Variable Responsive Wettability Films via Electrospinning Induced by Solvents

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Three kinds of interesting distinct wettability films are fabricated by a facile electrospinning technique. The films are composites of poly(N-isopropylacrylamide) and polystyrene but different precursor solvents. By taking advantage of the conformational changes of poly(N-isopropylacrylamide) chains and polystyrene chains in different solvents, the films exhibit responsive wettability variation to temperature.

1. Introduction

Smart interfacial materials with special wettability have attracted considerable attention in recent years due to their importance for both fundamental research and practical applications [1–4]. Fruitful achievements have been proposed in many areas, for example, superhydrophobic surfaces used for self-cleaning and low-adhesion [5, 6] and superhydrophilic surfaces used for antifouling and biomedical devices [7]. Furthermore, special wettability surfaces that can respond to external environment stimuli (e.g., temperature, light, pH, electrical field, solvent, and magnetic field) [8–13] have been reported through various methods, such as sol-gel method, the plasma method, template method, electrospinning method, surface-initiated atom-transfer radical polymerization, hydrothermal approach, self-assembled monolayers, electrochemical deposition, and layer-by-layer technique [14–20]. Nevertheless, most of the smart surfaces fabricated are still limited to laboratory. With the unceasing in-depth exploration and consideration of these functional materials, it is of particular important to develop a facile method and manufacture on large scale.

Electrospinning has been widely recognized as an efficient and promising technique of preparing polymer micro/nanofibers in recent years [21, 22]. Researchers found that the structure and property of electrospinning fibers can be influenced by many factors, including polymers’ solubility, molecular weight, solvent, the solution properties (e.g., viscosity, elasticity, conductivity, and surface tension), and ambient parameters (e.g., temperature, humidity, and air velocity) [23–27], while it is well known that the solvent is an important factor affecting the morphology of fibers. Examples include that Megelski et al. investigated the influence of different polymer/solvent systems on the fiber micro-/nanoporous surface morphology [24]. As far as mentioned above, many researches have been interested in the influence of polymer/solvent on the fiber surface morphology in the process of electrospinning; few people pay attention to the property of the fiber surfaces. In addition, heterogeneous materials are attractive because they may endow new function different to the intrinsic properties of two original materials. Herein, we designed and fabricated poly(N-isopropylacrylamide) (PNIPAAm)/polystyrene (PS) composite films with various wettability via electrospinning by using different precursor solvents. By taking advantages of distinct conformational changes of PNIPAAm chains and PS chains in different solvents, variable responsive wettability films have been successfully realized. The water contact angle (CA) of the PNIPAAm/PS composite films with N,N-dimethylformamide (DMF) or dichloroethene (CH₂Cl₂) precursor solution is completely different. The as-prepared PNIPAAm/PS composite film which is formed from DMF...
precursor solution showed superhydrophilicity both before and after increasing temperature. Inversely, the as-prepared PNIPAAm/PS composite film which is formed from CH$_2$Cl$_2$ precursor solution showed superhydrophobicity both before and after increasing temperature. Interestingly, in a proper proportion of PNIPAAm and PS, the water CA of the composite films in which the solvent is tetrahydrofuran (THF) in precursor solution could switch between superhydrophobic and superhydrophilic when changing the temperature. Distinct conformation of PNIPAAm chains and PS chains in different precursor solvents results in various wettability via electrospinning. It is important for the transformation of polymeric precursor solution into fibers during the process of electrospinning.

2. Experimental

2.1. Preparation of Polystyrene (PS) Films. PS (homopolymer, $M_w = 230,000$, Aldrich) was dissolved in solvents by stirring for 4 h to form 10 wt% transparent solution. The solvents are DMF, CH$_2$Cl$_2$, and THF (A.R.), respectively, which were purchased from Beijing Yili Fine Chemical Co., Ltd. About 2 mL of the precursor solution was placed in a 5 mL syringe equipped with a blunt metal needle of 0.7 mm inner diameter. The solution feed rate is about 0.5 mL/h. The needle was connected to a high voltage generator, and a grounded metallic plate covered with a sheet of aluminum foil served as a collecting substrate. The distance between the needle tip and collector was 10–20 cm, and the voltage was set at 15–20 kV.

2.2. Preparation of PNIPAAm/PS Composite Films. Preparation of PNIPAAm/PS composite films was similar to that of PS film. The PNIPAAm (poly(N-isopropylacrylamide), Mn = 20000–25000, Aldrich) and PS were mixed and dissolved in DMF, CH$_2$Cl$_2$, and THF, respectively, and stirred for 4 h. The proportion of PNIPAAm, PS, and solvent is 2:10:90 (PNIPAAm/PS/solvent).

