Multifunctional superhydrophobic composite materials with remarkable mechanochemical robustness, stain repellency, oil-water separation and sound-absorption properties

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ABSTRACT

Superhydrophobic materials have attracted immense commercial and academic interests in recent years. However, the poor mechanical durability has restricted their practical applications where high durability is required. Here, a facile one-pot synthesis method was reported to fabricate multifunctional superhydrophobic composite materials with remarkable mechanochemical robustness, stain repellency, oil-water separation and sound-absorption. Their mechanical and chemical durability could be greatly improved by chemically adhering epoxy resin microspheres (ERMs) on 3-D porous skeleton structures of latex sponge. The materials could retain superhydrophobicity after going through sandpaper abrasion, ultrasonication, multiple knife scratch, tape peeling and finger wiping, and exposure to UV irradiation and high temperature. The materials are able to maintain the repellency against strong acid and alkali droplets. The combined excellent mechanical properties, liquid repellency & selectivity, and other functional properties displayed by this type of material have made it a strong candidate for a range of industrial applications.

Keywords: superhydrophobic composite materials; mechanochemical robustness; multifunction; recoverable; sound-absorption

1. Introduction

Superhydrophobic materials, with contact angle larger than 150° and sliding angle smaller than 10° [1-3], have attracted tremendous attention in recent years owing to their excellent properties of self-cleaning [4-6], anti-fogging [7], oil-water separation[8-10], anti-corrosion [11] and delayed frosting [12]. Surface roughness and surface hydrophobicity are the two prerequisites to form an ultra-hydrophobic surface [13]. Hierarchical structures accompanied by low surface energy materials could render surfaces with large static contact angles ($>150^\circ$) with water droplets [14, 15]. Various methods have been used to fabricate superhydrophobic surface, such as chemical vapor deposition, electrospinning, layer-by-layer assembly, etching, lithography, and so on [16-18]. However, their poor mechanical durability, a critical factor affecting the lifespan, has restricted large-scale applications of these superhydrophobic surfaces. The micro/nano-scale surface structures were inherently fragile and could be easily damaged in practical applications (such as physical scratch and sunlight radiation), which would result in the loss of superhydrophobicity. Thus, improving the mechanical robustness of the superhydrophobic coatings had been a focus in the past research.

To date, some strategies have been put forward to expand the lifespan of superhydrophobic surfaces. One strategy was to endow the surface with self-healing ability. The lost superhydrophobicity could be healed by external stimulus, including heating [19, 20], organic solvents [21], humidity [22] and mechanical forces [23]. However, the use of hydrophobic agents, such as poly- or perfluoroalkyl and

long-chain fatty amines, was either expensive or harmful to the environment and health. In addition, the healing ability relied on the content and nature of self-healing agent. Another strategy was to bond functionalized hydrophobic nanoparticles to the applied object, such as the commercial superhydrophobic coatings “NeverWet” spray. However, the mechanical durability of these coatings were limited by the strength of the bonding between the substrate and the coatings [24, 25].

Making a bulk material with superhydrophobicity throughout the whole volume allows it to retain its properties even after any mechanical damage. For example, after the top layer is damaged or removed upon scraping, the newly exposed surface possessing the same low-energy rough structures will be able to maintain the superhydrophobicity [26]. The common method to fabricate a bulk superhydrophobic material was to add hydrophobic nanoparticles into the bulk materials under a high pressure at room temperature or at high temperatures [27-29]. For example, Zhang [28] mixed TiO_2 nanorods and SiO_2 nanoparticles in a polypropylene (PP) solution to prepare $\text{TiO}_2/\text{SiO}_2/\text{PP}$ composite powders. A bulk superhydrophobic material was obtained by pressing these powders into a mold under a pressure of 25 MPa at room temperature. Zhu [29] created a CNT-PTFE bulk material by pressing the mixture of CNTs and PTFE in a mold under a pressure of 256 kPa at 390 °C. The use of high pressure and/or high temperature would increase construction difficulty and limit the practical applications. In addition, simple physical mixing of these hydrophobic particles would reduce mechanical strength of the bulk materials, resulting in a compromise in mechanical durability.

Here, a simple and effective solution immersion method was presented to build multifunctional superhydrophobic epoxy composites with excellent wear-resistance, mechanical strength, stain repellency, oil-water separation and sound-absorption properties. Epoxy resin microspheres (ERMs) formed in this reaction system could chemically adhere to latex porous skeleton. This superhydrophobic material was denoted as ERM@Latex. ERM@Latex could be made into free-standing bulk or sheet form, or could be further anchored onto different substrates without using adhesives. These surfaces could maintain superhydrophobicity even after sandpaper abrasion for 3000 cm, ultrasonication for 60 min, multiple knife scratch, tape peeling and finger wiping, UV-irradiation for 300 h, heating at 300 °C, and soaking in acidic/alkali solutions. Excellent mechanochemical robustness and multifunctionality have enabled the ERM@Latex materials to possess the versatility for a number of practical applications.

2. Materials and methods

2.1. Materials

Tetraethoxysilane (TEOS) (AR, 98%) was purchased from Guangzhou Chemical Reagent Factory. Hexamethyldisilazane (HMDS) (AR, 98%) was purchased from Meryer. Ethanol (AR, $\geq 99.7\%$) were purchased from Sinoparm Chemical Reagents Co., Ltd. Bisphenol A epoxy resin (E-44) and low molecule polyamide curing agent (650) were purchased from Yueyang petrochemical plant, China. Latex sponges (Dunlop latex) were provided by Wenzhou Xinshili Latex Factory. Trypan blue, methyl orange and phenolphthalein were purchased from Aladdin. Oil Red O was

purchased from Adamas. Distilled water was prepared by a water purification system (UPH-II-20T). Qualitative filter paper was purchased from Hangzhou specialty paper Co., Ltd. Polyurethane sponge was provided by Jiangsu Huayi foam technology Co., Ltd. Cotton textile were bought from a local supermarket.

