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Effect of salt concentration in spinning solution on fiber diameter and mechanical property of electrospun styrene-butadiene-styrene tri-block copolymer membrane

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HIGHLIGHTS

- The relationship of electrospun fiber diameter and salt concentration was depicted in a wide range.
- A critical salt concentration of decreasing fiber diameter was revealed.
- Mechanical strength of SBS electrospun membrane was enhanced most at the critical concentration.

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ABSTRACT

Electrospun nanofiber is regarded as a promising candidate for many high-end applications due to its advantageous unique structure. Ultrafine fiber and good mechanical property are essential to ensure its performance. In this work, tunable ultrafine diameter and significantly enhanced mechanical strength of electrospun Styrene-butadiene-styrene tri-block copolymer (SBS) membrane are attained by means of the addition of LiBr into SBS solution dissolved in tetrahydrofuran/dimethylformamide (THF/DMF). Solution conductivity is found to grow in two steps with the increasing lithium bromide (LiBr) concentration and a critical point is observed at the ultralow concentration of 0.005 wt%, sharp increase below it but modest increase above it. Interestingly, the diameter of electrospun fiber shows a significant reduction with increase of LiBr concentration below this critical point but minor fluctuation above this. Welded structure is observed between adjacent fibers and the degree of welding goes deeper with increase of salt concentration. Accordingly, the mechanical strength of electrospun membrane is gradually enhanced and reaches to the highest value of 5.7 MPa at the critical concentration, with enhancement of 134% in comparison with pure electrospun SBS membrane, and then declines when further adding LiBr. TEM observation confirms more oriented and distinct self-assembly domains in the finer fibers, which contribute greatly to the property enhancement for electrospun SBS membrane obtained below critical concentration. The finding of critical concentration is important for the preparation of high performance electrospun membrane by adding salt in the spinning solution.

1. Introduction

In recent decades, nanofiber membrane has been widely used in various fields owing to their unique extraordinary performances such as large specific surface area, high porosity and interconnected pores, which cater to the very requirements of elaborated nanotechnology. Compared with other methods [1–3] of fabricating nanofiber, electrospinning attracts much more interest and is highly thought of in applications including but not limited to sensor [4–6], tissue engineering scaffold [7–9], filtration [10–12], oil/water separation [13–15], shape memory [9,16,17], lithium battery [18–20].

Thermoplastic elastomers has also aroused great concerns by the merits of excellent processing property and outstanding elastic stretching property, combined features of plastics and rubber without any vulcanization. Styrene-butadiene-styrene tri-block copolymer (SBS) is a kind of popular thermoplastic elastomer with distinctive properties such as great elastic recovery ratio, tunable mechanical properties by changing the S/B ratio and further modification on the carbon-carbon double bond. By virtue of these advantages, electrospun SBS membrane has been paid more and more attention in fields such as membrane

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distillation [21,22], stretchable device component [23,24], stretchable sensor [4,5,25], superelastic superhydrophobic material [26], interlaminar or interfacial adhesion [27,28]. Nevertheless, some challenging issues are still restraining its potential in further applications and remain to be overcome, and one of most urgent challenges is to enhance mechanical property, which is exactly expected but absent in most cases.

Generally, there are two main approaches to enhance mechanical strength of electrospun membrane, one of which is enhancing mechanical property of individual fiber and the other is fabricating crosslinked structure. According to the former approach, incorporating reinforced agents into nanofibers to promote the mechanical property is a common way. However, reinforced nanofillers like carbon nanotube, boron nitride and cellulose nanocrystal are difficult to be homogeneously dispersed in polymer and tend to bring about poor interfacial adhesion with matrix, where physical or chemical modifications [29–31] are quite demanded to enhance the mechanical properties or thermal conductivity of nanocomposites. In addition, concerning to individual nanofiber, fiber diameter shows a closed correlation with mechanical property. As demonstrated in literature [32–34], the modulus of individual nanofiber increase exponentially when fiber diameter decrease. The distinct mechanical property improvement was attributed to higher degree of molecular orientation in fiber with reduction of diameter, which was confirmed in researches [35,36]. As for the latter approach, physical bonding structure between adjacent fibers was demonstrated to be fabricated by thermally treatment [8,37], vapor treatment [38,39] or immersing treatment [40]. Lee, S. J. et al. [37] immersed electrospun poly (3-caprolactone) (PCL) scaffold in Pluronic F127 solution at different temperature and improved biomechanical properties after thermally bonding. Li, H. et al. [38] exposed PCL membrane in dichloromethane vapor and appropriately fused and welded fibers at the fiber cross points by manipulating exposure time, and the mechanical strength of welded membrane increased from 9 MPa to 15 MPa. However, methods mentioned above tend to lead to dimension shrinkage, porosity declining or devastated nanofiber morphology and add complexity to production. Besides, chemical crosslinking was also developed to enhance mechanical performance of electrospun SBS membrane. Sam van der Heijden et al. [41] immersed electrospun SBS membrane into phenyl − triazolinediones (TAD) and bifunctional TAD solution in order to introduce phenyl groups and chemical cross-links onto fiber surface, and by varying contents of cross-linker, tunable mechanical property was obtained at the expense of strain at break.

