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Preparation of fibrous electrospun membranes with activated carbon filler

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Abstract

Immiscible solvents blend suspensions applied to produce fibrous polymer membranes heavy filled with activated carbon (AC) particles by electrospinning method. The continuous phase of the suspension is a solution of polyacrylonitrile (PAN) in polar solvent (dimethylsulfoxide (DMSO)), the dispersed phase is suspended in non-polar solvent (hexane) AC particles. An ionic liquid 1-ethyl-3-methylimidazolium acetate (EmimAc) added to both phases to improve the electrospinning process and enhance the electrical conductivity of the electrospun mat. These types of membranes developed as electrode materials for energy storage devices.

In this study, we obtain electrospun membranes with up to 60 wt. % of activated carbon content, AC particles are connected between each other by PAN nanofibers, and covered with PAN nanofibrous mesh.

Introduction

Conductive carbonous materials intensively used for production of polymer composites. Recently electrospinning of polymer composites functionalized by different fillers are actively studied [1]. Most often fillers are dispersed in polymer material before processing [2], or material coated [3] or impregnated with fillers [4]. The first method has good homogeneity of properties through the final material, but filler particles are covered by the polymer what decreases functionality of the filler (electrical conductivity, absorption properties, etc. [5]. The second approach keeps the filler particles uncovered but the uniform distribution of particles through the volume of the product demands sophisticated impregnation techniques [6].

What concerns electrospinning of carbon-filled polymers, heavy load of carbon significantly increases the viscosity of solution that makes electrospinning process too complicated [7]. Another problem is absorption of solvent by carbon particles and thus increasing local concentration of polymer chains near the particles that leads to deposition of polymer onto the surface of particles. Electrospinning of such fluids is complicated, has low productivity and final product has not uniform morphology.

The different approach for electrospinning fluids preparation to avoid complications mentioned above could be used [8]. To keep the good fibre generation from the polymer solution, it should be spun from the proper solvent, and simultaneously, the electrospinning fluid should contain carbon particles separated from polymer chains. This problem could be solved by the preparation of the immiscible solvents blend electrospinning suspension.

We propose a new method for the electrospinning fluid preparation. The electrospinning of this type of fluids will combine both good fiber generation and high load of carbon filler with uniform particle distribution through the electrospun material. This method allows achieving electrospun mat of fine nanofibers with high load of carbonous material. The electrospinning fluid is a suspension with two phases: continuous phase is a solution of polyacrylonitrile in DMSO dispersed phase is a suspension of activated carbon particles in hexane. DMSO and hexane are not miscible, PAN soluble in DMSO and insoluble in hexane.

Materials and methods

Polyacrylonitrile 150 kDa molecular weight purchased from Polysciences Inc. DMSO purchased from Sigma Aldrich. Porous coconut shell activated carbon YP-80F, purchased from Kuraray Co. Ltd. 1-buthyl-3-methylimidazolium acetate ionic liquid synthesized in the laboratory by the methods described elsewhere [9] [10].

The sonication of suspensions is done by Bandelin Sonopuls sonification device with 3 mm MS-73 probe at frequency 20 kHz, amplitude 50% and 9 pulsed cycle, 70W generator.

The rheology studied by means of Anton Paar Physica MCR501 rheometer using cone-plate measuring geometry (cone angle = 2°). All measurements carried out in nitrogen atmosphere at temperature 21 °C. The gap = 0.051 mm was used. The oscillation tests were performed at angular frequencies $\omega = 1 \div 600$ rad/s with strain = 5% determined from the linear viscoelasticity region in the amplitude sweep test at a frequency of 1 Hz.

The homogeneity of suspensions studied by means of optical microscope Carl Zeiss Axioskop 2 in transition mode with polarized light. The morphology of fibrous mats studied by the scanning electron microscopy at Zeiss EVO MA15 in secondary electron and reflected beam regimes. To improve the image quality samples were sputtered with gold.

Electrospinning done at self-made setup, it consists of a needle pump, a high voltage supply and a grounded rotating drum collector covered with an aluminum foil. A voltage 17 kV, a distance between needle and the collector 15 cm, a pumping rate 0.7 ml/h, a needle 0.6 mm diam.

Suspension preparation

9 wt. % PAN solutions in DMSO were made by mechanical mixing at 45°C.

9 wt. % AC suspensions in hexane first mechanically mixed, then sonicated for 1 hour. A water bath used to keep suspensions cold and prevent fast evaporation of hexane. The sonication done in three intervals of 20 minutes, after each interval, the suspension weighted and the amount of evaporated hexane added to keep the concentration constant. Both liquids mechanically mixed in needed ratio and sonicated for 1 hour by the procedure described above. The stability of suspensions examined by the optical microscopy and by rheology tests.

