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Spectromechanical Properties of Polymeric Gel Electrolytes and Blends

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Summary: In this paper we studied the spectro-mechanical properties of polymer gel electrolytes and blends by means of shear rheology. These electrolytes were obtained by immobilizing EC/PC/$LiClO_4$ solutions in a polymeric matrix of PEO, PAN and PMMA, respectively. Two structural and thermoreversible transitions, a *strong-to-weak gel* and a *gel-to-sol*, were revealed and discussed. Moreover, PMMA-PVdF blends have been studied as a function of the different polymeric ratios in order to obtain the best compromise between ionic conduction and mechanical properties. Interesting mechanical properties were observed at some intermediate blend compositions.

Keywords: blends; conductivity; gels; lithium batteries; shear rheology

Introduction

Polymer electrolytes have stimulated worldwide interest due to promising applications such as solid-state rechargeable lithium-ion batteries, super capacitors, electrochromic windows and sensors.[1–3] The representative polymer electrolytes are based on lithium salts dissolved in high molecular weight polyethylene oxide (PEO). These materials are solvent-free and the cations are coordinated to the electron lone pairs of the ether oxygen's. Unfortunately, PEO shows a much higher crystalline degree at room temperature. It implies that PEO-based polymer electrolytes have a very low ionic conductivity ($\sim 10^{-7}$ S cm^{-1}) at room temperature,[4] that is a drawback for their applications.

Numerous methodologies have been developed in order to enhance the room temperature conductivity of this solid electrolyte. One method is to include into the system plasticizer molecules, such as propylene carbonate (PC) and ethylene carbonate (EC).[5–7] This method was extended to other polymers, like poly (methylmetacrylate) (PMMA),[8] poly (acrylonitrile) (PAN),[9] poly(vinilicloride) (PVC)[10] and poly(vinilidenefluoride) (PVdF),[11] where a large amount of plasticizer is required to dissolve the salt, resulting in materials known as polymer *gel* electrolytes.[12,13] In these gels a liquid solution (for instance, PC and/or EC solutions of a lithium salt) is immobilized in the polymeric matrix and the increasing of ion mobility is associated with the phase structure changes of the polymeric materials, in particular with the amorphous phase.[14–16] On the other hand, because of a phase separation between the polymer matrix and the encapsulated electrolyte solution, a leakage problem can arise. Blending[17,18] is one of the approaches utilized to overcome this drawback. This method was adopted for the present study. The polymer blend electrolytes consist of at least two polymers: one that absorbs the electrolyte's active species and the second one that is tougher and sometimes, substantially inert, which enhances the mechanical integrity of the polymer blend. In general, a negative change in free energy is crucial for miscibility of polymer blends. This requirement is met by blends of PMMA and PVdF.[19]

In this study, we put in comparison the linear viscoelastic properties of various gel

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electrolytes based on PEO, PAN, PMMA and PMMA-PVdF blends at various polymeric ratios. The lithium perchlorate salt ($LiClO_4$) was chosen since it exhibits a smaller dissociation energy, while an EC/PC mixture was adopted as plasticizing solvent.

Experimental Part

Samples Preparation

All the polymer electrolytes were prepared by the solvent casting technique and are listed in Table 1. In the table are also reported the conductivity values of all the samples at two representative temperatures, 25 °C and 100 °C.

*PEO- $LiClO_4$- EC (**sample A**)*: was prepared from PEO (Aldrich, average molecular weight 5×10^6), $LiClO_4$ (Aldrich) as salt, and EC (Aldrich) as plasticizer molecule. All the components were dissolved in acetonitrile. The solution was stirred for 24 h at room temperature and then to cast on a Teflon plate so that the solvent was allowed to evaporate slowly for 2–3 days. The synthesis procedures gave dimensionally stable membranes of a typical thickness ranging between 400 and 600 μm.

Their composition is usually expressed as $LiX.P(EO)_x$, where LiX is a generic lithium salt and x is the number of ether oxygens per salt molecule. In this paper the results are presented for $LiClO_4.P(EO)_{10}$ (PEO:Li = 10:1) and the quantities of EC is 1:1 with respect to the polymer.

*PAN- $LiClO_4$- EC-PC (**sample B**)*: an appropriate amount of $LiClO_4$ was first dissolved in a mixture of EC and PC with a fixed molar ratio EC/PC of 1/0.4, while the salt content in the solution was expressed as O/Li molar ratio[20] calculated by the following formula:

$$O/Li = \frac{\text{mass of solvent}}{\text{mass of salt}} \times \frac{\text{Mw of salt}}{\text{Mw of solvent}} \times n$$

where n is the number of 'interactive' oxygen atoms per molecule of the solvent (for EC and PC, $n = 1$). Sample B has an O/Li = 10/1, i.e. 10 molecules of plasticizers and 1 of salt.

PAN was slowly added, at room temperature, to the solution electrolyte and stirred for several hours until a homogeneous mixture was obtained. The PAN/solvent ratio used in the gels preparation was of 26/74 by mass. This ratio was chosen on the basis of the best polymer dissolution in the electrolyte solution. The formed mixture was then cast on an aluminium plate preheated at about 80 °C in order to promote a fast and complete dissolution and to promote the gel formation. Finally, on cooling at room temperature, a solid membrane is obtained.

