Cellulose Derivatives as Solid Electrolyte Matrixes

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SUMMARY: Cellulose derivatives like hydroxyethylcellulose (HEC) and carboxymethylcellulose (CMC) were submitted to the graftization reactions. The samples of HEC were grafted with monoisocyanate of poly(propylene oxide) (MPPO) and different diisocyanates of poly(ethylene oxide) (DPEO) and poly(propylene oxide) (DPPO) in the presence of $LiClO_4$. CMC was grafted with MPPO. These polyssacharides based samples were characterized by IR, NMR and thermal analysis (DSC and TGA). The samples of grafted polyssacharides derivatives showed glass transition temperatures (Tg) of –40°C for HEC/MPPO, -33°C for HEC/DPEO, –10°C for HEC/DPPO and 24°C for CMC/MPPO. The ionic conductivities of all samples were about 10^{-7}-10^{-6} S/cm at room temperature. The sample of CMC/MPPO presented conductivity value similar to HEC/DPPO but does not exhibit film-forming characteristic indicating its use as solid polymer electrolytes only in the pellet form.

Introduction

Polymer electrolytes with lithium salts dissolved in a polymer matrix have been widely studied ever since the pioneering works of Wright et al.[1] and Armand et al.[2] These materials represent a promising alternative for the substitution of liquid electrolytes and inorganic crystals used in batteries, sensors and electrochromic devices.[3,4] Most of the described systems are based on polyether chains containing $LiClO_4$ salt. Different organic or inorganic systems can be modified by graftization reactions with polyether chains in order to decrease its crystallinity and glass transition temperature and improving the stability, chain mobility and lithium ion conductivity. One example is the electrolytes based on poly(amide 6-b-ethylene oxide) that exhibit the conductivity in the range of 10^{-4} S/cm at 100°C.[5,6]

Cellulose is very attractive because of its abundance in nature. Its hydroxyethyl derivative is also interesting because of its film-forming and good mechanical properties.[7] The cellulose derivative chains can be modified by condensation (graftization) reaction of OH groups with mono or polyfunctional isocyanates making possible the generation of a great variety of

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networks.[8] The ionic conductivity results show that hydroxyethylcellulose based networks are very good candidates for solid polymeric electrolyte. The ionic conductivity of HEC sample grafted with poly (ethylene oxide) diisocyanate (DPEO) and doped with Li salt is about $2.08 \cdot 10^{-5}$ S/cm at 40 °C and $8.8 \cdot 10^{-4}$ S/cm at 60°C.[9]

In this work we present a study of the ionic conductivity of various solid electrolytes based on HEC and CMC grafted with oligoether-based isocyanates.

Experimental

Commercial samples of HEC under the names QP09H, QP4400, and QP30MH from UNION CARBIDE - Brazil, were characterized by determination of structural parameters (Table 1) using techniques already reported.[10]

Table 1. Hydroxyethylcellulose structural parameters.

Parameter	QP09H	QP4400	QP30MH
DS	0.8	0.9	0.5
MS	1.2	1.4	0.9
DP	260	1840	2470

Polyethylene oxide diisocyanate (DPEO), polypropylene oxide diisocyanate (DPPO) and polypropylene oxide monoisocyanate (MPPO) were synthesized from the corresponding Jeffamines (FLUCKA), following previous developed procedure.[11] The solid elastomeric electrolytes were obtained by the reaction between the HEC and the isocyanates in different crosslink concentrations (Table 2).

Table 2. NCO/OH ratio and salt concentration on the various solid polymer electrolytes synthesized.

NCO	$\frac{NCO}{OH}$	QP09H			QP4400			QP30MH		
		Salt Concentration								
		A*	B**	C***	A	B	C	A	B	C
DPEO	0,4	12	6,8	3,0	12,6	7,3	2,9	12	7,3	2,8
	0,6	14	9,7	2,1	12	7,8	2,6	12	8,2	2,5
	0,8	14	10,2	2,0	12,5	9,1	2,3	12	9,1	2,3
DPPO	0,4	12,4	6,8	2,7	13,4	7,3	2,8	12,9	7,3	2,6
	0,6	12	7,8	2,4	12,8	8,3	2,3	12,6	8,3	2,3
	0,8	12,5	8,9	2,1	12,3	8,7	2,1	13,1	9,5	2,0
MPPO	0,4	12	8,1	2,0	12,8	8,6	1,9	12,6	8,7	1,8
	0,6	12	9,1	1,8	12,5	9,4	1,7	12,6	9,7	1,7
	0,8	11,7	9,4	1,7	12,2	9,8	1,6	12,4	10,1	1,6

