to the surface.

Wenzel model proposed that:

\[
\cos \theta_w = r \cdot \cos \theta_y \tag{2}
\]

In (2), \( \theta_w \) refers to the apparent contact angle, \( \theta_y \) refers to the intrinsic contact angle of the ideal smooth surface, and \( r \) refers to the surface roughness. When the surface roughness increases, the hydrophobicity of a hydrophobic surface or the hydrophilicity of a hydrophilic surface also increases. Because the Wenzel model is only suitable for the case of complete infiltration of droplets on the surface.

The Cassie-Baxter model considers the presence of air when the droplet contacts the solid surface \[10\], and proposed based on the Wenzel model that:

\[
\cos \theta_c = f \cdot \cos \theta_y + f - 1 \tag{3}
\]

In (3), \( \theta_c \) is the apparent contact angle, \( \theta_y \) is the intrinsic contact angle of the surface, \( f \) is the percentage of the solid-liquid interface area to the total area \[11\]. Therefore, reducing the solid-liquid interface area (increasing the solid-gas interface area) will increase the surface hydrophobicity.

The illustration of the three models is shown in Figure 1.

![Figure 1](image.png)

2. Preparation of superhydrophobic surfaces by copolymerization

Copolymerization refers to the polymerization of two or more compounds into a substance under certain conditions. Generally, there are three situations in which a superhydrophobic surface is obtained by copolymerization - modification, directly synthesis of superhydrophobic Copolymer, and preparation of superhydrophobic coatings or coatings.
2.1. Surface modification
There are about two methods for superhydrophobic modification of surfaces. One is to copolymerize the materials with low surface free energy on the rough surfaces, the other is to construct rough micro-nanostructures on the surfaces of hydrophobic materials. In modification, it is often achieved by free radical graft copolymerization on the surfaces.

Table.1 Surface modification

| Name                    | Method                  | Raw Materials                                                                 | Result                                      |
|-------------------------|-------------------------|-------------------------------------------------------------------------------|---------------------------------------------|
| Zhao Li et al. [12]     | copolymerization        | α-methylstyrene (AMS), butyl methacrylate (BMA), multi-walled carbon nanotubes (MWCNT) | AMS-co-BMA (PAB) contact angle = 165°     |
|                         |                         |                                                                               | sliding angle < 3°                          |
| Wang Meishu et al. [13] | copolymerization        | polydimethylsiloxane (VPDMS), Octavinyl-T8-silsesquioxane (VPOSS), Polysiloxane, cotton fiber | contact angle = 164°                      |
|                         |                         |                                                                               | microstructure observed by SEM            |
| Taijun He et al. [14]   | micro-nanostructure     | trifluoro ethyl methacrylate, divinylbenzene, PET saturated polyester fabric | Stable superhydrophobic property           |
|                         |                         |                                                                               | contact angle = 161°                      |
|                         |                         |                                                                               | sliding angle = 8°                         |
| Wang Qingjun et al. [15]| radiation-induced       | hexafluoro propene / ethyl methacrylate (HFP/EMA)                           | contact angle = 153°                      |
|                         | copolymerization        |                                                                               |                                             |

2.2. Copolymer synthesis
In addition to modification, superhydrophobic surfaces can also be obtained by direct preparation of superhydrophobic copolymers, in which the emulsion and solution polymerization method are often used, getting required superhydrophobic copolymers through repeated washing, filtration and precipitation. Among the studies, the preparation of fluorinated acrylate copolymers is the most common.

