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A statistically designed study of ternary electrolyte polymer material (PEO/LIClO$_4$/ethylene carbonate)

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Statistically designed mixture experiments were performed for the ternary electrolyte polymer system poly(ethylene oxide) (PEO) - lithium perchlorate - ethylene carbonate (EC). Ionic conductivities and crystalline/glass transition temperatures were measured for 15 ternary mixtures of varying ingredient proportions. Although conductivity increases with salt concentration, the plasticizer/polymer ratio is important in determining conductivities at higher salt proportions. A quadratic mixture model provides an accurate description of how conductivity at room temperature changes with varying ingredient proportions. It predicts a maximum conductivity for a 0.50 PEO, 0.21 LiClO$_4$, 0.29 EC (weight fractions) mixture. A special cubic model is found to be most appropriate for representing how the corrected transition temperature values depend on ingredient proportions. The temperature dependence of conductivity was measured for some of the mixtures. The same composition exhibited higher conductivities at room temperature and up to 100 °C. The VTF parameters for the plasticized systems were compared with those of non-plasticized ones. © *2000 Kluwer Academic Publishers*

1. Introduction

The configuration of an electrochemical device requires an electrolyte providing a medium for exclusive moving ions. Traditionally aqueous acid or salt solutions have been used. The necessity of extending the electrochemical stability window above the domain of the reduction-oxidation potential of protons has led to the use of aprotic organic solvents. In this case a highly delocalized negative charge is used, such as in ClO_4^-, $CF_3SO_3^-$ and BF_4^- to increase the corresponding salt solubilities, generally lithium salts are chosen for their electrochemical gain.

The incorporation of high salt concentrations in flexible polymers results in complex formation with the salts, observed either in solution or solid state. In the solid state, films of electrolytic polymer permit extensive technologically advantageous miniaturization of electrochemical devices [1].

Poly(ethylene oxide) - PEO - is the matrix most studied for lithium salts. The oxyethylene sequence forms entropically-favored five-membered rings and as a consequence, has been characterized as a good solvent for a majority of cations [2]. Among the developed electrolyte polymeric materials, those based on simple homopolymers, lattices, copolymers, polymer mixtures and ternary polymer-salt-plasticizer or polymer-salt-filler systems are predominantly investigated [3].

The addition of plasticizers has been proposed with the objective of reducing crystallinity and increasing segmentational mobility that could lead to better ionic conductivity [4–6]. For conventional polymeric materials, the introduction of non-volatile liquids that are compatible with intractable polymers is frequent, in order to reduce processing temperatures and make these polymers more flexible. Generally, for these materials, the plasticizers are low molecular weight liquids with phthalic esters being predominantly used as thermoplasticizers (eg. dioctyl phthalate). Of the various effects provoked by the plastifying process, the lowering of T_g with a proportionate weakening of intermolecular interactions and an increase in free volume of the system are the most pronounced.

The choice of an adequate plasticizer for polymeric electrolyte systems is based on compatibility and electrochemical stability criteria, and organic compounds such as ethylene or propylene carbonate or poly-(ethylene glycol) oligomers are preferred [3]. With the use of these materials plasticizer-polymer interactions are involved as well as plasticizer-salt ones, making their investigations considerably more complex [6–9].

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With increases in plasticizer concentrations there occur conductivity increases, as well as reductions in mechanical property qualities, when the matrix is linear. As such the choice of ternary system compositions should be carefully made to obtain optimized properties. Various experimental factors, such as thermal history and the type of solvent evaporation process, can decisively affect the final properties.

Above aproximately 30 wt% of plasticizer the mechanical properties become rather unpractical in the case of an host polymer linear chain [3]. Thus, this limit is frequently observed. On the other hand, in the case of a crosslinked matrix, which can be swollen with plasticizer, even more than 60 wt% of liquid can be combined with a polymer/salt system. This kind of material is called "gel polymer electrolyte".

Gel and linear chain based polymer electrolytes are significantly different materials. While gel conductivity, as typical liquid electrolytes, can surpass 10^{-2} S·cm^{-1} [6], the linear based ones frequently do not exceed 10^{-4} S·cm^{-1} at room temperature [8, 9]. Studies of gel electrolytes have shown that the plasticizer acts, not only on the polymer chain, but is probably also interacting with the salt producing a dissociation increase [6, 10].

The active field of gel polymer electrolytes covers materials based in networks of polyethers as well as in other host polymers such as poly(vinylidene fluoride) [11], poly(methylmethacrylate) [12] or poly(acrylonitrile) [13]. The main drawbacks of gel polymer electrolytes are their poor electrochemical stabilities, since liquids are frequently the major component, and the problem of processing in thin films [3].