2.2. Preparation of silica sol

Hydrophobic silica sol was prepared first [30]. TEOS (2.1 mL) was dripped into ethanol (30 mL). After being vigorously stirred for 10 min, HMDS (2.0 mL) was slowly added to the above mixture and stirred for 0.5 h. Then deionized water (3.0 mL) was dropped into the mixture with the same stirring rate at room temperature. The reaction of the mixture was carried out with stirring for 2 h to form a transparent sol. The aging of silica sol for three days was needed before it was used.

2.3. Preparation of superhydrophobic composite materials on different substrates

The simple one-pot fabrication route of superhydrophobic latex composite materials (ERMs@Latex) was illustrated in Fig. 1. Epoxy resin (1.25 g) and polyamide (0.46 g) were dissolved in silica sol (20 ml) with magnetic stirring until a homogeneous epoxy mixture was formed. The mixture was heated and kept at different temperatures (15, 25, 35, 45, 60 °C). Then a piece of latex spoon was immersed in the mixture. The curing reaction of epoxy and amine was carried out in the system at the different temperatures with stirring. Epoxy resin microspheres appeared, adhered, grown and cured on the latex skeletons. After 24 h, the wet latex was taken out and washed with ethanol. Finally, the latex was dried in air for 24 h. The obtained materials were

named as ERM@Latex-T, where T was the reaction temperature (15, 25, 35, 45, 60 °C).

In the drying process, if the samples had been flipped for several times, the obtained superhydrophobic materials were free-standing with no adhesiveness to base surfaces. If the wet latex has not been flipped in the drying process, the material could adhere on the base surface with strong bonding strength. If the wet latex was compressed first and then dried, a sheet-like superhydrophobic material would be obtained. The thickness of these sheet-like materials could be adjusted by changing the compressing pressure. The sheet-like materials could be either free-standing or anchored firmly on any substrate surfaces.

The latex sponge was not the only matrix to prepare superhydrophobic composite materials. The fabrication of polyurethane sponge composite materials (named as ERM@PU), textile composite materials (named as ERM@Textile) and filter paper composite materials (named as ERM@Paper) under the reaction temperature of 45 °C were also performed using the same method as for the ERM@Latex.

To better illustrate the comprehensive performance of superhydrophobic composite materials, a control group was prepared. Epoxy mixtures containing epoxy resin, curing agent and silica sol were reacted for 24 h under different temperatures (15, 25, 35, 45, 60 °C). Then the epoxy mixtures were coated on smooth glass surfaces which were called control groups (ERM@Glass).

2.4. Characterization

The morphology of latex porous structures and other matrix materials before and

after ERMs adhering was observed by scanning electron microscope (SEM, SU8010, HITACHI, Japan). Fourier transform infrared spectrometry (FTIR, Tensor II, Germany) was performed to measure the components of the reaction system. The wettability was measured by a contact angle system (Theta, Sweden) at ambient temperature with a 6 μ l droplet. The slide angles were measured by tilting the samples with a static droplet of 10 μ l. When the water drop started to roll from the surface, the tile angle was recorded as the sliding angle. Compression tests were performed on a texture analyzer (TMS PRO ILC-S 1000N) equipped with a 1000 N load cell and a loading speed of 30 mm/min at room temperature. Compressive strength could be calculated from the obtained stress-strain curves. The thermal conductivity was measured by a Hot Disk Thermal Constants Analyzer (TPS 2500s) with a measurement time of 40 s. Sound-absorption test was carried out in a SW477 impedance tube (Beijing China prestige Sound Technology Co. Ltd., China).

The mechanical robustness was evaluated by sandpaper abrasion, ultrasonication, tape peeling, knife scratch and finger wiping. The chemical stability of ERMs@Latex-T was evaluated by UV-irradiation, heating under high temperature, and droplet test with strong acid (pH=1) and alkali (pH=14) solutions. The details of experimental methods were listed in supporting information.

Experimental data of ERMs@Latex-60 were reported here unless otherwise noted. Other samples prepared under different temperature were also characterized and listed in supporting information.

3. Results and discussion

3.1. Characterization of superhydrophobic latex composite materials

The one-pot fabrication route includes three key components for different purposes. The first was epoxy resin (E44) and its curing agent, which were used as adhesive agents and were the source of surface roughness (producing ERMs). The second was the hydrophobic silica sol acting as a dispersing agent, which helps to form the ERMs with good dispersibility. The speculated formation pathway of silica particles and ERMs are shown in Fig. 1a and Fig. 1b, respectively. The detailed reaction equations for silica [31] and the curing reaction of epoxy resin [32] are shown in Fig. S1a and Fig. S1b, respectively. The formation mechanism of ERMs in the epoxy resin system had has been explained previously [30]. At the early stage, microgels with dimensions of 10-50 nm were generated and they grew up to secondary gels (200-500 nm) (Fig. 1b). The silica sol dispersant cut the contact between gels. These gels grew up as stand-alone units as the curing process continues. Thus, the dispersive ERMs were generated. The third key component was latex sponge used as a carrier for the ERMs, which could enhance the mechanical strength of superhydrophobic materials. The one-pot fabrication route of superhydrophobic latex composite materials (ERMs@Latex-T) was shown in Fig. 1c. The morphology of latex porous structures before (Fig. 1d) and after (Fig. 1e) the ERMs adhering was observed using SEM.