*PMMA- $LiClO_4$- EC-PC (**sample C**)* and *PMMA-PVdF- $LiClO_4$- EC-PC (**samples D**)* : the required amounts of PMMA, for the gel electrolytes, and PMMA-PVdF (various blend ratios, 80:20, 70:30, 60:40, 40:60, 30:70), for the blend electrolytes, (both Aldrich) were dissolved in anhydrous tetrahydrofurane (THF). After complete dissolution, the electrolyte solution, composed

Table 1.
Composition and ionic conductivity of the studied systems.

Samples	Composition Polymers/salt/plasticizers	Conductivity (S/cm) at 25 °C	Conductivity (S/cm) at 100 °C
A	PEO/$LiClO_4$/EC	2.5×10^{-4}	$3{,}3 \times 10^{-3}$
B	PAN/$LiClO_4$/EC-PC	1×10^{-3}	$3{,}8 \times 10^{-3}$
C	PMMA/$LiClO_4$/EC-PC	2.7×10^{-4}	$2{,}5 \times 10^{-3}$
D_{20}	PMMA:PVdF $_{(80:20)}$/$LiClO_4$/EC-PC	2.9×10^{-4}	3×10^{-3}
D_{30}	PMMA:PVdF $_{(70:30)}$/$LiClO_4$/EC-PC	3.4×10^{-4}	$3{,}8 \times 10^{-3}$
D_{40}	PMMA:PVdF $_{(60:40)}$/$LiClO_4$/EC-PC	3.6×10^{-4}	$4{,}2 \times 10^{-3}$
D_{60}	PMMA:PVdF $_{(40:60)}$/$LiClO_4$/EC-PC	1×10^{-4}	$3{,}2 \times 10^{-3}$
D_{70}	PMMA:PVdF $_{(30:70)}$/$LiClO_4$/EC-PC	5×10^{-5}	$1{,}2 \times 10^{-3}$

of $LiClO_4$ in a mixture of EC and PC with a molar ratio EC/PC of 1/0.4, was added. The salt content in the solution was 10/1 in terms of O/Li molar ratio. Finally, the polymers/plasticizers [PMMA:(EC-PC) and (PMMA-PVdF)/(EC-PC)] weight ratio was of 1:2. The films were achieved by casting the solution on the glass plate in air at room temperature to favour the evaporation of THF. The membranes were dried in a temperature-controlled oven at 50 °C for several hours to remove traces of residual solvent.

Experimental Techniques

Conductivity Measurements:
The ionic conductivity of all the films was measured by impedance spectroscopy using a A*utolab PGSTAT 30 Frequency Response Analyser* over the frequency range from 0.1 Hz to 1 MHz and a home-made conductivity cell.

Dynamic Mechanical Spectroscopy:
DMS experiments were realized by a controlled-strain rheometer (Rheometrics RFS III) and plate-plate geometry. The plate diameter was 25 mm. A Peltier temperature control unit was calibrated to give a temperature in the sample within 0.1 °C of the preset value. Frequency sweep tests were performed between 0.1 and 16 Hz in the temperature range 25–140 °C. The temperature sweep experiments were performed at 1 Hz and with a rate of increase of 2 °C/min.

All the dynamic experiments were made in the linear viscoelastic region (previously determined by strain sweep tests at the same temperatures).

Results and Discussion

The spectromechanical proprieties of polymer electrolytes were studied by small oscillatory shear within the linear viscoelastic region which was well defined by strain sweep tests. In this paper two kinds of experiments were mainly analyzed: *temperature sweep* and *frequency sweep tests*.

PEO Based Gel (Sample A)

The temperature dependence of G′ and G″ for sample A is showed in Figure 1a. This time cure was performed from 25 °C up to 100 °C, at 1 Hz and 1% strain. In this temperature range the dynamic moduli are completely parallel and flat, and denote the presence of a stiff material with a greatly compact microstructure.

Normally, if a material is sheared over long enough times, it starts to flow.[22] This behaviour recalls what happens with temperature changes where the material becomes softer once it is heated. This relation is expressed as the idea of time-temperature equivalence,[23] and the so-called *time-Temperature Superposition (tTS) principle*[24] is normally used to enhance the frequency window. This procedure was applied to frequency-sweep experiments executed from 25 to 100 °C, by using an oscillating frequency from 0.1 to 16 Hz.

The resulting master curve is showed in Figure 1b. The dynamic data were reduced at the reference temperature of 25 °C. *tTS* method has allowed to extend the frequency range to four order of magnitude (10^{-3} Hz up to 16 Hz). The mechanical spectrum at 25 °C supports the results reported in the time cure test (Figure 1a): the material behaves like an elastic solid which is typical of a *strong gel*.

The model of Winter and Chambon[25,26] establishes that the gel point during gelation process can be accurately determined as the point at which the viscoelastic moduli are interrelated with the frequency (ν) as: $G'(\nu) \sim G''(\nu) \sim \nu^n$. In the case of sample A, the trends of G′ and G″ are parallels giving a ratio $G'/G'' \cong 10$ and a relaxation exponent $n \to 0$ (*strong gel*).

