



Contents lists available at ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

Original Research Paper

Formation of nanoparticle added functional polymer network membrane via micro-phase separation process

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ARTICLE INFO

Article history:

Received 7 September 2015
 Received in revised form 17 December 2015
 Accepted 28 December 2015
 Available online xxx

Keywords:

Network membrane
 Carbon nanoparticle
 Micro-phase separation

ABSTRACT

Electro-conductive membranes formed by carbon nanoparticle network array were fabricated via micro-phase separation process in the polymer system of cellulose acetate/acetone/water ternary solution. Micro-phase separation technique is the most common method for preparation and production of polymeric membrane. With the formation of polymer network, added nanoparticles became network by the drive of non-solvent owing to thermodynamic and compatible properties between particles and ternary solution. Meanwhile, the nanoparticle surface properties affected the binding force of neighbor particles for the continuous nanoparticle network structure. Heat treatment on the membrane aims at removing polymer from. Thus, electro-conductive nanoparticle network membrane can be facilely prepared.

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1. Introduction

Functional nanoparticle network with isotropic array, hydrophobicity and electrical conductivity have attracted much attentions due to its feasible application in conducting material and electromagnetic shielding area. Such particle array has been conventionally fabricated by photo-etching, directly printing on the substrate, and woven polymeric fiber with electro-conductive particles [1]. However, these processes are wide range and require precise nano-technology. To obtain desired network structures, simple and effective method should be taken into consideration.

Micro-phase separation technique is the most common method for preparation and production of polymeric membrane [2]. The dry cast process, as one of phase separation process, typically needs ternary reaction system including polymeric substance, its good-solvent with relatively low boiling point, and its non-solvent with higher boiling point [3]. When the ternary solution is casted onto a substrate, good solvent first starts to vaporize. Then the solute polymer molecules separate from its non-solvent due to the decreasing of solubility in the solution. The non-solvent that has rather higher surface energy [4] than the polymer tends to decrease its surface area in the solution; thus, polymer molecules are deposit themselves around the non-solvent phase. After removing the non-solvent by vaporization, 3D polymer network still remains as membrane morphology. For ternary system

components, hydrophobic cellulose acetate (CA) was most frequently being chosen to form polymer membrane by micro-phase separation process [5] for its hydrophobicity, chemical stability and environmental friendly. Cast polymer solution of cellulose acetate, acetone and water was investigate due to the thermodynamic possibility and adjustable [2,6,7].

Composites modified by addition of certain fillers like mineral [8], metal powders [9,10], graphite fiber [11] and carbon black (CB) [12], are currently be evaluated due to polymer's property improvement around polymer toughness, intensity and functional applications such as thermal conductive [13], electrical conductive [14] and so on. Researches were focused on how to improve dispersibility of particles and to explore the inner binding force of particles and polymer to fabricate particle unordered arrayed membrane, while by micro-phase separation process, nanoparticles array in ordered so that porous network membrane was easily prepared.

Considering about electro-conductivity and affinity with cellulose acetate, carbon is substantially less conductive than metal powders, while its inoxidizability when formed with polymer has a significant advantage than metal materials. Meanwhile, Van der Waals' force of high specific area carbon particle ensures the attraction of neighbor particles nearly stick together with a reasonable amount [15] for thermal and electrical conductive.

Carbon nanoparticle as filler added into cellulose acetate was chosen in this study and fabricated network membrane by micro-phase separation process to improve polymer electro-conductivity. When carbon nanoparticles were added into ternary

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system for micro-phase separation to prepare nanoparticle network membrane, with the formation of CA polymer network, carbon nanoparticles become network by the drive of non-solvent, which owing to thermodynamic and compatible properties between particles and ternary solution; meanwhile, nanoparticle surface properties affected the binding force of particles. Thus, CA network membrane with carbon nanoparticle added could be facily prepared. After removing polymer composition by heating, functional property of electro-conductivity was measured. The ratio of ternary system, amount of carbon nanoparticle and heat treatment temperature has been investigated to optimize the morphology of network membrane.

2. Materials

Initial wet membranes were prepared by dry-casting method on quartz substrates (1.5 * 25 * 70 mm), using mol weight 50,000 g/ml cellulose acetate (CA, Aldrich Chemical Company Inc., acetyl content: 39.8 wt.%, Mn: 30,000) as polymer, acetone (Wako Pure Chemical Industries, Inc. Analytical grade, b.p.: 56.5 °C) as the good-solvent and distilled water as the non-solvent. Hereafter, the ratio of polymer and non-solvent weight percent in the ternary solution were abbreviated as P and N. Hydrophobic carbon nanoparticles (70 nm diameter, Lion Corporation) was filled into ternary system solution to prepare blend polymer membranes.

