

Simple Route To Get Very Hydrophobic Surfaces of Fibrous Materials with Core–Shell Latex Particles

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ABSTRACT: The aim of this article is to report the creation of artificial, robust, and very hydrophobic materials with core–shell polyurethane–polydimethylsiloxane or polyurethane–poly(*n*-butyl acrylate) polymer microparticles. These latexes were prepared by polyaddition in cyclohexane with commercial or synthetic steric stabilizers. An easy one-step method based on the filtration of the colloidal particles

was developed to obtain water-repellent fibrous materials such as paper or textiles that maintain stable properties even after several washing/drying cycles. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2772–2777, 2008

Key words: colloids; core-shell polymers; films; polyurethanes; surfaces

INTRODUCTION

The wettability of a solid can be conventionally controlled by the chemical composition and geometric microstructure (or nanostructure) of its surface. Nature gives us a few examples of extreme water repellency, such as lotus leaves, which show a multiscale structure.¹ The surface of these plants is also self-cleaning as water drops can roll over it, collecting and removing dust or other debris. Because they could bring a lot of convenience into our daily life or in industry,² superhydrophobic materials have attracted considerable research interest in the last decade. Several biomimetic ultrahydrophobic materials have been prepared by the creation of rough surfaces with low surface free energy. Two approaches have been commonly used. The first one is to pattern hydrophobic surfaces by mechanical machining,³ micromolding texturation,^{4,5} plasma etching,⁶ or nanosphere lithography.⁷ For instance, Bico et al.⁴ fabricated a superhydrophobic material by texturing a surface with periodic, micrometer-size silica features (e.g., wells, plateaus, channels, and flat mesas) produced on a substrate with a micromolding technique. The other one is to cover structured surfaces with hydrophobic molecules,^{8,9} polymers,¹⁰ or met-

als.¹¹ For example, Erbil et al.¹² reported a simple and inexpensive method to form a superhydrophobic coating using polypropylene, which can be applied to a large variety of surfaces. Other methods have also been reported, such as the solidification of alkylketene dimmers.¹³ Han et al.¹⁴ fabricated superhydrophobic coatings with poly(*t*-butyl acrylate)-*b*-polydimethylsiloxane-*b*-poly(*t*-butyl acrylate) triblock copolymers, which formed micelles in selective solvents. Our approach involves a new and easy method of creating robust and very hydrophobic materials with a multiscale structure based on the deposition of core–shell polyurethane (PUR) particles on textiles or paper.

The preparation of PUR materials in the form of calibrated microspheres has been performed by a polyaddition reaction in a dispersant medium (cyclohexane).^{15–18} The stabilization of the precipitating polymer is due to the presence of a reactive polymer (surfmer) in the dispersant phase, which reacts with the growing polymer and remains covalently bonded to the final particle. The obtained dispersion is a latex. The filtration of the microparticles onto various fibrous substrates gives rise to very hydrophobic surfaces with a multiscale structure. We present here the study of the influence of several parameters such as the polydispersity of the core–shell particles and the nature of the shell [e.g., polydimethylsiloxane (PDMS) or poly(*n*-butyl acrylate) (*Pn*BA)] on the high water repellency of the resulting filtrates.