2.3. Characterization. The morphology and structure features of the composite films were characterized by field emission scanning electron microscopy (FE-SEM) (JEOL JSM-6700F) at 3.0 kV. Contact angle was measured on a data-physics OCA20 contact angle system at ambient temperature. The temperature was controlled by a superthermostat (Julabo F25, Germany). Water droplet (about 2 $\mu$L) was dropped carefully onto the samples. The average CA values were obtained by measuring five different positions of the same sample.

3. Results and Discussion

The PS films were prepared by electrospinning with a variety of PS/solvent solutions. Firstly, we prepared film I from
10 wt% PS/DMF solution by electrospinning. The typical filed emission scanning electron microscopy (FE-SEM) image of film I is shown in Figure 1(a). The numerous nanofibers with spindle beads are randomly oriented on the substrate which displays a network structure. Then, we investigated the wetting properties of film I. Film I is hydrophobic with a water CA of 140 ± 4° (inset of Figure 1(a)) which is much higher than the plat PS film owing to the rough structure of the as-prepared PS film. This result is corresponding to our previous work [18]. Afterwards, films II and III were fabricated from a 10 wt% solution of PS in CH$_2$Cl$_2$ and THF by the similar electrospinning process. Figure 1(b) shows the SEM image of film II which exhibits hierarchical structure with nanofibers and microparticles over the whole substrate. Figure 1(c) shows the SEM image of film III which displays numerous microparticles and a few nanofibers. We measured the wettability of the films with water CA of 144 ± 4° and 144 ± 3°. These results show that the as-prepared electrospun PS films are all hydrophobic because of the rough surface and hierarchical structure. The minor difference in surface structure is due to the influence viscosity and volatility with polymer in different solvents. Also, it will not affect the intrinsic hydrophobic-hydrophilic properties of original materials. Therefore, in order to study the facility we set the same weight proportion of the polymeric precursor solution during the experiment below.

Then, PNIPAAm/PS/solvent solution (2:10:90 w/w/w) was used to fabricate composite films IV, V, and VI in which the solvents are DMF, CH$_2$Cl$_2$, and THF, respectively. Figures 2(a), 2(b), and 2(c) show the typical SEM images of films IV, V, and VI. The morphology of the films is not completely identical with the same polymer composition. Concretely, the nanofibers are randomly oriented on the surface of film IV which has a network structure like a spider’s web. Compared with the surface of film I, the spindle beads are instead of the numerous uniform nanofibers. It can be easily understood by the addition of PNIPAAm leading to the increase of the viscosity [19, 28]. The surface of film V (Figure 2(b)) is almost covered with nanofibers except for a few spindle beads. The microparticles in film II surface almost disappear in the surface of film V when adding PNIPAAm. Figure 2(c) is the SEM image of film VI showing numerous microspheres and nanofibers distributed densely over the surface. It is obvious that the amount of nanofibers increases compared with the SEM image of film III without PNIPAAm. Films IV, V, and VI are prepared with the same polymer composition by electrospinning from different PNIPAAm/PS/solvent precursor solutions. These SEM results show that the surface morphology is not completely uniform with the same polymer composition. The amount of the microspheres and nanofibers is distinct mainly by the reason of the viscosity of precursor solution with different
Next, the wetting properties of films IV, V, and VI were investigated. At 20°C, the water CA of the films IV, V, and VI is about 0°, 133 ± 3°, and 6 ± 5°, respectively (Figure 3). Then, the water CA is 0°, 142 ± 5°, and 152 ± 3°, respectively, when the temperature is changed to 50°C (Figure 3). Surprisingly, the change of the water CA along with increasing the temperature is completely distinct. The as-prepared film IV, which was added to PNIPAAm in PS/DMF solution, is superhydrophilic according to heating up the surface. Differently, the surface of film V from PNIPAAm/PS/CH₂Cl₂ precursor is hydrophobic along with the temperature alteration. While the water CA of the film VI from PNIPAAm/PS/THF precursor switched from 6 ± 5° to 152 ± 3°, the temperature changed from 20°C to 50°C.

It is well known that PNIPAAm is a thermo-responsive polymer which has fabricated many thermo-responsive materials by some methods [19, 29, 30]. The mechanism of the stimuli-responsive is explained by the competition between intermolecular and intramolecular hydrogen bonding below and above the lower critical solution temperature (LCST) of

Figure 3: Photographs of water-droplet shape on the PNIPAAm/PS composite films at 20°C and 50°C. (a), (b), and (c) correspond to films IV, V, and VI in which the solvent of precursor solution is DMF, CH₂Cl₂, and THF, respectively. The wettability of PNIPAAm/PS composite films prepared from different precursor solutions is completely distinct when increasing the temperature. The wettability of the PNIPAAm/PS films is both superhydrophilic and superhydrophobic and switches from superhydrophilic to superhydrophobic according to the change in the temperature when the solvents are DMF, CH₂Cl₂, and THF, respectively.

