

Improvement of Mechanical and Electrical Properties of Poly(ethylene glycol) and Cyanoresin Based Polymer Electrolytes

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Abstract: Ionic conductivity and mechanical properties of a mixed polymer matrix consisting of poly(ethylene glycol) (PEG) and cyanoresin type M (CRM) with various lithium salts and plasticizer were examined. The CRM used was a copolymer of cyanoethyl pullulan and cyanoethyl poly(vinyl alcohol) with a molar ratio of 1:1, mixed plasticizer was ethylene carbonate (EC) and propylene carbonate (PC) at a volume ratio of 1:1. The conductive behavior of polymer electrolytes in the temperature range of 298–338 K was investigated. The PEG/LiClO₄ complexes exhibited the highest ionic conductivity of $\sim 10^{-5}$ S/cm at 25 °C with the salt concentration of 1.5 M. In addition, the plasticized PEG/LiClO₄ complexes exhibited improvement of ionic conductivity. However, their complexes showed decreased mechanical properties. The improvement of ionic conductivity and mechanical properties could be obtained from the polymer electrolytes by using CRM. The highest ionic conductivity of PEG/CRM/LiClO₄(EC-PC) was 5.33×10^{-4} S/cm at 25 °C.

Keywords: Poly(ethylene glycol) (PEG), Cyanoresin, Polymer electrolytes, Ionic conductivity, Mechanical properties

Introduction

The current interest in the polymer electrolytes consisting of polymer, lithium salt and low molecular weight organic plasticizer has been increased due to their high ionic conductivity and wide application such as lithium batteries, sensors, capacitors and actuating systems [1-10]. In the application of polymer electrolytes to actuators, electrochemical actuators using conductive polymer and electrolytes have been proposed by Baughman [11], Pei [12] and Otero [13]. However, these electrochemical actuators required electrolytes solutions, and they operated absolutely in aqueous environments [13,14]. In recent years, the actuators using various electrolyte complexes, which enable operation in air, were investigated by several research groups [15-17]. The ideal actuator should respond to an electrical signal such as voltage or current and should be required cyclic bending movement. However, it is difficult to achieve an ideal actuator because of mechanical properties of polymer electrolytes.

Since Wright [18] reported high ionic conductivity for poly(ethylene oxide) (PEO)-lithium salt complexes, the polymer electrolytes consisting of PEO and lithium salt have been extensively investigated in order to improve their ionic conductivity and mechanical properties. The PEG can easily solvate various inorganic salts by interaction with polar ether groups in the main chain, and it can form homogeneous solutions by coordinating effectively with dissociated cations [18-20]. However, despite high ionic mobility of PEG-salt complexes with low glass transition temperature, its ionic conductivity is as low as 10^{-7} – 10^{-8} S/cm at room temperature because the PEG tends to crystallize or forms crystalline complexes. Therefore, various studies have been performed to reduce

the crystallinity of polymer electrolytes [21-25]. The plasticization of polymer electrolytes is a common method to improve the ionic conductivity with reduced crystalline phase of polymer electrolytes. However, the major drawbacks of the plasticized polymer electrolytes are known as the solvent volatility and the poor mechanical properties due to high degree of plasticization [26-29]. Therefore, the improvement of mechanical properties sustaining high ionic conductivity is required for plasticized polymer electrolytes.

Cyanoresins are one of the most promising materials for electrical field owing to their high dielectric constants [30]. Their four types are called CRS, CRV, CRM, and CRU. CRS is cyanoethyl pullulan. CRV is cyanoethyl poly(vinyl alcohol). CRU is cyanoethyl sucrose which is used as plasticizer. CRM is a copolymer of cyanoethyl pullulan and cyanoethyl poly(vinyl alcohol). In general, cyanoresin has an excellent solubility in organic solvents and a highly transparent film can be easily fabricated. Furthermore, the CRM has 300 kg/cm² of tensile strength and 55 % of elongation at break (these data were reported by Shin-Etsu Chemical Co.). Therefore, it was expected that poor mechanical properties of polymer electrolytes could be overcome by blending with cyanoresin.

