

Polymer Electrolytes Based on Poly(ethylene glycol) and Cyanoresin

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ABSTRACT: Polymer electrolytes based on a mixed polymer matrix consisting of poly(ethylene glycol) (PEG) and cyanoresins with lithium salt and plasticizer were prepared with an *in situ* blending process to improve both the mechanical properties and the ionic conductivity (σ). The PEG/lithium perchlorate (LiClO_4) complexes, including blends of cyanoethyl pullulan (CRS) and cyanoethyl poly(vinyl alcohol) (CRV), exhibited higher σ 's than a simple PEG/ LiClO_4 complex when the blend compositions of CRS/CRV were 5 : 5 or 3 : 7 or than CRV alone. When the CRS/CRV blend was compared with a copolymer of cyanoethyl pullulan and cyanoethyl poly(vinyl

alcohol) (CRM) in the same molar ratio, the σ values of the polymer electrolytes containing the CRM copolymer series were slightly higher than those of the CRS/CRV blends containing PEG/ LiClO_4 complexes. Moreover, the addition of cyanoresin to PEG/ LiClO_4 /(ethylene carbonate-propylene carbonate) polymer electrolytes provided better thermal stability and dynamic mechanical properties. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2402–2408, 2007

Key words: conducting polymers; functionalization of polymers; polyelectrolytes

INTRODUCTION

Conductive polymers and materials have been widely investigated recently because of their potential application in developing electrochemical industries.^{1–9} Since Baughman¹⁰ suggested a potential application of conductive polymers to artificial muscles, conductive polymer actuators have been investigated extensively but have mainly been used in liquid electrolytes.^{11,12} Recently, conductive polymer actuators with solid-state electrolytes instead of liquid electrolytes have been investigated by several research groups.^{13–15} Actuators with solid-state electrolytes, which can operate in air, are suitable for an ideal conductive polymer actuator, which should be controlled by an electrical signal, either voltage or current.

Poly(ethylene glycol) (PEG) has a high solvating ability for inorganic salts and shows homogeneous solution mixing because of interactions with polar ether groups and coordination with dissociated cations.^{16–18} However, PEG tends to crystallize at room tempera-

ture, and PEG–salt complexes exhibit a low ionic conductivity (σ) at room temperature.

In general, because σ in the matrix of polymer electrolytes is controlled by an amorphous phase,¹⁹ the existence of a highly resistive crystalline phase with various salts decreases σ . Therefore, studies have been performed to reduce the formation of the crystalline phase in polymer electrolytes and to increase the segmental mobility of the host polymer through grafting,²⁰ copolymerization,²¹ network formation,²² and plasticization of the polymer matrix.²³ The greatest advantage of plasticization over the other methods is the relatively higher σ obtained; however, the major drawback of plasticized electrolytes has been their poor mechanical properties, which are caused by the high degree of plasticization and diffusion out of the plasticizer with long-time use at high temperatures.^{24–27}

Cyanoresins are among the most promising materials for electrical fields because of their high dielectric constants. There are four types of cyanoresins available commercially: cyanoethyl pullulan (CRS), cyanoethyl poly(vinyl alcohol) (CRV), a copolymer of cyanoethyl pullulan and cyanoethyl poly(vinyl alcohol) (CRM), and cyanoethyl sucrose, which is used as a plasticizer. In general, cyanoresins have excellent solubility in organic solvents and are easy to fabricate as films. Furthermore, they are highly transparent and exhibit good mechanical properties when they are

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made into films.²⁸ CRS, CRV, and CRM have tensile strengths of 450, 90, and 300 kg/cm², respectively, and elongations at break of 4.8, 500, and 55% elongation at break, respectively (these data were reported by Shin-Etsu Chemical Co., Chiyoda, Tokyo, Japan). Therefore, we expected that poor mechanical properties and low σ of polymer electrolytes could be overcome by blending with cyanoresins.

In general, polymer electrolytes that can endure cyclic bending movements when a voltage is applied to an actuator must maintain moderate mechanical properties. However, previous polymer electrolytes have exhibited poor mechanical properties and thermal stabilities. Therefore, to improve the mechanical properties and σ , polymer blends consisting of PEG and cyanoresins with lithium salts were prepared by an *in situ* blending process. The blend compositions and working temperatures affecting σ are discussed. In addition, the thermal stability and mechanical properties of the prepared polymer electrolytes were investigated.

