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Research Article

Physical Structure Induced Hydrophobicity Analyzed from Electrospinning and Coating Polyvinyl Butyral Films

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Surface wettability of a film plays a critical role in its practical applications. To control the surface wettability, modification on the physical surface structures has been a useful method. In this paper, we reported the controlling physical surface structure of polyvinyl butyral (PVB) films by different film-forming methods, spin-coating, bar-coating, and electrospinning. The wettability of these PVB films was examined, and the surface morphologies and roughness were investigated. The results indicated that coating PVB films were hydrophilic, while electrospun films were hydrophobic. The physical surface structure was the key role on the interesting transition of their surface wettability. Theoretical analyses on these results found that the coating PVB films showed different mechanism with electrospun ones. These results may help to find the way to control the PVB film surface wettability and then guide for applications.

1. Introduction

The wetting behavior of solid surfaces by a liquid as a very important aspect of surface properties has been a focused interest for a long time [1–4] and has shown a wide variety of practical applications in various fields, such as protecting clothes [5], medical care [6–8], and filtration [9]. Consequently, great efforts have been made to find the way to control the surface wettability [10–13].

According to the term biomimetic, “lotus leaves effect” indicates that the cooperation of hierarchical structures and other specific components on the natural surfaces results in the desired wettability [1–3, 14]. Moreover, from the theoretical view, such as Young’s equation [15], Wenzel model [16], and Cassie model [17], the surface roughness plays a critical role in surface wettability [18–21]. Furthermore, the rough surface is extended to porous surfaces and even micro-nano structures [22–24]. To achieve these structures, especially in film structures, several methods are developed such as solution cast and electrospinning [5–10, 19, 21].

Among various materials, polyvinyl butyral (PVB), which is characterized by high adhesion to glass, excellent mechanical strength, excellent biocompatibility, nontoxicity, and good solubility in alcohol, has been applied to many fields such as an adhesive interlayer in safety glass, wound dressing, and coating film [5–7, 10, 11]. Moreover, PVB shows both hydrophobic and hydrophilic properties due to its chemical structure with both vinyl butyral group and vinyl hydroxyl group [10, 25]. And previous study has suggested that electrospun PVB nanofibrous structures and patterns showed larger water contact angle (WCA) than that of the solution casting film [7, 10, 11]. However, these works most focus on the electrospun PVB meshes and rarely discuss the comparison of the structures between the different methods.

In this paper, we focused on the comparison of PVB films made by several methods, spin-coating, bar-coating, and

Table 1: The SWCA of the prepared PVB films by different methods.

Methods		SWCA (°)	SWCA (°)	SWCA (°)	ASWCA (°)
Concentrations/parameters		8 wt%	10 wt%	12 wt%	
	250 r/s	77.767	78.800	78.900	
Spin-coating	300 r/s	74.300	82.600	79.933	78.593
	350 r/s	76.033	82.733	76.267	
	6 μm	86.438	83.297	84.303	
Bar-coating	8 μm	81.255	82.626	81.437	83.067
	10 μm	81.093	81.360	85.796	
	15 cm	135.833	130.833	131.933	
Positive electrospinning	20 cm	132.167	133.600	129.700	132.404
	25 cm	131.667	135.400	130.500	
	15 cm	131.033	135.733	130.867	
Negative electrospinning	20 cm	128.633	135.100	133.367	131.615
	25 cm	128.300	133.233	128.267	

electrospinning. The WCAs on these films were measured and the morphologies and surface roughness of them were also examined. By analyzing these results, we want to find a way to control the surface wettability.

2. Materials and Methods

2.1. Materials. Polyvinyl butyral (PVB) (MW~100,000, Sinopharm Chemical Reagent Co., Ltd., China) was dissolved in ethyl alcohol (analytical reagent, 99%) at 8 wt%, 10 wt%, and 12 wt% firstly and then stirred for 2 h at room temperature.

