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polymer

Polymer 48 (2007) 7455–7460

www.elsevier.com/locate/polymer

Polymer Communication

Fabrication of super-hydrophobic film from PMMA with intrinsic water contact angle below 90°

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Received 21 July 2007; received in revised form 18 October 2007; accepted 26 October 2007
Available online 30 October 2007

Abstract

Super-hydrophobic film is commonly prepared from hydrophobic materials. Poly(methyl methacrylate) (PMMA) is considered as a hydrophilic polymer (intrinsic contact angle below 90°) with the water contact angle (CA) of ∼68°. However, a super-hydrophobic PMMA film with CA of ∼154° was obtained by treating polystyrene (PS) and PMMA blended film in a warm selective solvent, cyclohexane. The surface was characterized by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and infrared spectroscopy (FT-IR). The results show that the conversion from the hydrophilic surface to a super-hydrophobic one is due to the cooperation of the micro-, nano-structure and the side group reorientation in the PMMA chains at the topmost.

Keywords: Super-hydrophobic; Phase separation; Reorientation

1. Introduction

In the last decade, study of super-hydrophobic surface has attracted much attention because its importance in both fundamental research and practical applications [1–6]. Different kinds of materials, such as organic, inorganic and hybrid materials have been developed to prepare super-hydrophobic surfaces. Among them, polymers were widely used to create super-hydrophobic surfaces via diverse methods, such as template synthesis [7], solution method [8] and solvent-induced crystallization [9], plasma polymerization or etching [10], electrohydrodynamics technique [11] and mechanical treatment [12,13], etc. In general, a material is called hydrophilic when the intrinsic water CA (CA on its flat surface) is smaller than 90°, and a material is called hydrophobic when the intrinsic water CA is greater than 90°. The surface wettability is determined by both surface chemistry and roughness. Super-hydrophobic surfaces are commonly prepared via constructing rough micro-, nano-structure on hydrophobic materials [4,14–19], and various kinds of high-performance hydrophilic materials are unfortunately excluded. It is desirable to develop strategies for preparing super-hydrophobic surfaces not only from hydrophobic materials but also from hydrophilic ones. However, reports concern to construction of super-hydrophobic surfaces from hydrophilic polymers especially suitable for large-area preparation, are still limited [9,20]. Process of polymer phase separation offers a simple method to obtain suitable composition with micro/nano-sized morphologies [21–26]. Erbil and co-workers [8a] have reported the preparation of super-hydrophobic surface from hydrophobic polymer polypropylene based on this process. Actually, by choosing polymer composition and then using selective solvents, both surface component and morphology can be controlled. Here, we propose a phase separation and selective solvent treatment method to prepare super-hydrophobic surface from a hydrophilic polymer, PMMA, without surface modification of low-surface-energy materials such as fluorides. It may provide an effective way to fabricate super-hydrophobic surfaces from broad hydrophilic polymers.

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doi:10.1016/j.polymer.2007.10.038

2. Experimental section

A mixture of PMMA ($M_w = 93.9$ kg/mol, $M_w/M_n = 1.82$) and polystyrene (PS, $M_w = 194.9$ kg/mol, $M_w/M_n = 2.25$) (PS/PMMA = 70/30, w/w) was dissolved in tetrahydrofuran (THF) to form a 5 wt% solution. Polymer film was made by spin-cast the solution on glass slide by ~2000 rpm at room temperature. Then it was exposed to enough cyclohexane at 70 °C for 20 min. Samples were all characterized after storage in a clean chamber for 12 h, or specified.

The surface morphology was characterized by scanning electron microscopy (SEM, Hitachi JEOL JSEM-6700F, 3.0 kV, Japan). The film and its surface chemical composition were characterized via infrared spectroscopy (FT-IR, BRUKER EQUINOX 55) and X-ray photoelectron spectroscopy (XPS, VG Scientific ESCALab220i-XL), respectively. The contact angles were measured on Contact Angle System (OCA20, Dataphysics Co., Germany).