PAN Based Gel (Sample B)

Figure 2 shows the temperature evolution of the mechanical moduli of sample B. At low temperature (20–60 °C) both moduli decrease slowly with increasing T and the

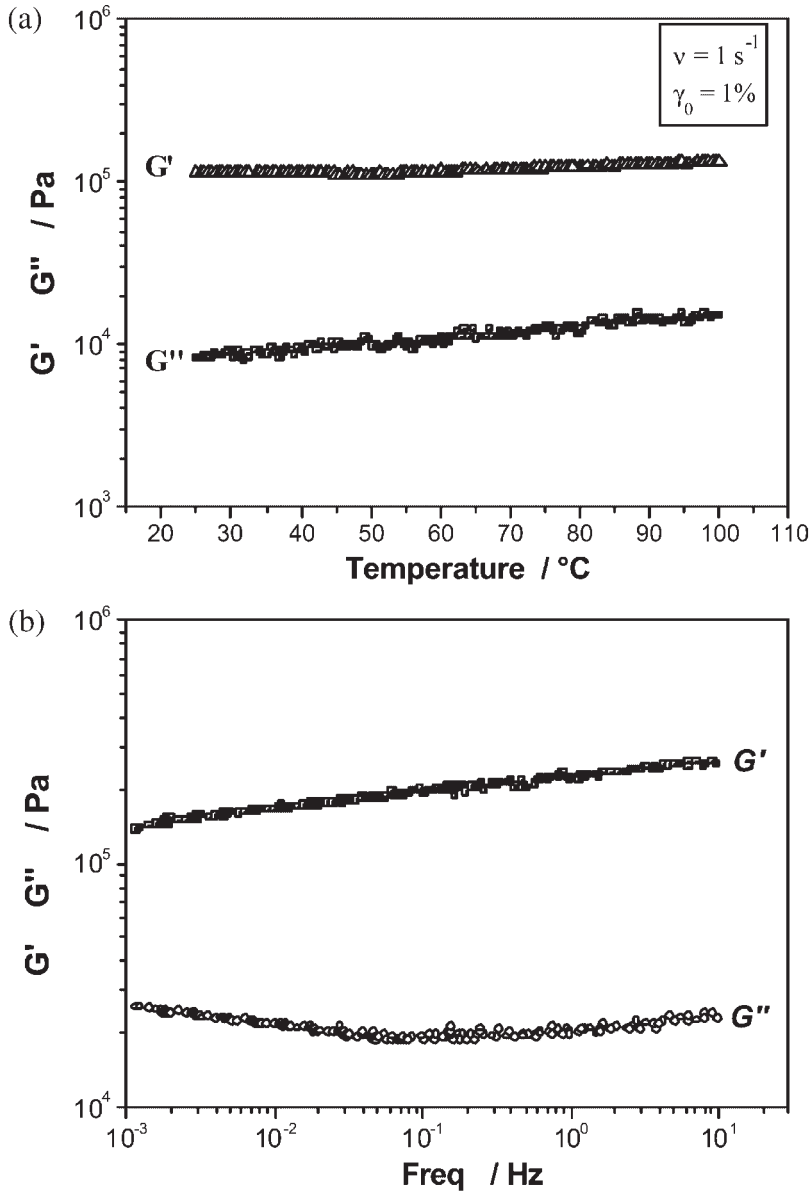

Figure 1.
Temperature sweep test from 25 °C to 100 °C (a) and *master curve* in the temperature range 25–110 °C, reduced at 25 °C (b) relative to the sample A.

storage modulus G′ exceeds significantly the loss modulus G″. In this temperature range, gel behaves elastically and its microstructure remains unchanged (*strong-gel*). The storage modulus starts to decrease upon increasing temperature above 70 °C and crosses over with the loss modulus at ca. 110 °C. In this temperature range G′ reduces its initial value to $\approx 1 \times 10^4$ Pa, showing an evident structural change that corresponds to a decreasing elastic response. The crossover point of 110 °C represents the temperature which is necessary to disrupt the gel network structure

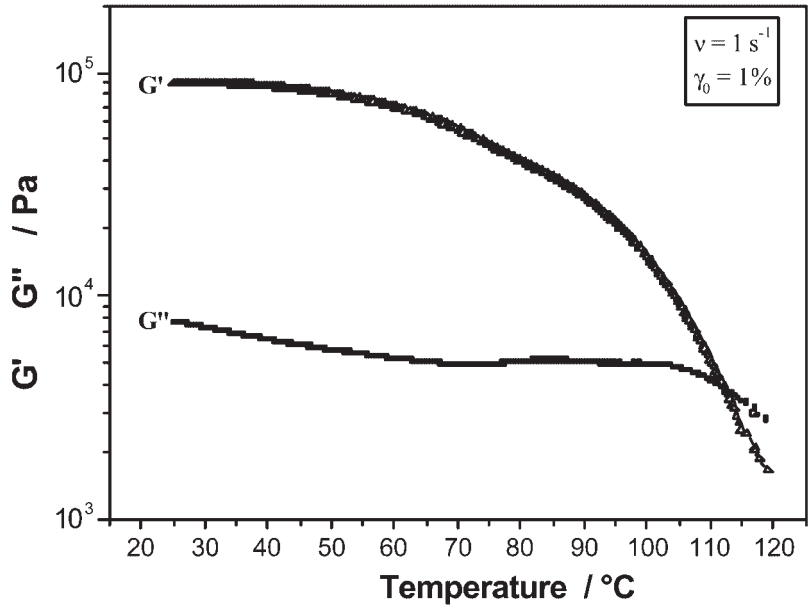

Figure 2.
Temperature sweep test from 25 °C to 120 °C performed on the sample B.

and the point where the sample starts to flow. Finally, far beyond the crossover point, G″ exceeds G′ which drops to small values with a further temperature increase.

