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Influence of humidity and polymer additives on the morphology of hierarchically porous microspheres prepared from non-solvent assisted electrospraying

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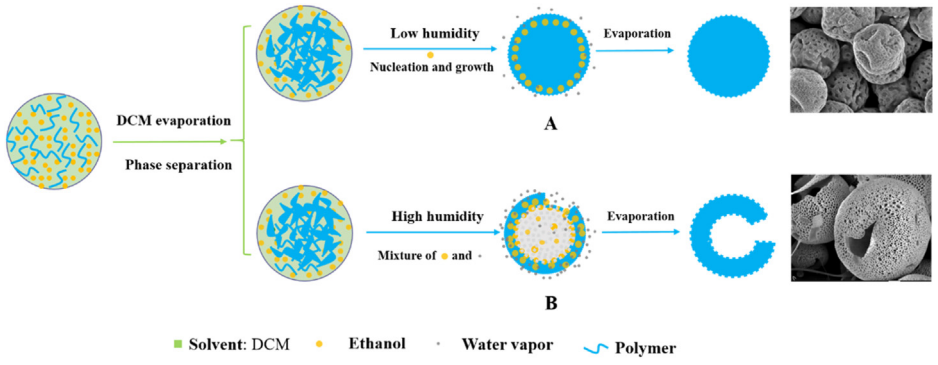
HIGHLIGHTS

- Hierarchically porous microsphere was prepared by non-solvent assisted electrospraying.
- Humidity could influence both the surface pore and microstructure of the microspheres.
- Surface morphology of the microspheres could be tuned by choosing different polymer additives.

GRAPHICAL ABSTRACT



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ABSTRACT

Porous polymer microspheres have attracted great interest in many potential fields of application, such as controlled drug release, catalysis, and scaffolds, due to their high surface to volume ratio, low density, permeability, etc. It is desirable to control the porous structure of the microspheres to meet their application requirements. In this study hierarchically porous microspheres were prepared by the technique of non-solvent induced phase separation (NIPS) during electrospraying. Porous and/or hollow microspheres were prepared by using different non-solvents. The influence of humidity on the surface morphology and microstructure by vapor induced phase separation and breath figure effect were investigated. Microspheres with an irregularly hollow structure was observed with the increase of humidity, when ethanol was used as the non-solvent. On the other hand, the polymer additives in the solution could also affect the NIPS and thus the surface morphology of the electrosprayed microspheres. It was found that the microstructure of both the microsphere and surface pores varied little when the polymer additives were not soluble in the non-solvent (hexanol). When polyvinyl pyrrolidone (PVP – soluble in the hexanol) was used as the polymer additive, dimples on the microsphere surface were formed.

1. Introduction

Porous polymer microspheres have recently received great attention because of their special features such as large specific surface area, low density, and permeability, which allow them to

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find applications in the field of controlled drug release, catalysis, scaffolds, selective separation, chemical sensors, etc. [1–5] A popular method to prepare porous microsphere is the heterogeneous polymerization using the immiscibility of two or more liquids, in which a porogen is often incorporated [6–9]. In spite of many advantages, a large number of emulsifiers or stabilizers are usually required for the heterogeneous polymerization, which inevitably introduces impurities and thus may deteriorate material performance. Furthermore, the polymerization is usually complicated and needs elaborate manipulation. For example, the geometry of the monomer droplets is closely related with the interfacial tension that should be carefully controlled. Therefore, it is of high importance to explore a simple and versatile method to prepare polymer microspheres with porous structures. Electrospraying, a modified version of electrospinning, has been developed for the preparation of polymer, inorganic and hybrid particles [10–13]. Generally, porous polymer microspheres can be formed based on the thermally induced phase separation (TIPS) [14], vapor induced phase separation (VIPS) [15,16], and breath figure effect resulting from the cooling of the rapid evaporation of the volatile solvent [15,17,18]. Porous microspheres could also be formed by electrospraying polymer solution onto a collector immersed in a non-solvent bath, during which mass exchange between the residual solvent in the droplet and the non-solvent would occur, causing the phase separation, i.e., non-solvent induced phase separation (NIPS). The NIPS was regarded as the main mechanism for the generation of the porous microstructure [19,20]. Nevertheless, the obtained microspheres are usually irregular and non-uniform; Also, it is not easy to control the porous structure of the microspheres.