In this research, in order to improve the mechanical properties of the polymer electrolytes with high ionic conductivity, the CRM was incorporated in PEG-lithium salts-plasticizer complexes by *in situ* blending process. The effects of blend compositions, salt types, and measurement temperatures on the ionic conductivity and the mechanical properties of polymer electrolytes were investigated.

Experimental

Materials

PEG with molecular weight of 20,000 g/mol were purchased

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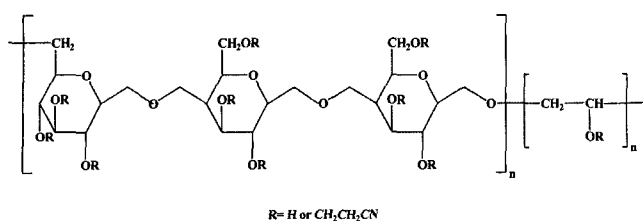


Figure 1. Chemical structure of cyanoresin (CRM).

from Fluka Chemie GmbH., Steinheim, Switzerland and dehydrated *in vacuo* at 100 °C for 24 hrs before use. CRM used was a copolymer of cyanoethyl-pullulan and cyanoethyl-poly(vinyl alcohol) with a molar ratio of 1:1 and obtained from Shin-Etu Chemical Co., Ltd., Tokyo, Japan, its chemical structure was shown in Figure 1. Lithium perchlorate (LiClO₄), lithium tetrafluoroborate (LiBF₄) and lithium trifluoromethanesulfonate (LiCF₃SO₃) were purchased from Sigma Aldrich Inc., St. Louis, MO, USA, and they were dried each *in vacuo* for 24 hrs before use. Ethylene carbonate (EC) and propylene carbonate (PC) with high purity (>99 %) were purchased from Acros Organics Co. (Morris Plains, NJ, USA) as the mixed plasticizer with volume ratio of 1:1. Acetone (Dae Jong Chemicals & metals Co., LTD., Siheung, Korea) was used as solvent for *in situ* blending method.

Preparation of Polymer Electrolyte Complexes

The polymer electrolyte complexes were prepared by *in situ* blending method at room temperature under a nitrogen atmosphere. The reaction was performed by stirring at 55 °C for 6 hrs, and then the excess solvent was removed to 3~5 % solution by distillation of the blends solution. The residual solvent of the distilled blend solutions was removed *in vacuo* at 40 °C for 24 hrs. The lithium salts concentration was represented by molar ratio of solvating unit for PEG to lithium salts as follows: 0.5, 1.0, 1.5 and 2.0. The mixed plasticizer composed of EC and PC with weight ratio of 1:1 were prepared, their contents of 5, 10, 15, 20, 25 and 30 wt% were prepared by *in situ* blending method and were defined as follows; EC-PC contents (wt%) = (weight of incorporated EC-PC/weight of the polymer matrix) × 100. The CRM contents were calculated by the blends composition of PEG to CRM when the sum of PEG and CRM weights are fixed to 2 g, and their contents were 5, 10, 15 and 20 wt%.

Ionic Conductivity Measurement

The complex impedance measurement of polymer electrolytes were performed using a frequency response analyzer (IM6, Zahner Eletrik) coupled to IBM-PC compatible computer over the frequency range of 1 kHz~1 MHz in temperature range of 298~338 K and with the constant applied signal amplitude of 200 mV, using ITO glass as a blocking electrode. The ionic conductivity of polymer electrolytes were calculated from the bulk resistance in the complex impedance diagram

as the following equation (1),

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

where, l is the thickness of the polymer electrolyte film (average film thickness: 0.022 ± 0.002 cm); R_b is the bulk resistance of the sample, and A is the surface of the polymer electrolyte film.

Dynamic Mechanical Properties

The dynamic mechanical properties of the polymer electrolytes were performed by an Advanced Rheometric Expansion System instrument (Rheometric Scientific, Co.) equipped with parallel-plate type over the frequency range of 0.05-450 rad/s at shear strain amplitude of 5 % at 65 °C. The sample size of the polymer electrolytes were 25 mm in diameter and 1 mm in gap of plates.