In short, at ca. 65 °C the gel network exhibits a structural change of the type "strong-to-weak" and at ca. 110 °C the relative magnitude and shape of dynamic moduli indicate the beginning of a gel-sol transition. On cooling, the system is able to recover the structure and to become a strong gel again.

In the temperature interval 25–120 °C a complete set of mechanical spectra were obtained for the PAN-based gel by frequency-sweep experiments. Figure 3 reports the dynamic viscoelastic data reduced at two temperatures, which correspond to the different gel states (strong and weak gel) discussed before. Figure 3a shows the master curve of the gel obtained by applying the *tTS method* on the frequency tests performed from 25 °C up to 60 °C and reduced to the reference temperature of 25 °C. Figure 3b reports the master curve corresponding to the temperature range 65–105 °C (below the crossover) and referred to 100 °C. The first one evidences the independence of G′ from the frequency over a wide range of time scales and his really high value respect to G″. The second one shows a quite different viscoelastic trend: below the frequency of 10^{-2} Hz, G′ is higher than G″, while the moduli approach each other at higher frequencies.

This behaviour highlighted a viscoelastic response far from a strong-gel network and much more correlated to frequency spectra recorded in polymer melts or polymer concentrated solutions.

PMMA Based Gel (Sample C)

The mechanical proprieties of sample C are summarized in Figures 4a and 4b. Figure 4a shows the temperature sweep test performed from 25 °C up to 140 °C. As the PAN-based gel, even this system shows a characteristic behaviour of a strong-gel type material at room temperature where the elastic modulus (G′) predominates of almost one order of magnitude the viscous modulus (G″). Increasing the temperature, G′ decreases considerably and crosses over with G″ at ca. 120 °C (*gel-sol* transition).

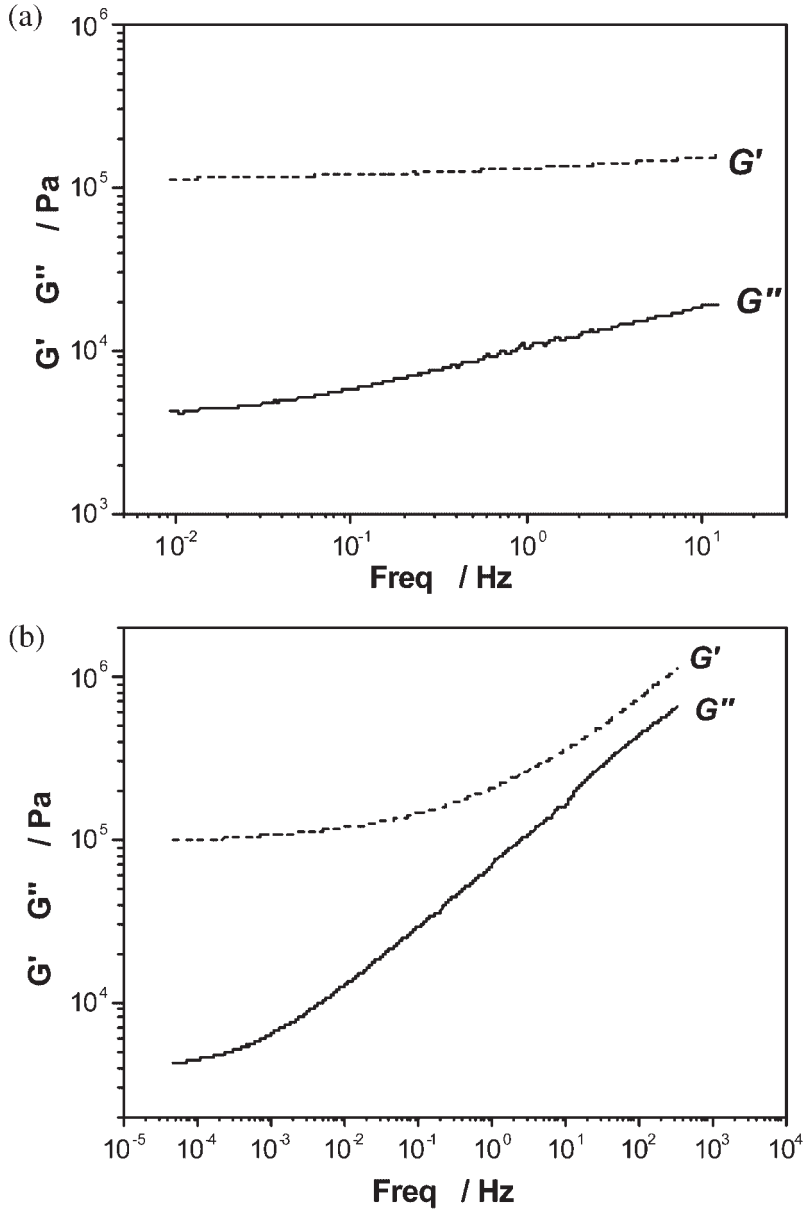

Figure 3.
Master curves from 25 to 60 °C reduced at 25 °C (a) and from 65 to 105 °C reduced at 100 °C (b) relative to the sample B.

The inversion of the moduli over this temperature implies that the material becomes softer or more viscous. The sample C is a thermoreversible gel, i.e. the temperature evolution of the viscoeleastic moduli on cooling is very similar to the one observed in the heating scan.

