

폴리아크릴로니트릴/셀룰로오스 아세테이트/*N,N*-디메틸포름아미드 용액의 유변학적 특성

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The Rheological Properties of Poly(acrylonitrile)/ Cellulose Acetate Blend Solutions in *N,N*-Dimethyl Formamide

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초록: 폴리아크릴로니트릴(PAN)과 셀룰로오스 아세테이트(CA) 블렌드/디메틸포름아미드(DMF) 용액의 유변학적 특성을 온도와 블렌드 조성비에 대하여 조사하였다. 모든 고분자 용액이 온도 변화에 따라 매우 특징적인 유변학적 거동을 보였다. 8 wt% 용액의 경우 20~60 °C 온도범위에서 온도의 증가와 더불어 용액의 점도가 증가하고 손실탄젠트값이 감소하였다. 20 °C에서는 용액의 물성이 블렌드의 조성에 영향을 받았으나 40 및 60 °C에서는 조성비가 용액 물성에 미치는 영향이 크게 감소하였다. 더 높은 온도에서의 더 긴 분자 이완시간으로부터 온도가 증가함에 따라 분자간력에 의한 물리적 구조 형성이 촉진된다는 것을 알 수 있었다. 이러한 유변학적 특성에 대한 원인은 묽은 용액의 특성으로부터 유추할 수 있었다. 고분자 용액의 고유점도가 온도가 증가함에 따라 감소하였다.

Abstract: The rheological properties of poly(acrylonitrile) (PAN) and cellulose acetate (CA) blend solutions in *N,N*-dimethyl formamide (DMF) were investigated in terms of temperature and blend composition. The solutions exhibited a very characteristic rheological behavior with variation of temperature. 8 wt% solution showed an increase of viscosity and a decrease of loss tangent as temperature was increased over the temperature range of 20 and 60 °C. At 20 °C the physical properties of the solutions exhibited dependence on the blend composition. At 40 and 60 °C, however, the effects of blend ratio on the physical properties notably diminished. The longer relaxation time at higher temperature indicated that the formation of physical structures resulting from intermolecular interactions was promoted with increasing temperature. The odd rheological responses were further elucidated by measuring of the physical properties of dilute solutions. The intrinsic viscosity of the solutions suggested that the coiled chain dimension was reduced with increasing temperature.

Keywords: poly(acrylonitrile), cellulose acetate, blend, solution, rheological properties.

Introduction

Polymer blends have been extensively studied in both academic and industrial aspects because polymer blending is a common and convenient way of developing new materials with designed properties which cannot be obtained by a single polymer alone.^{1,2} Poly(acrylonitrile) (PAN) is mainly used to produce films or fibers.^{3,4} In recent years, there have been lots of efforts to develop newly advanced materials based on these products.⁵ One of the examples is a carbon nanofiber which can be used in portable electronics, mobile phones,

electric vehicles, and other electronic devices. It is promising to prepare a porous carbon nanofiber of large surface area for these purposes. On the whole, the nanofibers are prepared by electrospinning. Carbonization of a polymer blend would produce a porous carbon material. Thus it may be helpful to use a blend precursor nanofiber to obtain porous carbon nanofiber. However, it is well known that PAN is rarely compatible with most other polymers due to the strong dipole-dipole interactions of nitrile groups.^{6,7} On the other hand, cellulose acetate (CA) is compatible with several synthetic polymers having electron-rich pendant group and frequently used as matrix materials having advantages as film formers.^{8,9} So CA was selected as the blend component of PAN and *N,N*-

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dimethyl formamide (DMF) was chosen as a co-solvent of the two polymers. As a preliminary study to the electro-spinning of PAN/CA solutions in DMF, their rheological properties of the blend solutions in DMF were investigated in terms of blend ratio and temperature.