3. Results and discussion

Cyclohexane is a solvent for PS and non-solvent for PMMA. The as spin-cast film was transparent and turned to translucent after subjected to the treatment with warm cyclohexane, indicating the possible formation of micro-structured in the film by removing of PS phase. FT-IR spectrum shows that PMMA is the only component of the film after treated in 70 °C cyclohexane for 20 min (Fig. S1) [27]. While PMMA is a hydrophilic material with water contact angle (CA) of merely 67.8 ± 1.4° (CA < 90°) on its smooth surface, the treated film is super-hydrophobic with the water CA as high as 154.3 ± 3.9° (Fig. 1).

The surface morphology of the porous film observed by SEM is shown in Fig. 2. It is indicated that the film holds a porous structure. The domains are from tens of nanometers to several micrometers. The final surface morphology is determined by the phase separation of the as spin-cast film and selective solvent treatment. The phase separation of the as spin-cast film is affected by a number of factors, such as molecular weight and distribution, blend composition, solvent and evaporation rate, solution concentration and substrate affinity, etc. [21–26]. Polymers with narrow molecular weight distribution are often used in the phase separation morphology studies in order to make clear the molecular weight affection or to obtain uniform structures. To demonstrate the low-cost and large-area fabrication of super-hydrophobic film in our experiment, commercially available PS and PMMA were adopted and the experimental parameters have been optimized according to the films' hydrophobicity.

THF is a better solvent for PS than for PMMA [24,26]. In the processing of spin-cast, with the evaporation of solvent, PMMA phase was quickly depleted from the solvent. Because of its lower weight fraction in the blend, PMMA may form micro/nano-particle dispersed in the PS-rich solution. With further evaporation of solvent, the PMMA particles necked and aggregated leading to the micro/nano-phase separated blend film. The phase morphology of the as-prepared film is not in thermodynamic equilibrium because of the quick evaporation of the solvent. The PS-rich phase still contains some amount of PMMA, and PMMA-rich phase also contains some amount of PS. The surface of the as spin-cast blend film is not very smooth observed by SEM. It generally agrees with the literature that such blend film typically exhibits a lateral phase morphology varying upon the preparation parameters [24,26]. The observation of SEM of blend films treated by selective solvent with different period of times (Fig. S2 in Supporting materials) shows that when exposed to a warm cyclohexane, PS was gradually dissolved away, and the porous PMMA film was formed. The proposed process for the porous film formation is illustrated in Fig. 3.

It has been known that surface roughness plays a very important role in wettability. The most accepted theories are Cassie model and Wenzel model [14]. The Cassie model should support very hydrophobic materials that at least with the intrinsic water CA above 90°. It can be expressed as:

$$\cos\theta_r = f_1 \cos\theta - f_2$$

where θ is the intrinsic CA; θ_r is the CA on a rough surface with the same material; f_1 and f_2 are the fractional interfacial areas of the solid material surface and the trapped air, respectively. The relationship between surface roughness and contact angle for slightly hydrophobic material (θ just above 90°) and hydrophilic material are commonly described with Wenzel equation:

$$\cos\theta_r = r \cos\theta$$

where r is the roughness factor. This equation indicates that when θ is smaller than 90°, θ_r decreases with increase of the surface roughness. If θ is higher than 90°, θ_r will increase

