Regular Aligned Porous Waterborne Polyurethane Composite Obtained by a Directional Freeze-Drying Process

Hong He[1,2], Jiale Xie[1,2,*], Jianfeng Tang[1] and Tingting Zhou[1]
[1] Faculty of Materials and Energy, Southwest University, Chongqing 400715, People's Republic of China
[2] Institute for Clean Energy & Advanced Materials, Faculty of Materials and Energy, Southwest University, Chongqing 400715, P.R. China
[*]Corresponding author

Abstract—**Regular aligned porous waterborne polyurethane (WPU) composites were simply obtained by a directional freeze-drying process in the study. The morphology of the WPU composite can be tailored with different concentration of the WPU dispersion and freezing rate. Very regular aligned pores along the immersion direction can be obtained when the concentration of WPU dispersion is 20 wt.%. In addition, the periodicity of the aligned pores can be tuned by the freezing rate such as the temperature of cryogenic liquid or immersing velocity. The periodicity of the aligned pores increases when the immersed velocity decreases and the temperature of the cryogenic liquid increases. With the theory of Mullins-Sekerka, the periodicity of the aligned pores can be accurately calculated.**

Keywords-directional freeze-drying process; concentration; freezing rate; regular; aligned pores; waterborne polyurethane

I. INTRODUCTION

Porous polymeric materials are typically produced either by thermal- or solvent-induced phase-separation process [1-3]. And, materials with aligned porous structures have potential applications in catalysis, chemical sensors, and tissue engineering [4,5]. Controlled formation of these structures with different pore size is important because the structures have a great influence on their properties.

The directional freeze-drying process, based on freezing of water slurries and subsequent freezing-drying steps, has proved to be an easily-controlled route to fabricate aligned porous materials with two-dimensional surface patterns or three-dimensional monolithic structures [6,7]. This novel process does not involve any chemical reaction and can avoid potential complications associated with by-products or purification procedures[8-10]. Nowadays, the directional freeze-drying process has been used to prepare aligned porous materials such as chitosan/vacuum-stripped grapheme, poly(3,4-ethylenedioxythiophene), poly(styrenesulfonate), poly(vinyl alcohol), etc[4,11,12]. Although porous poly(vinyl alcohol) composite obtained by a directional freeze-drying process has been reported recently[3,4,5], regular aligned porous waterborne polyurethane composite obtained from waterborne polyurethane (WPU) dispersion by a directional freeze-drying process have not been investigated yet. We report herein the influence of concentration and freezing rate on the morphology of the WPU composite obtained by a directional freeze-drying process.

II. EXPERIMENTAL

The main materials used in the study were waterborne polyurethane (WPU) dispersion. The WPU dispersion with the concentration of 40 wt.% was Bayhydrol PR240, a commercial product of Bayer Group Corporation, Germany. And, distilled water was added into Bayhydrol PR240 to obtain different concentrations of WPU dispersion. To obtain homogeneous dispersion, the dispersion was mixed by high speed stirrer for 30 minutes and followed by an ultrasonic vibration for about 1 minute. Then the dispersions were put into a glass container with flat bottom and slowly immersed into the cryogenic ethanol or liquid nitrogen at a fixed velocity. The method of fabricating the device by the directional freeze-drying process was accorded to the reference [9]. When the dispersions were frozen completely, the solid specimens were then sublimated at low pressure for 24 hours with a LGJ-10D freeze-dryer produced by Four-ring Science Instrument Plant Beijing Co., Ltd. (China). To observe the microstructure of the WPU composite, the obtained specimens were frozen in liquid nitrogen for one hour, and then were quickly impact fractured parallel to the aligned direction. The freshly broken surfaces were sputter coated with gold and then observed by a Hitachi S-3500N scanning electron microscopy.

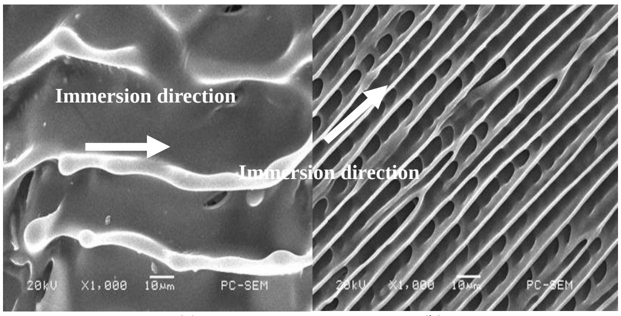
III. RESULTS AND DISCUSSION

A. *Effect of Concentration on the Morphology of the WPU Composite Obtained by A Directional Freeze-Drying Process*

1) liquid nitrogen used as the cryogenic liquid by a directional freeze-drying process