EXPERIMENTAL

Materials

PEG with a molecular weight of 20,000 g/mol was purchased from Fluka Chemie GmbH (Steinheim, Switzerland) and was dehydrated *in vacuo* at 100°C for 24 h before use. The cyanoresins used were CRS, CRV, and two from the CRM series (molar ratios = 5 : 5 and 3 : 7); they were obtained from Shin-Etsu Chemical Co., Ltd. (Tokyo). Their chemical structures are shown in Figure 1. Lithium perchlorate (LiClO₄), lithium

tetrafluoroborate (LiBF₄), and lithium trifluoromethane sulfonate (LiCF₃SO₃) were purchased from Sigma Aldrich, Inc. (St. Louis, MO), and each was dried *in vacuo* for 24 h before use. Ethylene carbonate (EC) and propylene carbonate (PC) of high purity (> 99%) were purchased from Acros Organics Co. (Morris Plains, NJ) as a mixed plasticizer with volume ratio of 1 : 1. Acetone was obtained from Dae Jong Chemicals & Metals Co., Ltd. (Siheung, Korea) as a solvent for the *in situ* blending process.

Preparation of polymer electrolyte complexes

The polymer electrolyte complexes were prepared by an *in situ* blending process at room temperature under a nitrogen atmosphere. The PEG, cyanoresin, and EC/PC were mixed with acetone and stirred for 3 h at room temperature. The lithium salt was dissolved in acetone, and the solution was added quickly to the previous polymer blend under a nitrogen atmosphere. The process was performed by stirring at 55°C for 6 h, and then, the excess solvent was reduced to 3–5% of the solution by distillation of the blended solution. The residual solvent was then removed *in vacuo* at 40°C for 24 h. The CRS/CRV blends were prepared with weight ratios of 3 : 7, 5 : 5, and 7 : 3, respectively, and their contents were calculated by the blend composition of PEG to CRS/CRV blend when the sum of PEG and CRS/CRV weights were fixed at 2 g, and their contents were 5, 10, 15, and 20 wt %. The CRM series were also prepared with the same concentrations as the CRS/CRV blends. The sample codes for the cyanoresins examined in this research are listed in Table I. The intrinsic viscosity of CRS, CRV, S-co-V55,

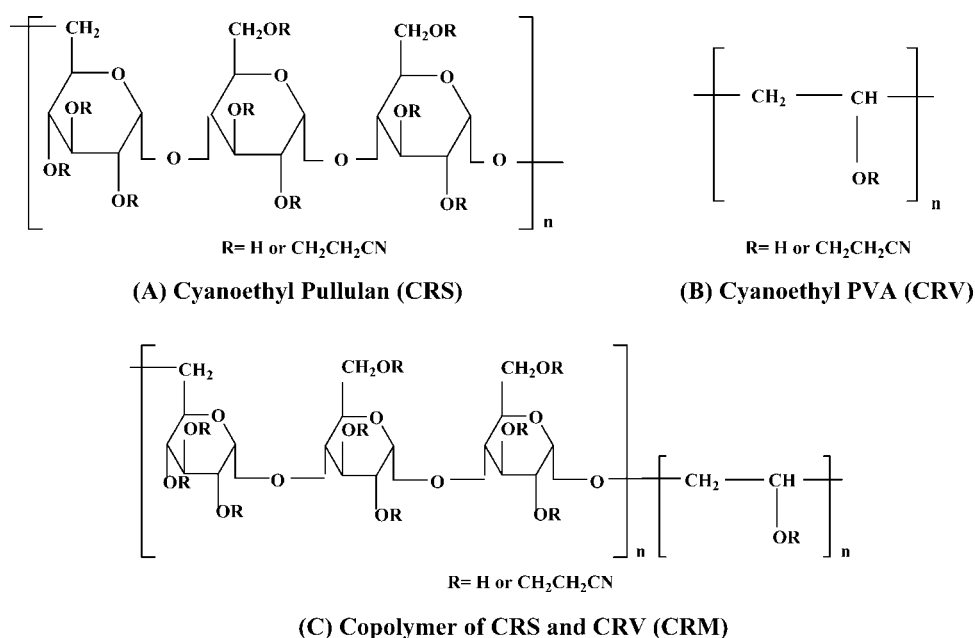


Figure 1 Chemical structures of the cyanoresins.