Linear chain polyether based solid polymer electrolytes continue to present fundamental and commercial interests [14]. The phase structures, ionic associations, conductivities and electrochemical behaviours, as a function of concentration and temperature, have been carefully studied [1–3, 14]. This paper intends to provide contributions about the effect of low plasticizer concentration additions on conductivity and thermal parameters associated with amorphous and crystalline phases, for one of the most studied polymer electrolyte systems, e.g., PEO/LiClO$_4$. The linear polymer and the range of plasticizer concentration was selected to produce a totally miscible polymer/salt /plasticizer system, in which all the solvent species participate in the conduction process [6].

The conductivity isotherms of a binary polymer electrolyte frequently exhibit a maximum at a given concentration, which depends on several factors. Among these factors the most discussed are the reduced mobility of the amorphous phase, which results in increasing T_g values [15, 16], and the growth of ionic aggregation when salt concentration is raised [17,18]. The effect of simultaneously increasing plasticizer content at various different salt concentrations on the structure and conductivity is a subject not yet carefully explored in the polymeric electrolyte field.

The wide study of network polyether/salt/plasticizer carried out by the Australian group of MacFarlane, Forsyth *et al.* [6, 19–23] has frequently used a fixed salt concentration of 1 mol·kg^{-1}, upon which plasticizer content is varied. The 1 mol·kg^{-1} of salt is not the composition at which maximum conductivity is attained for their binary system, which is 0.6 mol·kg^{-1} [19]. These authors have frequently studied plasticizer content up to 60 wt%, and very interesting results have been obtained with the use of powerful techniques such as FTIR, DMTA, NMR and PALS (Positron Anhilition Lifetime Spectroscopy) [6, 19–21, 23]. The difficulties for comparing results when both salt and plasticizer concentrations are changing in a linear way can be observed in some of this group's recent work [20, 22]. Other groups have also studied linear variations of salt and plasticizer contents [24, 25]. However, it is not obvious how to extrapolate their conclusions to other regions of the concentration surface of the ternary diagram, which is important for understanding the system behaviour well.

The goal of obtaining more general information about ternary mixtures in these intricate systems is approached in this paper with the use of statistical tools. Results are presented for a statistically designed set of experiments for the polyethylene oxide/ lithium perchlorate/ethylene carbonate (PEO/LiClO$_4$/EC) mixture. This ternary mixture was previously characterized thermally and electrically, for five compositions with fixed salt proportions (23% w/w) and increasing plasticizer concentrations (between 10 to 60% w/w). Under our experimental conditions, a conductivity gain with maintenance of thermal stability was observed [26], but this was accompanied by mechanical property degradations. This behaviour motivates further investigations with variations of proportions of plasticizer and salt.

This work reports an investigation of statistically chosen mixtures with sample concentrations for all regions of the ternary diagram of potential interest. The salt concentration limits were established considering the range of maximum conductivity frequently observed in polymer electrolytes [19, 27]. The plasticizer content was not raised above 30 wt% to limit the degradation of mechanical stability and to maintain a polymer related mechanism of conductivity [6] for the material.

The number of distinct samples used in the design, as well as the number of replicate points, were chosen as a compromise between operational convenience and statistical rigor. Four duplicate points were used so that accurate assessment of experimental error could be made. Without replicate information it is not possible to identify significant response variations, owing to composition changes from random variations that occur naturally in measurement processes. Commonly used techniques for electrolyte characterization, Differential Scanning Calorimetry (DSC) and impedance measurements, were also used.

Statistical mixture models have been extensively developed during the past forty years [28]. These models, in contrast to models for statistically independent variables that are normally used in factorial designs and response surface analyses [29], are applicable to studies with redundant parameters and have found application in the chemical and related sciences [30–36] For the present study the sum of the weight fractions of polymer, salt and plasticizer add to one (or 100%) and knowledge of two fractions yields the third. Rather than arbitrarily exclude one of the weight fractions from model building, the redundancy condition can be introduced into the more familiar statistical models for independent variables to form mixture models. Mixture models can always be identified by the fact that they do not contain a constant term, as do conventional models for independent variables. The choice of component proportions for the samples investigated are made such that the mixture parameters contain a minimum of propagated error arising from the inevitable experimental error involved in measurements.