Morphology of the specimen fractured along the immersion direction using different concentrations of WPU dispersion is shown in Figure 1. The velocity immersed into liquid nitrogen was 4 mm/min. Figure 1 shows that, when the concentration of the WPU dispersion was 5 wt.%, there was only a trend to orientate along the immersion direction and no aligned pores can be seen in the photograph [Figure 1 (a)]. But when the concentration of the WPU dispersion increased to 20 wt.%, the morphology shown in Figure 1 (b) was very regular aligned pores along the immersion direction, and, the average width of these pore channels was about 8 μm, the thickness of the pores' wall was about 2 μm. The morphology of the WPU composite with regular aligned pores was different from the poly (vinyl alcohol) composites obtained by a directional freeze-drying process reported in the reference [5, 13]. Compared with the poly(vinyl alcohol) composites obtained by a directional freeze-drying process with the same processing condition, the width of the pores' channels and thickness of the walls were similar to that of poly(vinyl alcohol) composites, but there were no pillars formed between the pore channels.

Typically, a directional freeze-drying process consists of the freezing, storage in the frozen state for certain time, and defrosting of low- or high-molecular-weight precursors, and colloidal systems which is initially either from a water solution, suspension or hydrogel[14-16]. The formation of crystalline ice causes most solutes originally dispersed in the aqueous suspension is expelled to the boundaries between the adjacent ice crystals. This is followed by sublimation of the ice by the freeze drying. This process can produce aligned pores which can be templates for scaffolds from the spaces occupied by the ice crystals [Figure 1(b)][4-6]. For a directional freeze-drying process, ice grows from the bottom and the WPU particles are excluded from the ice and aggregate between the growing ice crystals. When the freezing is completed, removal of the orientated ice by sublimation leads to forming aligned porous structure (Figure 2).



(a) (b)

FIGURE I. MORPHOLOGY OF THE SPECIMEN OBTAINED BY DIFFERENT CONCENTRATIONS OF WPU DISPERSION. THE VELOCITY OF IMMERSING INTO LIQUID NITROGEN IS 4MM/MIN. (A) 5 WT.%, (B) 20 WT.%

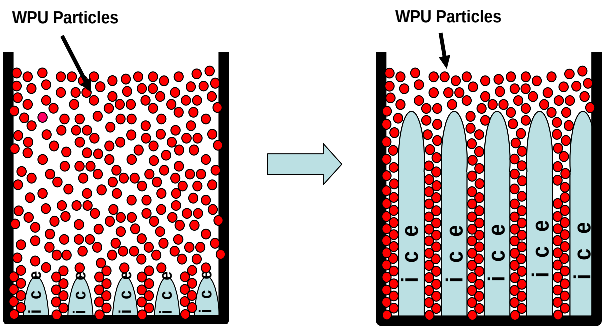


FIGURE II. SCHEME DIAGRAM SHOWING A DIRECTIONAL FREEZE-DRYING PROCESS

Figure 2 shows that the formation of aligned pores by the directional freeze- drying process resides in the ability to form ice crystals during the directional immersion of an aqueous solution/dispersion into the cryogenic liquid. For the aligned pores of poly (vinyl alcohol) composites obtained by a directional freeze-drying process, the formation of the pillars is because of the difference in the fundamental constitutional unit of the solution/dispersion compared with WPU dispersion. For a poly (vinyl alcohol) solution, it is the macromolecule chains been expelled to form aligned pores. The long macromolecules of poly (vinyl alcohol) were not easy to be expelled by the ice crystals, and some of the growing solvent crystals may be encapsulated in the concentrated solute. The pillars in the poly (vinyl alcohol) composite result from the side branches formed when the long macromolecules freeze-concentrated around the primary ice crystals.