Fig. 1. (a) Speculated formation pathway of silica. (b) Speculated formation pathway of ERM. (c) Schematic illustration of the one-pot synthesis procedure of ERM@Latex-T. SEM images of latex porous structures before (d) and after (e) ERM adhering. (f) The high magnification image of (e). The reaction temperature of the sample was 25 °C.

The effect of reaction temperature on the morphology and size of ERM was investigated. ERM with dimension larger than 5 μm were formed in the system at low temperature (15 or 25 °C, see Fig. S2a and Fig. S2b). With increase in temperature, the size of ERM was reduced. When the temperature was higher than 35 °C, the dimension of ERM was smaller than 5 μm (Fig. S2c and Fig. S2d). ERM

with the size smaller than 2 μm (marked by white cycle in Fig. S2f) were observed when the reaction temperature was 60 $^{\circ}\text{C}$. The smaller size of ERMs under higher temperature was due to the better solubility of epoxy resin and smaller the size of gel formed in the reaction system with increasing reaction temperature. Thus, the sizes of cured ERMs were also decreased. The temperature also influenced the extent of reaction of the epoxy resin. The curing of epoxy resin was related to the ring-opening reaction of glycidyl of epoxide by amine (Fig. S1b). No infrared characteristic peak of glycidyl of epoxide around 912 cm^{-1} was observed when the temperature was higher than 35 $^{\circ}\text{C}$ (Fig. S3). This implies that the curing reaction of epoxy resin was complete at this temperature or higher.

The EDX mapping of pristine latex skeletons and ERMs@Latex-T skeletons prepared under different reaction temperatures were shown in Fig. S4. It could be found that mainly C and O were found on pristine latex skeletons. While on ERMs@Latex-T skeletons, elemental C, N, O and Si distributed homogeneously across skeleton surfaces. The presence of N element was ascribed to ERMs, and Si was derived from the silica sol. These results confirmed the formation of ERMs and silica, and their adhesion on latex skeleton surfaces.

The ERMs@Latex-T samples were superhydrophobic after being manually abraded for 2 or 3 times using sandpaper (1000 Cw). No fluorinated polymers were used in the whole process, which decreased the manufacturing cost and could be considered safe to human health. The mechanism of superhydrophobicity was due to the hydrophobic ERMs and hydrophobic silica sol adhering on latex skeletons, which not only

roughened the skeleton surfaces but also decreased the surface energy. Plenty of $-\text{Si}(\text{CH}_3)_3$ groups are grafted on silica surfaces, resulting in the hydrophobicity of silica sol (Fig. 1a). The hydrophobicity of ERMs has been proved in our previous work [30]. Polyamide curing agent was made by reacting a dimer fatty acid with excess low molecular weight of aliphatic amines. The dimer fatty acid was a strong hydrophobic chain segment, which could improve the water resistance of epoxy resin. Thus, the hydrophobicity of curing products (ERMs) could attribute to the long methylene chain (hydrophobic chain segment) from polyamide. Thus, the rough structures (due to the adhesion of ERMs and silica) and their low surface energy properties worked together to render the composite materials superhydrophobic. The contact angles of all these ERMs@Latex-T samples were larger than 150° and their sliding angles were less than 10° , showing superhydrophobicity (Fig. 2a). It was worth mentioning that the preparation methods of latex composite materials in this study was versatile, and could be adopted for different types of superhydrophobic materials meeting different demands for practical applications. For example, samples could be made into standing-alone bulk materials (Fig. 2b). Alternatively, the wet latex could be bonded onto a substrate with the help of the adhesive nature of epoxy resin. The bonding process occurred spontaneously in the drying process of wet latex due to some residual active groups of epoxy resin (Fig. 2c). The low stiffness of the wet latex allows it to be compressed and then dried into a plate or sheet-like superhydrophobic material (Fig. 2d).

The robust bonding strength of the sample to a substrate was due to the bonding of

multiple hollow pillars formed by latex skeleton on the substrate surface. The discontinuous crack propagation in the debonding process gives rise to a higher adhesion compared to a uniform material [33].

Fig. 2. (a) The contact angles and sliding angles of ERM@Latex-T samples. (b) Standing-alone superhydrophobic bulk material. (c) Superhydrophobic material adhered onto a substrate. (d) A sheet-like superhydrophobic material. (e) Optical images of the compression performance for the latex sponge. (f) Optical images of the compression performance for ERM@Latex-60. (g) The compressive stress-strain curve of ERM@Latex-60. The scale bars in (b-f) are 10 mm.

The compressive strength of materials was crucial for many applications. The initial latex sponge was soft and could be compressed easily (shown in Fig. 2e). However, after adhering ERMs and curing of the epoxy resin on the sponge skeletons, the obtained composite materials were much harder and stiffer. Fig. 2f showed that no appreciable deformation for ERM@Latex-60 under a load of 500 g. The compressive stress-strain curve of ERM@Latex-60 was shown in Fig. 2g. At the beginning, the

stress-strain curve was relatively steep, which meant that a smaller amount of deformation with the incremental stress occurred [9]. After the elastic linear stage, the compressive strength of ERM@Latex-60 was around 1.22 MPa. The mechanical strengths of other four samples (0.78, 1.08, 0.53, 0.66 MPa) were also measured by the compression test and displayed in Fig. S5. The different yield strength was related to the extent of reaction in the epoxy resin, which was explained in supporting information.