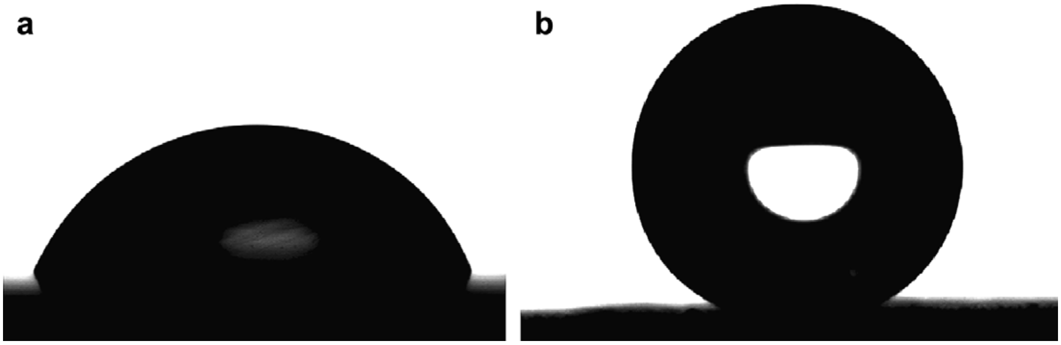

Fig. 1. (a) Water droplet on a pure flat PMMA film with CA of 67.8 ± 1.4°; (b) water droplet on the warm cyclohexane treated film with CA of 154.3 ± 3.9°.

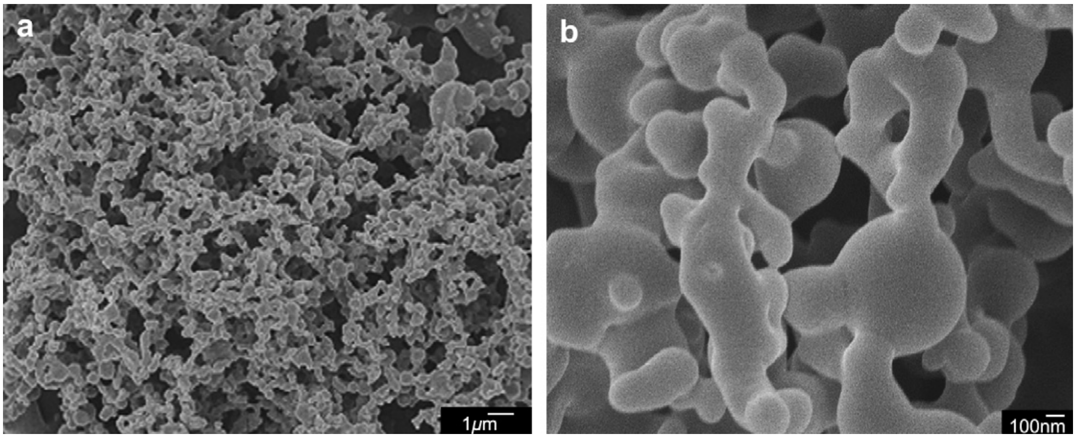

Fig. 2. SEM images of the as-prepared porous film with different magnifications. The film is made by spin-cast and selective solvent treatment.

with the roughness increase. That is, a rough surface made by material with intrinsic water CA higher than 90° should be more hydrophobic even super-hydrophobic, whereas a rough surface made by material with water CA lower than 90° should be more hydrophilic even super-hydrophilic. However, the porous PMMA film in present experiment was super-hydrophobic. If the water droplet set on the surface by Wenzel model, it should show very high sliding angle or even be pinned [14c]. The sliding angle measured for the porous film was ∼22°. That is far from Wenzel model but more close to Cassie model.

To understand this unconventional result, both surface morphology and surface composition, the two main factors governing the surface wettability, are considered. XPS was used to determine the film surface chemistry. The detection angle in the experiment was 15°, which could give valuable information of the conformation of the macromolecules at the surface. Fig. 4(a and b) illustrates the C 1s spectra of the porous film and the pure flat PMMA film, respectively. These spectra are fitted by a combination of Gaussian peaks. The C 1s spectra are resolved into three components with different bonding states, and the corresponding relative peak parameters of the fitted peaks are given in Table 1. The values in the last column of the table denote the ratio of carbon atoms in hydrophobic groups (C–C and C–H) to that in hydrophilic groups (C–O and O–C=O) on the surface. The data indicate that the percentage of hydrophobic groups on the porous micro-, nano-structured film is greater than that of the untreated pure flat PMMA film.