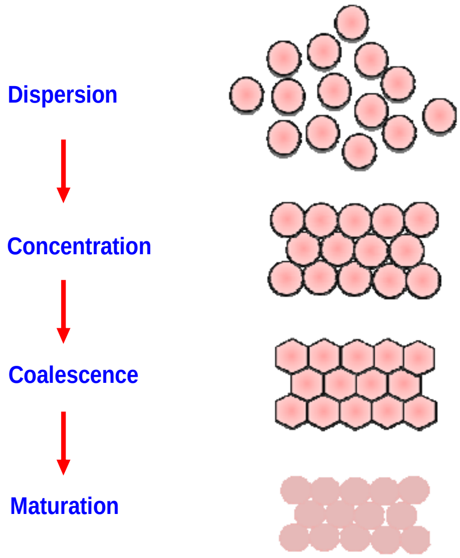


FIGURE III. THE ACCUMULATED PROCESS OF WATER POLYURETHANE DISPERSION

For the formation of the WPU composites with aligned pores by a directional freeze-drying process, the solidification process of water polyurethane dispersion is shown in Figure 3. It is not macromolecule chains, but nano-particles of WPU in the dispersion expelled by the ice crystals which results in regular aligned pores. During the directional-freeze process, the water crystal nucleus occurred homogeneously on the bottom of the container firstly, and then, grew along the direction of the temperature gradient. Simultaneously, the WPU particles which can not be taken into the ice crystal lattice were excluded and forced to concentrate at the moving freezing front. Through this process, the WPU filled with the aligned ice crystals was created. After removal of the aligned ice crystals by sublimation at low pressure, the aligned porous structure was obtained. The particles accumulated process of water polyurethane dispersions (WPU) were mainly generated by the enclosed force and adhesive force of the polar groups in the molecules. The film-forming mechanism is that the polymer particles assemble together to form a film due to the evaporation of water and solvent, not the solidification of –OH and –NCO. These factors result in the regular aligned pores of the WPU composites.

2) The cryogenic ethanol at -70℃ used as the cryogenic liquid

Morphology of the specimen fractured along the immersion direction using different concentration of WPU dispersion immersed into cryogenic ethanol at -70℃ is shown in Figure 4. The immersing velocity was also 4 mm/min. The morphology in Figure 4(a) & (c) shows that,when the concentration of the WPU was 10 wt. % or 40 wt. %, there was only a trend to orientate along the immersion direction. However, when the concentration of the WPU dispersion was 20 wt%, the morphology shown in Figure 4(b) was very regular aligned pores along the immersion direction, and the average width of these pore channels was about 24 µm and the thickness of the pores' wall was about 3 µm. The average width of the porous channels and thickness of the pores' wall were much larger than the width and thickness when immersed in liquid nitrogen with the same condition [Figure 1(b)].

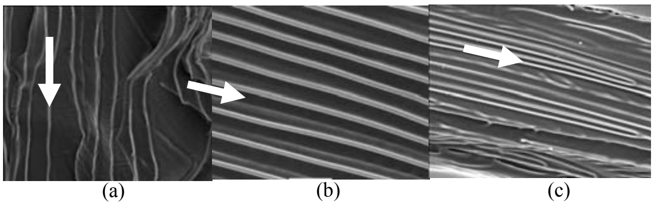


FIGURE IV. MORPHOLOGY OF THE SPECIMEN WITH DIFFERENT CONCENTRATIONS OF WPU DISPERSION IMMERSED INTO -70℃ ETHANOL. THE IMMERSING VELOCITY IS 4MM/MIN. (A) 10 WT.%, (B)20 WT.%, (C)40 WT.%

The very low concentration of WPU dispersion, which means the content of WPU solute was very low, would result in that the aligned pores can not form continuously. There was only a trend to orientate in the morphology of 10 wt. % WPU dispersion. On the other hand, when the concentration of WPU was much higher (such as 40 wt. %), the resistance of WPU solute expelled by the ice front increased, and this resulted in that the ice crystals could not be formed completely during the solidification process, and eventually the regular aligned pores can not be formed. In this way, the morphology can be tailored by adding different contents of solute in the solution.

B. Effect of the Freezing Rate on the Morphology of the WPU Composite Obtained by a Directional Freeze-Drying Process

Figure 4(b) shows that the morphology of the specimen obtained by the WPU dispersion with 20 wt. % solute was very regular aligned pores along the immersion direction. The average width of these pore channels was about 24 µm, and thickness of the pores' wall was about 3 µm. The average width of the pore channels and thickness of the pores' wall were larger than the width and thickness when immersed into liquid nitrogen [Figure 1(b)]. This means that the temperature of cryogenic liquid can affect the average width of the pore channels and thickness of the pore's wall.

To explore the effect of temperature of the cryogenic liquid on the average width of the pore channels and thickness of the pores' wall, the WPU dispersion with the concentration of 20 wt. % was immersed into the cryogenic ethanol with the velocity of 1 mm/min at different temperatures. The morphology of the specimen is shown in Figure 5.