In our previous work, we proposed a facile method, i.e., non-solvent assisted electrospraying, to produce microspheres with hierarchical surface pores [21]. The solvent and non-solvent evaporated successively during electrospraying as long as the non-solvent possessed a higher boiling point than the solvent, and the surface pores were finally formed due to NIPS. Many factors including the polymer solution concentration, weight ratio between non-solvent and polymer, and the non-solvent properties affected the morphology of both the microsphere and its surface pores. The formation of the hierarchical pores was attributed to the combination of VIPS, TIPS, NIPS and the breath figure effect. The environment humidity plays a very important role determining the porous structure of the microspheres, because the moisture may be mixable with the solvent and/or non-solvent and thus influence the multiple phase separation as well as the breath figure effect, which has been extensively investigated in porous nanofibers. [18,22–24] The influence of the humidity on the porous microstructure of the microspheres prepared by electrospraying is, however, seldom reported. Therefore, it is necessary to study the influence of humidity on the surface morphology and microstructure of the microspheres, in order to gain more insights of the pore formation mechanisms.

In this study, we choose dichloromethane (DCM) as the solvent, and hexanol, ethanol, and propanediol as the non-solvent. Both ethanol and propanediol is able to absorb water vapor easily, but the water absorption capability for hexanol is very weak. As a result, the use of different non-solvent can give rise to different mechanisms for the surface pore generation at different humidity. The moisture as an external factor can only exert influence on the surface of the solution droplet. To understand what happens inside the droplet solution during the non-solvent assisted electrospraying, and hence further fine-tuning of the surface morphology of the electrosprayed microspheres, polymer additives were added to the solution to study their influence on the non-solvent induced phase separation and thus the surface morphology from the macromolecular movement perspective. Our studies indicated that the structure of both the microsphere and surface pores varied little when the polymer additives were not miscible with the non-solvent (hexanol). When the polyvinyl pyrrolidone and polyethylene glycol, which were soluble in the hexanol, were used as the polymer additives, the dimple structure on the microsphere surface was obtained.

2. Experiment

2.1. Materials

Polymethylmethacrylate (PMMA) was obtained from Chi Mei company (Mw = 11 2000). Dichloromethane (DCM), ethanol, hexanol and propanediol were purchased from Sigma-Aldrich Corporation, and used as received. The physical properties of the solvent and non-solvents including the boiling point, viscosity, solubility parameter and surface tension are listed in Table S1 in the supporting information. Polyvinyl pyrrolidone (PVP, Mw = 10 000, 54 000 and 130 0000), polycaprolactone (PCL, M_w = 80 000), polyethylene glycol (PEG, M_w = 8000), and polycarbonate (PC), were purchased from Sigma-Aldrich Corporation, and used as received.

2.2. Electrospraying

For non-solvent assisted electrospraying, the solvent, non-solvents, polymer and polymer additives were mixed under the magnetic stirring for 2 h until the uniform solution was obtained. Note that the polymer concentration was 2 wt%, and the weight ratio between the non-solvent and polymer was 2:1, while the weight ratio between polymer additives and polymer varies from 1:50 to 1:2. The as-prepared polymer solution was then loaded into a syringe with a metallic needle for electrospraying. The electrospinning unit is located in a chamber, in which the humidity could be adjusted. The electrosprayed products were collected in a grounded aluminum foil, which was 12 cm far from the metallic needle. The voltage and the flowing rate for the electrospraying was 12 kV and 1 ml/h. The relative humidity was controlled ranging from 15% to 75%.

2.3. Morphology characterization

The morphologies of the electrosprayed microspheres were characterized by a field emission scanning electron microscope (FESEM JSM6335) operated at 5 kV.

3. Results and discussion

3.1. Influence of humidity on the morphology and microstructure of the microspheres

It was reported in our previous work that the PMMA microspheres were irregular and usually collapsed if the non-solvent was not used, and many tiny pores with the diameter of a few tens of nanometers were present on the microsphere surface [21]. The thermally induced phase separation (TIPS) and breath figure effect might be responsible for the generation of pores on the microsphere surface. When the non-solvent was used, the pore size increased to a few hundred nanometers as shown in Fig. 1, which displays the morphologies of the porous microspheres electrosprayed at different humidity. It was found that the microsphere size was independent of the humidity, because the diameter of the microspheres was mainly determined by the solution properties (the solution concentration, surface tension, etc.) and electrospraying parameters (the voltage, flow rate, etc.) [25–27]. On the other hand, the humidity could affect the surface topography of the electrosprayed microspheres. The surface was very rough without evident pore for-