Actually, adding salts into polymer spinning solution is considered to be an effective way to decrease the fiber diameter. It was reported that adding salt into spinning solution generated welded structure at the cross points, but no further studies were conducted to clarify its effects on properties of electrospun membranes [34,42,43]. More importantly, the conductivity of spinning solution through adding salts could make a great difference to fiber diameter and the varying trends of fiber diameter with salt concentration were not consistent in different literature. For the most part, as demonstrated in literature [42–44], fiber diameter exhibited a remarkable reduction when adding salt into spinning solution and it was illustrated that high conductivity led to strong stretching in electric field and contributed greatly to diameter reduction. However, studies [45,46] showed a completely different trend wherein fiber diameter increased when raising conductivity by adding salts into spinning solution. These different results could be caused by the high-content salts above 0.1 wt% added in these researches [42–49], where conductivity of solution worked not alone but accompanied by the simultaneous great changes of viscosity and surface tension of spinning solution. Additionally, high-content salts would be expelled out of polymer and resulted in rough surface and defects [43] inside fiber. Therefore, it is quite demanded to figure out the clear correlation between fiber diameter and salt concentration, and an appropriate lower salt concentration will be preferred to realize performance optimization of electrospun membrane. According to Debye-Hückel interionic attraction theory [50], ions in electrolyte tend to be surrounded by other ions with opposite charges which is called ion atmosphere and strong interactions exist between adjacent ions. We suppose that there should be a critical salt concentration, below it ions is supposed to be completely free from attractions with other ions and above it ions are bound to each other and dispersed inhomogeneously in solution. So it is necessary to extend the range of salt concentration to very dilute solution to find the critical point, and to investigate how the critical concentration affects the fiber diameter and mechanical property of electrospun membranes.

In this study, inorganic salt LiBr was added into SBS spinning solution in a broad concentration range (0.0001 wt% to 0.2 wt%). LiBr is selected as the adding salt because of its strong ionization in organic solvents and could enhance the conductivity of solution greatly at ultralow concentration. The solution conductivity was first measured with increasing of LiBr concentration to find out the exact varying trend and a critical salt concentration was observed where the increasing rate of conductivity changed obviously. Then the change of fiber diameter of electrospun membranes before and after the critical point was carefully analyzed. Finally the tensile property of the prepared electrospun membranes was investigated as function of salt concentration. The work is important for the preparation high-performance electrospun membranes by adding slat in the spinning solution.

2. Experiments

2.1. Materials

Styrene–butadiene–styrene (SBS) triblock copolymer (YH-791) with a weight-average molecular weight (Mw) of $1.7 \times 10^5\,g\,mol^{-1}$ was purchased from Baling Branch Corporation of SINOPEC, China, whose styrene to butadiene ratio is S/B = 30/70. Tetrahydrofuran (THF) and dimethylformamide (DMF) were supplied by Chengdu Kelong Chemical Reagent, China. Lithium bromide (LiBr) was purchased from Shanghai Alladin Reagent, China. All reagents were used without any further purification.

2.2. Sample preparation method

The SBS solution containing 14 wt% polymer was prepared by dissolving SBS in mixed solvents of THF and DMF at a fixed weight ratio of THF:DMF = 3:1 (wt:wt). When preparing SBS solutions with different LiBr concentrations, accurate concentration were guaranteed by dilution method, that is, dissolved LiBr in mixed solvents at light concentration firstly and then added a certain amount of LiBr solution into adjusted solution. Prior to electrospinning, the solution was magnetically stirred at room temperature for 12 h to obtain homogeneous solution.

All electrospun SBS fiber membranes were fabricated on an electrospinning unit Nanon-21 (MECC Corp., Japan) consisting mainly of plastic syringes with stainless steel capillary tip (inner diameter of 0.27 mm), a high-voltage power connected to the capillary tip and a metal collector covered with a piece of aluminized foil. Before electrospinning, the solution was fed into the syringe and then performed all the experiments under a voltage of 25 kV at 27 °C with a relative humidity of 50% or thereabouts. The feeding rate of solution and the distance between the tip and collector were fixed respectively at $1.5\,ml\,h^{-1}$ and 15 cm. All the obtained SBS electrospun membranes were dried in the vacuum oven at 40 °C overnight to completely remove the residual THF and DMF before other characterizations.

2.3. Characterization

2.3.1. Conductivity test

The conductivities of the solutions with different LiBr