2.2. Preparation of the Films. The PVB/alcohol solutions were used to produce films by spin-coating, bar-coating, and electrospinning, respectively. During spin-coating process, PVB/alcohol solutions were dripped onto cover slips (20 mm×20 mm) with 5 μl and then set on the spin-coater (KW-4A, Institute of Microelectronics of the Chinese Academy of Sciences). The spinning velocities were selected at 250 r/s, 300 r/s, and 350 r/s, and spinning time was set at 30 seconds. In bar-coating process, 10 μl PVB/alcohol solutions were dripped onto slide glasses (76 mm×26 mm), and the bars were selected with 6 μm, 8 μm, and 10 μm film thickness. For electrospun meshes, both positive electrospinning and negative electrospinning were processed. PVB/alcohol solutions were firstly loaded into syringes (5 ml) and then set on the electrospinning apparatus (DW-P303-1ACF5 (positive), DW-N303-1ACDF0 (negative), Dongwen, China), the electrospinning voltage was set at 15 kV and -15 kV, and the distances were selected at 15 cm, 20 cm, and 25 cm.

2.3. Characterization. The static water contact angles (SWCA) of the prepared films were examined by an optical tensiometer (Attension Theta, Biolin Scientific, Germany) with a 2 μL water droplet for three sites at room temperature and analysis was performed by fitting drops with a Young-Laplace formula using the Theta software. The surface roughness was also measured by optical tensiometer with 3D surface roughness module. The morphologies of the films were examined by a scanning electron microscope (SEM, Phenom ProX, Phenom Scientific Instruments Co., Ltd., China) at 10 kV, and all samples were coated with gold for 30 s before analysis. The fiber diameters were analyzed by Nano Measurer software. The Fourier transform infrared spectroscopy (FTIR) spectrums were measured by a Thermo Scientific Nicolet iN10 spectrometer.

3. Results and Discussion

To ensure the wettability of the prepared PVB films, SWCA were measured and shown in Table 1. One can find that the spin-coating and bar-coating PVB films showed hydrophilicity with SWCA <90°, while the electrospun films showed hydrophobicity with SWCA>90°, which agreed with the previous study [7, 10, 11]. Moreover, the bar-coating PVB films had larger SWCA than spin-coating ones generally. The SWCA of electrospun PVB films with positive electrospinning process is mostly larger than that of negative electrospinning. Nevertheless, as seen from Figure 1, the prepared PVB films showed similar absorption peaks, which indicated that these films had same chemical structures. It is interesting that the same material showed different wettability for its different film-forming methods.

To understand the interesting PVB film wettability, we firstly examined the morphologies of selected PVB films (10% concentration) with spin-coating 250 r/s, bar-coating 6μm, and positive and negative electrospinning with distance of 15 cm. As shown in Figure 2(a), the spin-coating PVB film showed a macroscopically relative smooth surface with SWCA 78.8°; the bar-coating film also had a smooth surface with SWCA 83.3° (Figure 2(b)). Both smooth films showed hydrophilicity. Meanwhile, both the positive and negative electrospun PVB films showed porous rough surfaces, as can be found in Figures 2(c) and 2(d), and the SWCA were 130.8° and 135.7°, respectively. Both the porous rough electrospun films showed hydrophobicity. According to these results, it seems that the surface roughness determined the wettability of the films.

For further investigation, we examined the roughness of the selected films, as shown in Figure 3. It is strange