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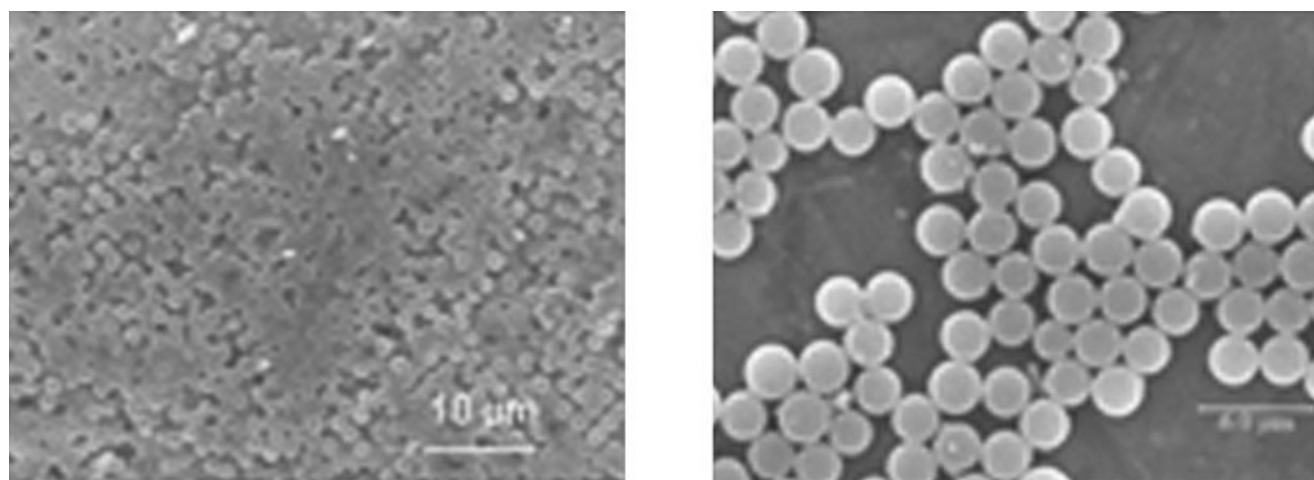


Figure 1 SEM views of 2.4- μm monodisperse PUR-PDMS particles (left) and 1.7- μm monodisperse PUR-PnBA particles (right).

EXPERIMENTAL

Synthesis of the PUR microspheres

Materials

Cyclohexane (99%; J.T. Baker, France) and dibutyl tin laurate (DBTDL; 98%; Sigma-Aldrich, France) were used as received; a 1% stock solution of the catalyst was prepared by the dissolution of 2.43 mmol of DBTDL in 25 g of paraffin (Sigma-Aldrich). Toluene-2,4-diisocyanate (TDI; Sigma-Aldrich) was purified by distillation *in vacuo*. Ethylene glycol (EG; 99%; Sigma-Aldrich), monohydroxy-terminated polydimethylsiloxane (PDMS-OH) of 4670 g/mol ($\geq 99\%$; Sigma-Aldrich), and PDMS-OH of 1000 g/mol ($\geq 99\%$; generously provided by the Polymer Technology Group, Berkeley, CA) were used as received.

Mono- or dihydroxy-terminated poly(*n*-butyl acrylate) (PnBA-OH_{*x*}; *x* = 1 or 2) stabilizers for the synthesis of PUR-PnBA particles were prepared by atom transfer radical polymerization, as previously reported by us.^{15,16} In this article, PnBA-OH of 13,000 g/mol was synthesized and used as a reactive steric stabilizer.

Procedures

PUR synthesis was carried out in a 250-mL jacketed glass reactor fitted with a reflux condenser, a sampling device, and a nitrogen inlet tube. Different procedures were followed according to the stabilizer used with a [NCO]/[OH] ratio of 1.1.¹⁵⁻¹⁸

Synthesis of PUR-PnBA particles

The reactor was charged with 2 equiv of TDI with respect to the OH functions (57 mg) and the tierce of the solvent (12 g). The mixture was allowed to react

in the presence of DBTDL as the catalyst (0.3 g of a 1% solution in paraffin) at 60°C under vigorous stirring for a few minutes.

PnBA-OH stabilizer (0.75 g) in cyclohexane (24 g) was then added dropwise over 1 h, and EG (1.86 g) was added in one lot and allowed to react for 30 min. The rest of the TDI was added over 4 h, and the mixture was kept at 60°C over a period of 6 h.

Synthesis of PUR-PDMS particles

The reactor was charged with the catalyst (DBTDL; 0.3 g of a 1% solution in paraffin), EG (1.86 g), and stabilizer (0.75 g). The mixture was then stirred at a speed of 500 rpm at 60°C over 1 h. TDI (4.8 mL) was added over 4 h, and the mixture was kept at the same temperature and under the same stirring conditions over a period of 6 h. All the latexes were washed 3 times by centrifugation/redispersion cycles in cyclohexane and dried *in vacuo*.