Result and Discussion

Ionic Conductivity of Polymer Electrolyte Complexes

In the polymer electrolyte, ionic conductivity (σ) can generally be defined as equation (2),

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

where, n_i is the number of ions of species i ; e is the electric charge, and μ_i is the mobility of i ions. Equation (2) shows that the ionic conductivity can be varied as the variety of mobility for the charged carriers and the charged species. The ionic conductivity of the PEG/LiClO₄ complexes with various salt concentrations and the temperature dependence of the ionic conductivity were shown in Figure 2. The PEG/LiClO₄ complexes exhibited the higher ionic conductivity at the salt concentration of 1.5 M than 2.0 M. This tendency

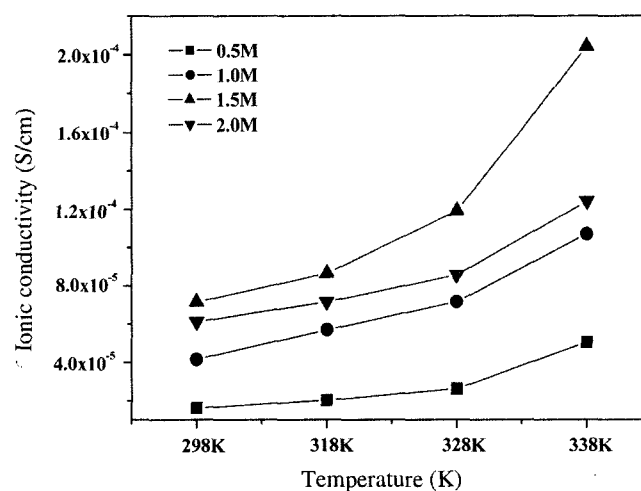


Figure 2. Salt concentration dependence of ionic conductivity for PEG/LiClO₄ complexes at different temperature.

can be explained in terms of ion-ion interactions [31]. As the salt concentration is increased from 0.5 M to 1.5 M, the mutual distance between ions decreases with the increasing number of charged carriers until the minimum distance of ions can resist for ion-ion interactions, therefore, ionic conductivity of polymer electrolytes are increased. However, at the high salt concentration of 2.0 M, ion pairs or ion clouds can be formed by significant interaction between ions, resulting in the reduction of ionic conductivity. In addition, the ionic conductivity of polymer electrolytes are increased with the increasing temperature, since the free volume is expanded, and the chance of ion pair or ion cloud formation is decreased simultaneously, providing more active chain mobility in the polymer matrix [32]. The PEG/LiClO₄ complexes exhibited the ionic conductivity of 7.15×10^{-5} S/cm at 25 °C with the salt concentration of 1.5 M. It is difficult to use for polymer electrolytes because of low ionic conductivity. Therefore, to improve the ionic conductivity of polymer electrolytes, the mixed plasticizer (EC/PC) was added to the polymer electrolytes complexes consisting of PEG and LiClO₄ prepared by *in situ* blending method.

The effect of plasticizer content on the ionic conductivity of the PEG/LiClO₄/(EC-PC) complexes were shown in Figure 3. In general, as the amount of plasticizer increased, the ionic conductivity of polymer electrolytes increased and the highest ionic conductivity of 4.05×10^{-4} S/cm (25 °C) was achieved when 30 wt% plasticizer was added. These results can be explained by the segmental motions of the host polymer chain. As the EC-PC blends are low molecules, they are incorporated well in the matrix of polymer electrolytes, and then the polymer chain exhibit flexibility with the segmental motions of the polymer chains in the polymer electrolytes [33]. Therefore, the chain flexibility effectively ensures the solvation of cations and provides suitable solvation entropy to transport ions [34].

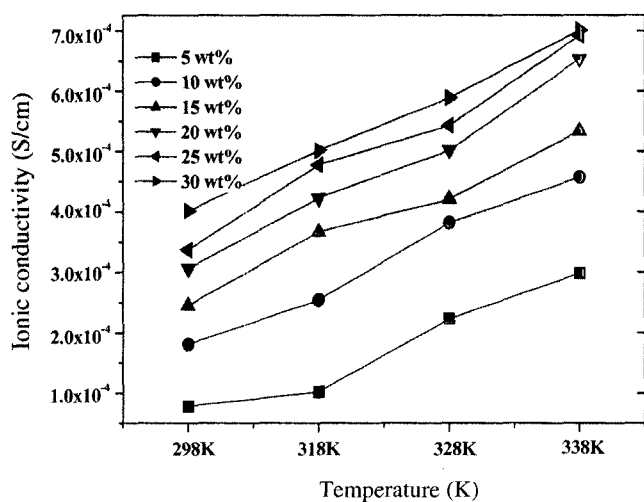


Figure 3. Plasticizer content dependence of ionic conductivity for PEG/LiClO₄/(EC-PC) complexes at different temperatures.

