

Polymer Electrolytes Based on Poly(vinylidene fluoride-hexafluoropropylene) and Cyanoresin

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Abstract: Lithium gel electrolytes based on a mixed polymer matrix consisting of poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) and cyanoresin type M (CRM) were prepared using an *in situ* blending process. The CRM used in this study was a copolymer of cyanoethyl pullulan and cyanoethyl poly(vinyl alcohol) (PVA) with a mole ratio of 1:1. The mixed plasticizer was ethylene carbonate (EC) and propylene carbonate (PC) with a volume ratio of 1:1. In this study, the presence of PVDF in the electrolytes helps to form a dimensionally stable film over a broad composition range, and decreases the viscosity. In addition, it provides better rheological properties that are suitable for the extrusion of thin films. However, the presence of HFP has a positive effect on generating an amorphous domain in a crystalline PVDF structure. The ionic conductivity of the polymer electrolytes was investigated in the range 298-333 K. The introduction of CRM into the PVDF-HFP/LiPF₆ complex produced a PVDF-HFP/CRM/LiPF₆ complex with a higher ionic conductivity and improved thermal stability and dynamic mechanical properties than a simple PVDF-HFP/LiPF₆ complex.

Keywords: ionic conductivity, poly(vinylidene fluoride-hexafluoropropylene), *in situ* blending.

Introduction

In recent years, ion conducting polymers have been investigated because of their potential applications in various electrochemical devices, such as high-energy-density batteries, electrochromic devices, capacitors, chemical sensors, and actuating systems.¹⁻¹¹ In the application of polymer electrolytes to actuators, electrochemical actuators using conductive polymers and electrolytes have been proposed by Baughman,¹² Pei,¹³ and Otero.¹⁴ However, these electrochemical actuators required electrolyte solutions, and they were perfectly operated in aqueous environments.^{14,15} Recently, actuators using various electrolyte complexes, which enable operation in air, have been investigated by several research groups.¹⁶⁻¹⁸ The ideal actuator should respond to an electrical signal such as voltage or current and should permit a cyclic bending movement. However, it is hard to achieve an ideal actuator because of the mechanical properties of polymer electrolytes.

As a result of our previous research, the ionic conductivity and mechanical strength of PEG/cyanoresin has been confirmed. However, it is not suitable for an electrochemical actuator because of its low mechanical strength and low ionic conductivity. Therefore, we have looked for a new

material for polymer electrolytes with good mechanical strength and good electrical properties.

Among the different choices of polymer electrolytes, the poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) polymer containing lithium salt solution with ethylene carbonate (EC)/propylene carbonate (PC) is a promising material for batteries based on polymers.¹⁹ Besides its good mechanical stability and easy film fabrication, it is possible to obtain a gel polymer electrolyte that shows conductivity as high as 10⁻³ S/cm.

However, PVDF-based polymer electrolytes suffer from poor interfacial stability towards lithium metal because fluorinated polymers are not chemically stable towards lithium, resulting in an interfacial reaction between lithium and fluorine that forms LiF and makes the PVDF-based electrolytes unsuitable for batteries using lithium metal as the anode.²⁰

Cyanoresin (Cyan) is a most promising material in the field of electricity because of its high dielectric constant. It is classified into four grades (CR-S, CR-M, CR-V, and CR-U) depending on its chemical composition (Figure 1). CR-S and CR-V are the commercial names of cyanoethyl pullulan and cyanoethyl PVA, respectively. CR-M is a copolymer of CR-S and CR-V with a 1:1 ratio. CR-U is the commercial name of cyanoethyl sucrose, used as a plasticizer of Cyan. Cyan has excellent solubility in organic solvents and shows ease of film fabrication. Furthermore, it is highly transpar-

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ent and exhibits good mechanical properties when it is made into a film.²¹

In order to improve the poor interfacial stability of PVdF-HFP, the polymer electrolyte complex needs another chemical bonding material. In our previous research, there were obvious interactions between polymer and Cyan, such as hydrogen bonding,²¹ and those results support the fact that interfacial stability was improved by Cyan.