Experimental

Materials. PAN and CA were purchased from Aldrich Co. (USA), whose molecular weight was 140000 and 50000, respectively. The degree of substitution of CA, the average number of hydroxyl groups substituted per anhydroglucose unit, was 2.5, which means acetyl content of cellulose acetate was 39.7 wt%. DMF was purchased from Dukan Co. (Korea). PAN, CA, and DMF were used without further purification. PAN and CA were dissolved in DMF with stirring for 6 hrs at 60 °C.

Measurement of Rheological Properties. Reduced and inherent viscosities of the polymer solutions were measured at 20, 40 and 60 °C by Ubbelohde viscometer (Schott Co.) over the concentration range, 0.1 ~ 0.6 g/dL. The solution was kept for 5 min prior to measurement to ensure the stabilization at the measuring temperature. Intrinsic viscosity was evaluated from the reduced and inherent viscosity data.

Dynamic rheological properties of the polymer solutions were measured by Advanced Rheometric Expansion System (ARES, Rheometric scientific). In rheological measurement, the concentration of solution was 8 wt%. The parallel-plate geometry with a diameter of 50 mm for solutions was used. The plate gap and strain level were 1 mm and 5%, respectively. Heavy mineral oil (Aldrich Co.) was used to prevent the evaporation of the solvent during measurement from the samples. Dynamic frequency sweep measurement was conducted over the angular frequency range of 0.05 to 500 rad/s at 20, 40 and 60 °C.

Results and Discussion

Rheological Properties of Blend Solutions. Figure 1 presents the dynamic viscosity curves of 8 wt% PAN/CA blend solutions at 20, 40, and 60 °C. It is seen that increasing CA content in the blends decreased the dynamic viscosity of the solutions. This indicates that PAN and CA have some limited compatibility in the solution. That is, if there exist specific interactions leading to miscibility between the two polymers the dynamic viscosity would not decrease monotonously. It is because the specific interactions would change the apparent molecular of the polymers. However, the blend solutions exhibit almost a linear decrease of the dynamic