3.2. The mechanical and chemical robustness of superhydrophobic latex composite materials

3.2.1 The mechanical robustness tests

To evaluate the mechanical robustness of superhydrophobic materials, a series of mechanical tests were performed. Knife scratch, file abrasion, sandpaper abrasion, finger-wiping and tape-peeling, pressure and high-speed water droplet impinging tests were common used methods [24, 34-36]. In this paper, the sandpaper abrasion, knife-scratch (Movie S1), finger-wiping (Movie S2), and tape-peeling (Movie S3) tests were performed to evaluate the mechanical robustness of composite materials. After these tests, the physical look or shape of the samples was altered, but they still kept superhydrophobicity (Fig. 3a-e). In the process of sandpaper abrasion test, samples loaded with 100 g weight were placed face-down on a piece of sandpaper (grit no.1000 Cw) and moved for 300 cm. This process was defined as one abrasion cycle. Water contact angles and sliding angles were measured for every cycle. 10 cycles were repeated and a total of 3000 cm abrasion distance was generated. The

change of contact angle and sliding angle for ERM@Latex-60 is shown in Fig. 3f. It could be seen that it still exhibited robust superhydrophobicity after the 3000 cm abrasion. The wettability change of other four samples prepared with different temperatures after sandpaper abrasion is shown in Fig. S6. Samples with reaction temperature higher than 35 °C possessed better abrasion resistance. Retention ratio and weight loss per unit area of the five samples after sandpaper (1000 Cw) abrasion for 3000 cm were used to further quantify the abrasion resistance displayed in Fig. S7. The retention ratio was $\beta = m_1/m_2 \times 100\%$, where m_1 referred to the sample mass after abrasion for a distance, and m_2 referred to the original sample mass. The weight loss per unit area was $\delta = (m_2 - m_1)/A$, where A was the abrasion area of samples. With the increase of temperature, the retention ratio of samples decreased and the weight loss per unit area increased. However, all these samples displayed high retention ratios after the abrasion test, showing limited damage by sandpaper abrasion.

Fig. 3. (a) Sandpaper abrasion (1000 Cw) test. (b) Knife-scratch test. (c) Finger-wipe test. (d) Tape-peeling test. (e) The water repellency of sample after undergoing the tests from (a) to (c). (f) The contact angle and sliding angle of ERM@Latex-60 after sandpaper abrasion for up to 3000 cm. (g) The contact angle and sliding angle of ERM@Latex-60 after tape-peeling for up to 60 times. The scale bars in (a)-(e) are 10 mm.

The tape-peeling test result of the ERM@Latex-60 was shown in Fig. 3g. The contact angle and sliding angle were recorded for every 10 peelings. Tape-peeling displayed a larger influence on the performance degradation of ERM@Latex-60 than the sandpaper abrasion. This could be due to the components of the adhesive cloth were adhered to the ERM@Latex surfaces after the repeated peeling processes. These residues from the adhesive are more hydrophilic, and would reduce the hydrophobicity of the samples. However, the hydrophobicity could be easily recovered by abrasion using sandpapers. The exposed surface after sandpaper abrasion showed a contact angle larger than 150° and sliding angle smaller than 10°.

again as shown in Fig. 3g (marked by a red vertical arrow). The tape-peeling test was also conducted on other four samples prepared with different temperatures as shown in Fig. S8. Some samples gradually lost water-repellence after the repeated peeling processes. Similar to ERM@Latex-60, their superhydrophobicity could also be recovered by sandpaper abrasion. Thus, samples prepared in this paper were easily recoverable after contamination.

The excellent mechanical strength was attributed to the composite structures of these samples. **First**, the ERMs were chemically adhered on the latex skeleton surfaces, ensuring a good bonding between them. The robust bonding strength could be proved by an ultrasonic experiment. Five samples were immersed in a beaker with absolute ethanol which could wet samples completely. Then the beaker was sealed and put in an ultrasonic cleaner and sonicated (100 Hz) for 30 and 60 min. SEM images of ERM@Latex-25 are shown in Fig. 4(a)-(c). The ERMs were largely intact after the ultrasonication for 60 min. ERM@Latex-25, ERM@Latex-35, ERM@Latex-45 were able to maintain a contact angle larger than 150° and sliding angle less than 10° (Fig. 4d). **Second**, it was interesting to know that the epoxy microspheres could fully permeate into the inside domain of latex sponge and uniformly deposited on skeleton of the sponge. Fig. S9 shown the SEM images of internal sections of ERM@Latex-T samples which were cut by a knife (Fig. S9f). The black circles marked the fracture positions of samples cut by a knife. This would be particularly useful once a significant thickness of the surface layer is worn out. The SEM images of sample surfaces before and after sandpaper abrasion are shown in Fig.

5. It could be found that abrading the outside sample surfaces could lead to newly exposed internal surfaces with similar roughness. Thus, ERMs fully permeating into the inside domain of latex sponge could ensure the superhydrophobicity of the whole materials. **Third**, the coatings were reinforced by the tangles of latex skeleton to ensure that shear forces caused by friction could largely dissipate into the entire coating instead of the local places. The sandpaper abrasion experiments on control groups (Fig. S10) could indirectly demonstrate the reinforcement effects of these 3D latex skeletons. Except for the coating prepared under 15 °C, epoxy resin coatings on smooth glass surfaces had contact angle larger than 150 ° and sliding angles smaller than 10°, presenting the superhydrophobicity. However, their superhydrophobicity could not be kept after sandpaper abrasion. After one cycle abrasion (300 cm), large area of bare glass surfaces exposed resulting in the dramatic reduction of contact angle. While for ERMs@Latex samples, they could keep superhydrophobicity after 10 cycles (3000 cm) abrasion. Thus, the reinforcement effect of these 3D latex skeletons was very obvious to prepare excellent wear-resistant superhydrophobic materials.