For the stability control of PAN in DMSO + AC in Hexane suspension, the viscosity measured right after the preparation, in 12 and 24 hours after the preparation. Visually the suspension is stay homogeneous. It was found the viscoelastic behavior of the suspension at day 1 is almost identical to one on day 2. At day 3 the aggregation is observed, thus we suppose the suspension once prepared has to be electrospun within 24 hours.

Results and discussions

For comparison, we prepared roll-mill casted electrode, electrospun one solvent DMSO suspension and DMSO-hexane immiscible solvents blend suspensions.

On Figure 1 SEM, images of roll-mill casted electrode shown. The electrode consists of AC particles (big gray particles image (a)) conductive carbon black (small round shape agglomerated particles image (b)) blended with polytetrafluoroethylene (PTFE) binder. The AC load is 94 wt. %.

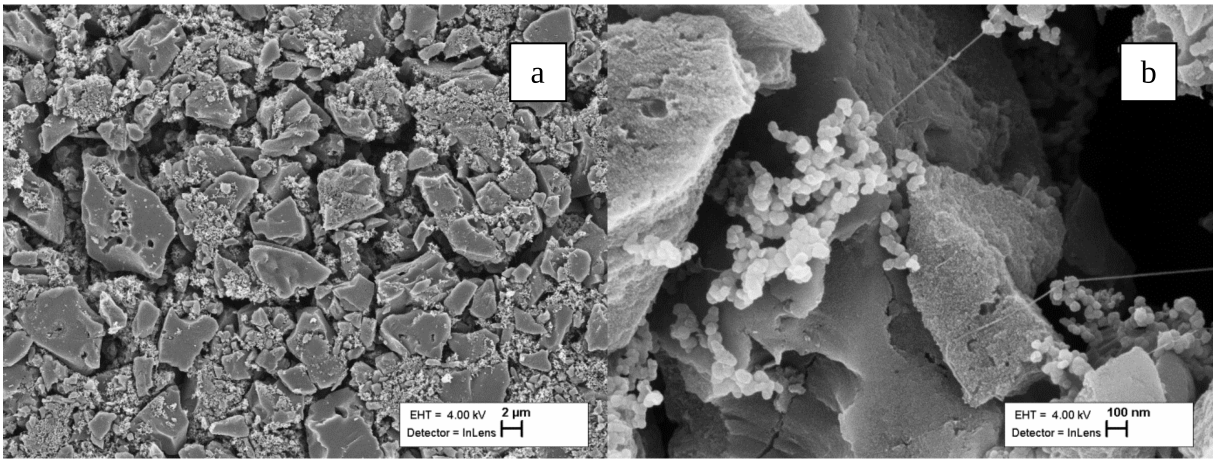

Figure 1. SEM image of PTFE-AC (ratio 6:94) roll-mill casted electrode

On Figure 2 the electrospun mat produced from PAN+AC suspension in DMSO is shown: AC particles are covered by PAN; thin fibers contain AC particles inclusions.

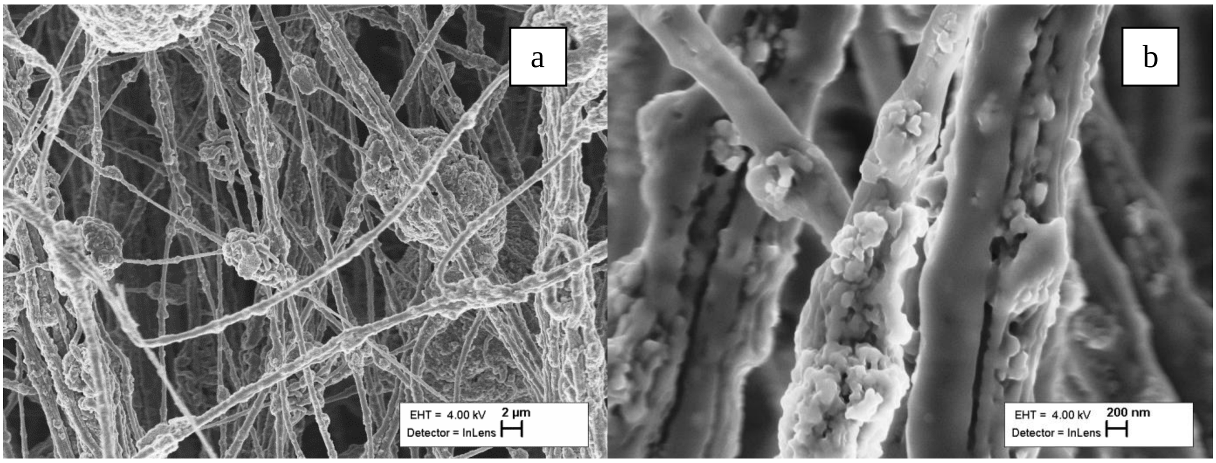

Figure 2. SEM image of PAN-AC (ratio 50:50) electrospun mat

In Figures 3 and 4 SEM images of mat electrospun from immiscible solvents, blend suspensions shown. The mats consist of separate uniform fibers, but PAN covers AC particles, one could notice that polymer coating is not uniform, it is porous and porosity decreases with AC content increase. Probably the evaporation of hexane absorbed inside AC particles prevents formation of uniform PAN coating.