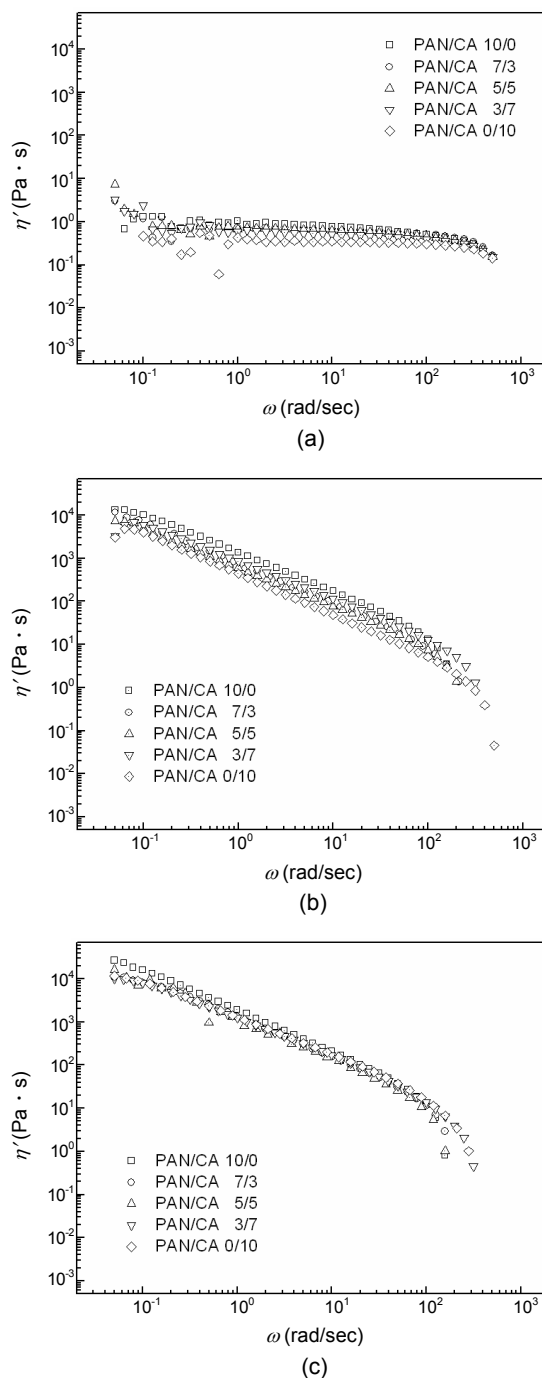


Figure 1. Dynamic viscosity curves of 8 wt% PAN/CA blend solutions in DMF: (a) 20; (b) 40; (c) 60 °C.

viscosity with CA content. This can be further supported by the fact that two polymers are immiscible at an arbitrary blending ratio when the difference in the solubility parameters between them is greater than 0.5 (cal/cm³)⁻². The solubility parameters of PAN and CA are reported to be 15.4 and 10.9 (cal/cm³)⁻², respectively.¹⁰ Consequently, PAN and CA in DMF are thermodynamically immiscible. According to Wang *et. al.*,¹⁰ however, a dynamically stable blend solution can be obtained

even if there is a tendency of phase separation due to the high viscosity of the blend solution and the slow movement of macromolecular chains. The limited compatibility suggested by rheological properties seems to result from this phenomenon.

It is a general rule that the dynamic viscosity of a polymer solution is decreased with increasing temperature. However, it should be noted in Figure 1 that increasing temperature increases dynamic viscosity of PAN and PAN/CA solutions. In addition, it should also be noted that increasing temperature makes the solutions increase the Bingham character. This means that the polymer solutions get more nonhomogeneous with increasing temperature. This seems to originate from the change in solubility of the polymers to the solvent with temperature. To elucidate the odd behavior of viscosity with temperature, the physical properties of dilute PAN/CA/DMF solution systems were measured.

The intrinsic viscosity of polymer solutions is usually studied under extremely diluted conditions where polymer chains are separated by large distances and the interactions between them are reduced to be negligible.¹¹ Important information on the chemical nature of polymers is revealed by the viscosity of a polymer in the dilute polymer solutions because it reflects the physicochemical state of individual polymer chains.¹²⁻¹⁴ Table 1 lists values of intrinsic viscosity of PAN/CA solutions in DMF at several temperatures. Intrinsic viscosity is diminished with increasing temperature at each PAN/CA blending ratio, suggesting that apparent volume of individual polymer decreases with increasing temperature. In other words, a coil dimension of individual polymer is decreased with increasing temperature. Such coil shrinkage reflects reduction of solubility of the solvent to the polymer. In addition, increasing the

CA content in the blends decreases intrinsic viscosity as well. These facts suggest that increase of temperature and reduction of CA content may increase the inter-, intra- chain interactions through the polar groups attached to the backbone because coil shrinkage renders their interactions much easier. In consequence, the higher dynamic viscosity at higher temperature comes from increased pseudostructures resulting