TABLE I
Codes of the Solution Blends and the Copolymers for the Cyanoresins

Sample type	Sample code	CRS	CRV
Solution blends (CRS/CRV)	SV73	7	3
	SV55	5	5
	SV37	3	7
Copolymers (CRM)	S-co-V73	7	3
	S-co-V55	5	5

and S-co-V37 were 1.0047, 0.9441, 1.0308, and 1.0108 dL/g, respectively, at 30°C, with dimethyl formamide as a solvent. The lithium salt concentration was represented by the molar ratio of the solvating unit for PEG to lithium salts as follows: 0.5, 1.0, 1.5, and 2.0, respectively. The mixed plasticizer composed of EC and PC with weight ratio of 1 : 1 was prepared, and concentrations of 5, 10, 15, 20, 25, and 30 wt % were prepared by the *in situ* blending process and were defined as follows:

$$\text{EC/PC content (wt \%)} = \frac{\text{Weight of incorporated EC/PC}}{\text{Weight of the polymer matrix}} \times 100$$

σ Measurement

The complex impedance measurements on the polymer electrolytes were performed with a frequency response analyzer (IM6, Zahner Elektrik, Kronach, Germany) coupled to a PC-compatible computer over the frequency range 1 kHz–1 MHz and the temperature range 298–338 K, with a constant applied signal amplitude of 200 mV, with an indium tin oxide glass-blocking electrode. The isothermal σ dependence on time was measured for 3 h at 338 K. σ 's of the polymer electrolytes were calculated from the bulk resistance (R_b) in the complex impedance diagram as

$$\sigma = \frac{l}{R_b A} \quad (1)$$

where l is the thickness of the polymer electrolyte film (average $l = 0.023 \pm 0.002$ cm) and A is the surface area of the polymer electrolyte film.

Dynamic mechanical properties

The dynamic mechanical properties of the polymer electrolytes were measured with an Advanced Rheometric Expansion System instrument (Rheometric Scientific Co., Epsom, Surrey, UK) equipped with parallel plates over the frequency range 0.05–450 rad/s at shear strain amplitudes of 5% at 65°C. The sample size of the polymer electrolytes was 25 mm in diameter with a 1-mm gap between the plates.

RESULTS AND DISCUSSION

σ of polymer electrolyte complexes

In the polymer electrolyte, σ could be defined as

$$\sigma = \sum n_i e \mu_i \quad (2)$$

where n_i is the number of ions of species i , e is the electric charge, and μ_i is the mobility of the ions of species i . Equation (2) shows that σ varies with the mobility of the charged carriers and the charge on the species.

Recently, many studies on σ of PEG-containing polymer electrolyte complexes have been reported because of PEG's high solvating and diffusing ability.¹⁶ From the preliminary experiment, σ of the PEG/LiClO₄ complex was 7.15×10^{-5} S/cm at 25°C with a salt concentration of 1.5M, and that of the PEG/LiClO₄/(EC/PC) complex increased up to 4.05×10^{-4} S/cm (25°C) when 30 wt % plasticizer was added. However, the mechanical properties and thermal stability of the polymer electrolytes were expected to decrease with increasing plasticizer content because of the chain slippage of the polymer electrolytes and their inability to endure cyclic bending in a conductive polymer actuator.²⁹ Therefore, to overcome these defects, new polymer electrolyte complexes were prepared by the blending of PEG with various cyanoresins.