Table.2 Copolymer synthesis

| Name                  | Method                | Raw Materials                                                                 | Result                                      |
|-----------------------|-----------------------|-------------------------------------------------------------------------------|---------------------------------------------|
| Wei Haiyang et al. [16]| microemulsion        | perfluoroalkyl ethyl acrylate, methyl methacrylate                            | contact angle = 151°-160°                   |
|                       | polymerization        |                                                                               |                                             |
| Gao Chen et al. [17]  | microemulsion         | methyl methacrylate (MMA), butyl acrylate (BA), 7.6% fluorinated acrylate     | contact angle = 158°                       |
|                       | polymerization        |                                                                               |                                             |
| Xianqian Shang et al. [20]| microemulsion     | Vinyl functional SiO2 particles (Vinyl−SiO2), styrene (St), And tridecafluoroctyl methacrylate (FOMA) | contact angle = 171° (highest in the current studies) |
|                       | polymerization        |                                                                               |                                             |
| Xiaoyan Li et al. [18]| solution polymerization| methacrylic acid, methyl methacrylate, perfluoroalkyl ethyl methacrylate     | contact angle = 157°                       |
|                       | polymerization        |                                                                               |                                             |
| Wang Jing [19]        | solution polymerization| 2-acrylamide-2-methylpropanesulfonic acid (AMPS) with sulfonic group, fluorine-containing monomer hexafluoro butyl acrylate (F6BA), functional monomer γ-glycidyl methacrylate (GMA) with epoxy group/ long-chain alkyl monomer octadecyl acrylate (SA), Polyaniline (PANI) | contact angle = 163.4°                     |
|                       | polymerization        |                                                                               |                                             |

2.3. Preparation of superhydrophobic coatings and paints
The preparation of superhydrophobic coatings and paints reduces the cost of superhydrophobic properties, which works simply by attaching the coating to the surfaces of the material that has the need for waterproofing. AhmedMeskini et al. [21] had obtained cyanide containing fluorovinyl ether by free radical homopolymerization, realizing the preparation of superhydrophobic coatings.
Table 3: Preparation of superhydrophobic coatings and paints

| Name                  | Method                        | Raw Materials                                                                 | Result                                                                 |
|-----------------------|-------------------------------|-------------------------------------------------------------------------------|------------------------------------------------------------------------|
| Ozbay et al. [22]     | fluorinated organics          | hydrophilic and hydrophobic fumed silica powder, perfluoroalkyl ethyl acrylate | contact angle = 162°                                                  |
|                       |                               | (Zonyl TA-N), styrene-butadiene rubber (SBR)                                  |                                                                        |
| Yanan Xing et al. [23]| fluorinated organics          | perfluoroalkyl ethyl acrylate, 3-(trimethoxy methyl silyl) propyl methacrylate | contact angle = 152°                                                  |
|                       |                               |, cotton fabric                                                                |                                                                        |
| Lifen Hao et al. [24] | fluorinated organics          | nano-SiO2 comb-like fluorosilicone copolymer (FPFAS-SiO2)                     | contact angle = 163.5°, sliding angle = 7°, micro-nano composite structure |
| Benfeng Zhu et al. [25]| surface microstructure       | acrylate monomer, vinyl trimethoxysilane (VTMS), silanized polyacrylate (PSA),| contact angle = 155.7°, sliding angle = 4°                            |
|                       |                               | hydroxyl-terminated polydimethylsiloxane (HTPDM), silanized polyacrylate (CPA) |                                                                        |
| Zhang Jing et al. [26] | superhydrophobic coating      | epoxy resin (EP), hydroxyl-terminated polymethylphenylsiloxane (HT-PMPS), SiO2| contact angle = 154°, sliding angle = 5° (After soaking for 15 h, contact angle = 151°; after soaking for 50 h, contact angle = 132°) |
|                       | copolymerization              | particles, MWCNTs                                                             |                                                                        |
| Zhengguang Sun et al. [27] | superhydrophobic coatings   | fumed silica, phenyltrimethoxysilane (PhTMS)-(2,3-propylene oxide) propyltrimethoxysilane (EPTMS) | contact angle = 156.1°, sliding angle = 3°                             |
| Yifan Si et al. [28]  | mussel adhesion               | trimethylsilyl group                                                           | an environmentally-friendly superhydrophobic coating                   |

3. Preparation of superhydrophobic surfaces by copolymerization and its application

The application of superhydrophobic surfaces prepared by copolymerization mainly depends on its characteristics of waterproofing and oil-water separation. Due to limitations, the applications in corrosion resistance and anti-icing are relatively rare [4].