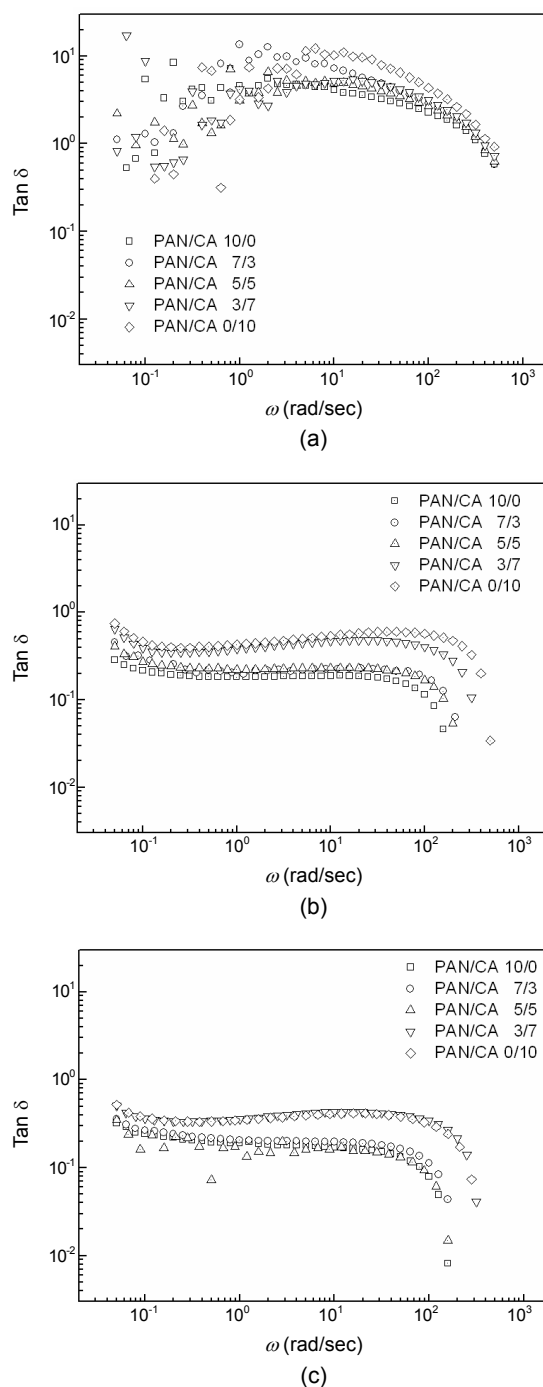


Figure 2. Loss tangent curves of 8 wt% PAN/CA blend solutions in DMF: (a) 20; (b) 40; (c) 60 °C.

Table 1. Intrinsic Viscosity of Dilute PAN/CA/DMF Solutions

Ratio of PAN/CA (by weight)	Measuring temperature (°C)	Intrinsic viscosity
10/0	20	1.73
	40	1.59
	60	1.24
7/3	20	1.55
	40	1.43
	60	1.15
5/5	20	1.50
	40	1.26
	60	1.08
3/7	20	1.49
	40	1.27
	60	0.94
0/10	20	1.40
	40	1.17
	60	0.96

from increased intermolecular interactions. Figures 1(b) and 1(c) show more noticeable Bingham behavior.

Plot of loss tangent ($\tan \delta$) against frequency may give an important clue to elucidating the elastic behavior under stresses because $\tan \delta$ is a quantitative measure of solid-like elastic or liquid-like viscous properties of a system under given stresses.¹⁵ The $\tan \delta$ curves of PAN/CA solutions are plotted against frequency in Figure 2. At 20 °C the solutions show fluid character whereas they show gel character at 40 and 60 °C. The solid-like elastic property in Figures 2(b) and 2(c) reflects the strong physical structure induced by secondary bonding as previously mentioned.

The disappearance of lower Newtonian flow region is indicative of the presence of 3-dimensional pseudostructure, giving rise to a positive yield stress, the minimum energy required to break pseudostructure. It is recognized that yield behavior of heterogeneous systems is well characterized by adopting the modified Casson plot defined by Eq. (1)

$$G''^{1/2} = G_y^{1/2} + K\omega^{1/2} \quad (1)$$

in which G_y stands for yield stress and K is constant.¹⁶ Table 2 lists the values of yield stress of the solution systems. As predicted, the yield stress is increased with increasing temperature or with decreasing CA content. The heterogeneity of the solution systems can further be ascertained by modified Cole–Cole plot, a logarithmic plot of storage modulus (G') versus loss modulus (G''). It is recognized that an isotropic homogeneous polymer solution system gives a temperature-independent master curve whose slope of this plot is 2 but a heterogeneous polymer solution system gives a slope less than 2.¹⁷ The slopes in Figure 3 are less than 2, indicating the solution system is a heterogeneous system, suggesting the presence of physical structure in the polymer solutions through polar interactions between the polymer chains.