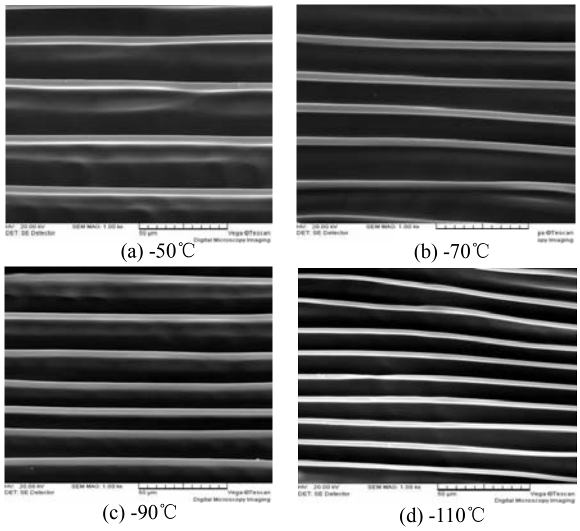


FIGURE V. MORPHOLOGY OF THE SPECIMEN IMMERSED INTO CRYOGENIC ETHANOL AT DIFFERENT TEMPERATURE. THE LOWERING VELOCITY IS 1MM/MIN

Figure 5 shows that, when the concentration of WPU was 20wt.%, all the morphology of specimen immersed into cryogenic ethanol separately at -110, -90, -70, -50℃ with the velocity of 1 mm/min by a directional freeze-drying process were regular aligned pores. In fact, all the morphology of specimen immersed into cryogenic ethanol separately at -110, -90, -70, -50℃ with the velocity of 4, 7 or 10 mm/min were also regular aligned pores in our results. In addition, the periodicity of the aligned pores, which is defined as the sum of the width of pore channels and thickness of the pore's wall, at different immersing velocity and temperature of cryogenic liquid is shown in Figure 6. It shows that the periodicity of the aligned pores increases when the immersed velocity decreases or the temperature of the cryogenic liquid increases.

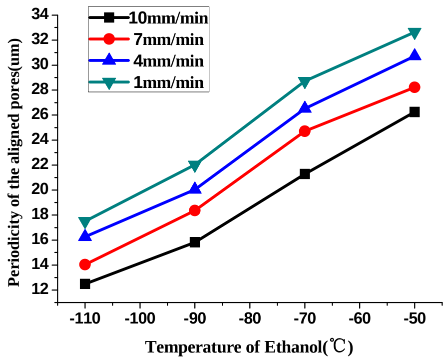


FIGURE VI. THE PERIODICITY OF THE ALIGNED PORES IMMERSED INTO CRYOGENIC ETHANOL AT DIFFERENT TEMPERATURE OR IMMERSING VELOCITY

The aligned pore structure can be explained by the phase separation that occurs during the freezing process. For WPU dispersion, the regular aligned pores were formed by the WPU particles expelled by the ice crystals. The ice crystals can more easily grow up with the lower immersing velocity or higher temperature of cryogenic liquid because of the lower temperature gradient[17]. This is the reason why the periodicity of the aligned pores increases when the immersed velocity decreases or the temperature increases. And, freeze concentration of WPU causes constitutional super-cooling at the interface, leading to Mullins-Sekerka instability with a well-defined wavelength by which the WPU concentrates between the ice crystals. The Mullins-Sekerka instability wavelength, which defines the primary periodicity of the templated structure, is governed by competition between the destabilizing solute interfacial concentration gradient and the surface energy that opposes cell formation. In this way, the periodicity of the aligned pores can be accurately calculated by the equation in the reference[5, 13, 18]. By the equation, the calculated value matches well with the periodicity of the aligned pores in Figure 6. Therefore, it is possible to fine-tune this periodicity by adjusting the freezing rate such as the temperature of cryogenic liquid or immersing velocity.

IV. Conclusions

Regular aligned porous waterborne polyurethane (WPU) composite can be obtained simply by a directional freeze-drying process. The morphology of the WPU composite can be tailored by the concentration of the WPU dispersion and freezing rate. And, by a freeze-drying process, when the concentration of WPU dispersion is 20 wt.%, very regular aligned pores along the immersion direction can be obtained.

When the concentration of WPU dispersion is 20 wt.%, the periodicity of the aligned pores can be tuned by the freezing rate such as the temperature of cryogenic liquid or immersing velocity into cryogenic liquid. The periodicity of the aligned pores increases when the immersed velocity decreases or the temperature of the cryogenic liquid increases. With the theory of Mullins-Sekerka, the periodicity of the aligned pores can be accurately calculated.