However, generally the mechanical property of polymer electrolytes was decreased by increasing plasticizer contents [34]. We expected that this disadvantage may exhibit the defect such as the slip phenomenon of prepared polymer electrolytes and difficulty for sustaining cyclic bending movement of actuator in preparing conductive polymer actuator. Therefore, new polymer electrolytes were prepared by the addition of CRM.

Effect of CRM Blending

In order to improve the mechanical properties as well as ionic conductivity of the polymer electrolytes, CRM was applied in PEG/LiClO₄/(EC-PC) complex. As shown in Figure 4, the ionic conductivity of PEG/CRM/LiClO₄/(EC-PC) complexes were increased up to the CRM contents of 15 wt% and decreased over its content of 20 wt% at 25 °C. The reasons of the increasing ionic conductivity of PEG/CRM/LiClO₄/(EC-PC) complexes with CRM contents may be assumed that the CRM may contribute to the improvement of solvating ability or may act as solvating units in the polymer electrolytes. However, the ionic conductivity of PEG/CRM/LiClO₄/(EC-PC) complex with 20 wt% of CRM content were decreased. As shown in Figure 5, the morphology of polymer electrolytes was significantly affected by CRM contents. CRM, white particles, were dispersed well when CRM was incorporated in polymer matrix from 5 to 15 wt%. However, we observed that CRM was aggregated to one side of polymer matrix. It is probably due to the formation of hydrogen bond between the cyanoethyl polyvinyl alcohol (PVA) and cyanoethyl pullulan units in the CRM repeat unit. The formation of hydrogen bonding between pullulan and poly(vinyl alcohol) were reported by Kim *et al.* [35] They reported that the hydrogen bonding is formed by the combination of OH group between pullulan and PVA, and it is increased with increasing pullulan contents in the pullulan/PVA blends. Therefore, it is

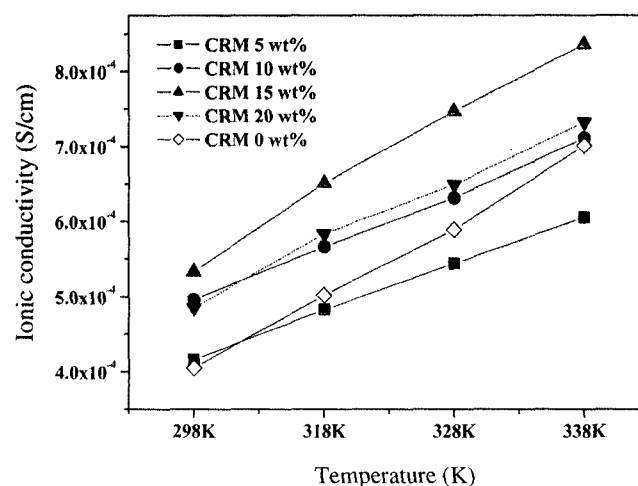


Figure 4. Cyanoresin content dependence of ionic conductivity for PEG/CRM/LiClO₄/(EC-PC) complexes at different temperatures.