2. Experimental

Samples were prepared with PEO (Aldrich) of average molecular weight of 1,000,000 g/mol. Anhydrous $LiClO_4$ and EC (Aldrich) were used as received. Solutions containing the three components, in the desired proportions, were prepared by stirring in acetonitrile. Dry samples were obtained by casting these solutions in Petri dishes, evaporating at ambient pressure and temperature, followed by vacuum evaporation for 24 h at 60 °C. Samples were stored in desiccator and the dry procedure was repeated before each kind of characterization.

The statistically designed experiments [28] A–K are presented in Table I. The H through K samples were prepared and characterized in duplicate. The experimental region established on the basis of preliminary results is defined by the proportion limits in weight fractions:

$$0.50 \leq C_{\mathrm{PEO}} \leq 0.86 \quad 0.07 \leq C_{\mathrm{salt}} \leq 0.29$$
$$0.07 \leq C_{\mathrm{EC}} \leq 0.29$$

This region corresponds to the polygon in the concentration triangle of Fig. 1. Besides samples corresponding to component proportions given by the vertices of the polygon and two side centroids, four mixtures in its interior were investigated. All these mixtures are macroscopically homogeneous and transparent with variable dimensional resistance.

The total ambient temperature ionic conductivities (at 25 °C) were obtained in a sandwich format cell (INOX/electrolyte/INOX) by complex impedance spectroscopy using an HP4192A instrument in the 50 Hz to 10 MHz frequency range. DSC 2920 and SDT 2960 systems of TA instruments were used for the thermal analyses. The DSC measurements were programmed to identify phase structures present in the material at ambient temperatures with tempering between this temperature and −120°C followed by heating at 10°C/min until 150°C in Helium atmosphere with approximately 5 mg of sample in a sealed aluminum crucible. Thermogravimetric analysis (TG) was carried out under nitrogen at 10°C/min between ambient temperature and 500°C.

3. Results and discussion

3.1. Ionic conductivity at room temperature

The ionic conductivities, for the ternary system $PEO/LiClO_4/EC$, in Table I show variations between 1×10^{-6} S cm^{-1} (samples A and G) and 3×10^{-4} S cm^{-1} (samples D and E) with the mechanical properties of the latter samples completely degraded. Linear, quadratic and special cubic statistical mixture models were evaluated to explain the variance in the conductivity values. However, all of these models resulted in very large discrepancies between experimental results and predicted conductivity models. Since the conductivity values span two orders of magnitude and their logarithms are often used in modeling, mixture model regression was applied to the logarithms of the values in Table I. A quadratic mixture model provided the best statistical fit and a model equation of

$$\log \mathrm{cond} = \underset{(\pm 0.89)}{-8.02x_{\mathrm{PEO}}} \underset{(\pm 11.94)}{- 36.61x_{\mathrm{salt}}} \underset{(\pm 11.94)}{+ 5.97x_{\mathrm{EC}}} \underset{(\pm 18.21)}{+ 56.62x_{\mathrm{PEO}}x_{\mathrm{salt}}} \underset{(\pm 18.21)}{- 10.86x_{\mathrm{PEO}}x_{\mathrm{EC}}} \underset{(\pm 24.96)}{+ 41.59x_{\mathrm{salt}}x_{\mathrm{EC}}} \quad (1)$$

was calculated. The numbers in parentheses below the model coefficients are 95% confidence intervals of the standard errors and can be used to test the significance of the terms in the model. For example, the x_{PEO}, x_{salt}, $x_{\mathrm{PEO}}x_{\mathrm{salt}}$ and $x_{\mathrm{salt}}x_{\mathrm{EC}}$ terms have coefficients with absolute values that are larger than their estimated intervals and can be taken to exist at the 95% confidence level. On the other hand it is highly improbable that the log conductivity data has a linear dependence on the plasticizer proportion or on the interaction between the polymer and plasticizer proportions. As such, their terms can be removed from the above model equation since the absolute values of their coefficients are smaller than their confidence interval values.

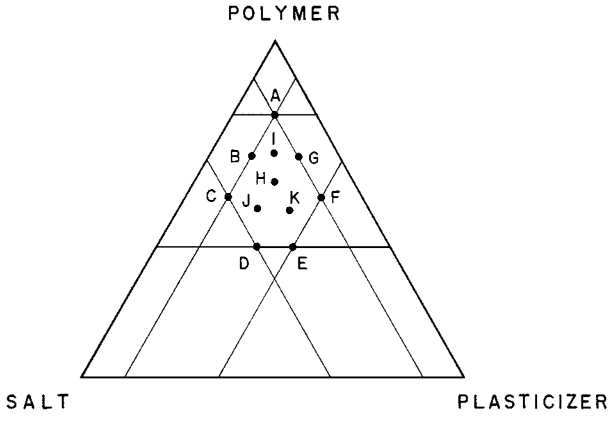

Figure 1 $PEO/LiClO_4/EC$ concentration triangle.