Fig. 4. Ultrasonic vibration test for ERM@Latex-25. (a) SEM image before ultrasonic vibration. (b) SEM image after ultrasonic vibration for 30 min. (c) SEM image after ultrasonic vibration for 60 min. (d) The contact angles and sliding angles after ultrasonic vibration for 60 min. The scale bars in (a)-(c) are 10 μm and in (d) is 10 mm.

Fig. 5. The SEM images of ERM@Latex before (a-e) and after (f-j) sandpaper (1000 Cw) abrasion. These samples are prepared at different temperature: (a) (f) 15 °C, (b) (g) 25 °C, (c) (h) 35 °C, (d) (i) 45 °C and (e) (j) 60 °C. The scale bar was 50 μm .

Latex sponge was very important to prepare robust superhydrophobic composite materials. However, latex sponge was not irreplaceable. Matrixes that possessed 3D rough microstructures could be used as a substitute for latex, which also proved the versatility of the present strategy. Here, polyurethane sponge, textile and filter paper were used as examples. Fig. S11-S13 showed the SEM images of the three substrate materials before and after ERMs adhering. The contact angle for polyurethane sponge was nearly 70° . For textile and filter paper, water could completely penetrate into the materials, showing contact angles of 0° . After the reaction with epoxy mixtures, it could be clearly seen that all these microstructures (polyurethane skeletons, textile threads and paper fibers) were closely adhered with small ERMs and silica particles. These composite materials all exhibited superhydrophobicity and robust mechanical strength. Sandpaper abrasion tests were conducted on the three composite materials. The ERMs@PU had excellent wear-resistance just like ERMs@Latex samples. ERMs@PU still kept superhydrophobicity (Fig. S14e) and displayed high retention ratios (Fig. S14f) after 3000 cm abrasion test, which showed the limited damage by sandpaper abrasion. The ERMs@Textile also showed good wear-resistance. However, the composite material surfaces were highly distorted and the exposed textile threads on surfaces tended to impede the move of small droplets. Thus, its contact angles and sliding angles could not be measured. Alternatively, the mobility of larger water droplets extruded from a dropper and the spherical shape of static water droplets on the material surface could be used as the tracer. After ten cycles of sandpaper abrasion, droplets still kept spherical and easily moved away from slightly inclined surface,

demonstrating the superhydrophobicity (Fig. S14d). For ERM@Paper, it could keep superhydrophobic after 2 cycles of abrasion processes. After knife scratch and tape peeling tests on the three composite materials, they still retained the excellent water repellency (Fig. S14 (a)-(c)). Thus, matrixes possessed 3D rough microstructures could help to reinforce the wear-resistance of superhydrophobic materials.

3.2.2 The chemical stability tests

Chemical stability in various extreme environment is a very important characteristic of superhydrophobic materials for practical applications [24, 37]. Three independent experiments, namely heating under high temperature, UV-irradiation, and droplet tests with strong acidic (pH=1) and alkaline (pH=14) solutions, were performed to investigate the chemical stability of the five samples. Fig. 6a shown the contact angles and sliding angles of samples after heating under 150 °C and 300 °C for 30 min. Samples of ERM@Latex-35, ERM@Latex-45, ERM@Latex-60 kept superhydrophobicity with contact angles larger than 150° and sliding angles smaller than 10° (Movie S4). Fig. S15 shows a very small mass loss (~1.5%) after 150 °C annealing. These samples remained white color under this condition (Fig. 6b). After heating at 300 °C, their mass loss increased to ~23%, indicating the heat-induced partial decomposition of samples. The color of samples changed to black under this condition (Fig. 6c). Their mechanical properties were also degenerated after the treatment at 300 °C. Despite the degenerated mechanical properties, samples of ERM@Latex-35, ERM@Latex-45, ERM@Latex-60 still kept their superhydrophobicity proving their excellent chemical stability. The thermal profile of

the curing epoxy resin and ERM@Latex-T samples were listed as follows. Fig. S15b and S16c showed the thermogravimetric analysis (TG) of epoxy curing product (without latex sponge) and ERM@Latex-T samples, respectively. No obvious weight losses were observed before 200 °C; after 200 °C, epoxy resin and ERM@Latex-T samples had dramatic weight decrease, indicating the heat-induced decomposition. The weight losses for ERM@Latex-45 and ERM@Latex-60 were less than other samples, indicating their better thermal stability.

Fig. 6 (a) The contact angles and sliding angles of the five samples after annealing at 150 °C and 300 °C for 30 min, respectively. (b) Digital photograph of samples after being heated at 150 °C for 30 min. (c) Digital photograph of samples after being heated at 300 °C for 30 min. (d) The contact angle and sliding angle of ERM@Latex-60 after UV-irradiation for up to 300 h. The scale bars in (b) and (c) are 10 mm.