Figure 4b shows the master curve of the sample C obtained by frequency sweep tests collected from 25 °C up to 110 °C (below the crossover temperature); the linear viscoelastic data were reduced to the reference temperature of 25 °C. At this reference temperature the crossover

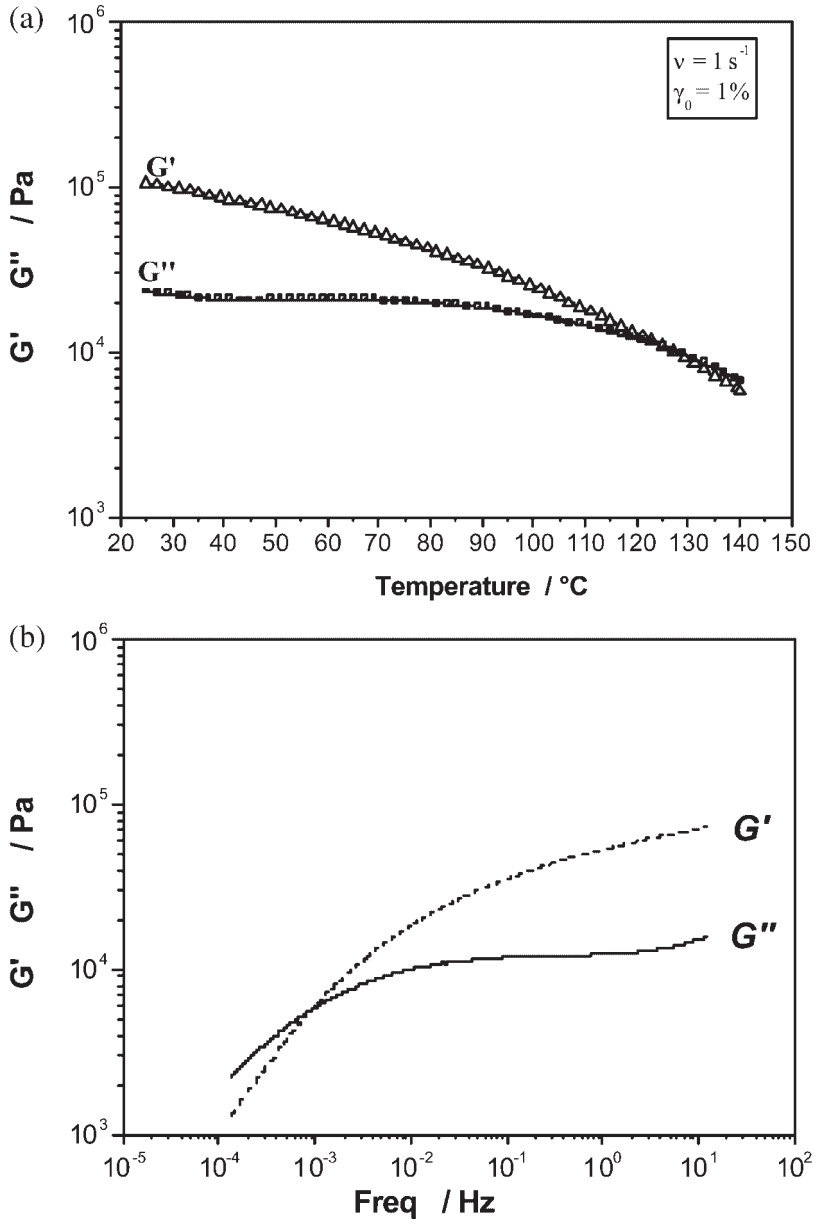

Figure 4.
Temperature sweep test from 25 °C to 140 °C (a) and *master curve* in the temperature range 25–110 °C reduced to 25 °C (b) relative to the sample C.

between G′ and G″ is found at frequency lower than 10^{-3} Hz and the material behaves liquid-like. The storage and loss moduli show a plateau region by increasing the frequency: this trend may be associated to the concept of an entangled network for a rubber-like material.

PMMA-PVdF (80:20) Blend (Sample D_{20})

Typically, the blending of at least two polymers implies morphological changes of the resultant polymeric matrix, whose effect is substantially a lowering of its crystalline fraction with respect to the film obtained with only one polymer. This could

also explain the higher conductivity in sample D_{20} with respect to sample C, as showed in Table 1, both at 25 °C and 100 °C. From a dynamic-mechanical point of view, when the crystalline degree of a polymeric system decreases, both the storage and the loss moduli values decrease.[27,28] Temperature sweep test for sample D_{20} is reported in Figure 5a. At room temperature, G′ and G″ have the same order of magnitude as the one we have seen previously for sample C.