First, various lithium salts were applied to select an appropriate salt type for the PEG/cyanoresin system. The effect of salt type on σ of PEG/S-co-V55/lithium salt/(EC/PC) complexes are shown in Figure 2. σ of the PEG/S-co-V55/LiCF₃SO₃/(EC/PC) complex was lower than those of the PEG/S-co-V55/LiBF₄/(EC/PC) and PEG/S-co-V55/LiClO₄/(EC/PC) complexes over the temperature ranges studied. This result may have been due to the larger hydrated radius of the anion for LiCF₃SO₃ compared to the two other lithium

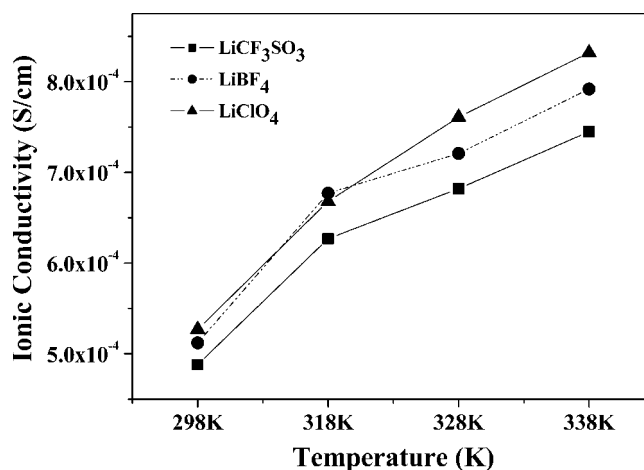


Figure 2 σ of PEG/S-co-V55/salt/(EC/PC) complexes with different salts.

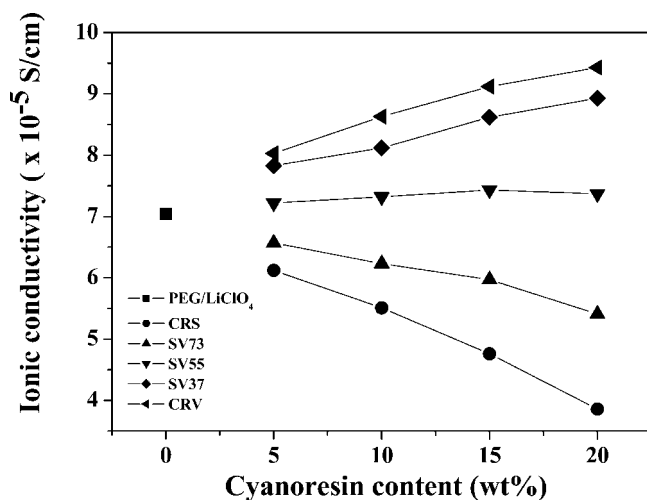
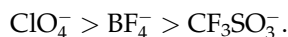


Figure 3 σ of various cyanoresin compositions for PEG/(CRS/CRV)/LiClO₄ complexes at 298 K.

salts, LiBF₄ and LiClO₄. The complex containing LiClO₄ exhibited the highest σ . In general, the degree of dissociation of the lithium salt is dependent on the association tendency of the anions with Li⁺; therefore, as the hydrated radius of the anion increases, the interaction between cation and anion increases, and the ion diffusion or ion mobility in the polymer matrix decreases. The dissociation tendency in nonaqueous aprotic solvents increases in the following order^{30,31}:



From these results, LiClO₄ was selected as the PEG/cyanoresin polymer electrolyte.

Effect of cyanoresin content and composition

Two types of cyanoresin, CRS and CRV, were mixed in different weight fractions. σ 's of the PEG/(CRS/CRV)/LiClO₄ complexes with various cyanoresin contents are shown in Figure 3. The PEG/(CRS/CRV)/LiClO₄ complexes exhibited higher σ 's than the PEG/LiClO₄ complex when the CRS/CRV samples were SV55, SV37, and CRV, respectively. σ of these complexes increased with increasing CRS/CRV cyanoresin content. The PEG/CRV/LiClO₄ complex exhibited the highest σ of 9.42×10^{-5} S/cm when CRV was at 20 wt % at 25°C. Generally, σ of the PEG/(CRS/CRV)/LiClO₄ complexes improved as the CRV component increased in the CRS/CRV blends. It seemed that CRV might have contributed to the ion mobility and may have acted as solvating units in the polymer electrolytes.^{32,33} Generally, viscosity and dielectric constant influence the ion mobility and solvating ability in the matrix.³⁴ Because the intrinsic viscosities of CRS and CRV were 1.0047 and 0.9441 dL/g, respectively, the ion mobility of CRV was greater than that of CRS.