Higher ionic conductivity is an important factor in polymer electrolytes. However, that is not sufficient to make a given polymer electrolyte into a suitable practical actuator. Therefore, polymer electrolytes based on PVdF-HFP and Cyan were prepared to improve the previous polymer electrolytes which exhibited poor mechanical properties and thermal stability.

In this research, PVdF-HFP/CR-M blend polymer electrolytes have been prepared with EC and PC as plasticizers and LiPF_6 , LiBF_4 , and LiClO_4 as salts. In addition, PVdF-HFP/CRM composite electrolytes were prepared by an *in situ* blending process to improve their mechanical properties.

Experimental

Materials. PVdF-HFP with a molar mass of 400,000 g/mol was purchased from Sigma Aldrich Inc., St Louis, MO, USA, and dehydrated *in vacuo* at 100 °C for 24 h before use. The cyanoresins used were CR-M (a copolymer of cyanoethyl pullulan and cyanoethyl PVA with a mole ratio of 1:1), obtained from Shin-Etu Chemical Co., Ltd., Tokyo, Japan; the chemical structures of the three polymers are shown in Figure 1. Lithium hexafluorophosphate (LiPF_6), lithium tetrafluoroborate (LiBF_4), and lithium perchlorate (LiClO_4) were purchased from Sigma Aldrich Inc., and were dried *in vacuo* for 24 h before use. EC and PC of high purity (> 99%) were purchased from Acros Organics Co.,

Morris Plains, NJ, USA, as the mixed plasticizer with a volume ratio of 1:1. Acetone was obtained from Dae Jong Chemicals & Metals Co., Ltd., Korea, as the 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 PVdF-HFP, cyanoresin, and EC-PC were mixed with acetone and stirred for 3 h at room temperature. After the lithium salt was dissolved in acetone, this solution was added quickly to the above polymer blend under a nitrogen atmosphere. The process was performed by stirring at 25 °C for 6 h, and then the excess solvent was removed to 3-5% solution by distillation of the blended solution. The residual solvent of the distilled blend solutions was removed *in vacuo* at 40 °C for 24 h. Their compositions were calculated from the ratio of PVdF-HFP blend to CRM blend when the sum of PVdF and CRM masses was fixed at 1.2 g, their contents being 2, 3, 4, and 5 wt%. The total portion of plasticizer contents and salt contents was fixed at 40 wt%. The lithium salt concentrations were recorded by weight ratio of lithium salt as follows: 10, 8.75, 7.5, 6.25, and 5 wt%. The mixed plasticizers, composed of EC and PC with a volume ratio of 1:1 were prepared, their contents of 30, 31.25, 32.5, 33.75, and 35 wt% were prepared by an *in situ* blending process, the composition being defined as follows: EC-PC contents (wt%) = (weight of incorporated EC-PC/weight of the polymer matrix) \times 100. The sample codes for the various compositions examined in this research are listed in Table I.

Ionic Conductivity Measurement. The ionic conductivities of the polymer electrolytes were evaluated by the complex impedance method using a frequency response analyzer (HP4192, Hewlett Packard) coupled to an IBM-PC compatible computer over the frequency range of 1 kHz to 1 MHz

