PVA/PAN/DMSO Solution의 온도에 따른 유변학적 특성

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Temperature dependant rheological properties of PVA/PAN/DMSO solutions

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Introduction

Polymer systems are made up of chemical bonds along the polymer chains and physical bonds across the polymer chains. The former includes covalent bonds and the latter results from hydrogen bonding, dipolar bonding, or Van der Waals forces. The type of physical bonding has huge effects on the physical properties of polymers. Particularly with the systems in which hydrogen bonding has dominant effect, the physical properties are strongly dependent not only on the molecular weight and concentration of polymer but also the kind of solvent systems[1].

Hydroxyl group of Poly (vinyl alcohol) (PVA) produces inter- and intra-molecular hydrogen bonding[2,3]. The content of hydrogen bonding is greatly affected by stereoregularity of hydroxyl group[4]. Specially designed syndiotactic-rich PVA exhibits rheological responses unbelievably different from general-purpose PVA due to more effective hydrogen bonding between adjacent chains as we already reported[4-6]. Thus, hydrogen bonding has a profound effect on the rheological and mechanical properties of the polymer, which is large determined by the density and spatial arrangement of hydroxyl groups may bring about complicated phenomena such as phase separation and gelation[5-8], which means the solution properties exhibit time-dependence. Thus, processing conditions (solvent, concentration, dissolving temperature, salt, etc) should be carefully adjusted in spinning or film casting to obtain desired properties[9-12]. The blends of PVA and poly (acrylonitrile)(PAN) are expected a very unusual responses resulting from strong intermolecular interactions. In the blend solutions PAN may play a paramount role in rheological responses because it may disturb effective hydrogen bonding between hydroxyl groups. To understand the role of PAN in the solutions, we investigate the rheological properties of PVA/PAN/dimethyl sulfoxide (DMSO) solutions.

Experimental

The PVA powder (Mw = 89,000 ~ 98,000 , Aldrich Chem. Co., USA) with a high degree of hydrolysis (99%) was used. Prior to use, the PVA powder was dried in vacuum oven for 24 hours. Commercial-grade PAN and DMSO (Aldrich Co.) were used without further treatment. PVA and PAN were dissolved in DMSO at 60 ℃, 75 ℃ for 4 hours with stirring. Total concentration of PVA and PAN in DMSO was set to 12 wt%. PAN content was 0, 20, 40, 60, 80, 100 wt% based on the weight of PVA. Dynamic rheological properties were measured by Advanced Rheomertic Expansion System (ARES, Rheometric Scientific. Co.) at 60 ℃. Parallel plate geometry was adopted whose diameter and gap were 50 and 1 mm, respectively. Frequency ranged from 0.05 to 500 rad/s. Prior to testing, the specimens were hold for 5 min to eliminate the thermal and shear histories.

Results and discussion

Figures 1 and 2 present the logarithmic plot of η' of PVA/PAN/DMSO solutions at 60 ℃, which were dissolved at 60 ℃ and 75 ℃, respectively. Both systems exhibit non-Newtonian flow behavior. The viscosity of polymer solution generally increases with increasing PAN content. At 40 wt% PAN, however, viscosity appear the lowest value at 60 ℃. Such phenomenon corresponds to the tendency of tan δ in figures 3 and 4 which clearly exhibit that tan δ gives maximum at 40 wt% PAN. However, this phenomenon is not clearly evidenced in the solutions prepared at 75 . This suggests that the temperature of preparing solutions has a very profound effect on the solution properties. Figures 5 and 6 present the storage modulus (G′) of PVA/PAN/DMSO solution dissolved at 60 ℃ and 75 ℃, respectively. They have high G′ value and only slight different values of G′ are observed with increasing frequency. They are responsible for the strong gel-like structure.

