PREPARATION OF SYNDIOTATIC POLY(VINYL ALCOHOL) NANOCPMPOSITE WITH ZIRCONIUM OXIDE AND BARIUM SULFATE

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Abstract

Syndiotactic poly(vinyl alcohol) (PVA)/zirconium oxide (ZrO_2) and PVA/barium sulfate ($BaSO_4$) composite were prepared to find possibilities of polymeric embolization coils for replacing metallic coils. Complex viscosity of s-PVA composite solutions showed shear thinning behavior and that of s-PVA/ZrO_2 solutions showed Newtonian behavior at low angular frequency. After making coil shape by wounding the fibers on the glass or metal rod, the s-PVA coils were annealed to retain the original coil shape.

1 Introduction

Poly (vinyl alcohol) (PVA) is a semi-crystalline polymer frequently used as biomaterials [1, 2]. Embolization materials are usually forms of particles, metallic coil and detachable balloon [3] and the embolization coil is made of tungsten or platinum. It is needed to replace metallic coils for polymeric materials because the metallic coils have some problem in biocompatibility and side effect, and high production cost.

In this work, syndiotactic PVA (s-PVA) solutions mixed with zirconium oxide (ZrO_2) and barium sulfate ($BaSO_4$) were prepared. Rheological properties of the solutions were investigated and s-PVA/ZrO_2 and s-PVA/$BaSO_4$ composite coils were prepared.

2 Materials and testing methods

S-PVA was polymerized by copolymerization of vinyl acetate (VA) and vinyl pivalate (VPi) of which molar ratio was 8:2. The number average degree of polymerization was and the degree of saponification was and 99.9%. Syndiotacticity of the PVA was 56% which was obtained from NMR spectroscopy. S-PVA solution was made using dimethyl sulfoxide (DMSO) and water. S-PVA and DMSO/water (8/2, v/v) were mixed and stirred at 90°C for 5 h. The concentration of s-PVA was fixed at 13wt%. Polymer solution was filtered and sonificated to remove air bubble. Rheological properties were measured by cone and plate rheometer. Shear rate ranged from 0.1 to 1,000 rad/sec. Measuring temperature was 100°C. S-PVA solutions containing ZrO_2 and $BaSO_4$ were spun by using gel-spinning apparatus. Gel-spun filament was deposited in DMSO/water solutions and maintained for 24 hours for solvent extraction. Coil was prepared by winding the s-PVA filament onto metallic rod of which diameter was around 100 μm. To retain coli shape, it was annealed.

3 Results and discussion

Figure 1 shows complex viscosity data as a function of radial frequency for s-PVA/ZrO_2 and s-PVA/$BaSO_4$ composite solutions. The complex viscosity decreased with increasing frequency showing shear thinning behavior. The degree of shear thinning of s-PVA/$BaSO_4$ composite solutions is larger than that of s-PVA/ZrO_2 solutions. At low shear rate of less than 10 rad/s, the complex viscosity of s-PVA/ZrO_2 solutions show close to Newtonian behavior. However, the viscosity of s-PVA/$BaSO_4$ decreases with increasing radial frequency from the low frequency.

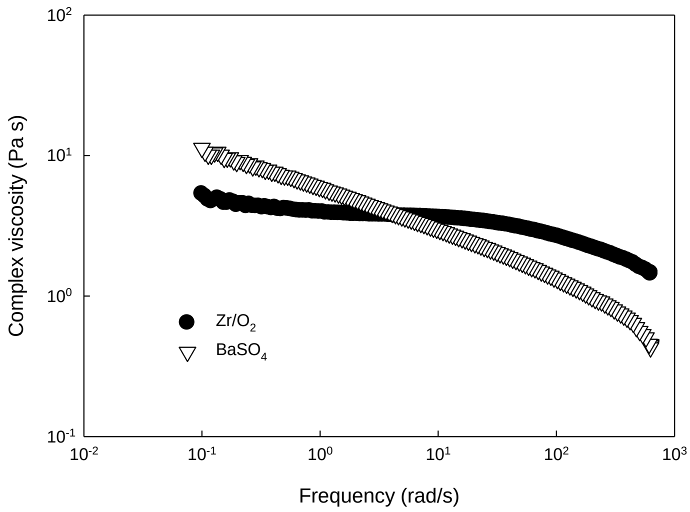

Figure 1. Complex viscosity of s-PVA composite solutions.