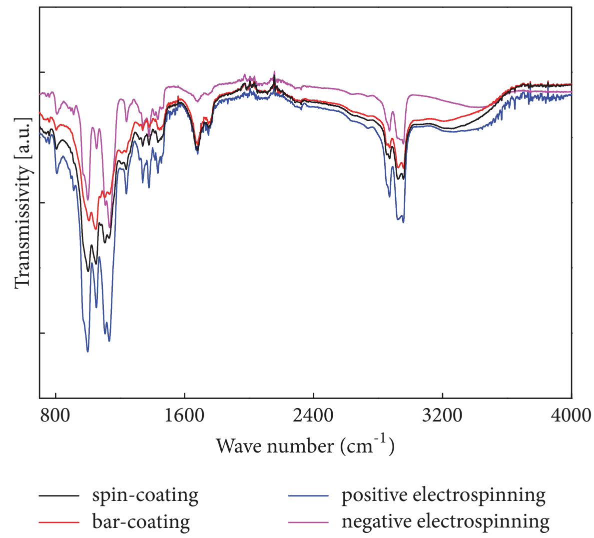
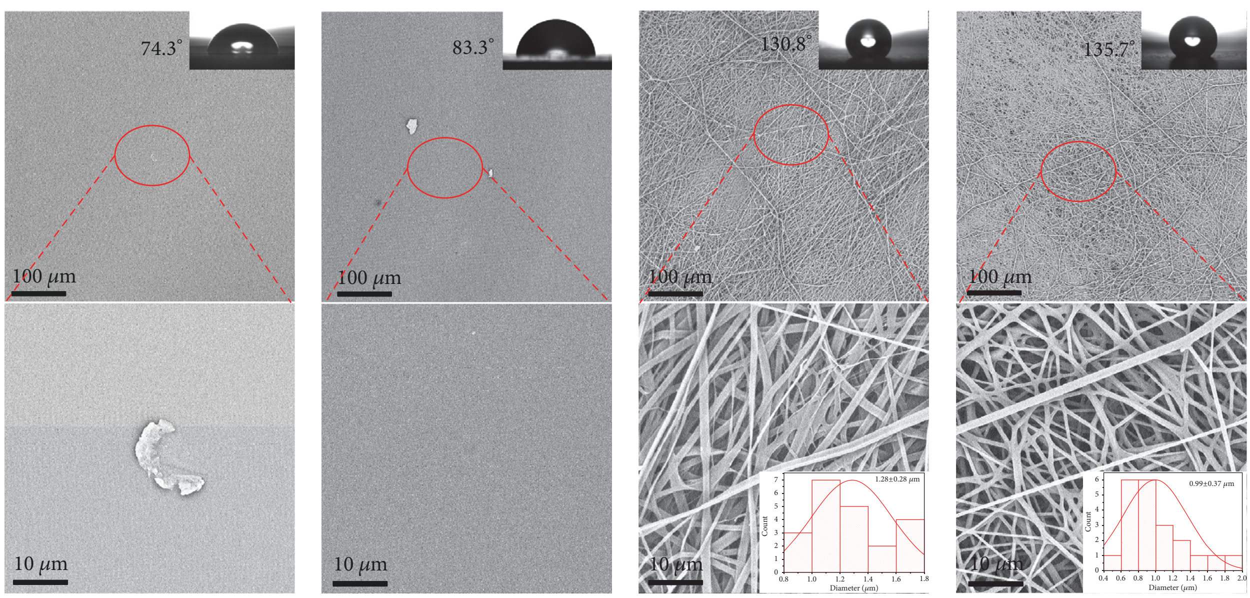


FIGURE 1: FTIR spectra of PVB films made by different methods.