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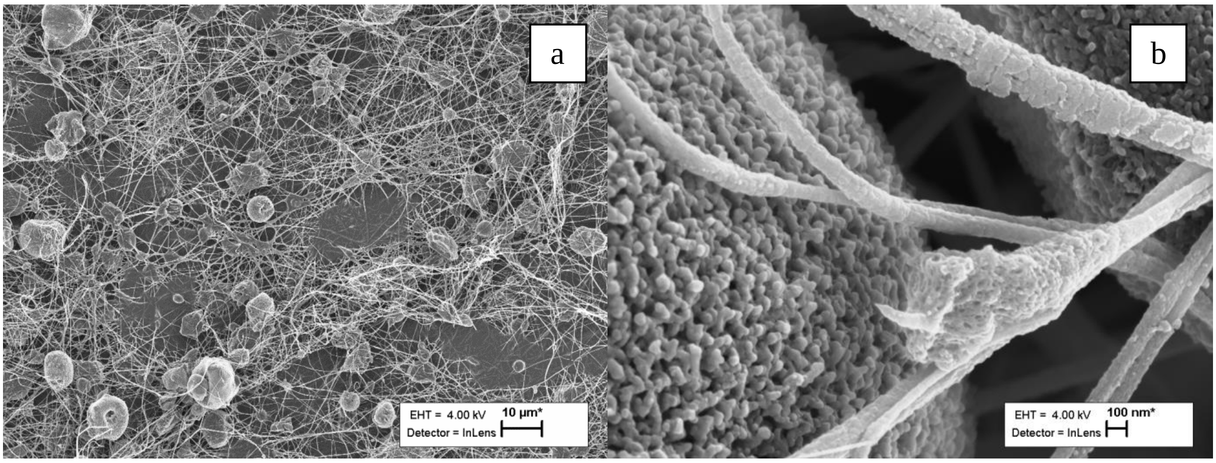

Figure 3. SEM image of PAN-AC (ratio 50:50) electrospun mat (separated PAN and AC)

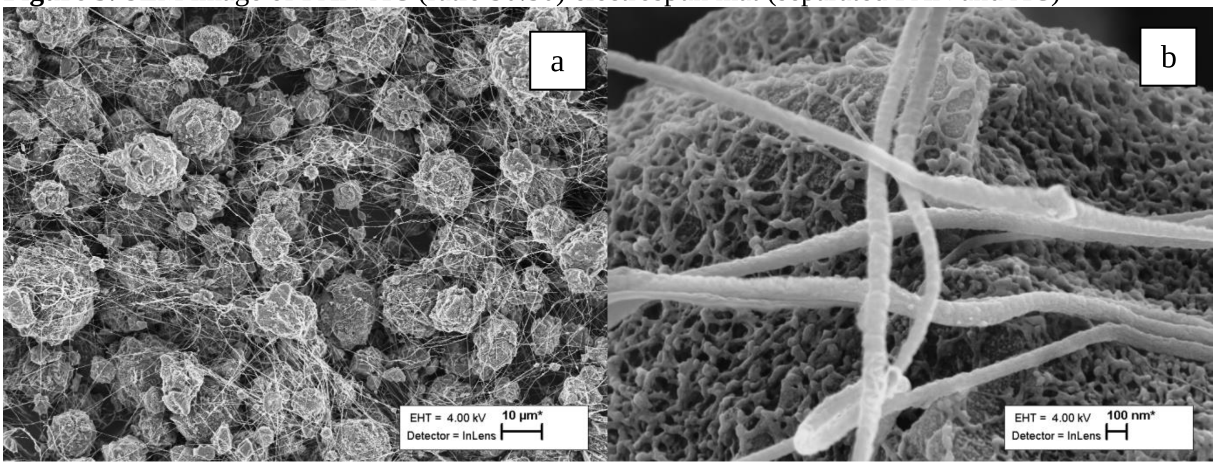

Figure 4. SEM image of PAN-AC (ratio 40:60) electrospun mat (separated PAN and AC)

Conclusion

We conclude that polymer chains cannot migrate from DMSO phase into hexane, but AC particles obviously can. As proven by SEM images, some AC particles migrate into DMSO solution of PAN and absorbs polymer on their surfaces.

The electrospinning of suspensions in which the polymer and the filler are separately dissolved or dispersed in non-mixable solvents relatively effective. Electrospun mats contain fine thin fibers and evenly distributed AC particles covered by porous layer of polymer.

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