| Name                  | Method                        | Raw Materials                                                                 | Result                                                                 |
|-----------------------|-------------------------------|-------------------------------------------------------------------------------|------------------------------------------------------------------------|
| Hongyan Zhai et al. [29] | free radical copolymerization | methyl acrylate, hydroxyethyl methacrylate, dodecyl heptyl methacrylate,      | excellent waterproof performance, light weight and good transparency  |
|                       |                               | vinyl trimethoxysilane, benzoyl peroxide                                       |                                                                        |
| Shouying Huang [30]   | one-step copolymerization of mussel adhesion | polyurethane                                                                  | superhydrophobicity and oil absorption                            |
| Qian Wei et al. [31]  | in-situ polymerization        | graphene (GE), FMS sponge                                                     | superhydrophobicity and superlipophilicity, contact angle = 158.9°    |
| Iman Noshadi et al. [32] | copolymerization              | divinylbenzene (DVB), sodium p-styrene sulfonate                              | mesoporous polymer solid acid catalyst (p-PDVB-SO3H) which showed superhydrophobicity and lipophilicity to triolein and methanol |
| Qi Sun et al. [33]    | copolymerization              | Nmurp-styrene sulfonyl-1-diphenyl ethylenediamine (V-TsDPEN), divinylbenzene | highly efficient trimethylbenzene (TsDPEN-Ru)                          |

4. Summary and prospect of preparing superhydrophobic surfaces by copolymerization

The preparation process of superhydrophobic surfaces by copolymerization is relatively mature. In addition to the improvement of hydrophobicity, it also involves the stability and tolerance of superhydrophobic surfaces, the applicability of modification methods and even the environmental protection. In addition, in terms of the hydrophobic forms, asymmetric and switchable superhydrophobic surfaces also have great research significance.
4.1. Development of asymmetric superhydrophobic surfaces

In the process of material development, asymmetric surfaces have significant research value due to broadening the scope of materials’ application. Its preparation mainly depends on polymer coating, interfacial condensation, plasma polymerization, dynamic formation or surface modification to make an extremely thin layer attached to different supporting layers. The methods of obtaining superhydrophobic surfaces by polymer coating has been introduced detailedly in the “2.3. preparation of superhydrophobic coatings and paints”, but the researches on other methods to develop asymmetric surfaces are relatively lacking.

Table 5 Asymmetric superhydrophobic surfaces

| Name                  | Method               | Raw Materials                                                                 | Result                        |
|-----------------------|----------------------|-------------------------------------------------------------------------------|-------------------------------|
| Guanghui Xi et al.    | copolymerization     | methacrylic acid 2, 2, trifluoroethyl ester, 2-trifluoroethyl methacrylate(TFMA), 2-isocyanate ethyl ester (IEM), divinylbenzene (DVB), cotton fabric | Superhydrophobicity contact angle = 151° |
| Yuan Gao et al.        | Graft copolymerization | water-soluble polyvinyl alcohol (PVA), perfluoro-2-dimethyl-3-dimethyl-3-dioxononoyl fluoride | PVA asymmetric membrane contact angle = 126° |

4.2. Development of switchable superhydrophobic surfaces

The switchable superhydrophobic surfaces makes the hydrophobicity of the material surfaces reversible under certain conditions. This kind of surfaces broadens the application range of superhydrophobic surfaces and superhydrophobic materials due to its higher flexibility.

Table 6 Switchable superhydrophobic surfaces

| Name                                      | Method               | Raw Materials                                                                 | Result                                    |
|-------------------------------------------|----------------------|-------------------------------------------------------------------------------|-------------------------------------------|
| Thierry Darmanin et al.                   | copolymerization     | EDOT monomer containing carboxyl group (EDOT-COOH), EDOT monomer containing dodecyl chain (EDOT-O-H12) | reversible superhydrophobic surface       |
| Gabriela Ramos Chagas et al.             | pH treatment         | carboxyl groups, Py-COOH, Py-nF6                                             | reversible superhydrophobicity           |
| Sabri Taleb et al.                       | electrochemical      | 3,4-ethylenedioxyppyrole (EDOP) derivatives, fluorinated chains, pyridinium groups | reversible hydrophobic surface           |
| Haiguang Zhu et al.                      | Free radical         | melamine-formaldehyde, methacrylate monomer                                  | SP-MF sponge contact angle = 155.5°       |

In summary, there is a large research space for process and technical means in the developing for asymmetric superhydrophobicity. Finding suitable materials and developing asymmetric superhydrophobic surfaces are elements in current researches. For switchable superhydrophobic surfaces, the hydrophobicity of the current surfaces varies due to the differences in acid-base, voltage, radiation etc. Reducing the switching threshold of hydrophobicity is an issue requiring in-depth studies.

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