UV-durability test was conducted by exposing to UV light for 300 h at room temperature. The wetting behavior was examined at every 60 h. Fig. 6d shows the contact angle and sliding angle of ERM@Latex-60 as a function of UV-irradiation time. After irradiation for 300 h, the sample exhibited a contact angle above 150° and a sliding angle below 10°. UV-durability tests on other four samples prepared under different temperatures were also conducted as shown in Fig. S8. It could be clearly seen that all these samples had excellent UV-durability. The longtime UV-irradiation had no influence on their superhydrophobicity, except for a slight change of their color from white to faint yellow. Chemical stability test with strong acid (pH=1) and alkali (pH=14) droplets was performed by positioning these droplets onto the five samples for up to 60 min as shown in Fig. S17 and Fig. S18. These droplets became smaller due to water evaporation. As the contact time increased, the contact angles of acidic/alkaline droplets decreased to below 150° for ERM@Latex-15, ERM@Latex-25. While for samples of ERM@Latex-35, ERM@Latex-45 and ERM@Latex-60, their contact angles still remained above 150°.

Through the above analysis, we discovered that samples of ERM@Latex-35, ERM@Latex-45 and ERM@Latex-60 had better wear-resistance and chemical stability, compared with samples of ERM@Latex-15 and ERM@Latex-25. The reason was that the curing reaction of epoxy resin was more complete at higher temperature (see the FT-IR spectra in Fig. S3). More hydrophilic groups were consumed from epoxy resin improving the anti-wettability of samples. The total coverage of the silica sol on them increased the roughness of skeleton surfaces, which

enhanced the superhydrophobicity of samples.

3.3. Practical applications of these superhydrophobic composite materials

The excellent anti-wetting properties of the latex composite materials could be used to repel dust particles and stain liquids. As shown in Fig. 7a and Movie S5, dust particles collected from construction sites were carried away immediately by the moving droplets in air. The fouled sample was clean again as more water flowed over the surface, suggesting a good self-cleaning property in air. Fig. 7b and Movie S6 shown the self-cleaning experiment in oil. Dust particles in oil also could be easily carried away by passing water droplets, suggesting a good self-cleaning property in oil. The anti-wetting properties of samples were tested by various liquids. Stain liquids including wine, milk, soy sauce, coffee, acid and alkali water could stand on surfaces with nearly spherical shapes as shown in Fig. 7c. The contact angles and sliding angles of coffee, milk, wine and sauce on sample surface are shown in Fig. 7d. The four stain droplets possessed contact angles larger than 150° and sliding angles smaller than 10° , showing excellent stain-repellence. These stain liquids dropping on slightly inclined sample surfaces moved away quickly either in air (Movie S7) or when immersed in oil (Fig. 7e, Movie S8). In addition to superhydrophobicity, these samples also possessed superhemophobicity. Blood drops could stand on sample surfaces with nearly spherical shapes (Fig. 7c). Fig. 7f and Movie S7 shown that blood droplets placed onto a slightly inclined sample surface could move away quickly without leaving any residue behind. All these experiments indicated very low friction between stain liquids and sample surface. Thus, the prepared

superhydrophobic and superhemophobic composite material is a very promising candidate for advanced engineering materials with antifouling functionality.

Fig. 7. (a) Self-cleaning experiment in air. Fouling powder could be easily carried away by passing water droplets. (b) Self-cleaning experiment in oil. Fouling power in oil (hexane) could be easily carried away by passing water droplets. (c) Stain liquids standing on a material with nearly spherical shapes. These liquids included wine, milk, soy sauce, coffee, acidic and alkaline solutions. (d) The contact angles and sliding angles of stain liquids, including wine, milk, sauce and coffee. (e) Stain liquids dropped on a material surface in oil could move away quickly. (f) The mobility of blood droplets on a material surface. The scale bars in (a)-(d) and (f) were 10 mm.

The 3-D porous structures of superhydrophobic materials could endow them a wide range of practical applications. Fig. 8 showed that oil could be separated from water immediately by the composite material (Movie S9). Oil contaminants left inside the

structures could be easily removed by evaporating, which made the material reusable. In addition, these materials perform well in a continuous oil-water separation test. A syringe was used here to simulate the continuous process.

These materials also displayed good sound absorption property. Fig. 9a showed the sound absorption coefficients of the bare latex materials and the five samples under high frequencies ranging from 800 to 6300 Hz. The sound absorption coefficients of all samples were higher at high frequencies. The bare latex materials, ERM@Latex-15, ERM@Latex-25 and ERM@Latex-45 showed greater sound-absorption in the range of 3000-6300 Hz and the latter three samples had larger sound absorption coefficients compared with the bare latex materials. ERM@Latex-35 and ERM@Latex-60 showed good sound absorption ability in the 2000-5000 Hz range. The good sound absorption performances were attributed to the existence of micro pores. When the sound waves entered these porous materials, the diffuse refraction or reflection were enhanced and the vibration of the hole walls were increased, resulting in the effective attenuation of the sound waves.

The composites were potentially good thermal resistance materials. Fig. 9b listed the thermal conductivity of the five samples. Among them, ERM@Latex-35 had the smallest thermal conductivity of 0.066 W/m k and ERM@Latex-25 had the largest value of 0.095 W/m k. The thermal conductivity of all samples have met the requirement for thermal insulation materials [38]. The existence of the micro pores (Fig. 1) disrupted the thermal conduction paths, which in turn gave the composite materials a low thermal conductivity [39].

Fig. 8. The simulation of continuous separation of oil from water by syringe pumping. Hexane was used as oil dyed by Oil Red O.

Fig. 9. (a) Sound-absorbance performance tests for the bare latex materials and the five samples (b) The thermal conductivity of the five samples.