During the heating scan, G′ and G″ are parallel and slowly decrease up to 100 °C. At this temperature, differently from

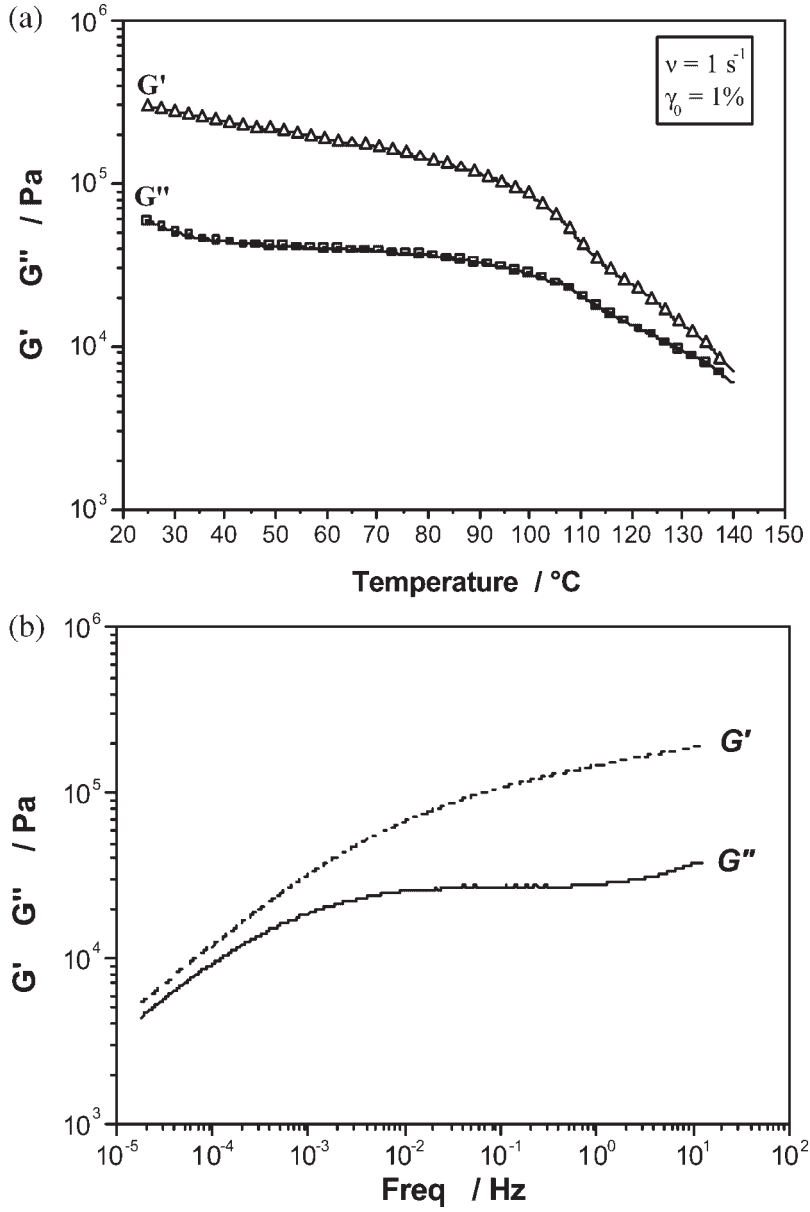

Figure 5.
Temperature sweep test from 25 °C to 140 °C (a) and *master curve* in the temperature range 25–140 °C reduced to 25 °C (b) relative to the sample D_{20}.

PMMA-based gel, G′ and G″ show a sensitive jump and reduce their initial value to $\approx 1 \times 10^4$ Pa when the temperature of 140 °C is reached.

This particular behaviour can be interpreted as a clear loss of elasticity as a consequence of a *strong-weak* gel transition at about 100 °C. However, no crossover between the moduli was found up to 140 °C; it will very probably be further. The absence of a *gel-sol* transition in this temperature range suggests excellent system stability in sight of electrochemical applications.

The *tTS* procedure worked very well for the sample D_{20} over all temperature range (25–140 °C). The master curve obtained at the temperature reference of 25 °C is reported in Figure 5b. The frequency dependence of G′ and G″ is indicative of a solid-like response in the whole frequency range (10^{-5}–10^2 sec^{-1}). In comparison with the sample C, no *terminal flow behaviour* is reached, demonstrating that this blend is able to support shear strains on a long time scale.

PMMA-PVdF Blends (Sample D_{20}, D_{30}, D_{40}, D_{60}, D_{70})

PMMA/PVdF blend at several polymer ratios have been investigated in this section. Figures 6a and 6b show the temperature dependence of G′ and *G″* (25–140 °C), for all blends. Over the entire temperature range, G′ values are always higher then G″ and are almost independent from the frequency: *strong* gel behaviour. In the samples D_{30}, D_{40} and D_{60} both moduli were found more or less coincident, while D_{20} and D_{70} samples show the lowest and the highest dynamic moduli values, respectively.

Previous studies[29–31] on PMMA/PVdF blends showed a phase separation consisting both of an amorphous and crystalline domain when the percentage of PVdF is above 50%.[32] In other words, the amorphous domain, where PMMA and PVdF are blended, coexists with pure PVdF crystalline domains. Ordinarily, high values of viscoelastic moduli are expected for systems with high crystallinity degrees. The blend D_{70} shows the moduli highest values, confirming a crystalline growth in the polymeric matrix attributable to the elevated content of PVdF. The D_{20} sample shows the opposite behaviour indicative of a higher amorphous morphology.

Figure 7 reports the frequency sweep tests for the blend samples. For clarity, we plotted separately G′ vs. *frequency* (a) and G″ vs. *frequency* (b), at 50 °C. These plots confirm the rheological behaviour observed in the temperature sweep test. The very soft character of D_{20} is highlighted by the marked slope of G′ which follows a power law $G'(\nu) \sim \nu^3$ which is emblematic of a *weak ge*l structure.[33] Finally, it is interesting to underline that the G′ profile of the sample D_{40} is completely flat in all the frequency range investigated. This behaviour is indicative of a good mechanical stability associated to a *strong gel* character.