TABLE I Summary of results for the PEO/LiClO$_4$/EC ternary system

	weight fraction of								
Sample	Polymer	Salt	Plasticizer	Cond./S·cm^{-1}	T_g^{a}/°C	T_m^{b}/°C	ΔH_m^{c}/J·g^{-1}	T^{*d}/°C	Mechanical properties
A	0.86	0.07	0.07	1×10^{-6}	−57	59	86	−47	+
B	0.75	0.18	0.07	2×10^{-5}	−48	58	5	−48	+
C	0.64	0.29	0.07	3×10^{-5}	−67	—^{e}	—	−67	−
D	0.50	0.29	0.21	3×10^{-4}	−67	—	—	−67	−
E	0.50	0.21	0.29	4×10^{-4}	−68	—	—	−68	−
F	0.64	0.07	0.29	4×10^{-5}	−72	51	56	−64	+
G	0.75	0.07	0.18	1×10^{-6}	−53	57	78	−45	+
H^{f}	0.66	0.17	0.17	7×10^{-5}	−56	39	11	−56	±
H2				8×10^{-5}	−63	44	25	−63	+
I	0.76	0.12	0.12	1×10^{-5}	−58	53	62	−51	+
I2				2×10^{-5}	−59	53	77	−50	+
J	0.60	0.25	0.15	7×10^{-5}	−71	—	—	−71	−
J2				1×10^{-4}	−69	—	—	−69	−
K	0.60	0.15	0.25	2×10^{-4}	−50	44	3	−50	±
K2				2×10^{-4}	−63	61	113	−49	−

[a] ±2 °C of accuracy [b] melting temperature taken on the peak [c] melting heat [d] corrected temperature considering crystallinity influence [e] without crystalline phase [f] samples H to K in duplicate.

Perhaps the statistical relevance of the 95% confidence intervals should be emphasized in another way. For example, the 18.21 95% interval value for the polymer-salt interaction coefficient of 56.62 means that if the experimental design is evaluated repeatedly 95% of the results will give a $x_{\text{PEO}}x_{\text{salt}}$ coefficient between 38.41 and 74.83. For this reason it seems highly probable that this coefficient is positive and there exists a synergetic interaction between the polymer and salt proportions for conductivity.

The analysis of variance for this model is presented in Table II. There is some evidence for lack of fit at the 95% confidence level since the mean square of lack of fit/mean square of pure error ratio is 8.0 whereas $F_{5,4} = 6.3$. However the lack of fit is not severe, by statistical measures, and is caused mostly by sample G which has a minimum log conductivity value of −6.00 whereas the model predicts a value of −5.48. The predicted values for the conductivities of the other samples are much closer to the measured values as can be seen in Fig. 2. There, constant value conductivity contour curves are shown as a function of mixture component proportions, along with the measured conductivity values for the mixtures studied. With the exception of sample G, the largest discrepancy occurs for sample E with calculated and measured log. of conductivities of −3.07 and −3.40, respectively. The above model explains 93% of the total variance in the log conductivity data. If the measured conductivity of the G sample is removed from the data set, the resulting adjusted quadratic model shows no lack of fit whatsoever and explains 98% of the explainable variance. The values of the coefficients of the significant terms in this model for the reduced data set are similar to those in Equation 1, since they differ by quantities less than their corresponding 95% confidence interval values. For this reason interpretations of the relative importance of the component proportions on the conductivity values are essentially the same for both models.

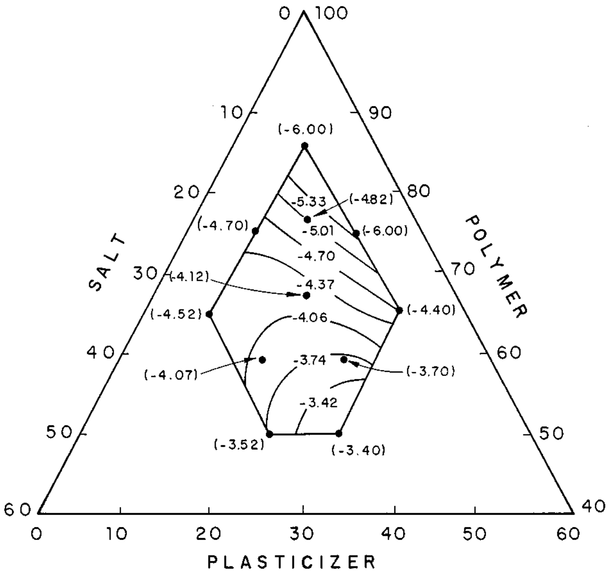

Figure 2 Predicted conductivity contour lines for the quadratic model of Equation 1.