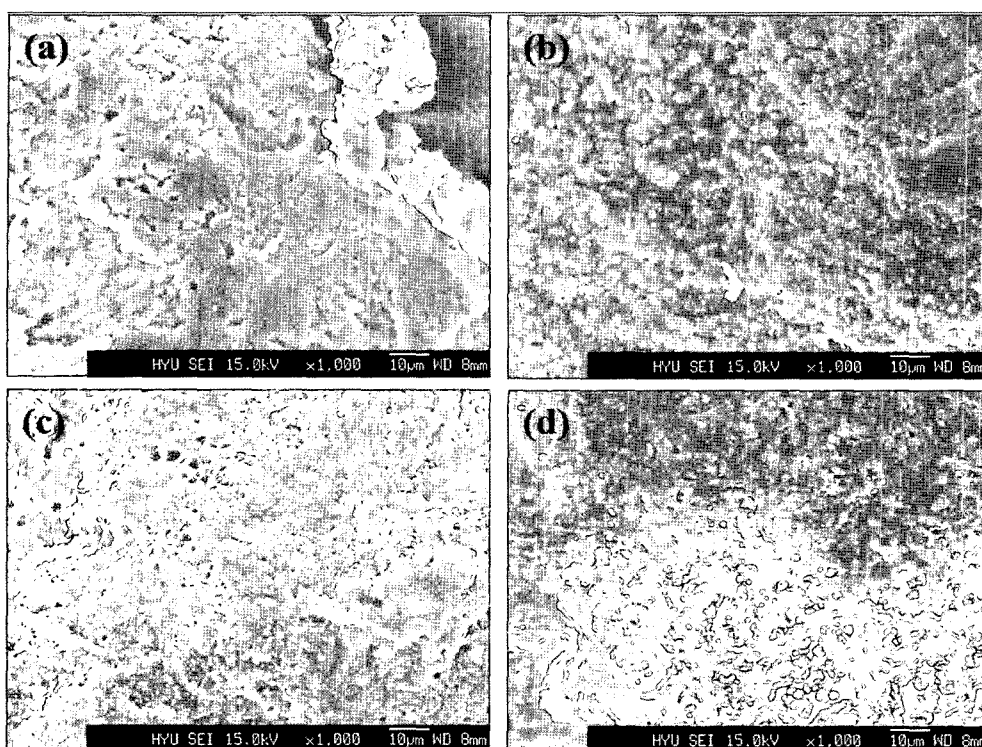


Figure 5. FE-SEM image of PEG/CRM/LiClO₄/(EC-PC) complexes: (a) CRM 5 wt%, (b) CRM 10 wt%, (c) CRM 15 wt%, (d) CRM 20 wt%.

thought that the miscibility of PEG and CRM is good when the CRM content is up to 15 wt%, in the saturation content above 15 wt% of CRM, the hydrogen bond is formed because the interaction of cyanoethyl PVA and cyanoethyl pullulan is overwhelmed dispersibility between PEG and CRM. Therefore, the ionic conductivity of polymer electrolyte containing 20 wt% of CRM is decreased by heterogeneous morphology.

Moreover, the effect of salt types on the ionic conductivity of the polymer electrolytes was studied by comparing two types of polymer electrolytes consisting of the same composition ratio of the highest ionic conductivity for the PEG/LiClO₄/(EC-PC) complexes and PEG/CRM/LiClO₄/(EC-PC) complexes prepared with different salts. The ionic conductivity of the PEG/LiClO₄/(EC-PC) complex, the PEG/LiBF₄/(EC-PC) complex, and the PEG/LiCF₃SO₃/(EC-PC) complex were shown in Figure 6. The ionic conductivity of the PEG/LiCF₃SO₃/(EC-PC) complex was lower than those of the PEG/LiBF₄/(EC-PC) and PEG/LiClO₄/(EC-PC) complexes over the temperature ranges studied. This result may be due to the larger hydrated radius of anion for LiCF₃SO₃ compared to other two lithium salts LiBF₄ and LiClO₄. The complex containing LiClO₄ exhibits higher ionic conductivity. In general, the degree of dissociation for the lithium salt is dependent on the association tendency of anions with Li⁺, therefore, as the hydrated radius of anion is enlarged, the interaction between cation and anion is increased, and then ion diffusion or ion mobility in the polymer matrix is decreased. The dissociation tendency in nonaqueous aprotic solvents increases in the

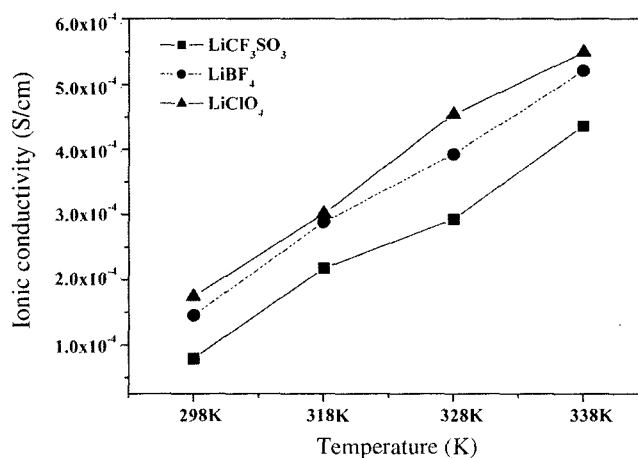
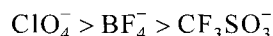