The morphology and the mechanical characteristics of these blends have considerable effects on the conductivity, i.e. on the lithium ions mobility, as showed in the plot of Figure 8. The conductivity range is between 10^{-4} and 10^{-2} S cm^{-1}, and in all the explored temperatures the maximum of the conductivity corresponds to the blend with intermediate composition of 40% PVdF and 60% of PMMA.

Conclusions

Mechanical properties of various gel electrolytes and blends of interest in the lithium batteries technology were studied by shear rheology.

The PEO-based gel demonstrated a really good mechanical stability from room temperature up to 100 °C. This strength and solidity is in a temporal spectrum, revealing a resistance to flow for very long times.

The rheological analysis of the PAN-based gel revealed two structural transitions: a *strong-weak gel* transition at 65 °C and a *sol-gel* transition at 110 °C. The first one involves to a loss of elasticity of the polymeric matrix; the sol-gel transition

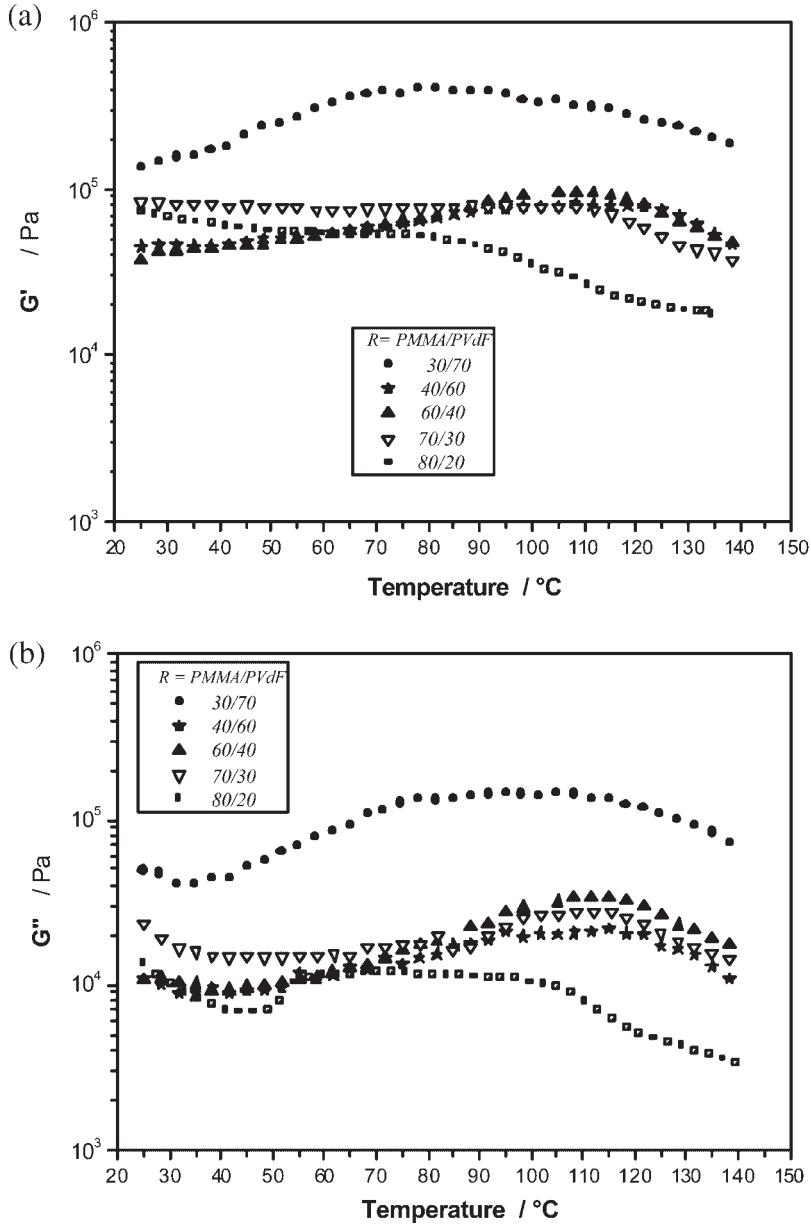

Figure 6.
G′ vs. temperature (a) and G″ vs. temperature (b) from 25 °C to 140 °C for all PMMA/PVdF blends.

occurs when the cross-links between the polymeric chains of the network weaken and the material starts to flow. However, both these transitions are thermoreversible and the gel state is recovered after every cooling cycles. Also PMMA-based gel showed a thermoreversible gel-sol transition at 120 °C, while it was not possible to exactly give a temperature at which the gel structure reduces its elasticity and the strong to weak gel transition occurs.

The addition of a certain amount of PVdF to PMMA, improved the thermo-mechanical properties of these electrolytes.