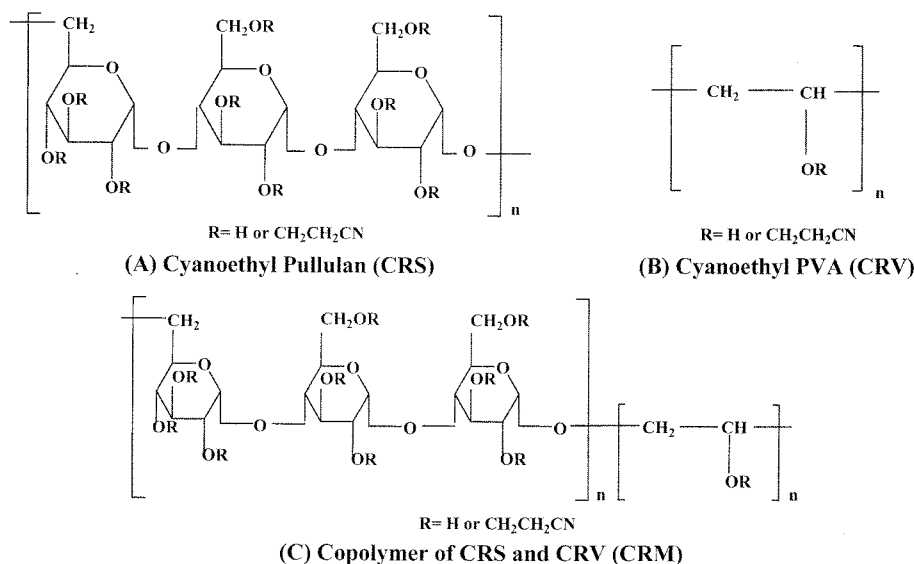


Figure 1. Chemical structures of cyanoresins.

Table I. Composition of Polymer, Additive, Plasticizer, and Lithium Salt

Sample	Polymer PVdF-HFP (wt%)	Additive CRM (wt%)	Plasticizer EC-PC (wt%)	Lithium Salt LiX (wt%)
PC1(LiBF ₄)	59	1	35	5
PC2(LiClO ₄)	59	1	35	5
PC3(LiPF ₆)	59	1	35	5
PC4(LiPF ₆)	59	1	33.75	6.25
PC5(LiPF ₆)	59	1	32.5	7.5
PC6(LiPF ₆)	59	1	31.25	8.75
PC7(LiPF ₆)	59	1	30	10
PC8(LiPF ₆)	60	0	31.25	8.75
PC9(LiPF ₆)	58	2	31.25	8.75
PC10(LiPF ₆)	57	3	31.25	8.75
PC11(LiPF ₆)	56	4	31.25	8.75
PC12(LiPF ₆)	55	5	31.25	8.75

in the temperature range 298-333 K, with an applied signal at amplitude of 200 mV. The ionic conductivity (σ) of the polymer electrolytes was calculated from the bulk resistance in the complex impedance diagram from eq. (1),

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

where, l is the thickness of the polymer electrolyte film (average film thickness: 0.020 ± 0.005 cm); R_b is the bulk resistance of the sample, and A is the surface area of the polymer electrolyte film.

Dynamic Mechanical Properties. The dynamic mechanical properties of the polymer electrolytes were measured using an Advanced Rheometric Expansion System instrument, Rheometric Scientific, Co., equipped with a parallel-plate-type accessory over the frequency range of 0.05-450 rad/s at a shear strain amplitude of 5% at 25 °C. The sample size of the polymer electrolytes was 50 mm in diameter and 1 mm in gap between the plates.

Thermogravimetric Analysis. Thermogravimetric analysis (TGA) of the polymer electrolyte complexes was carried out under an argon atmosphere from 20 to 800 °C at a heating rate of 10 °C/min with a TA Instrument 2960 (New Castle, DE) thermogravimetric analyzer.

Results and Discussion

Ionic Conductivity of Polymer Electrolyte Complexes.

The ionic conductivity of polymer electrolytes depends on various factors. These are the mobility and number of carrier ions in the complexes, as well as the availability of a connecting polar domain as the conduction pathway.¹ By optimizing these factors, high ionic conductivity may be achieved. In the polymer electrolyte, the ionic conductivity (σ) can be defined by eq. (2),