solvents and evaporation of the solution droplets during electrospinning process [23–25].
Figure 4 outlines the proposed mechanism of various wetting properties of the as-prepared electrospun films. The fabric structure of the film is mainly made from PS as a result of the majority proportion of precursor solution. While the spheres which represent PNIPAAm are distributed distinctly in various films IV, V, and VI, the chain diagram represents the idealized conformation between the PNIPAAm chain and solvent molecules in precursor solutions. As shown in Figure 4(a), DMF is a kind of familiar polar solvent and the value of polarity is 6.4. So in the mixture solution of PNIPAAm, PS, and DMF, the polar C=O and N–H groups in the PNIPAAm chain interact easily with the DMF molecules to form intermolecular hydrogen bonding. At the same time, the nonpolar C–H group in the PNIPAAm and PS tend to intertwist together. Then, in the transformation from polymer precursor solution to fibers with rapid solvent evaporation during electrospinning, the PNIPAAm chain is easily distributed on the surface of the fibers with the polar C=O and N–H groups barely. Although there are hydrophobic C–H groups of PS molecules surrounding the PNIPAAm molecules, the water drops can still move across the PS molecules and interact with C=O and N–H groups to form intermolecular hydrogen bonding. Therefore, the as-prepared film IV exhibits superhydrophilicity with the water CA of 0° at 20°C. When the temperature is changed to 50°C, the PNIPAAm chain cannot go around freely which results in the C=O and N–H groups still exhibiting the surface of the film. Consequently, the film IV is still superhydrophilic with the water CA of 0° when heating up the surface. Surprisingly, the wettability of film V from PNIPAAm/PS/CH₂Cl₂ precursor solution is completely different according to heating up the surface. The as-prepared film V is superhydrophobic both before and after increasing the temperature. It is well known that CH₂Cl₂ is a kind of nonpolar solvent and the value of polarity is 3.4. Both the C–H groups in PNIPAAm and PS will interact with CH₂Cl₂ molecular easily during electrospinning. Hence, the PNIPAAm chain is apt to shrink to form intramolecular hydrogen bonding between the C=O and N–H groups. After the process of electrospinning with rapid solvent evaporation, most of the fibers surface is occupied by hydrophobic C–H groups which accords with the water CA of 133±3°. When the temperature is raised above the LCST, the PNIPAAm chain more easily shrinks to form a compact and collapsed conformation. Thus, the film V shows hydrophobicity with the water CA of 142±5° at high temperature. Besides, the wettability of
film VI can be switched between superhydrophilicity and superhydrophobicity when changing the temperature. The polarity value of THF is 4.2 which is between DMF and CH$_2$Cl$_2$ and results in the fact that the PNIPAAm chain could distribute more freely in the PNIPAAm/PS/THF precursor solution (Figure 4(c)). Noticeably, the PNIPAAm chain could still swell and shrink freely on the surface of as-prepared film VI. So the wettability of film VI could be explained by the competition between intermolecular and intramolecular hydrogen bonding in PNIPAAm chain according to changing the temperature which have been studied in detail in our previous work [19].

Therefore, solvents play an extraordinary important role in the transformation from precursor polymer solutions to fibers which induce different physicochemical properties of the surface. In this work, the polar solvent DMF is likely to form intermolecular hydrogen bonding with PNIPAAm chain in precursor solution. The C=O and N–H groups are easily bared on the surface of the film. So the film IV is superhydrophilic both before and after increasing the temperature. Inversely, the PNIPAAm chain seems more favorable to form intramolecular hydrogen bonding when nonpolar solvent CH$_2$Cl$_2$ is used. And film V is hydrophobic when changing the temperature because most of the surface is occupied by C–H groups. The polarity of THF is between DMF and CH$_2$Cl$_2$; thus, there is no evident hydrogen bonding interaction in the PNIPAAm/PS/THF solution (Figure 4(c)). The PNIPAAm molecular could freely extend and shrink before and after increasing the temperature. The film VI could switch between superhydrophilicity and superhydrophobicity when the temperature is changed from 20°C to 50°C.

4. Conclusion

Variable responsive wettability films were fabricated by electrospinning by the result of solvents induced distinct distribution of hydrophilic groups and hydrophobic groups. Three kinds of PNIPAAm/PS films with the same polymer composition present extremely different wettability performance. The wettability of the PNIPAAm/PS films is both superhydrophilic and superhydrophobic and switches from superhydrophilic to superhydrophobic according to change in temperature when the precursor solvents are DMF, CH$_2$Cl$_2$, and THF, respectively. It could be explained by the competition between intermolecular hydrogen bonding and intramolecular hydrogen bonding in solutions with different solvents. It is the first example to fabricate composite films with same polymer composition but different properties by electrospinning. It gives us an inspiration that new functional and structure materials could be created with proper substance and solvent. It is quite important for the electrospinning research about the solvent induced factors and lays a foundation for the further application of electrospinning.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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