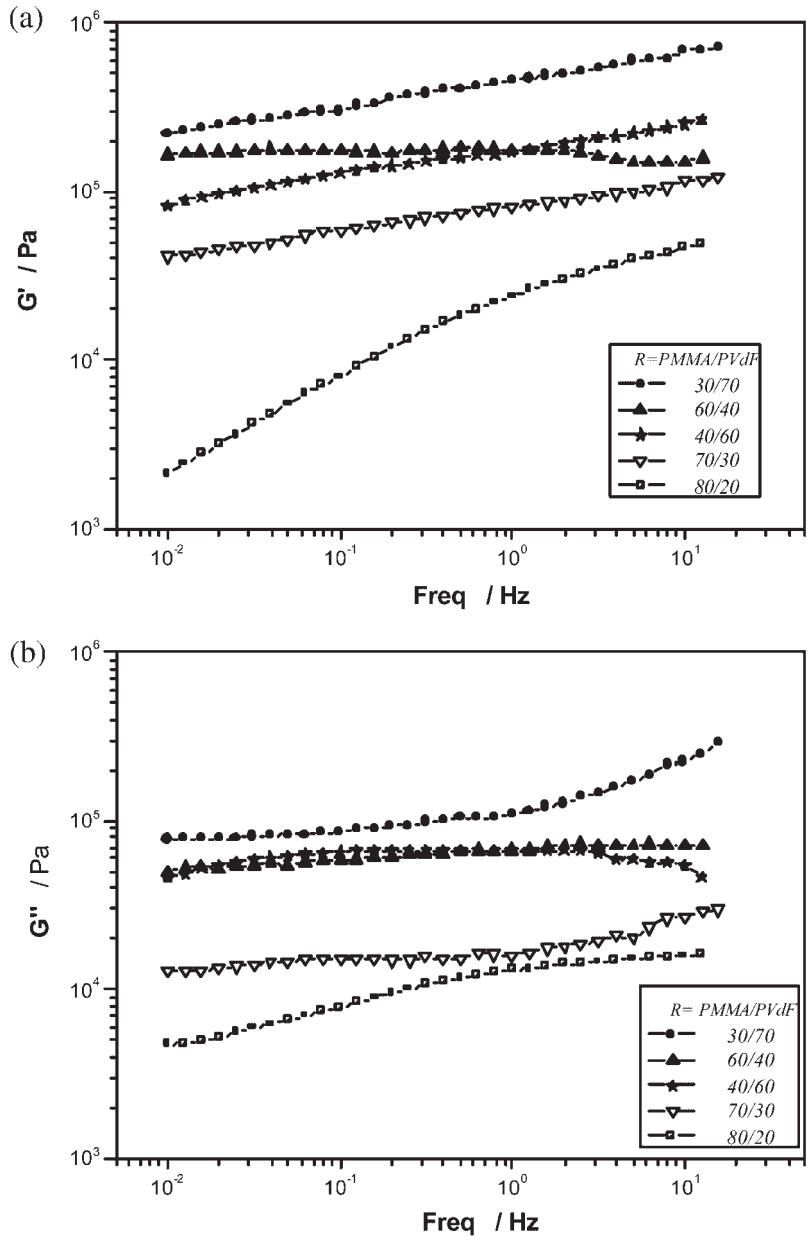

Figure 7.
Frequency sweep tests performed at 50 °C for PMMA/PVdF blends.

In fact, a stable gel phase for PMMA-PVdF blends is maintained up to 140 °C. At intermediate compositions and in the entire temperature range investigated, blends showed viscoelastic behaviour similar to, and typical of polymer strong gels. The particular composition of PMMA/PVdF = 60/40 is resulted to be the most favourable in ionic conduction. Morphological studies of these kind of blends were achieved by Scanning Electron Microscopy (SEM) in a previous paper.[31] It is worth

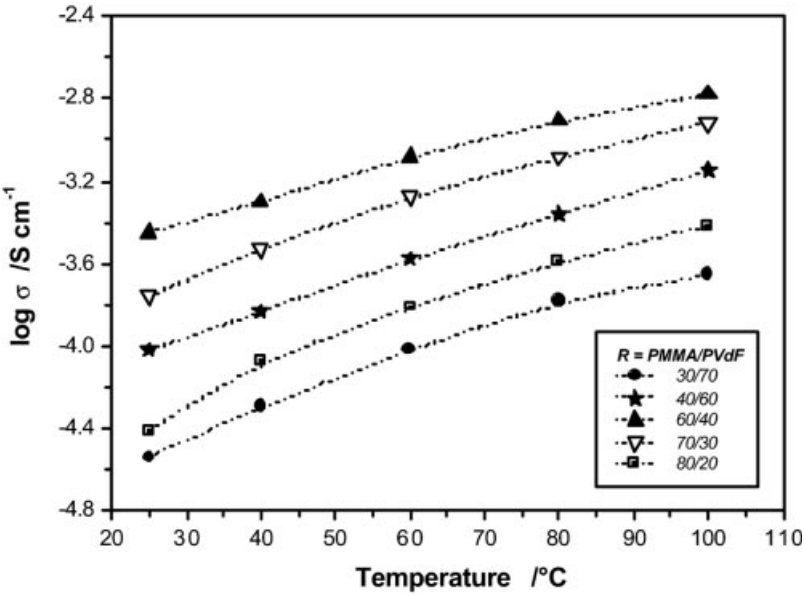

Figure 8.
Ionic conductivity of PMMA/PVdF blends electrolytes recorded from 25 °C up to 100 °C.

underlining that the best ionic mobility of lithium occurs in a gel that, in principle, is not the most amorphous one, but it has a semi-crystalline morphology with a compact and well-connected structure. The PMMA/PVdF blends at the polymeric ratios 80/20 and 30/70 showed the lowest and highest values of the moduli, respectively. These features can be associated to a different crystalline degree of their microscopic structures.

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