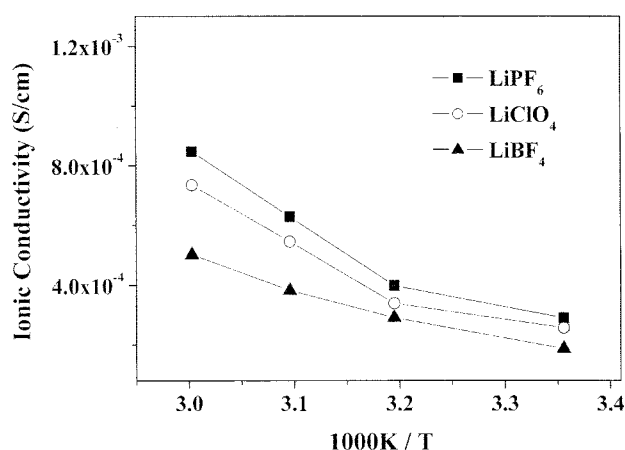


Figure 2. Ionic conductivity of PVdF-HFP/CRM/salt/(EC-PC) complexes with different salts.

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

where n_i is the number of ions of species i , e is the electric charge, and μ_i is the mobility of the i ions. Eq. (2) shows that the ionic conductivity varies as a function of mobility for the charged carriers and the charged species.

First, different lithium salts were applied to selected salt types for the PVdF-HFP/CRM system. Figure 2 shows the temperature dependence of ionic conductivity for different Li salts, LiBF₄, LiClO₄, and LiPF₆, for fixed salt content (5%). It is seen from Figure 2, for the system containing LiPF₆ as salt, that the ionic conductivity ranges from 10^{-4} to 10^{-3} S/cm for different temperatures. The ionic conductivity increases with an increase in temperature. From preliminary experiments on LiBF₄, LiClO₄, and LiPF₆, the films containing LiPF₆ offer the highest ionic conductivity. Because all of the anions are counterions of strong acids, the difference in conductivity is presumably due to the difference in

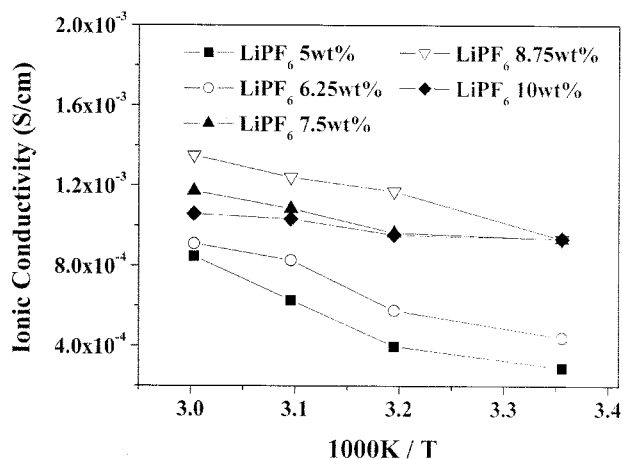


Figure 3. Ionic conductivity of PVdF-HFP/CRM/salt/(EC-PC) complexes with different salt contents.

lattice energies. LiPF_6 has the lowest lattice energy and therefore easier solvation of Li^+ ions by the polymer matrix, which facilitates higher ionic conductivity.²² Because of these results, LiPF_6 was selected as a salt of the best PVdF-HFP/CRM polymer electrolyte complex.

The variation of ionic conductivity as a function of plasticizer and salt with fixed polymer host (60 wt%) containing different contents of LiPF_6 and plasticizer are shown in Figure 3. The ionic conductivity increases with an increase in salt content, LiPF_6 , to a level down to 31.25 wt% of plasticizer and then decreases even further for increase in salt content at 10 wt%. The maximum ionic conductivity was found at 8.75 wt% of Li salt. This dependence is commonly explained in terms of ion-ion interactions and the effect of the plasticizer. As the concentration of Li salts is increased, the mutual distance between the ions decreases with the increasing number of charged carriers until ion-ion interactions become significant. Therefore, the higher the concentration, the stronger the ion-ion interaction, resulting in a change of free ions to ion pairs or to the formation of higher aggregates. Consequently, the ionic conductivity decreases as a result of the decrease of mobility, as well as the number of charged carriers. As the concentration of plasticizer decreased, the segmental motion of polymer chains decreased in polymer electrolytes. Decreased chain flexibility causes difficulty in solvating cations effectively and providing solvation entropy to transport ions. Because of these results, 8.75 wt% of LiPF_6 and 31.25 wt% of plasticizer were selected for the PVdF-HFP/cyanoresin polymer electrolyte.