*A=nO/nLi ($n\mathrm{O}_{\mathrm{HEC}}+n\mathrm{O}_{\mathrm{polyether}}$); **B=$n$O/$n$Li ($n\mathrm{O}_{\mathrm{polyether}}$); ***C=mol $\mathrm{Li}^{+}/\mathrm{dm}^{3}$ polyether

The $LiClO_4$ was introduced during the grafting reaction as described elsewhere.[9] The glass transition temperature (Tg) was determined through differential scanning calorimetry (DSC) measurements performed on a Setaram DSC92 analyzer. The experiments were realized on the temperature range from −140 to 100°C in air atmosphere and heating rate of 10°C/min. Conductivity measurements were carried on a SCHLUMBERGER 1272 impedance analyzer over a frequency range from 1 Hz to 10 MHz under vacuum.

CMC grafted with MPPO samples were obtained by suspension of CMC (0.5 g) in dimethylacetamide (DMAc) (25 ml) and futher addition of p-toluenesulphonic acid (0.4 g) at 60°C. Then the polypropylene oxide monoisocyanate (13 g) was added very slowly maintaining the temperature at 60°C. After that the product was washed with ethanol and pure water, and then dried in vacuum at 50°C. The CMC/MPPO samples were characterized by IR, DSC, TGA and electrochemical measurements.

Results and Discussions

Table 3 shows the Tg values determined from the DSC curves, where no other transition such as melting or crystallization was observed. Samples of DPEO grafted HEC present a constant Tg value around −33°C. This value is independent of the NCO/OH ratio or the salt concentration. This fact can be explained by the conjunction of two phenomena. The first one is that Tg value diminishes with the increasing amount of polyether introduced in the HEC chain until a limit value. After that the Tg becomes independent of the further increase in the degree of reticulation.[12] The second one is related to the salt such as $LiClO_4$ introduced to the forming network. An increasing amount of this salt into a given network produce a progressive increase in the Tg of the material which follows a relationship with salt concentration consistent with a physicochemical crosslinking operated by the cations until a limit value, around 1 mol Li^+/dm^3 polyether. From this a further increase of salt introduced leads to the presence of non-solvated cations that do not participate on this type of crosslinking.[12,13]

Table 3. Values of the glass transition temperature of the solid polymer electrolytes.

		Tg (°C)		
Isocyanate	**NCO/OH**	**QP09H**	**QP4400**	**QP30MH**
DPEO	0.4	-32	-34	-31
	0.6	-34	-31	-32
	0.8	-33	-35	-34
DPPO	0.4	-6	-9	-3
	0.6	-10	-3	-3
	0.8	-4	-5	-6
MPPO	0.4	-29	-34	-51
	0.6	-36	-41	-47
	0.8	-35	-46	-43

All the HEC/DPEO samples have the Tg value of about –30°C independent on the NCO/OH ratio. For the HEC/DPPO samples it was observed that the Tg values are higher when compared with HEC/DPEO samples that can be due to the ramification structure of polypropylene chain. For the HEC/MPPO the Tg value are similar to the HEC/DPEO samples for the small DP (260) of the polysaccharide chain (QP09H) and this value decrease for about –50°C for the DP of 2470 (QP30MH). All the Tg values for the HEC grafted samples were below the 0°C. The Tg value for CMC/MPPO sample was about 24°C.

Figures 1 to 3 show the Arrhenius plot of the solid polymer electrolytes synthesized in this work. The experimental values were fitted (solid lines) using Vogel Tamman Fulcher (VTF) equation. It can be observed that when different samples of HEC are grafted with the same isocyanate the values of the ionic conduction are very similar. It is interesting to note that for a same HEC the response of the film to the conduction experiments seems to be a function of the isocyanate used in the graft reaction. The best conductivity value achieved at 60°C for sample QP09H/DPEO, NCO/OH = 0.6 and $O_{polyether}/Li = 9.7$ was $\sigma = 2.82 \cdot 10^{-5}$ S/cm, for the sample QP09H/DPPO, NCO/OH = 0.8 and $O_{polyether}/Li = 8.9$ was $\sigma = 1.47 \cdot 10^{-5}$ S/cm e for the sample QP09H/MPPO, NCO/OH = 0.4 and $O_{polyether}/Li = 8.1$ was $\sigma = 1.24 \cdot 10^{-5}$ S/cm. The activation energy, Ea obtained for the most of samples were in the range from 18-20 kJ/mol and for some QP30MH samples this value was different. It can be explained that the experimental conductivity values were not very well fitted with VTF equation.