Moreover, because of CRV's high elongation at break (500%) and low tensile strength (90 kg/cm²), we expected that CRV would be flexible and soft, properties that can also improve ion mobility. On the other hand, the dielectric constants of CRS and CRV were 18.1 and 15.6, respectively; this indicated that CRS had a greater ion-solvating ability than CRV. However, σ 's of PEG/CRS/LiClO₄ complexes decreased with increasing CRS content. Even though CRS had a negative influence on σ by reducing ion mobility, it could contribute to its ion-solvating ability. In addition, from the structural standpoint, the somewhat stiff structure of pullulan,³⁵ the main chain of CRS, had a positive effect on the mechanical properties, as shown in previous research.²⁸ Therefore, both CRS and CRV were blended with PEG for further study.

The effect of plasticizer on σ 's of PEG/(CRS/CRV)/LiClO₄ complexes is shown in Figure 4. σ 's of PEG/(CRS/CRV)/LiClO₄ complexes were improved with 30 wt % EC/PC plasticizer. These results could be explained by the segmental motions of the host polymer chains. EC/PC blends were incorporated well in the matrix of polymer electrolytes, and the polymer chains, therefore, became more flexible because of the segmental motions of the polymer chains in the polymer electrolytes.³⁶ Increased chain flexibility ensured the effective solvation of cations and provided suitable solvation entropy to transport ions.²⁹

Comparison of solution blends and copolymer

The performances of the mixture of CRS, CRV, and their copolymer CRM (S-co-V) were compared. σ 's of PEG/(CRS/CRV)/LiClO₄/(EC/PC) complexes and PEG/(S-co-V)/LiClO₄/(EC/PC) complexes at different temperatures are shown in Figure 5. σ of the polymer electrolytes increased with increasing tempera-

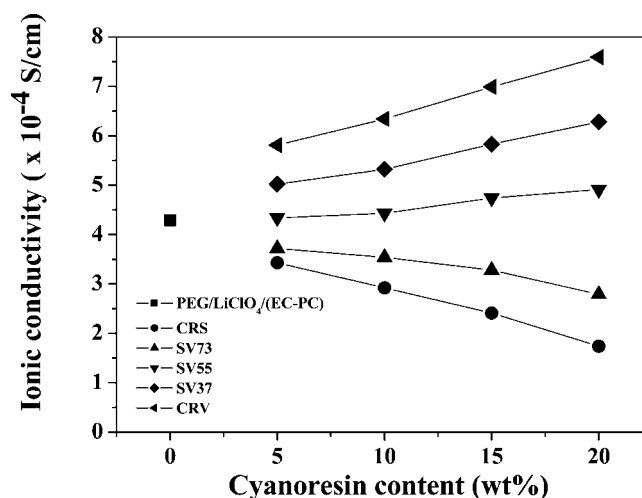


Figure 4 σ of various cyanoresin compositions and plasticizer additions for PEG/(CRS/CRV)/LiClO₄/(EC/PC) complexes at 298 K.

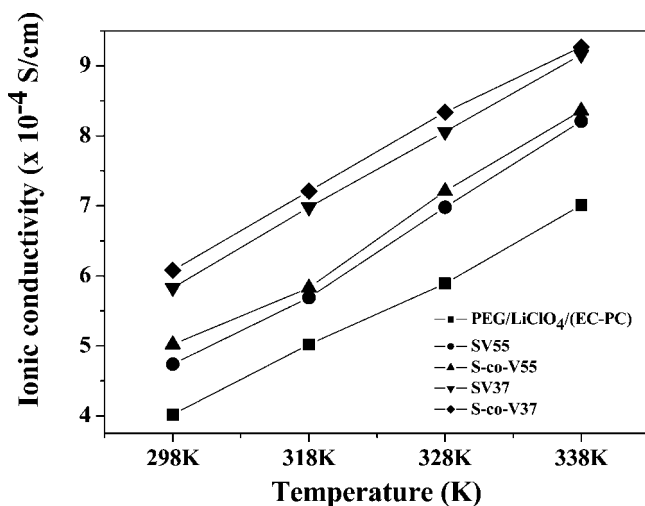


Figure 5 σ of PEG/cyanoresin/LiClO₄/(EC/PC) complexes with 15 wt % cyanoresin at different temperatures.