The ionic conductivity of the PVdF-HFP/CRM/ LiPF_6 complexes with various cyanoresin contents is shown in Figure 4. The PVdF-HFP/CRM/ LiPF_6 complexes exhibited higher ionic conductivity than the PVdF-HFP/ LiPF_6 complex. The ionic conductivities of these complexes increased with increasing CRM content. The PVdF-HFP/CRM/ LiPF_6 complex exhibited the highest ionic conductivity of 1.69×10^{-3} S/cm

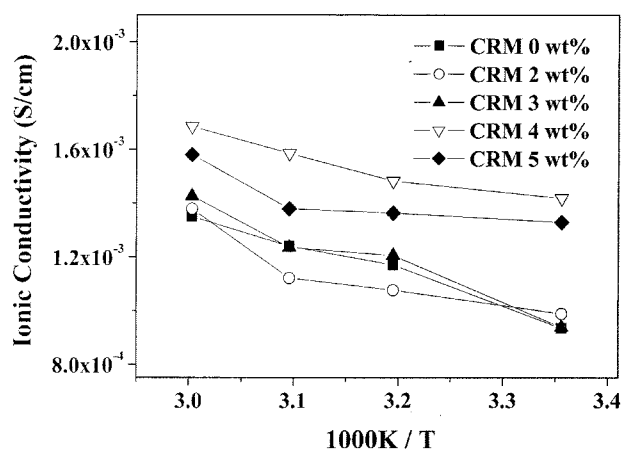


Figure 4. Ionic conductivity of PVdF-HFP/CRM/salt/(EC-PC) complexes with different CRM contents.

when the CRM content was 4 wt% at 333 K. However, we observed that the ionic conductivity of 5 wt% CRM decreased. This is probably due to the formation of a hydrogen bond between the cyanoethyl PVA and cyanoethyl pullulan units in the CRM repeat unit. The formation of hydrogen bonding between pullulan and PVA was reported by Kim *et al.*²¹ They reported that the hydrogen bonding results from the interaction of an O-H group between pullulan and PVA, which is increased with increasing pullulan contents in the pullulan/PVA blends. Therefore, it is noted that the miscibility of PVdF-HFP and CRM is good when the CRM content is up to 4 wt%; but above 4 wt% of CRM, hydrogen bonds are formed between cyanoethyl PVA and cyanoethyl pullulan, which reduces dispersibility between PVdF-HFP and CRM. Therefore, the ionic conductivity of polymer electrolyte containing 5 wt% of CRM is decreased by the heterogeneous morphology.

Dynamic Mechanical Properties of the Polymer Electrolyte Complexes. The storage modulus, loss modulus, and complex viscosities (G' , G'' , and η^* , respectively) of PVdF-HFP/CRM/ LiPF_6 complexes measured at 298 K are given in Figures 5 and 6, respectively. It is seen from Figure 5, for the complex containing CRM, that the storage modulus is 10^3 - 10^4 Pa s at 298 K for different CRM contents. The figure shows that G' and G'' remained approximately constant and G' dominated G'' over the frequency range measured. This is in good agreement with the definition of a gel given by Almdal *et al.*, which is that a gel is a material with a G' that exhibits a plateau extending to times in the order of seconds and a G'' in the plateau region.²³ These results indicate that all of the complexes exhibited gel-like behavior and have good mechanical strength. The PVdF-HFP/ LiPF_6 complex exhibited the lowest G' and G'' , and the G' and G'' for the complexes containing the CRM were higher than those of the PVdF-HFP/ LiPF_6 complex. This apparent increase in G' and G'' with the increase of CRM content is attributed to