3. Membrane preparation and characterization

The ternary solutions were casted onto quartz support and porous membranes were prepared due to the evaporation of acetone. Casted membranes were kept on stable condition for evaporation of non-solvent and residual good-solvent at room temperature with 20% humidity. Preparation of membrane was illustrated in Fig. 1. The cast thickness was 12 μm controlled by automatic bar coater (K Control Coater, RK PrintCoat Instruments Ltd.) at speed of 3 cm/s.

Accounting to the well affinity between particle/good-solvent and poor solubility of particle/non-solvent, hydrophobic carbon nanoparticles (70 nm diameter) were added to the ternary system to prepare blend polymer membranes at different concentrations (2.7, 4, 8 wt.%) with P3N15 solution component (e.g., P3N15 means the ratio of polymer and non-solvent are 3% and 15%, respectively). The preparation process was practically the same as initial membranes.

Prepared membranes were heated at 300 °C, 350 °C and 400 °C under argon atmosphere held with 2 h to remove cellulose acetate for obtaining particle network on substrate. After heat-treating, electro-conductivity of network membrane was measured by the Four-probe Van Der Pauw Method [16].

The surface morphology of dried membranes was examined by optical microscope (OLS4000, Olympus Corp.) and scanning

electron microscope (SEM, JSM-7000F, JEOL Ltd.). Samples were coated by Osmium (Osmium plasma coater OPC60A, Filgen, Inc.) for membrane morphology observation.

4. Results and discussion

Membrane morphology can be significantly affected by slight changes of dry-cast process and it is quite sensitive to preparation condition. Noting that the composition ratio dependence of ternary solution was the primary experimental aspect of membrane characteristic structure. Moreover, previous researches focused on cross-sectional view of relatively thick polymeric membrane that prepared in hundreds of micrometer since it contains large macrovoids or finger-like passageways [2]. To investigating the effect of casting solution composition to comprehensive thickness, 12 μm wet thickness membranes have been made in this work.

4.1. Membrane of CA/Ace/W ternary system

Fig. 2 shows the upper-face morphology of membranes prepared by micro-phase separation. The final membrane structures impacted by compositions of initial ternary solution were changed by means of the concentration controlling, which kept the good-solvent fix at 80 wt.% and the weight faction of polymer and non-solvent were P3N15, P4N14 and P5N13. The SEM images revealed ordered polygonal (pentagons and hexagons) unit network and also asymmetric pores surrounded by polygon from top-view. We believe that these self-assemble patterns were generated from Marangoni effect, which was induced by a fast evaporation process. Membrane of volatile solution deposited on substrate was subjected to a fast temperature variation between the substrate and free upper surface. Thus, the fluid couldn't conduct enough heat and a temperature gradient was created across the film. It means that the formation of polygon was driven by the Marangoni instability [3].

Focusing on the center of polygon, it can clearly see from there asymmetrical 3D porous network membrane was formed by micro-phase separation process. Fig. 2 indicates that with the increasing of P/N ratio in the initially casting solution, membrane structure varied from high porosity to practically pore-free. From Fig. 2(a) it can be seen that an isotopic membrane prepared from the P/N ratio of 3/15 is highly porous. During the membrane formation, polymer and non-solvent concentration gradients were formed along the membrane thickness. Fig. 2(b) shows the P4N14 membrane with fuzzy edge between individual polygons. The increase of polymer percentage led the pore size trend to be smaller than high percentage ones. The pore size and distribution turned to be homogeneous from Fig. 2(c) under the condition of highest polymer percentage, and the unit of pores could not be determined obviously. The coating wet thickness is 12 μm and the average dry thickness value obtained by optical microscope is 5 μm.

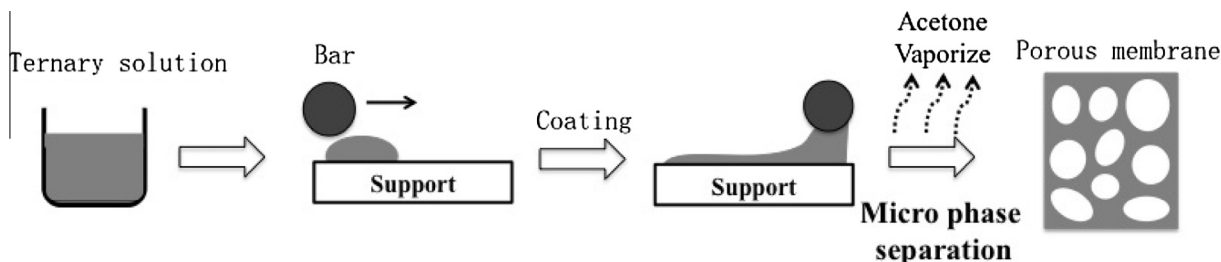


Fig. 1. Preparation process of porous membrane by micro-phase separation process.

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