As examples, Figure 1 shows scanning electron microscopy (SEM) pictures of monodisperse particles obtained in the presence of PDMS-OH (1000 g/mol) and PnBA-OH (13,000 g/mol). The particle average diameters and size distributions were estimated statistically by analysis of the SEM micrographs and are reported in Table I.

Elaboration of the superhydrophobic materials

Dried microparticles (white powder; 100 mg) were dispersed in 100 mL of cyclohexane by an ultrasonic method over 1 h. The suspension was then filtered on filter paper (no. 1, Whatman), a nylon membrane (Sefar, France; porosity = 5 μm), or a polycarbonate membrane filter (GE Osmonics Labstore (Minnetonka, MN); porosity = 10 μm) and dried at room temperature.

TABLE I
Measured Contact Angles of a 2- μ L Water Droplet Deposited at the Surface of Films Obtained by the Filtration of the Core-Shell Particles on Whatman Paper, a Polycarbonate Membrane, Cotton Linen, a Nitrocellulose Membrane, or a Nylon Membrane

	Contact angle ($^{\circ}$)				
	PDMS/1.7 μ m/ polydisperse (± 1 μ m) ^a	PDMS/2.5 μ m/ polydisperse (± 1.2 μ m) ^a	PDMS/2.1 μ m/ monodisperse (± 0.2 μ m) ^a	PnBA/3.3 μ m/ polydisperse (± 1.5 μ m) ^a	PnBA/1.7 μ m/ monodisperse (± 0.2 μ m) ^a
Whatman filter paper	133	141	140	131	132
Polycarbonate membrane	130	138	134	132	130
Nylon membrane	131	139	137	130	132
Nitrocellulose membrane	141	147	145	—	—
Cotton linen	139	145	137	—	—

^a Chemical nature of the shell of the particles/average diameter/size distribution.

To enhance the robustness of the filtrates versus washing/drying cycles, 800 mg of silicon gel (Rubson, France) was dissolved in cyclohexane before the filtration stage. The samples were washed with tap water (flow rate ~ 7 L/min) and dried at room temperature under air.

SEM

The size of the PUR particles and the microstructure morphology of the surface of the particulate films were estimated by SEM observations with a JEOL JSM-840 scanning electron microscope (France) oper-