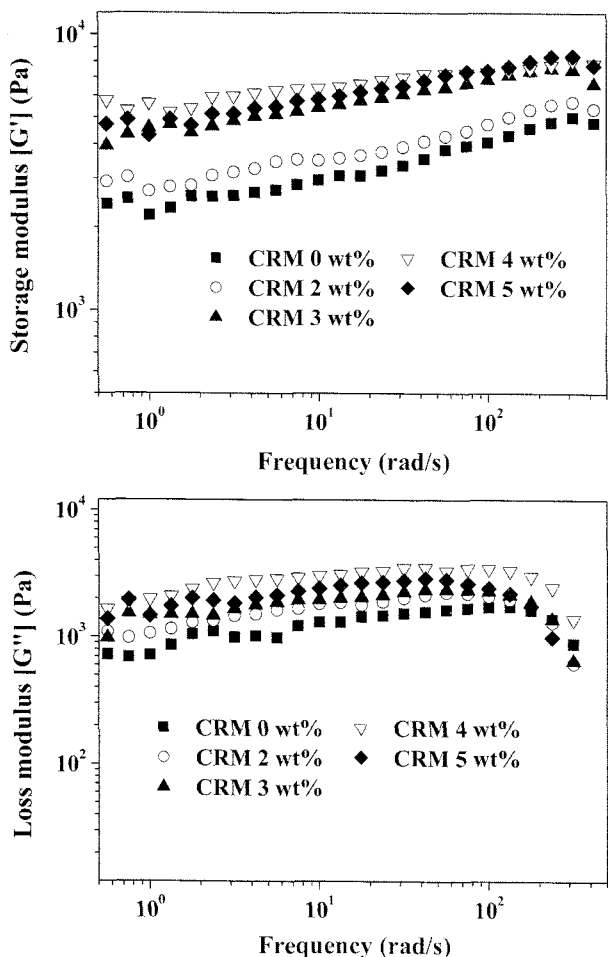


Figure 5. The storage modulus and loss modulus as a function of frequency for various polymer electrolytes.

hydrogen bonding between CRM and PVdF-HFP.²¹

The complex viscosity (η^*) of the prepared polymer electrolytes as a function of the frequency is shown in Figure 6. The η^* of all complexes exhibited shear thinning behavior. This is because the polymer chains are disentangled more and more because of chain slippage with increasing frequency; in addition, the polymer chain segments become oriented after disentanglement of the polymer chains. The η^* at low frequency increases with increase in CRM content because of formation of hydrogen bonding and entanglement of chains.

Thermal Stability. The thermal properties of the polymer electrolyte complexes were evaluated by TGA, the TGA thermograms being shown in Figure 7. In the thermograms of the polymer electrolyte complexes, the initial weight loss was observed between 50 and 100 °C and was attributed to the loss of moisture. A major weight loss was observed from 200 to 300 °C and was due to CRM degradation. Above 400 °C, the weight loss was related to main-chain degradation of PVdF-HFP.

It is generally accepted that reliable degradation tempera-

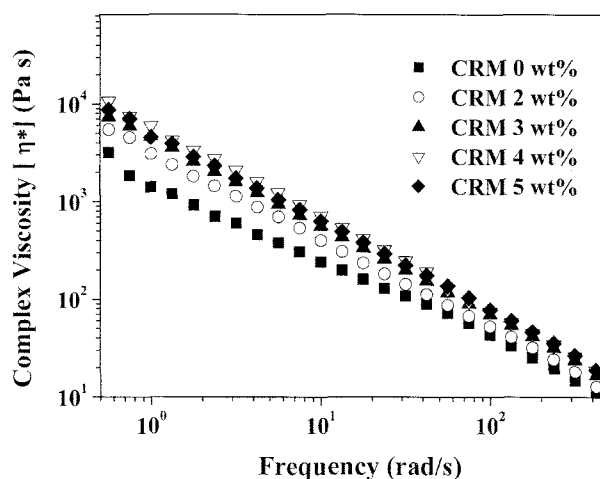


Figure 6. Complex viscosity as a function of frequency for various polymer electrolytes.