Figure 6. Ionic conductivity of PEG/salt/(EC-PC) complexes with different salts.

following order [36,37]:



As shown in Figure 7, the ionic conductivity of polymer electrolytes containing CRM with different salts were increased and same dissociation tendency for the different lithium salts were exhibited. As these results, it is suggested that the CRM does not have any negative influence on the ion mobility of different lithium salts in the matrix.

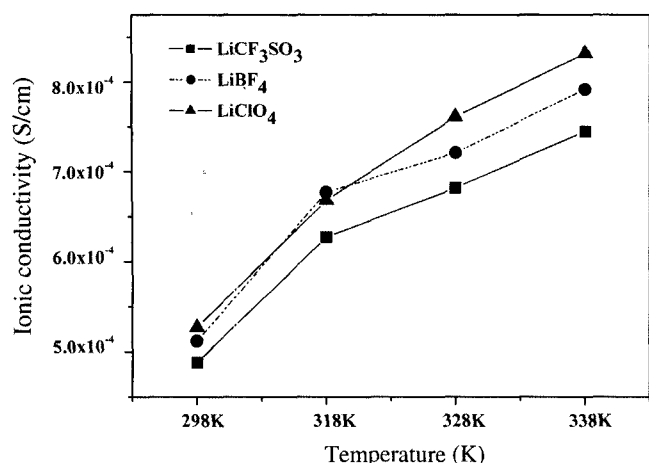


Figure 7. Ionic conductivity of PEG/CRM/salt/(EC-PC) complexes with different salts.

Dynamic Mechanical Properties of the Polymer Electrolytes Complexes

In general, polymeric materials exhibit a non-Newtonian behavior (the decrease in the viscosity with increasing shear rate or frequency), which was attributed to the anisotropy, including molecular disentanglement, stretching, uncoiling, elongation and orientation [38]. Enthalpy-driven elasticity effect may be explained by the fact that the increase in the distance between molecular chains by applied shear force led to higher change of energy rather than that of initial state without shear force, exhibiting the elasticity of polymers. In addition, the number of conformation decreased with decreasing degree of entanglement by applied shear force, leading to the decrease in the entropy [38,39].

The storage modulus (G') and the loss modulus (G'') of the prepared polymer electrolytes as a function of frequency were shown in Figure 8. The G' and G'' values of the PEG/LiClO₄ complex were significantly decreased by addition of EC-PC mixed plasticizer. In the complexes containing the CRM, the G' and G'' values of the prepared polymer electrolytes were significantly increased with increasing CRM contents. The values of G' approximately exceeded than G'' in all complexes with the frequency range measured. This behavior indicated that the all complexes exhibited gel-like behavior and good mechanical stability [38].

The complex viscosity (η^*) of the prepared polymer electrolytes as a function of the frequency was shown in Figure 9. The η^* of all complexes exhibited shear-thinning behavior, the polymer chains are disentangled due to slippage at low frequency, however, the segment between entanglements become oriented before disentangled at high frequency [38,39]. The η^* decreased monotonically as gel-like behavior [39] in the complexes with the increasing the frequency and display non-Newtonian behavior. It is probably due to the segments between entanglements become oriented before the entanglements can be disappeared. In addition, the η^* significantly