We wondered whether the flat pure PMMA film would also change its surface chemistry or wettability when subjected to the same process as that of the porous PMMA film. So the spin coated PMMA film was also treated by 70 °C cyclohexane for 20 min. The SEM image shows that the surface remained flat, but the CA of the treated film increased from 67.8° to 87.9° (Fig. S3 in Supporting material). The surface C 1s spectrum and the corresponding relative peak parameters of fitted peaks are shown in Fig. 4c and Table 1. The XPS data show an increase ratio of C 1s in hydrophobic groups after the treatment. These results suggest that group reorientation may occur

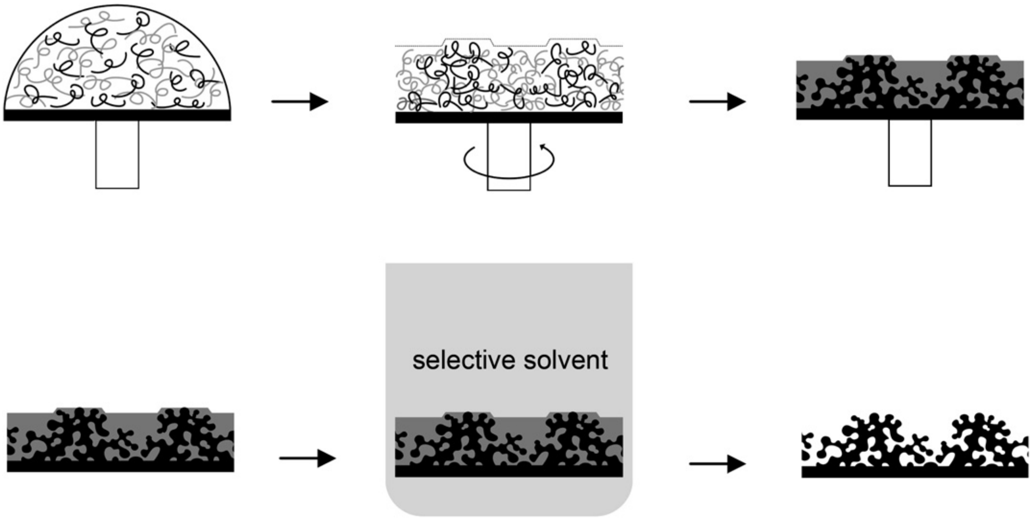

Fig. 3. Proposed mechanism of formation of the super-hydrophobic porous film. PMMA and PS correspond to black and gray, respectively. Initially, both polymers dissolve in the THF and form one phase. During spin-cast, phase separation occurs and, after evaporation of the solvent, micro- and nano-phase morphology forms. The blend film is then exposed to the selective solvent for PS and a porous PMMA film is obtained.