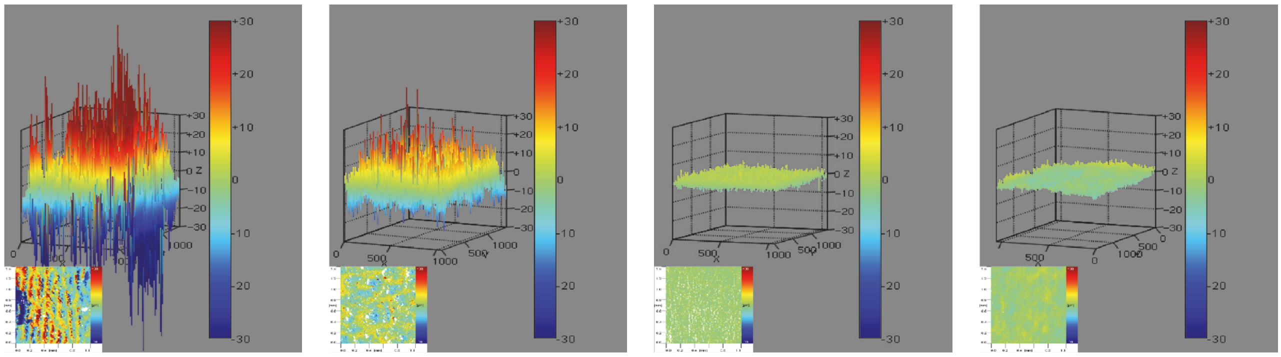
(a) (b) (c) (d)

FIGURE 2: SEM images of the PVB films made by spin-coating 250 r/s (a), bar-coating 6 μm (b), positive electrospinning 15 cm (c), and negative electrospinning 15 cm (d). The upper inset images showed the water droplet onto these films, and the lower inset images showed the electrospun fiber diameter distributions.

that the macroscopical smooth surfaces shown in Figure 2 have higher roughness than the electrospun films. In our opinion, this case may result from the different surface structures of the films that coating films showed relative dense surface structure, while electrospun films had porous surface structure, as can be seen in Figure 2. For the hydrophobilic coating PVB films [seen in Figures 3(a) and 3(b)], bar-coating ones showed higher roughness than the spin-coating ones with r=3.715>2.351, where r is the factor of the surface roughness. According to the Wenzel model [1, 22],

$$\cos\theta' = r\cos\theta_c, \quad (1)$$

where $\theta_c < 90^\circ$, the larger the factor of roughness r is, the smaller θ' will get, and the increasing roughness will make the film more hydrophilic. The case in coating PVB films followed the Wenzel model; consequently the bar-coating films with more roughness showed smaller SWCA than spin-coating ones. Meanwhile, for the electrospun films, the porous and micro-nano surface structures made the Wenzel model not work. As suggested in Figures 3(c) and 3(d) and Figures 2(c) and 2(d), the positive electrospun PVB film with more roughness (r=1.106) had smaller SWCA (130.8°) than that of negative electrospinning PVB film (r=1.076, SWCA 135.7°). In this case, the Cassie model, which gives a composite state



(a) (b) (c) (d)

Figure 3: 3D surface roughness of the prepared PVB films under spin-coating 250 r/s (a), bar-coating 6 μm (b), positive electrospinning 15 cm (c), and negative electrospinning 15 cm (d). The inset images showed the 2D surface roughness of these films.

that liquids are assumed to only contact the solid through the top of the asperities and air pockets are assumed to be trapped underneath the liquid [1, 22], may be considered; the function can be expressed as

$$\cos\theta' = -1 + f_s\left(1 + r\cos\theta_c\right), \quad (2)$$

where f_s are the area fractions of the solid on the surface. From (2), one can find that the smaller f_s is, the more hydrophobicity will be obtained. Specifically to the electrospun PVB films, the smaller the fiber diameter is, the smaller f_s will be achieved, and then higher hydrophobicity will be shown [5, 7, 10, 11]. From lower inset images in Figure 2, we can obviously find that negative electrospun PVB fibers had smaller diameters and less uniform and consequently exhibited higher SWCA.