Figure 4 show the Arrhenius plot for CMC/MPPO sample where can be observed that the conductivity values are very close to the HEC grafted samples. But the difference between this two kind of samples is in the appearance. The HEC samples are transparent films while the CMC/MPPO samples are white powder and the conductivity measurements are performed from the pellet samples.

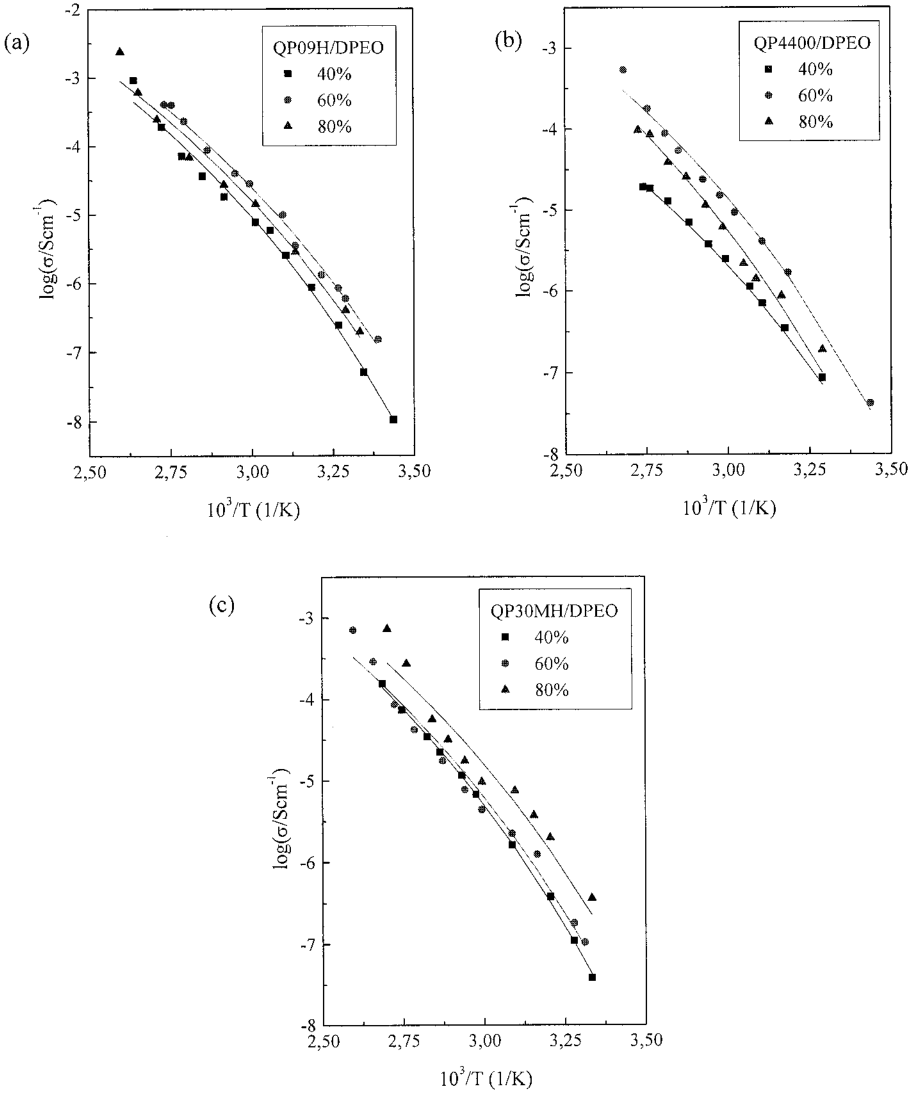

Figure 1. log σ vs. 10^3/T for solid electrolytes based in HEC grafted with DPEO (a) QP09H; (b) QP4400; (c) QP30MH.