4. Conclusions

In conclusion, a facile one-pot synthesis method was reported to fabricate mechanically robust superhydrophobic and superhemophobic composite materials. The mechanical and environmental durability were owing to the strong chemical bonding between the epoxy resin microspheres (ERMs) and the 3-D porous skeleton structures of latex sponge. The samples of ERM@Latex-35, ERM@Latex-45 and ERM@Latex-60 displayed better wear-resistance and chemical stability after severe mechanical and chemical durability tests. All the five samples exhibited a superior UV-durability after 300 h UV-irradiation. These superhydrophobic materials could be

made into free-standing bulk or thin plate samples. They could also be prepared to adhere onto a substrate during the curing stage. The excellent comprehensive performances including mechanochemical robustness, stain repellency, oil-water separation and sound-absorption properties have made these superhydrophobic materials a strong candidate for a range of industrial applications.

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Supplementary data

Supplementary data associated with this article could be found.

References

- [1] Y. Si, F. Yang, Z. Guo, Bio-inspired one-pot route to prepare robust and repairable micro-nanoscale superhydrophobic coatings, *J. Colloid Interf. Sci.*, 498 (2017) 182-193.
- [2] Y. Wang, Y. Shi, L. Pan, M. Yang, L. Peng, S. Zong, Y. Shi, G. Yu, Multifunctional superhydrophobic surfaces templated from innately microstructured hydrogel matrix, *Nano lett.*, 14 (2014) 4803-4809.
- [3] H. Liu, Y. Wang, J. Huang, Z. Chen, G. Chen, Y. Lai, Bioinspired surfaces with superamphiphobic properties: concepts, synthesis, and applications, *Adv. Funct. Mater.*, 28 (2018) 1707415.
- [4] Z. Liu, H. Wang, X. Zhang, C. Lv, C. Wang, Y. Zhu, Robust and chemically stable superhydrophobic composite ceramic coating repellent even to hot water, *Adv. Mater. Interfaces*, 4 (2017) 1601202.
- [5] Y.Y. Quan, L.Z. Zhang, Numerical and analytical study of the impinging and bouncing phenomena of droplets on superhydrophobic surfaces with microtextured structures, *Langmuir*, 30 (2014) 11640-11649.
- [6] Y.-Y. Quan, L.-Z. Zhang, Experimental investigation of the anti-dust effect of transparent hydrophobic coatings applied for solar cell covering glass, *Sol. Energy Mater. Sol. Cells*, 160 (2017) 382-389.

- [7] J. Lomga, P. Varshney, D. Nanda, M. Satapathy, S.S. Mohapatra, A. Kumar, Fabrication of durable and regenerable superhydrophobic coatings with excellent self-cleaning and anti-fogging properties for aluminium surfaces, *J. Alloys Comp.*, 702 (2017) 161-170.
- [8] J. Li, D. Li, Y. Yang, J. Li, F. Zha, Z. Lei, A prewetting induced underwater superoleophobic or underoil (super) hydrophobic waste potato residue-coated mesh for selective efficient oil/water separation, *Green Chem.*, 18 (2016) 541-549.
- [9] C. He, J. Huang, S. Li, K. Meng, L. Zhang, Z. Chen, Y. Lai, Mechanically resistant and sustainable cellulose-based composite aerogels with excellent flame retardant, sound-absorption, and superantiwetting ability for advanced engineering materials, *ACS Sustain. Chem. Eng.*, 6 (2017) 927-936.
- [10] M. Ge, C. Cao, J. Huang, X. Zhang, Y. Tang, X. Zhou, K. Zhang, Z. Chen, Y. Lai, Rational materials interface design at nanoscale towards intelligent oil-water separation, *Nanoscale Horiz.*, (2018).
- [11] N. Wang, D. Xiong, Y. Deng, Y. Shi, K. Wang, Mechanically robust superhydrophobic steel surface with anti-icing, UV-durability, and corrosion resistance properties, *ACS Appl. Mater. Interfaces*, 7 (2015) 6260-6272.
- [12] Y.Y. Quan, P.G. Jiang, L.Z. Zhang, Development of fractal ultra-hydrophobic coating films to prevent water vapor dewing and to delay frosting, *Fractals*, 22 (2014) 1440002.
- [13] X.-M. Li, D. Reinhoudt, M. Crego-Calama, What do we need for a superhydrophobic surface? A review on the recent progress in the preparation of superhydrophobic surfaces, *Chem. Soc. Rev.*, 36 (2007) 1350-1368.
- [14] F. Li, M. Du, Q. Zheng, Dopamine/Silica Nanoparticle Assembled, Microscale Porous Structure for Versatile Superamphiphobic Coating, *ACS Nano*, 10 (2016) 2910-2921.
- [15] L. Wen, Y. Tian, L. Jiang, Bioinspired super-wettability from fundamental research to practical applications., *Angew. Chem., Int. Ed.*, 54 (2015) 3387-3399.
- [16] N. Nuraje, W.S. Khan, Y. Lei, M. Ceylan, R. Asmatulu, Superhydrophobic Electrospun Nanofibers, *J. Mater. Chem. A*, 1 (2013) 1929-1946.
- [17] M. Wolfs, T. Darmanin, F. Guittard, Superhydrophobic nanofiber arrays and flower-like structures of electrodeposited conducting polymers, *Soft Matter*, 8 (2012) 9110-9114.
- [18] P. Tian, Z. Guo, Bioinspired silica-based superhydrophobic materials, *Applied Surface Science*, 426 (2017).
- [19] Y. Liu, Z. Liu, Y. Liu, H. Hu, Y. Li, P. Yan, B. Yu, F. Zhou, One-step modification of fabrics with bioinspired polydopamine@octadecylamine nanocapsules for robust and healable self-cleaning performance, *Small*, 11 (2015) 426-431.
- [20] H. Wang, Z. Liu, X. Zhang, C. Lv, R. Yuan, Y. Zhu, L. Mu, J. Zhu, Durable self-healing superhydrophobic coating with biomimic "chloroplast" analogous structure, *Adv. Mater. Interfaces*, 3 (2016) 1600040.
- [21] Y. Si, H. Zhu, L. Chen, T. Jiang, Z. Guo, A multifunctional transparent superhydrophobic gel nanocoating with self-healing properties, *Chem. Comm.*,