For the polymeric systems in which some pseudo-structures are involved, relaxation time (λ) under shear can be calculated by Eq. (2).¹⁸

$$J' = G' / ([\eta^*] \omega)^2 = \lambda / [\eta^*] \quad (2)$$

in which, J' and η^* are compliance and complex viscosity, respectively. The relaxation time of the solution systems is expected to be sensitive to the presence of pseudostructure.¹⁹ Some molecular order or physical structure is sure to increase the relaxation time.²⁰ Figure 4 indicates that in-

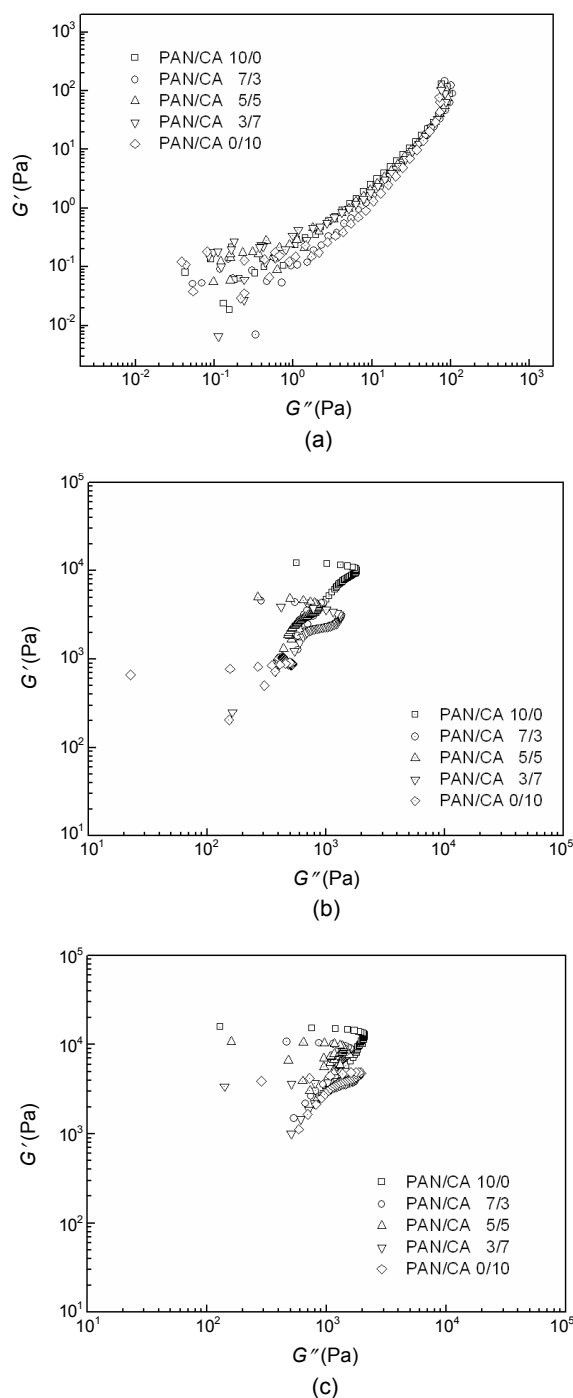


Figure 3. Modified Cole–Cole plot of 8 wt% PAN/CA blend solutions in DMF: (a) 20; (b) 40; (c) 60 °C.