ture because the expanded free volume allowed more active chain mobility in the polymer matrix.³⁷ When the σ 's for cyanoresin types incorporated in the PEG/LiClO₄/(EC/PC) system were compared, there was no significant difference, even though those of the copolymers of the CRM series were slightly higher than those of the CRS/CRV blends. σ 's of PEG/S-co-V55/LiClO₄/(EC/PC) and PEG/S-co-V37/LiClO₄/(EC/PC) complexes reached 5.02×10^{-4} and 6.19×10^{-4} S/cm, respectively, with 15 wt % CRM addition at 25°C. However, the CRM was expected to have a greater advantage over the blends of CRS and CRV in terms of processability and mechanical properties and σ through improved homogeneity of blend.

Thermal stability of the polymer electrolyte complexes

The changes in σ of various polymer electrolytes at 338 K over prolonged times are shown in Figure 6. Af-

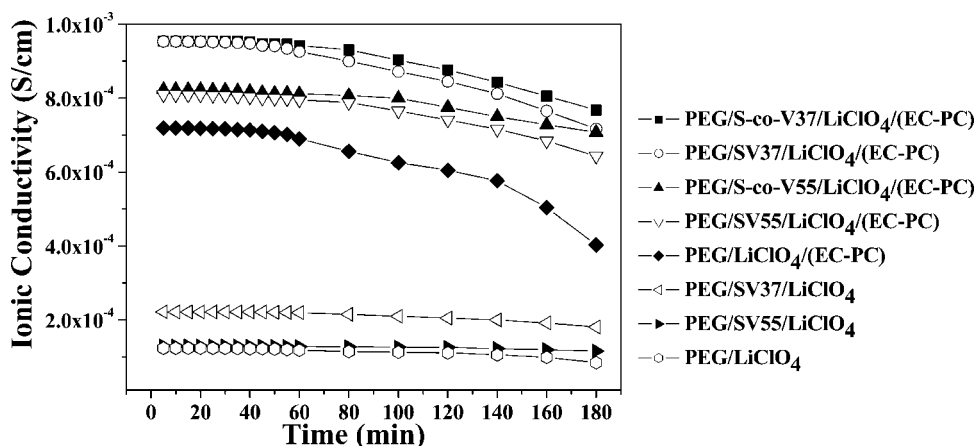


Figure 6 σ of PEG/cyanoresin/LiClO₄/(EC/PC) complexes with 20 wt % cyanoresin for prolonged times at 338 K.

ter 3 h of exposure at 338 K, σ 's of the PEG/LiClO₄, PEG/SV55/LiClO₄, and PEG/SV37/LiClO₄ complexes decreased by 5.1, 3.4, and 5.7%, respectively. Polymer electrolyte complexes without plasticizer exhibited small decrements of σ . However, σ of the PEG/LiClO₄/(EC/PC) complex decreased significantly, by 43.9%. This drawback may have been due to diffusion out of the plasticizer at a high temperature over a prolonged time. On the other hand, through blending with cyanoresin, the reduction in σ of the PEG/SV55/LiClO₄/(EC/PC) and PEG/SV37/LiClO₄/(EC/PC) complexes was reduced to 20.5 and 24.8%, respectively, compared to the PEG/LiClO₄/(EC/PC) complex. It seemed that the cyanoresin incorporated in the matrix may have contributed to the sustenance of the plasticizer. Jayathilaka et al.³⁸ reported that EC/PC existed in two different environments in polyacrylonitrile-based electrolytes. One region included pairwise interactions of EC/PC molecules and CN groups, and the other consisted of free EC/PC molecules. Because the CH₂CH₂CN group in the side chain of the cyanoresin had high polarity, EC/PC molecules were subject to pairing interactions by the CH₂CH₂CN group in the cyanoresin. In the blend composition of CRS/CRV, SV55 had more CH₂CH₂CN groups than SV37, and as a result, the PEG/SV55/LiClO₄/(EC/PC) complex exhibited less of a decrease in σ than the PEG/SV37/LiClO₄/(EC/PC) complex.