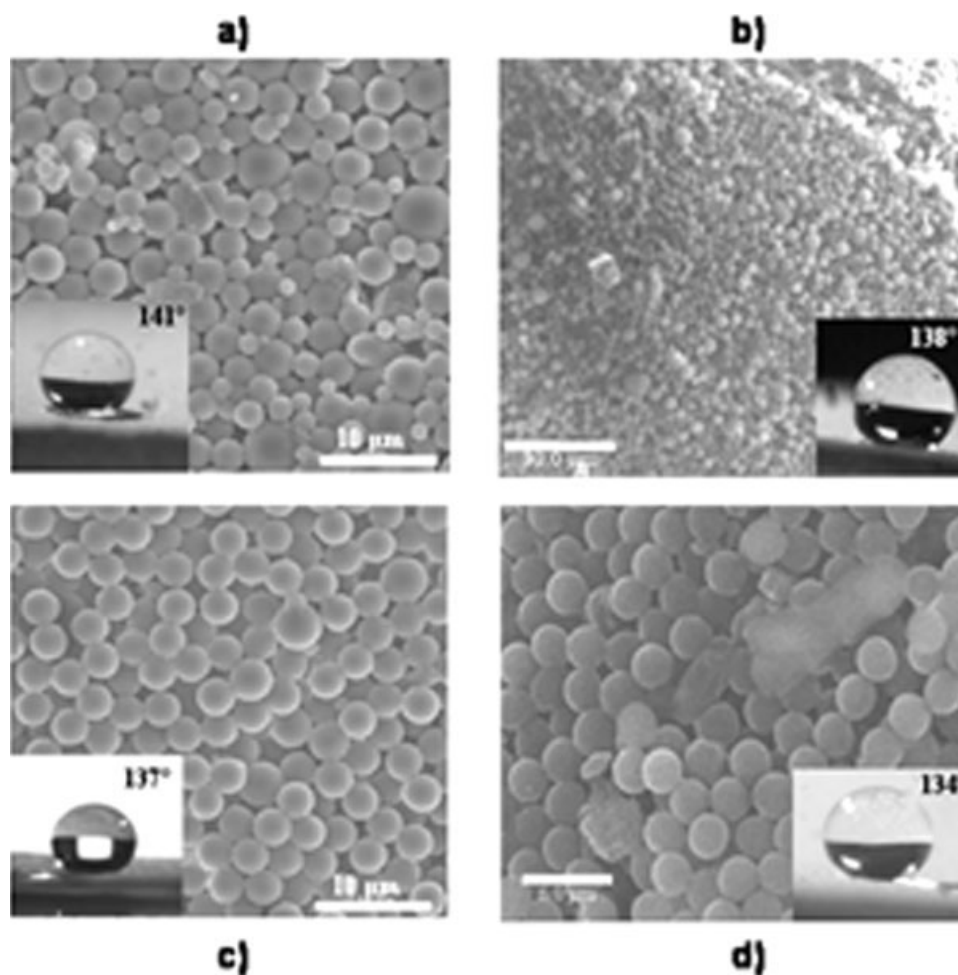


Figure 2 SEM pictures of (a) polydisperse PUR-PDMS particles on Whatman filter paper, (b) polydisperse PUR-PDMS particles on a polycarbonate membrane, (c) monodisperse PUR-PDMS particles on a polyamide membrane, and (d) monodisperse PUR-PDMS particles on a polycarbonate membrane. The inset images show the water contact angle of a 2- μ L water droplet on the corresponding filtrate surface.

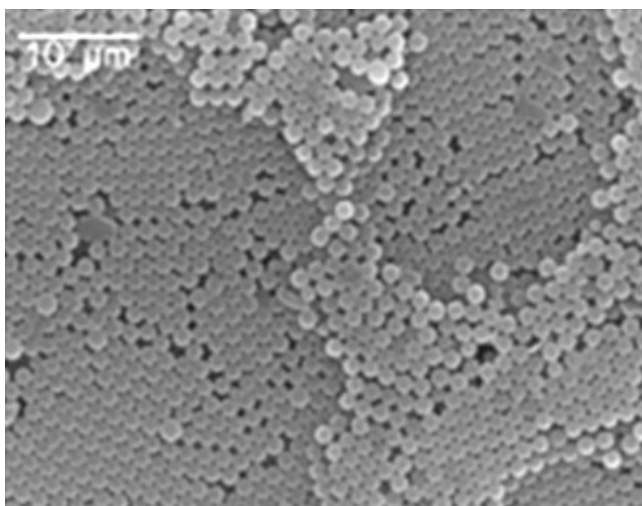


Figure 3 SEM picture of monodisperse PUR-*Pn*BA particles deposited on a glass slide.

ating at 10 kV. The specimens were gold-coated before examination.

Contact-angle measurements

Contact angles of 2 μ L of deionized water drops were measured with a goniometer at room temperature (DSA 100, Kruss, Germany).

RESULTS AND DISCUSSION

By observing a water droplet carefully deposited onto filter paper that had been used for the filtration of a suspension of monodisperse PUR-PDMS particles, we observed that it did not wet the substrate. Indeed, the contact angle between the droplet and the surface was found to be equal to 140° , indicating that the filtrate exhibited a very hydrophobic behavior. Similar results were obtained with PUR-*Pn*BA particles of a similar size (see Table I), indicating that the chemical nature of the shell of the particles had no noticeable influence on the water repellency of the corresponding filtrate. When viewed in an SEM image [see Fig. 2(a)], the filtrate showed a rough surface as the result of a random packing of the colloidal particles. It is in fact well known that water repellency depends not only on the chemical nature of the surface but also on its geometrical structure.^{4,5,7,11} Wetting properties on roughly textured surfaces can be described by the Wenzel¹⁹ or Cassie-Baxter²⁰ model. The first one assumes that the liquid fills up the grooves on a rough surface and states that, for an identically same increase in the free liquid area at the upper surface of the drop (i.e., the liquid-vapor-surface), a greater amount of actual surface is wetted under it on a rough surface versus