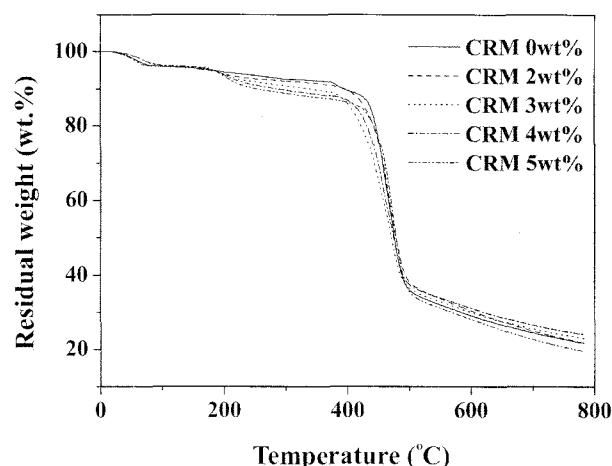


Figure 7. TGA thermograms of PVdF-HFP/CRM/salt/(EC-PC) complexes with different CRM contents.

tures, such as T_{max} and IPDT, can be used to assess a material's lifetime.²⁴ The integral procedural decomposition temperature (IPDT) was calculated as follows:

$$IPDT (^\circ C) = A^* K^* (T_f - T_i) + T_i$$

where A^* is the area ratio of the total experiment curve divided by the total TGA thermogram, K^* is the coefficient of A^* , T_i is the initial experimental temperature, and T_f is the final experimental temperature. The values of the IPDT parameters (A^* , K^*) and IPDT are listed in Table II. As shown in Table II, the PVdF-HFP/LiPF₆ complex had the lowest IPDT value (760.8 °C), and the PVdF-HFP/CRM/LiPF₆ complexes had a somewhat higher IPDT value than the PVdF-HFP/LiPF₆ complex. Therefore, it is possible to enhance the thermal stability of PVdF-HFP through blending with CRM. However, we observed that the IPDT value for 5 wt% CRM decreased. This is probably due to the formation of hydrogen bonding between the cyanoethyl PVA

Table II. Effect of CRM on the Thermal Stabilities of Polymer Electrolyte Complexes

CRM Content (wt%)	T_{max} (°C)	A	K	IPDT (°C)
0	458.14	0.6764	1.442	760.8
2	466.91	0.6745	1.480	778.6
3	471.04	0.6653	1.534	796.0
4	476.49	0.6705	1.566	819.0
5	473.42	0.6595	1.425	733.0

and cyanoethyl pullulan units in the CRM repeat unit. At concentrations above 4 wt% of CRM, weak hydrogen bonding (O-H) takes place and therefore, even though the number of hydrogen bonding sites is higher, the effective number of hydrogen bonding sites available for interaction with fluoride is reduced.

Conclusions

The PVdF-HFP/CRM polymer gel electrolytes complexed with a combination of EC and PC and three different lithium salts have been prepared and their ionic conductivities measured from 298-333 K. The ionic conductivity of the complexes had a range of 10^{-4} to 10^{-3} S/cm. The ionic conductivity of these complexes with LiPF_6 as salt exhibited the maximum ionic conductivity. The ionic conductivity of these complexes increased with increasing CRM content as a result of increased ion mobility. The dynamic mechanical properties showed that G' and G'' for the complexes containing CRM were higher than those of the PVdF-HFP/ LiPF_6 /EC-PC complex. This apparent increase in G' and G'' with increase in CRM content is attributed to hydrogen bonding between CRM and PVdF-HFP. The thermal stability increased with the addition of up to 4 wt% of CRM, whereas the polymer electrolyte complexes became dramatically unstable with more than 5 wt% CRM because of the strength of the hydrogen bonding. These behaviors can be used in the fabrication of new polymer electrolytes with good ionic conductivity, high mechanical strength, and thermal stability.

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