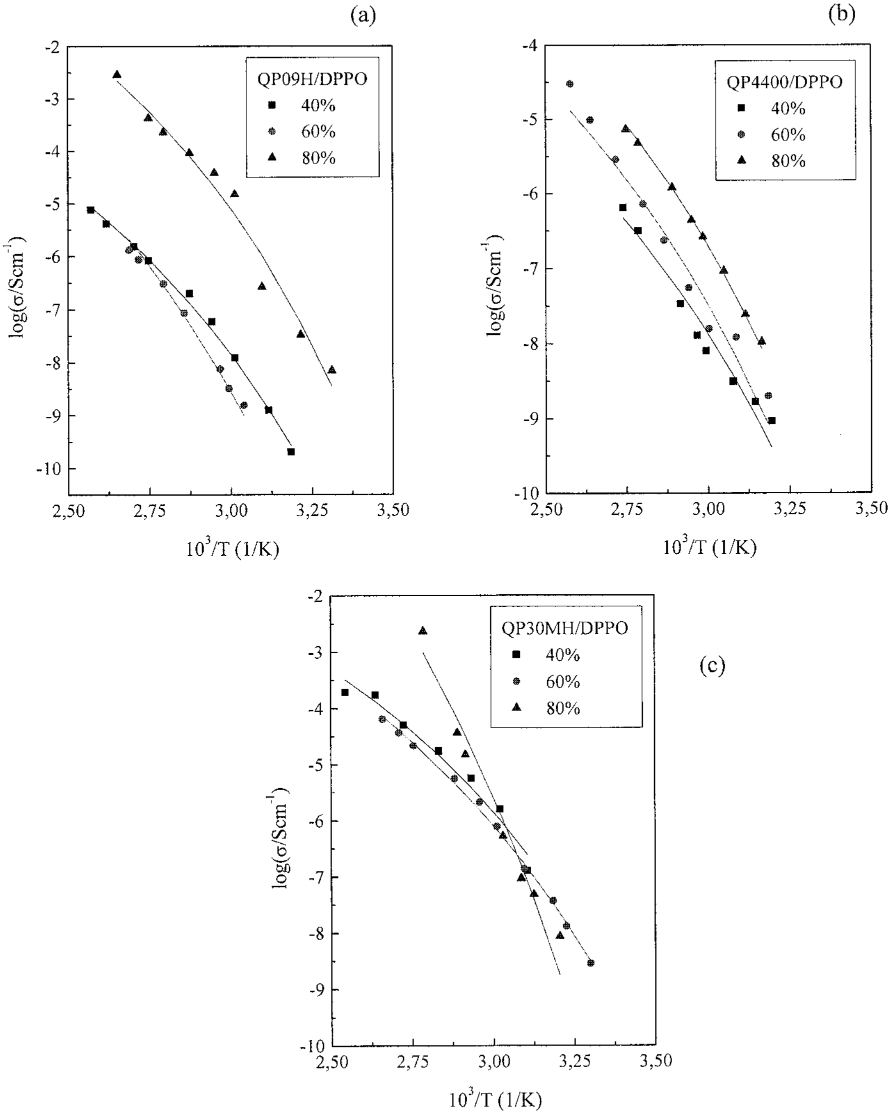

Figure 2. log σ vs. $10^3/T$ for solid electrolytes based in HEC grafted with DPPO (a) QP09H; (b) QP4400; (c) QP30MH.