a smooth area. Thus, the net energy decrease on wetting a water-repelling surface will be greater for the rougher surface than a smooth surface and thereby enhances its water repellency. In the approach of Cassie and Baxter, it is assumed that the liquid forms a composite surface on the rough substrate; that is, the liquid does not fill the grooves. In this case, the liquid-surface interface is actually an interface consisting of two phases, namely, a liquid-solid interface and a liquid-vapor interface.

As the filtration of polydisperse PUR-PDMS and PUR-*Pn*BA particles gave similar results in terms of the water contact angles (see Table I), one can conclude that the monodispersity in the size of the sample is not a key criterion for the creation of a very hydrophobic surface.

Because the filter paper is made of interconnected fibers (see Supplemental Fig. S1), we can thus think that the high water repellency of the filtrate is due to this special textured and porous internal structure. To verify this hypothesis, we deposited the PUR-PDMS and PUR-*Pn*BA core-shell particles onto a flat glass slide. Figure 3 shows a typical SEM image of the resulting films. One can clearly see that the surface topography is more uniform and smoother than on porous materials. A water contact angle close to 105° was measured in both cases, proving that the textured internal structure of the substrate is required to obtain a very hydrophobic material.

This result drives us to work with different fibrous materials, such as cotton linen or polyamide, nitrocellulose, and polycarbonate membranes, which also have a textured and porous structure (see Supplemental Fig. S2). Figure 2 shows the SEM images obtained for PUR-PDMS particles deposited on polyamide [Fig. 2(c)] and polycarbonate [Fig. 2(d)] membranes, together with optical micrographs (inset) indicating the corresponding water contact angle of the filtrate surface. In all cases, a high water repellency of the surface is observed (contact angle values between 130 and 140°).²¹ As a flat PDMS film spin-coated or obtained by a simple dipping process on these fibrous materials has a water contact angle of about 105° , which is in agreement with the result

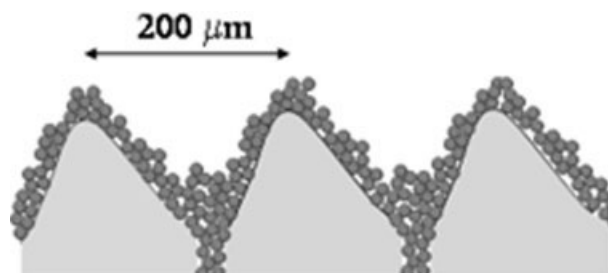


Figure 4 Schematic representation of the multilevel rough surface of the filtrate.

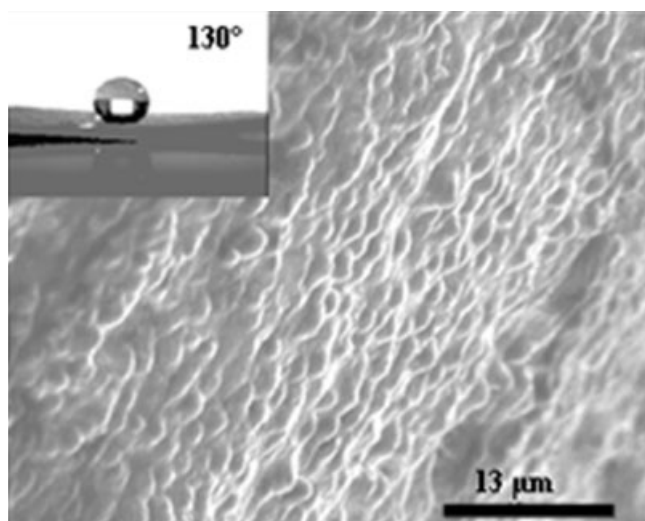


Figure 5 SEM picture of monodisperse PUR-PDMS particles embedded in a silicon joint film after filtration on Whatman paper. The inset image shows the water contact angle of a 2- μ L water droplet on the filtrate surface.