The decreases in σ of the PEG/S-co-V55/LiClO₄/(EC/PC) and PEG/S-co-V37/LiClO₄/(EC/PC) complexes were 14.0 and 19.5%, respectively. The differences were probably due to the fact that the copolymer CRM series had more entangled chains and CH₂CH₂CN groups than the CRS/CRV blends, which may have contributed to better holding of more EC/PC molecules. As these results show, the polymer electrolytes consisting of copolymers of cyanoresin exhibited good stability of σ for prolonged times at high temperatures.

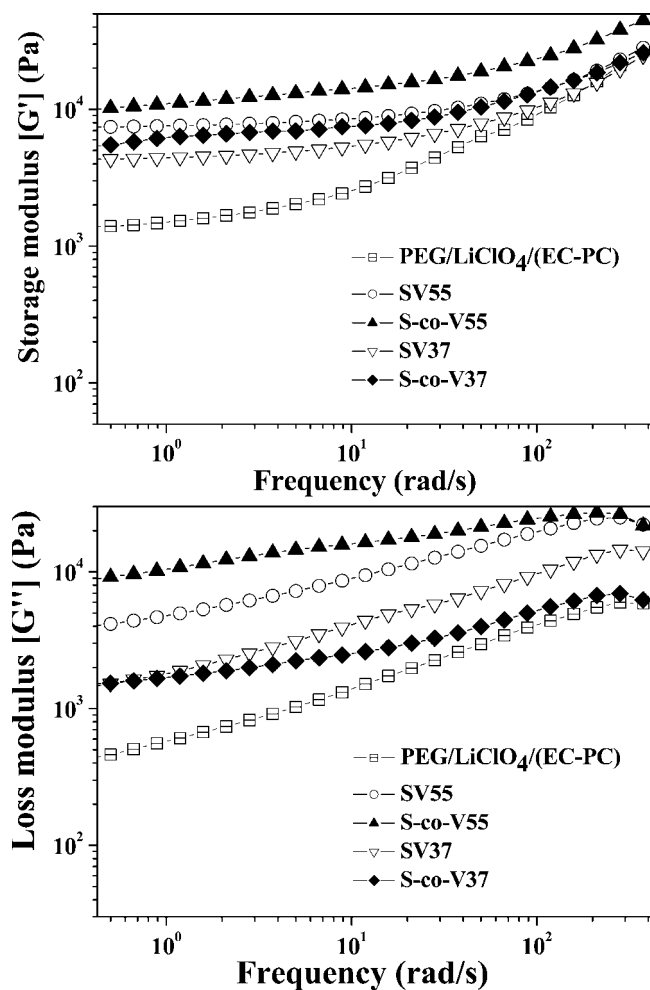


Figure 7 G' and G'' values as a function of frequency for various polymer electrolytes; 15 wt % cyanoresins was incorporated in the PEG/LiClO₄/(EC/PC) complex.

Dynamic mechanical properties of the polymer electrolyte complexes

The storage modulus (G') and the loss modulus (G'') values of the various polymer electrolytes as a function of frequency are shown in Figure 7. G' of all complexes increased with increasing frequency because of their elasticity. In general, enthalpy-driven elasticity effects may occur because the increase in distance between molecular chains caused by the applied shear force leads to higher changes of energy than those in the initial state without shear force, which exhibit the elasticity of polymers. In addition, the number of conformations decrease with decreasing degree of entanglement caused by the applied shear force, which leads to a decrease in entropy.^{39,40} The PEG/LiClO₄/(EC/PC) complex exhibited the lowest G' and G'' , whereas G' and G'' values for the complexes containing cyanoresins were higher than those of the PEG/LiClO₄/(EC/PC) complexes. The formation of hydrogen bonds between pullulan and poly(vinyl alcohol)