Table 2. The Value of Yield Stress of PAN/CA/DMF Solutions Obtained by Extrapolating to Zero Shear Rate on the Casson Plot

Ratio of PAN/CA (by weight)	Yield stress (τ_y) (Pa)		
	20 °C	40 °C	60 °C
10/0	0.04861	36.72109	39.35707
7/3	0.07700	23.84765	28.23750
5/5	0.09502	19.56295	28.88006
3/7	0.13422	13.64723	26.35334
0/10	0.00925	13.25442	26.23077

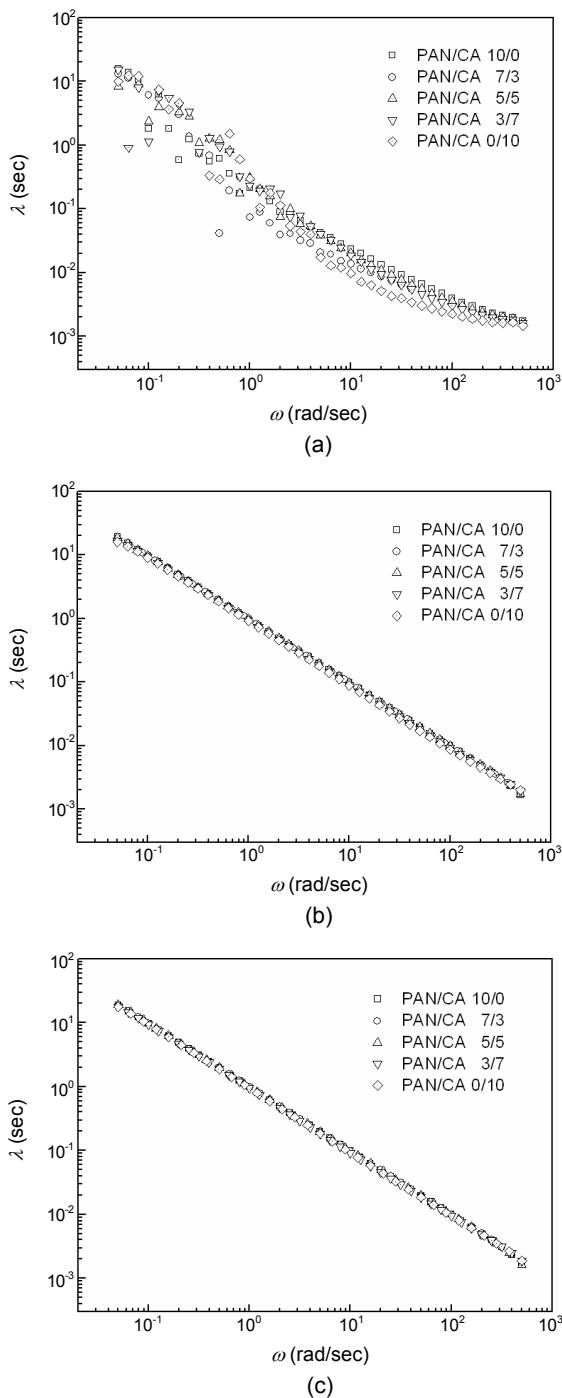


Figure 4. Relaxation time curves of 8 wt% PAN/CA blend solutions in DMF: (a) 20; (b) 40; (c) 60 °C.

creasing temperature lessens the effects of blend composition of the two polymers, which agrees with the loss tangent curves. That is, the weaker pseudostructure would be generated at 20 °C whereas very strong physical structure would be produced at 40 and 60 °C. Hence blending ratio independent relaxation time is observed at these temperatures because the effects of secondary bonding rule over

the individual molecular motions.

Conclusions

Increasing temperature increased the dynamic viscosity of PAN/CA blend solutions in DMF as is often the case with most other polar polymer systems. This could be explained by intrinsic viscosity data. On the whole, increasing temperature decreased the coil dimension of the polymers. Hence, there might be some phase separation of nano-scale at higher temperature, which made the polymer solution more heterogeneous. This suggests that the odd temperature-dependence of the rheological properties should be taken into account in the process design of the PAN and PAN/CA solutions in DMF. Thus these results can be effectively utilized as basic knowledge for the fabrication processes of PAN based blend solutions such as electrospinning, film casting, and fiber spinning.

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