previously reported by Khorasani and Mirzadeh,²² we can conclude that both the textured structure of the substrate and the presence of the colloidal core-shell particles are thus required to get a very hydrophobic surface. Indeed, through filtration of micrometer-size core-shell particles on fibrous materials, a multilevel rough surface is obtained (see Fig. 4) that looks like the one previously reported by Han et al.,¹⁴ who cast a poly(*t*-butyl acrylate)-*b*-polydimethylsiloxane-*b*-poly(*t*-butyl acrylate) copolymer micelle solution containing a small amount of water onto glass substrates. It is speculated that the high water repellency of the surface of the filtrate is partially due to the entrapment of air bubbles in the small pores situated between the colloidal particles. Moreover, we have observed that water drops rapidly skip over a slightly inclined surface of the filtrate. They also can be moved freely with a syringe without adhesion to the surface, therefore exhibiting a very low contact angle hysteresis, which is a high hydrophobicity criterion in the Cassie-Baxter model.²³

Thus, the very high hydrophobicity on the surface of the filtrates can be attributed to a Cassie-Baxter state.

Such fibrous materials with a very hydrophobic surface may have potential industrial applications such as new printing supports or textiles. However, their high water repellency must remain after several treatments such as washing and drying cycles. Unfortunately, our samples showed a tendency to slightly lose their very hydrophobic behavior after being washed copiously with 100 mL of water. SEM observations of the surface of the materials after these washing stages showed that most of the core-shell particles were removed from the surface. To enhance the robustness of the samples, we first tried to sinter the particles by a heating treatment (1 h at 100°C). Unfortunately, no improvement of the stability of the samples versus washing was observed. We thus followed a strategy previously developed by Quéré and coworkers,^{4,5} which consisted of cofiltration of a silicon gel with the core-shell particles. Figure 5 shows the surface of the resulting filtrate. The colloids were partially embedded in a homogeneous silicon film, appearing as micrometer-scaled hills. The contact angle value of a water droplet deposited onto this material was found to vary between 129 and 142° (see Table II). Moreover, it remained stable after five washing/drying cycles because the silicon film acted as cement, which prevented the removal of the particles. Similar results were obtained with all types of membranes that we used, and this opens the way for industrial applications.

The slight decrease of the water contact angle in comparison with the silicon joint-free filtrates could be explained by a lower quantity of trapped air in the pores between the colloidal particles, and this proves once more that the Cassie-Baxter model can describe the very hydrophobic behavior of our samples.

CONCLUSIONS

We managed to obtain robust, washable, and very hydrophobic materials through a new and easy process. Well-defined core-shell microparticles were

TABLE II
Influence of the Number of Washing/Drying Cycles on the Value of the Contact Angle ($\pm 2^\circ$) of a 2- μ L Water Droplet Deposited at the Surface of Films Obtained by the Cofiltration of 2.5- μ m PUR-PDMS Core-Shell Particles and a Silicon Gel on Whatman Filter Paper, a Polycarbonate Membrane, Cotton Linen, a Nitrocellulose Membrane, or a Nylon Membrane

	Contact angle ($^\circ$)					
	Without washing	After one cycle	After two cycles	After three cycles	After four cycles	After five cycles
Whatman filter paper	136	135	134	134	132	132
Polycarbonate membrane	133	133	132	132	130	130
Nylon membrane	129	126	125	125	125	125
Nitrocellulose membrane	142	142	142	142	140	140
Cotton linen	140	135	133	133	133	133

first prepared via polyaddition in a dispersant medium. These particles were deposited by filtration on fibrous materials to make them very hydrophobic. We showed that this property could be attributed to a Cassie-Baxter state. The cofiltration of a silicon joint with the core-shell particles allowed us to get very hydrophobic surfaces that were stable even after several washing/drying cycles, opening the way for industrial applications.

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