was reported by Kim and Choi.³⁵ They reported that hydrogen bonding was formed by the combination of OH groups between pullulan and poly(vinyl alcohol), and it increased with increasing pullulan content in the pullulan/poly(vinyl alcohol) blend. Therefore, in the CRS/CRV blends, the complexes having SV55 exhibited higher values of G' and G'' than the PEG/SV37/LiClO₄/(EC/PC) complexes because of the increase in hydrogen bonding. In addition, the CRM series had higher values of G' and G'' than the CRS/CRV blends because of the formation of hydrogen bonding and more entangled chains. Moreover, G' generally exceeded G'' in all of the complexes in the frequency range measured. This behavior indicated that all of the complexes exhibited gel-like behavior and good mechanical stability.³⁹

The complex viscosity (η^*) of the various polymer electrolytes as a function of the frequency is shown in Figure 8. η^* of all complexes decreased with increasing frequency and exhibited non-Newtonian behavior. In general, non-Newtonian behavior is attributed to anisotropy, including molecular disentanglement, stretching, uncoiling, elongation, and orientation.³⁹ η^* of the CRM series complexes exhibited the same tendencies as their intrinsic viscosities; their complexes had high η^* values because of the formation of hydrogen bonds and the entanglement of chains. In the CRS/CRV blends, η^* increased with increasing CRS content because CRS caused hydrogen bonding in the CRS/CRV blends.³⁵

η^* of all complexes exhibited shear-thinning behavior. The polymer chains were disentangled because of slippage at low frequency; however, the segments between entanglements became oriented before disentangling at high frequency.^{39,40} It may be this behavior that caused η^* to decrease monotonically and the

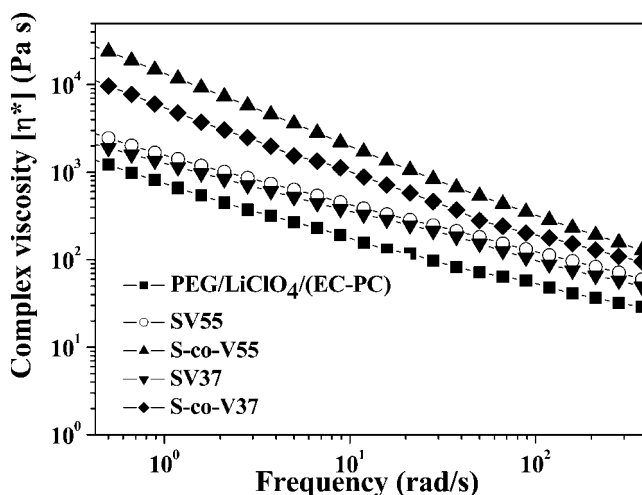


Figure 8 η^* as a function of frequency for various polymer electrolytes; 15 wt % cyanoresins was incorporated in the PEG/LiClO₄/(EC/PC) complex.

complexes to become gel-like⁴⁰ and display non-Newtonian behavior at higher frequencies.

CONCLUSIONS

New polymer electrolyte blends consisting of PEG, CRM, LiClO₄, and EC/PC, were prepared by an *in situ* blending method. In the comparison of CRS and CRV, CRS had a greater ion-solvating ability than CRV; however, CRS's high intrinsic viscosity and stiff structure caused a reduction in ion mobility. In contrast to CRS, CRV showed improved σ because of increased ion mobility. Cyanoresin copolymers and solution blends showed similar σ 's. However, the complexes containing CRM exhibited a better stability of σ than CRS/CRV blends over prolonged times at high temperatures because CRM complexes had more entangled chains and CH₂CH₂CN groups than the CRS/CRV blends, which may have contributed to the better holding of more EC/PC molecules. In addition, G' and η^* values of the complexes containing CRM were higher than those for the PEG/(CRS/CRV)/LiClO₄/(EC/PC) complexes.

In conclusion, CRM complexes had greater advantages than the CRS/CRV blends in terms of easier processing, better mechanical properties, and better σ of the resulting PEG/LiClO₄/(EC/PC) complex. Therefore, we expect that the fabrication of these new polymer electrolytes with their good σ and high mechanical properties will make it possible for them to be applied as electrolyte membranes for polymer actuators.

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