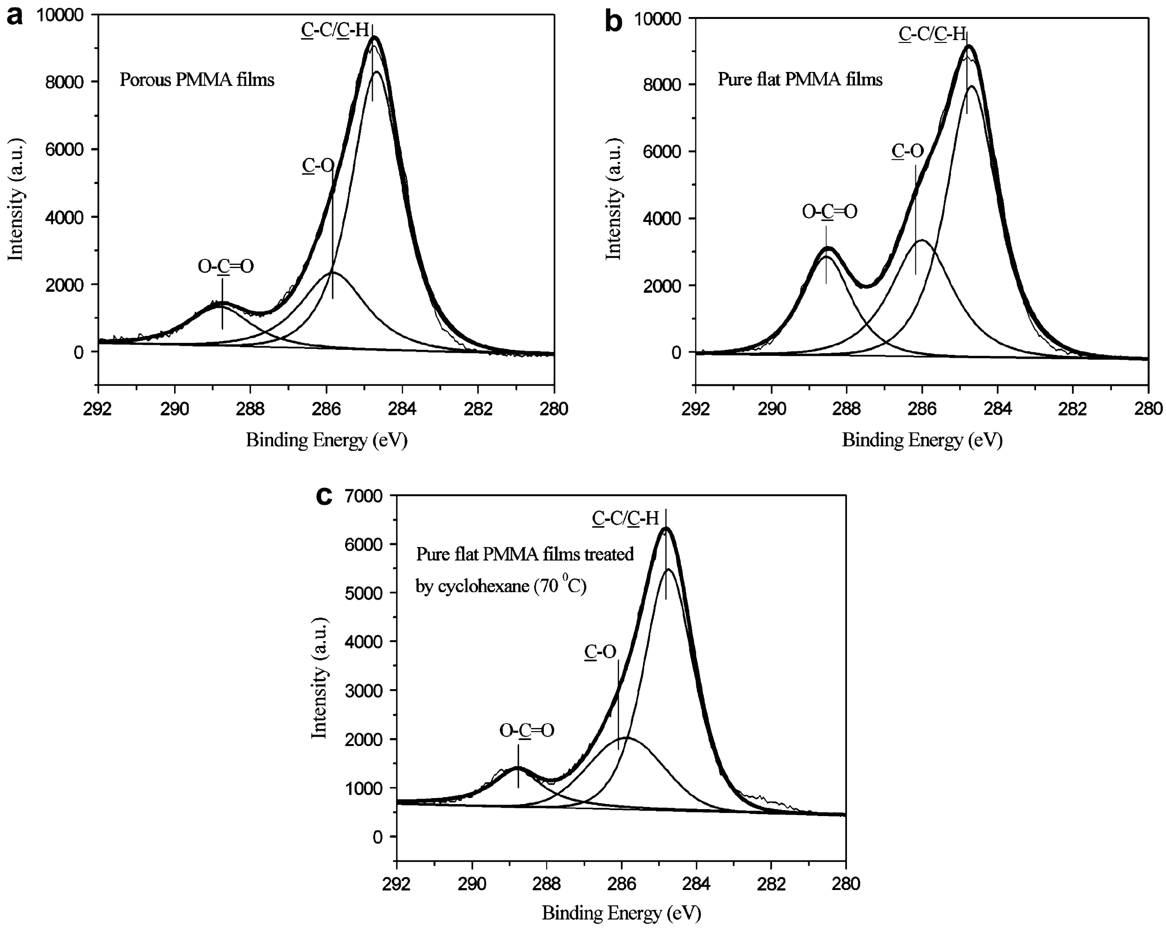

Fig. 4. XPS (15°) C 1s core spectra of (a) the porous micro-, nano-structure PMMA film; (b) the pure flat PMMA film; (c) film b treated with cyclohexane for 20 min at 70 °C.

during the cyclohexane treatment. The porous micro- and nano-structured film gives the highest ratio of carbon atom in hydrophobic groups. It is a reasonable result when both roughness (high surface area ratio) and group reorientation are considered. In the process of reorientation, some hydrophobic groups that sited below the surface moved onto the surface. Meanwhile, some hydrophilic groups that originally exposed to the air rotated underneath the surface. Fig. 5 illustrates the proposed mechanism.

The reorientation should be attributed by the self-adaptation of the polymer chain to minimize its surface free energy in heated cyclohexane, which was far from accomplishment in the quick film forming procedure. The polymer chain and groups were frozen at room temperature in the air. When treated by heated cyclohexane, the higher temperature and the hydrophobic selective solvent can promote the reorientation at the surface, even at temperature lower than its bulk glass transition temperature (T_g) [28]. Of course, it may take

Table 1
C 1s XPS (15°) parameters for pure flat PMMA film, pure flat PMMA film treated with cyclohexane at 70 °C and porous micro-, nano-structure film

Sample	C 1s	Binding energy (eV)	Peak area (%)	Ratio of (*C*−C + *C*−H) to (*C*−O + O−*C*=O)
Pure flat PMMA film	*C*−C/*C*−H	284.7	53.6	1.16
	C−O	286.0	27.7	
	O−*C*=O	288.5	18.7	
Pure flat PMMA film treated with cyclohexane at 70 °C	*C*−C/*C*−H	284.8	65.2	1.88
	C−O	285.9	25.1	
	O−*C*=O	288.8	9.7	
Porous micro-, nano-structure PMMA film	*C*−C/*C*−H	284.7	66.1	1.95
	C−O	285.8	22.8	
	O−*C*=O	288.8	11.1	

Carbon atoms contributed to the signal are italicized.