4. Conclusions

In conclusion, we have prepared several kinds of PVB films through spin-coating, bar-coating, and electrospinning. The FTIR spectra suggested that these films have the same chemical structures. Meanwhile, these films showed different wettability that coating films were hydrophilicity and electrospun films were hydrophobicity. SEM images indicated that the different films showed different physical surface structures, which may introduce the different wettability. Further investigation on the surface roughness confirmed that the wettability of coating films obeyed the Wenzel model, while the electrospun films agreed with the Cassie model. These results may help to understand the mechanism of the PVB films and then guide for its practical application.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

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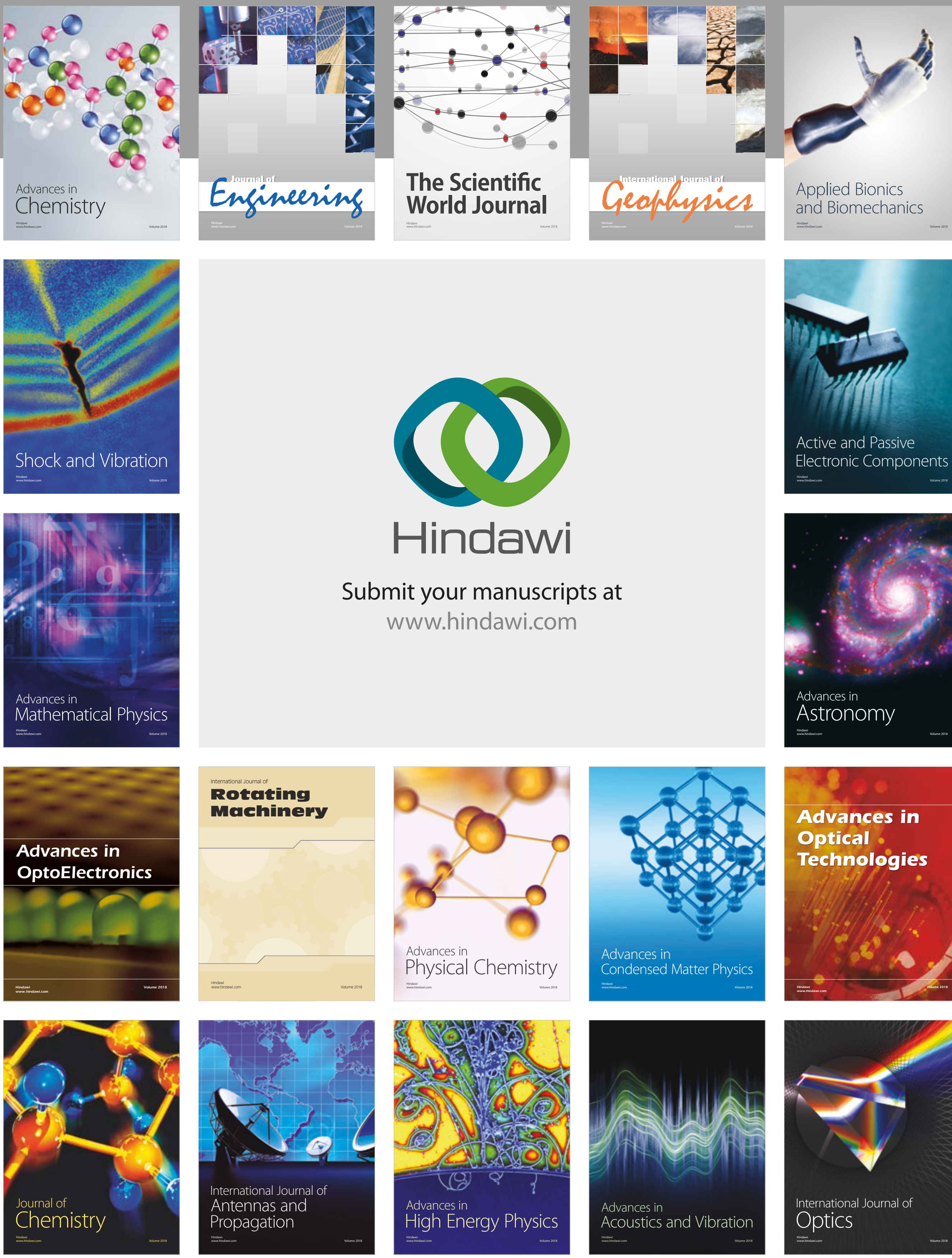
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