Acknowledgment

This work is financially supported by the research project of Commission of Science and Technology of Chongqing (Grant No. cstc2014kjrc-qnrc50006), Basic Research Foundation for the Central Universities (Grant No. XDJK2016C005 and XDJK2015C061) and Start Foundation for the doctors of Southwest University (Grant No. SWU112052), China.

References

[1] Liu, C.; Xia, Z.; Czernuszka, J. T. Design and development of three-dimensional scaffolds for tissue engineering. Chem. Eng. Res. Des. 2007, 85, 1051–1064.

[2] Gao, Y.; You, B.; Wu, L. Facile fabrication of hollow polymer microspheres through the phase-inversion method. Langmuir 2010, 26, 6115–6118.

[3] Liu, Q.; Huang, C.; Luo, S.; Liu, Z.; Liu, B. Production of micron-sized hollow microspheres by suspension polymerization of St-DEGDA (diethylene glycol diacrylate) with petroleum ether (90-120 degrees). Polymer 2007, 48, 1567–1572.

[4] Xu, X.; He, H.; Zhang, Y.; Zhang, D.; Yang, Z. Influence of Position on the Microstructure of Carbon Black/Polyvinyl Alcohol Composite Obtained by the Directional Freeze-drying Process. J. Macromol. Sci., Part B: Phys. 2014, 53, 568-574.

[5] Zhang, H.; Cooper, A.I. Aligned porous structures by directional freezing. Adv. Mater. 2007, 19, 1529-1533.

[6] Deville, S.; Saiz, E.; Nalla, R.K.; Tomsia, A.P. Freezing as a path to build complex composites. Science 2006, 311, 515-518.

[7] Chino, Y.; Dunand, D.C. Directionally freeze-cast titanium foam with aligned, elongated pores. Acta Mater. 2008, 56, 105-113.

[8] Deville, S.; Saiz, E.; Tomsia, A.P. Ice-templated porous alumina structures. Acta Mater. 2007, 55, 1965-1974.

[9] He, H.; Xu, X.; Zhang, D.; Zhang, Y. An aligned macro-porous carbon nanotube/waterborne polyurethane sensor for the detection of flowing organic vapors. Sensor Actuat. B-Chem. 2013, 176, 940-944.

[10] He, H.; Zhang, D.; Xu, X. Electrically Conductive Multiwall Carbon Nanotubes/Poly(vinyl alcohol) Composites with Aligned Porous Morphologies. J. Macromol. Sci., Part B: Phys. 2012, 51, 2493-2498.

[11] He, Z.; Liu, J.; Qiao, Y.; Li, C. M.; Tan, T. T. Architecture Engineering of Hierarchically Porous Chitosan/Vacuum-Stripped Graphene Scaffold as Bioanode for High Performance Microbial Fuel Cell. Nano Lett. 2012, 12, 4738−4741

[12] Kim, D.; Kim, Y.; Choi, K.; Grunlan, J.C.; Yu, C. Improved Thermoelectric Behavior of Nanotube-Filled Polymer Composites with Poly(3,4-ethylenedioxythiophene) Poly(styrenesulfonate). ACS Nano. 2010, 4 , 513–523

[13] Zhang, H.; Hussain, I.; Brust, M.; Butler, M.F.; Rannard, S.P.; Cooper, A.I. Aligned two- and three-dimensional structures by directional freezing of polymers and nanoparticles. Nat. Mater. 2005, 4, 787-793.

[14] Qian, L.; Willneff, E.; Zhang, H. A novel route to polymeric sub-micron fibers and their use as templates for inorganic structures. Chem. Commun. 2009, 3946-3948.

[15] Zhang, H.; Lee, J.; Ahmed, A.; Hussain, I.; Cooper, A.I. Freeze-align and heat-fuse: Microwires and networks from nanoparticle suspensions. Angew. Chem. Int. Edit. 2008, 47, 4573-4576.

[16] Catheline, A. L.; Colard, R. A.; Cave, N. G; James, A. C.; Stefan, A. F. Bon. Conducting nanocomposite polymer foams from ice-crystal-templated assembly of mixtures of colloids. Adv. Mater. 2009, 21, 2894–2898

[17] Qian, L.; Ahmed, A.; Foster, A.; Rannard, S. P.; Cooper, A. I.; Zhang, H. Systematic tuning of pore morphologies and pore volumes in macroporous materials by freezing. J. Mater. Chem. 2009, 19, 5212-5219.

[18] Deville, S. Freeze-casting of porous ceramics: A review of current achievements and issues. Advanced Engineering Materials. 2008, 10, 155-169.