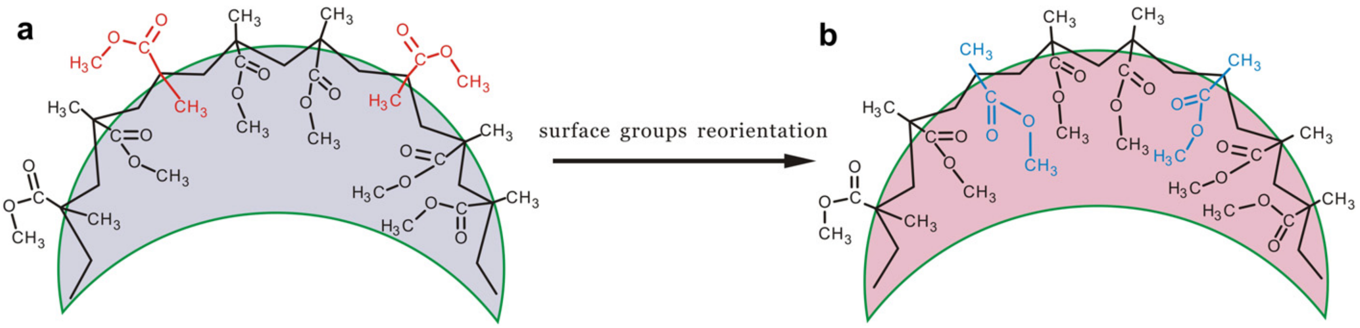

Fig. 5. Scheme of the different conformations of PMMA chain on the surface: (a) before and (b) after group reorientation. After the treatment, some comparative hydrophilic ester groups on the surface change their sites with CH_3 groups' undersurface. Most of the methyl groups are exposed outside the surface, while most hydrophilic ones are buried inside the surface.

longer time for the reorientation to occur than that near or above the T_g. In our experiments, the reorientation took ∼20 min to reach a stable state kinetically.

One may wonder how if the film is treated by a hydrophilic solvent, such as water. If the mechanism works, could it then become more hydrophilic? It has been reported that amphiphilic block polymers can respond to water and rearrange the block chain on the surface, thus the hydrophilicity altered [29]. Our mechanism can be considered similar to that of the block polymers, but with much smaller range of hydrophilic/hydrophobic blocks. Experiments showed that when the porous PMMA film was subject to water treatment (70 °C, 20 min, cooled in water), the film did become more hydrophilic. But the hydrophilicity declined with time, which was similar to that of amphiphilic block polymers for the time resolved rearrangement. Upon drying in room temperature for several hours, the water contact angles then kept almost unchanged. When measured after 12 h, the CA was $105.7 \pm 6.9°$ (Fig. S4 in Supporting material). This phenomenon gives a support to our mechanism from another aspect.

4. Conclusions

In conclusion, super-hydrophobic PMMA film with micro- and nano-structured surface was prepared effectively via phase separation and selective solvent method. Reorientation of the surface hydrophobic and hydrophilic groups in polymer chain occurred during the process. It is proposed that the cooperation of the micro-, nano-structure and the surface group reorientation leads to the super-hydrophobicity. This work shows that when super-hydrophobicity is needed, it is still possible to take advantage of high performances of hydrophilic polymers. This method is well repeatable, low-cost and has potential for practical application. The significance of this process also lies in that it will greatly broaden the range of materials that can be used for the fabrication of super-hydrophobic films.

Acknowledgement

This work is supported by the NSFC (grants 50573082, 20774101) and CMS-CX200603, ICCAS.

Appendix. Supporting material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2007.10.038.

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