- 51 (2015) 16794-16797.
- [22] Y. Li, S. Chen, M. Wu, J. Sun, All spraying processes for the fabrication of robust, self-healing, superhydrophobic coatings, *Adv. Mater.*, 26 (2014) 3344-3348.
- [23] Y. Liu, Y. Liu, H. Hu, Z. Liu, X. Pei, B. Yu, P. Yan, F. Zhou, Mechanically induced self-healing superhydrophobicity, *J. Phys. Chem. C*, 119 (2015) 7109-7114.
- [24] X. Zhang, D. Zhi, L. Sun, Y. Zhao, M.K. Tiwari, C.J. Carmalt, I.P. Parkin, Y. Lu, Super-durable, non-fluorinated superhydrophobic free-standing items, *J. Mater. Chem. A*, 6 (2018) 357.
- [25] Y. Lu, S. Sathasivam, J. Song, C.R. Crick, C.J. Carmalt, I.P. Parkin, Robust self-cleaning surfaces that function when exposed to either air or oil, *Science*, 347 (2015) 1132-1135.
- [26] D. Zhi, Y. Lu, S. Sathasivam, I.P. Parkin, X. Zhang, Large-scale fabrication of translucent and repairable superhydrophobic spray coatings with remarkable mechanical, chemical durability and UV resistance, *J. Mater. Chem. A*, 5 (2017) 10622.
- [27] B. Ge, Z. Zhang, X. Zhu, G. Ren, X. Men, X. Zhou, A magnetically superhydrophobic bulk material for oil removal, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 429 (2013) 129-133.
- [28] X. Zhang, Y. Guo, H. Chen, W. Zhu, P. Zhang, A novel damage-tolerant superhydrophobic and superoleophilic material, *J. Mater. Chem. A*, 2 (2014) 9002-9006.
- [29] X. Zhu, Z. Zhang, G. Ren, J. Yang, K. Wang, X. Xu, X. Men, X. Zhou, A novel superhydrophobic bulk material, *J. Mater. Chem. A*, 22 (2012) 20146.
- [30] Y.-Y. Quan, L.-Z. Zhang, Facile fabrication of superhydrophobic films with fractal structures using epoxy resin microspheres, *Appl. Surf. Sci.*, 292 (2014) 44-54.
- [31] F. Wang, X. Wang, A. Xie, Y. Shen, W. Duan, Y. Zhang, J. Li, A simple method for preparation of transparent hydrophobic silica-based coatings on different substrates, *Applied Physics A*, 106 (2011) 229-235.
- [32] K. Tsuchida, J.P. Bell, A new epoxy/epi-sulfide resin system for coating applications: curing mechanism and properties, *Int. J. Adhes. Adhes.*, 20 (2000) 449-456.
- [33] L. Xue, B. Sanz, A. Luo, K.T. Turner, X. Wang, D. Tan, R. Zhang, H. Du, M. Steinhart, C. Mijangos, M. Guttman, M. Kappl, A.d. Campo, Hybrid surface patterns mimicking the design of the adhesive toe pad of tree frog, *ACS Nano*, 11 (2017) 9711-9719.
- [34] W. Zhang, T. Xiang, F. Liu, M. Zhang, W. Gan, X. Zhai, X. Di, Y. Wang, G. Liu, C. Wang, Facile Design and Fabrication of Superwetting Surfaces with Excellent Wear-Resistance, *ACS Appl. Mater. Interfaces*, 9 (2017) 15776-15784.
- [35] A. Davis, S. Surdo, G. Caputo, I.S. Bayer, A. Athanassiou, Environmentally Benign Production of Stretchable and Robust Superhydrophobic Silicone Monoliths, *ACS Appl. Mater. Interfaces*, 10 (2018) 2907-2917.
- [36] H. Jin, X. Tian, O. Ikkala, R.H. Ras, Preservation of superhydrophobic and

superoleophobic properties upon wear damage, ACS Appl. Mater. Interfaces, 5 (2013) 485-488.

[37] J. Zimmermann, G.R.J. Artus, S. Seeger, Long term studies on the chemical stability of a superhydrophobic silicone nanofilament coating, Appl. Surf. Sci., 253 (2007) 5972-5979.

[38] U. Hunan, U. Tianjin, U. Tongjing, U. Southeast, Civil engineering materials, China Architecture and Building Press: Beijing, China, (2003) PP: 253–254.

[39] G. Gong, K. Gao, J. Wu, N. Suna, C. Zhou, Y. Zhao, L. Jiang, A highly durable silica/polyimide superhydrophobic nanocomposite film with excellent thermal stability and abrasion-resistant performance, J. Mater. Chem. A, 3 (2015) 713-718.

651 **Highlights**

- 652 ● A facile one-pot synthesis method was reported.
- 653 ● Non-fluorinated superhydrophobic latex composite materials were fabricated.
- 654 ● Remarkable mechanochemical robustness and multifunctionality were obtained.
- 655 ● The water repellency of materials was remained after suffering serious disruption.
- 656 ● The samples are easily recoverable after contamination.

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Graphical Abstract

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