Figure 2 shows storage modulus versus loss modulus called as Cole-Cole plot. Gradient of s-PVA/ZrO_2 solutions is larger than that of s-PVA/$BaSO_4$ solutions indicating that PVA/ZrO_2 solutions is more stable than s-PVA/$BaSO_4$ ones [4].

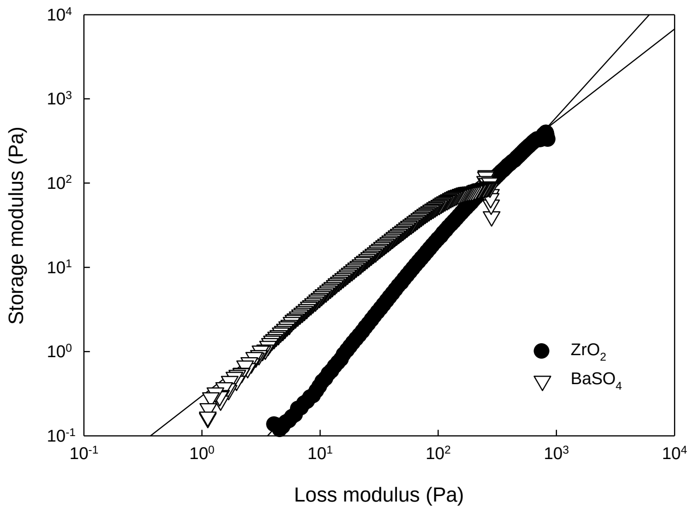

Figure 2. Storage modulus and loss modulus of PVA solutions versus shear rate.

Figure 3 shows shear viscosity versus shear rate. Like the complex viscosity, shear viscosity showed shear thinning behavior. Both the shear viscosity of s-PVA/ZrO_2 and s-PVA/$BaSO_4$ solutions showed Newtonian behavior at low shear rate of less than 1 s^{-1}. Shear rate range showing Newtonian behavior is large in the s-PVA/ZrO_2 solutions. From these results, it can be predicted that s-PVA/ZrO_2 solutions have better spinnability than s-PVA/$BaSO_4$ solutions. We confirmed that with repeated spinning trials.
Figure 4 shows VMS images of s-PVA/ZrO_2 and s-PVA/$BaSO_4$ composite coils. To make s-PVA composite coils, the filament was wound on the rod. The coils were annealed to retain coil shape after tensioning.

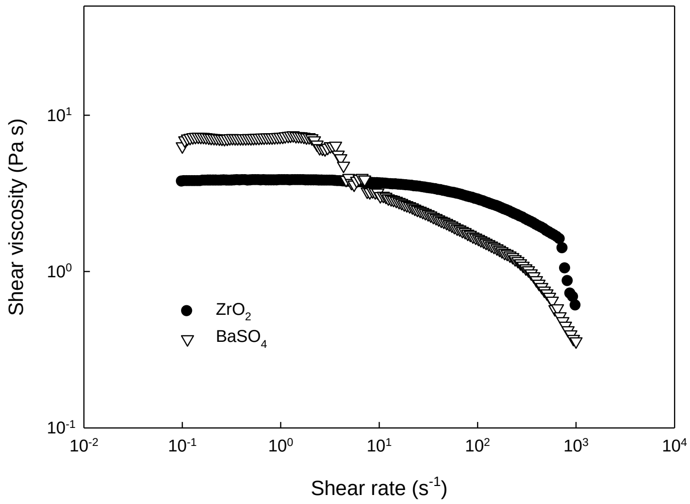

Figure 3. Shear viscosity of s-PVA solutions versus shear rate.

Figure 4. Photographs of coils made of s-PVA composite fibers.

4 Conclusions

S-PVA/ZrO_2 and s-PVA/$BaSO_4$ composite fibers were prepared to make embolization coils. Rheological properties of composite solutions showed shear thinning behavior. S-PVA/ZrO_2 composite solutions are more stable and better spinnability than s-PVA/$BaSO_4$ solutions. Polymeric embolization coils were successfully made by using s-PVA/ZrO_2 and s-PVA/$BaSO_4$ composite fibers. Annealing is important to retain coil shape after loading of some tension.

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