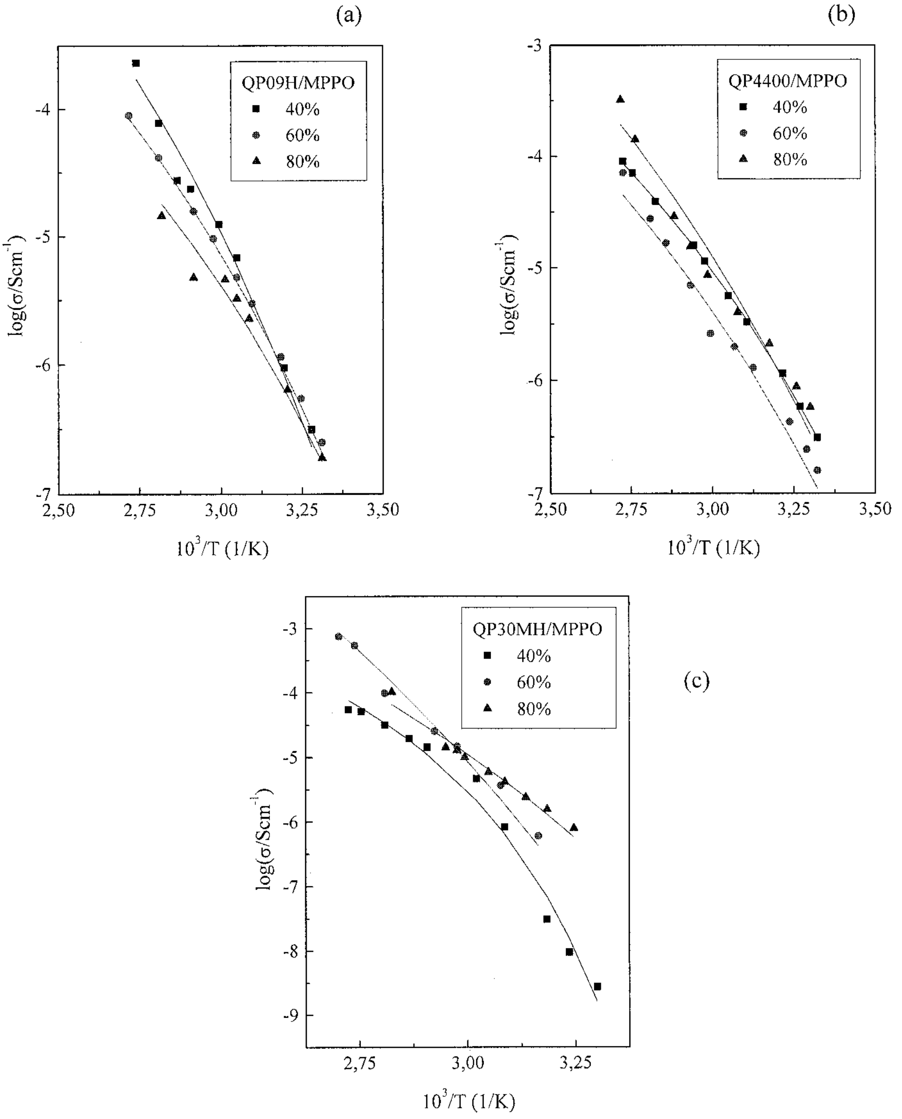

Figure 3: log σ vs. $10^3/T$ for solid electrolytes based in HEC grafted with MPPO (a) QP09H; (b) QP4400; (c) QP30MH.

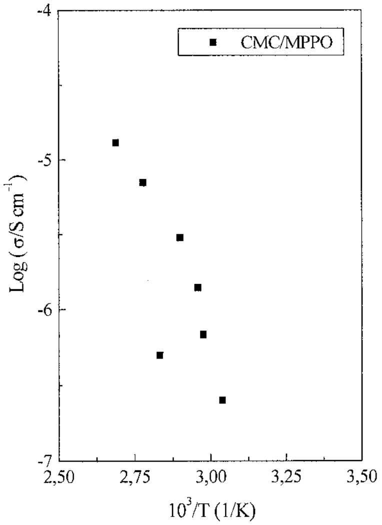

Figure 4. Arrhenius diagram for CMC grafted with poly(propylene oxide) monoisocyanate.

The analysis of the temperature dependence of conductivity shows that the behaviors that can be adjusted by typical curves of amorphous systems and the ionic conductivity can be explained by the mechanism that follows the free volume theory represented by Vogel Tamman Fulcher (VTF) or William Landel Ferry (WLF) models. These theories predict that the segmental motion of the elastomeric polymer assures the ion transport. According to these considerations, the WLF equation, represented below, can be applied to the systems studied here,

$$\log\frac{\sigma_T}{\sigma_{T_g}} = \frac{C_1\left(T - T_g\right)}{C_2 + \left(T + T_g\right)}$$

where σ_T and σ_{Tg} are the conductivity at temperatures T and Tg and C_1 and C_2 are the WLF parameters for the temperature dependence of the ionic conductivity. The C_1 and C_2 values obtained are shown in table 4. The deviations to the universal values, 17.4 and 51.6 K, respectively, indicate that the synthesized films are not tridimensionaly perfect.

Table 4. WLF constant values for the synthesized solid electrolytes.

		QP09H		**QP4400**		**QP30MH**	
	NCO/OH	$C_1^{T_g}$	$C_2^{T_g}$ **(K)**	$C_1^{T_g}$	$C_2^{T_g}$ **(K)**	$C_1^{T_g}$	$C_2^{T_g}$ **(K)**
DPOE	**0.4**	21	34	18	38	21	40
	0.6	17.8	44	17.3	40	15.7	24.7
	0.8	14.9	71	33	24	16.7	59.9
DPOP	**0.4**	21.9	74	20.6	92	14	41
	0.6	29	28	20	81	16.3	44
	0.8	-14.3	-54	17	43	-	-
MPOP	**0.4**	8.71	72	13.7	80	82	21
	0.6	17	43	15	107	24.2	145
	0.8	16	39	13.1	113	17.8	53

Conclusions

In this work we showed the electrochemical behavior of different solid electrolytes based on hydroxyethylcellulose grafted with oligo-ether isocyanates and of CMC grafted with PPO monoisocyanate. It was shown that the conductivity in these films is independent on the cellulose derivative structural parameters (MS, DS, and DP) but is related to the type of isocyanate used on the graft reaction. It was observed that the mechanism ruling the ionic conduction can be explained by the free-volume theory represented by a WLF equation, typical for amorphous electrolytes. The values of conductivity at ambient temperature suggest that the electrolytes described here can be used as an alternative to the traditional PEO ones.

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