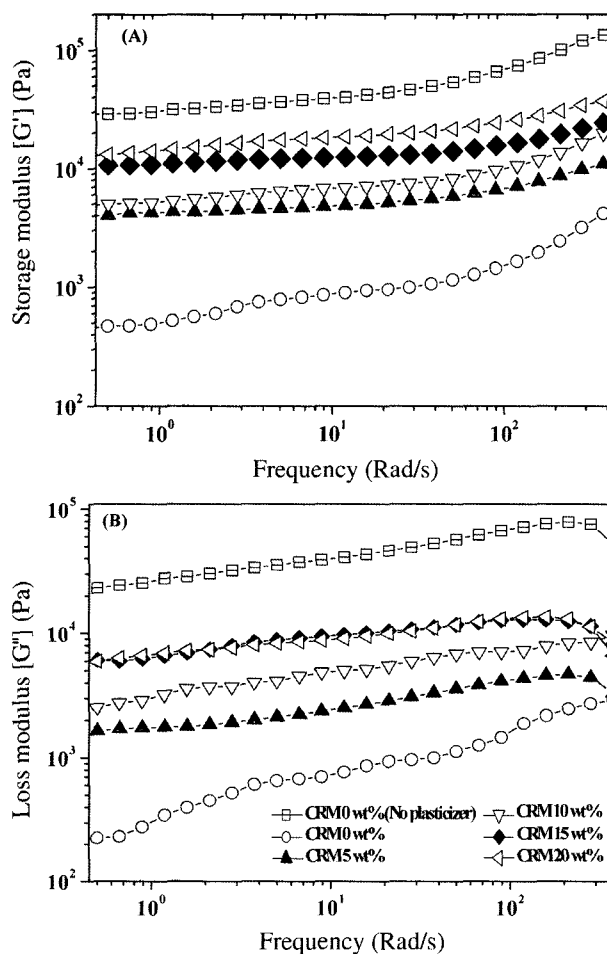


Figure 8. The storage modulus and loss modulus as a function of frequency for PEG/CRM/LiClO₄/(EC-PC) complexes; salt concentration and content of EC-PC are 1.5 M and 30 wt%, respectively.

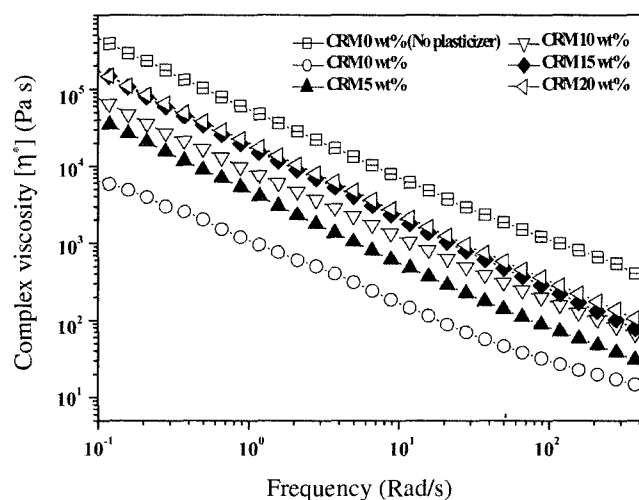


Figure 9. Complex viscosity as a function of frequency for PEG/CRM/LiClO₄/(EC-PC) complexes; salt concentration and content of EC-PC are 1.5 M and 30 wt%, respectively.

increased with increasing the CRM contents. The reason of the increasing G' and η' values with increasing the CRM contents may be affected by increasing the rigid polyethyl-pullulan group in the CRM structure.

Conclusion

New polymer electrolytes based on polymer blends consisting of PEG, CRM, LiClO₄, and EC-PC, were prepared by in situ blending method. The PEG/CRM/LiClO₄/(EC-PC) complexes exhibited higher ionic conductivity than that of the PEG/LiClO₄/(EC-PC) complexes at 25 °C. In addition, the CRM does not have any negative influence on the ion mobility of different lithium salts in the matrix, and the ionic conductivity of the PEG/CRM/LiClO₄/(EC-PC) complex was higher than those of PEG/CRM/LiBF₄/(EC-PC) and PEG/CRM/LiCF₃SO₃/(EC-PC) complex, because of the dissociation tendency for anion of lithium salts. As the CRM contents increased, the dynamic mechanical properties of the polymer electrolytes are improved, implying that the CRM improve the mechanical properties as well as the ionic conductivity of polymer electrolytes. Therefore, it is expected that the fabrication of new polymer electrolytes with good ionic conductivity and high mechanical properties makes it possible to realize their application as the electrolyte membrane to establish polymer actuator.

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