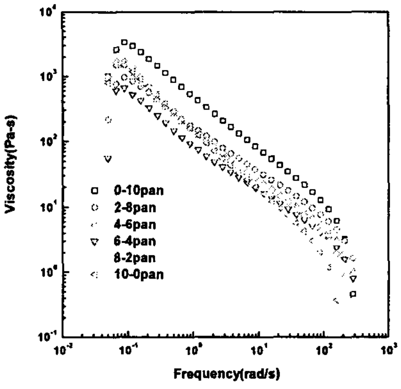

figure 1. Viscosity curves of PVA/PAN/DMSO solutions at 60℃

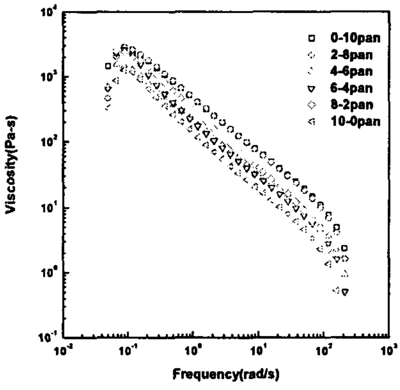

figure 2. Visocosity curve of PVA/PAN/DMSO solutions at 75℃

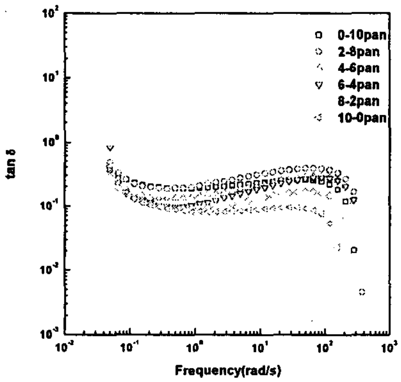

figure 3. tan δ curve of PVA/PAN/DMSO solutions at 60℃

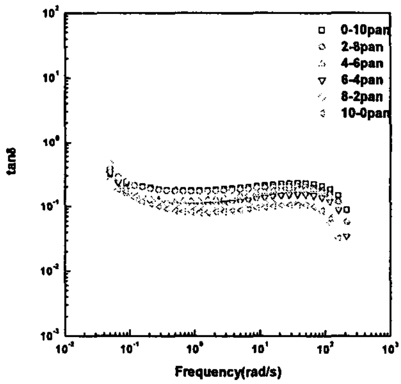

figure 4. tan δ curve of PVA/PAN/DMSO solutions at 75℃

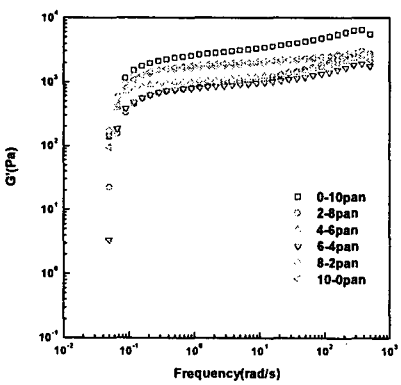

figure 5. storage modulus of PVA/PAN/DMSO solutions at 60℃

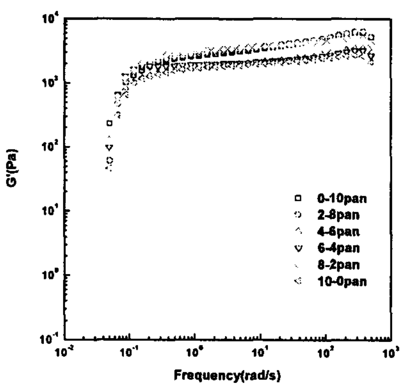

figure 6. storage modulus of PVA/PAN/DMSO solutions at 75℃

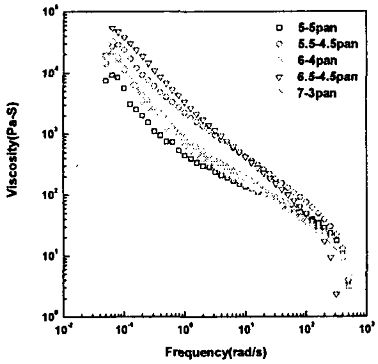

figure 7. Viscosity curve of PVA/PAN/DMSO solutions at 60℃

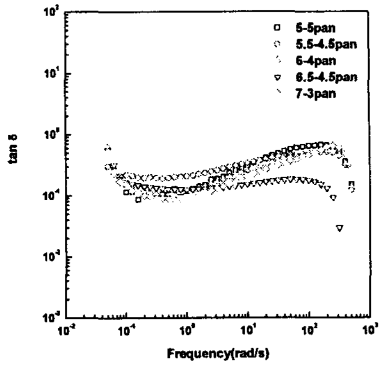

figure 8. tanδ curve of PVA/PAN/DMSO solutions at 60℃

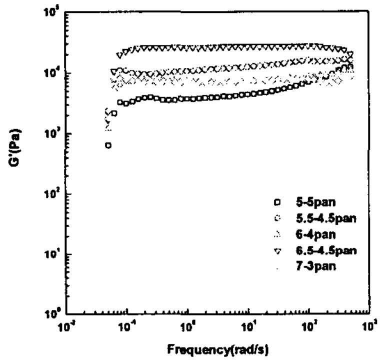

figure 9. storage modulus of PVA/PAN/DMSO solutions at 60℃

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