TABLE II Analysis of the variance for the regression of the log conductivity data as a quadratic function of the mixture proportions

Variance Source	Sum of Squares	Degrees of Freedom	Mean Square	*F* Test
Regression	8.19	5	1.64	22.5^{a}
Residuals	0.66	9	0.073	
Lack of Fit	0.60	5	0.12	8.0^{b}
Pure Error	0.06	4	0.015	
Total	8.85	14		

Percentage of explained variance = 92.6%.

Percentage of maximum explainable variance = 99.3%.

a) The 95% confidence *F* value for 5 and 9 degrees of freedom is 3.48. Since this value is smaller than the *F* test value in the above table the regression model is significant at the 95% confidence level if the residuals distribute normally.

b) The 95% confidence *F* value for 5 and 4 degrees of freedom is 6.3. This value is smaller than the *F* test value, 8.0, in the table and indicates a slight lack of fit.

The largest coefficients in Equation 1 are those for polymer-salt and plasticizer-salt interactions. Both coefficients are statistically significant well above the 95% confidence level. Since their signs are positive the interactions are synergetic. Not surprisingly the simultaneous presence of polymer and salt increases the conductivity more than one would expect based on their isolated contributions to this response. On the other hand, the synergetic interaction between plasticizer and salt is almost as large. Since the linear salt term is negative, these two interaction terms provide contributions that correctly predict conductivity increases for increases in the salt concentrations for the mixtures studied. The highest conductivity values in Table I occur for samples D and E with high salt proportions, 0.29 and 0.21. The lowest values were measured for samples A and G which have the smallest salt proportions. This behaviour can be seen more clearly in the triangular concentration graph of the conductivity contour lines of Fig. 2. Although predicted conductivity values are seen to increase with increasing salt concentrations, the increases are larger for proportions relatively rich in plasticizer at the expense of polymer. Even though the synergetic polymer-salt interaction term coefficient is larger than the plasticizer-salt one, the significant linear polymer term provides negative contributions to the log conductivity explaining this behaviour. Within the mixture region investigated here, the above equations predict that the highest conductivity value is expected to occur for the (0.50; 0.21; 0.29) mixture, equivalent to the one for sample E. Indeed this sample contains the highest plasticizer proportion of all samples in Table I. The model's predictive power was tested by making new measurements which will be discussed in the 3.3. section below.

3.2. Thermal analysis

The thermogravimetric analysis showed a weight loss at 100 °C lower than 3% for all samples. Moreover, the loss of plasticizer around 150°C with subsequent system stability until values up to about 300°C was observed.

Fig. 3 shows the DSC curve obtained for sample A. The melting temperatures were determined at the peak and the glass transition temperatures at the extrapolated beginning. The choice of reporting the T_g(onset) is justified by the large range of glass transition in some measured samples. The beginning of heat capacity variation was easier to determine in our experiments. The accuracy of the transition temperatures in a single measurement were ±1 °C for T_m and ±2 °C for T_g.

The influence of the plasticizer on the crystallinity and glass transition, as measured by DSC, can be seen in Table I. Samples K and K_2 showed very different thermal properties while their conductivities are the same. The relatively high degree of crystallinity of K_2 can be attributed to material microheterogeneities [18]. Since the DSC sample weight is approximately 5 mg it seems possible that the sample collected for K_2 presents a higher concentration of crystals in comparison to K. However, since the amount used in bulk conductivity measurements is greater than 200 mg, this measurement is not sensitive to microheterogeneities, producing an average value. It should be possible to perform another measurement with a more typical sample for K_2. However, the different degrees of crystallinity and T_g values of K and K_2 will be used, as described below, to design a useful parameter for later statistical treatment.

The same kind of experimental problem, e.g. microheterogeneities, may also be present in the other samples used for DSC measurements. For example sample C, with 29 wt% of salt, shows a lower value of T_g (Table I) than expected when compared with the literature results [15], even if we consider that the plasticizer content in the sample C is 7 wt%. However the purpose of this work is to develop an overall statistical treatment

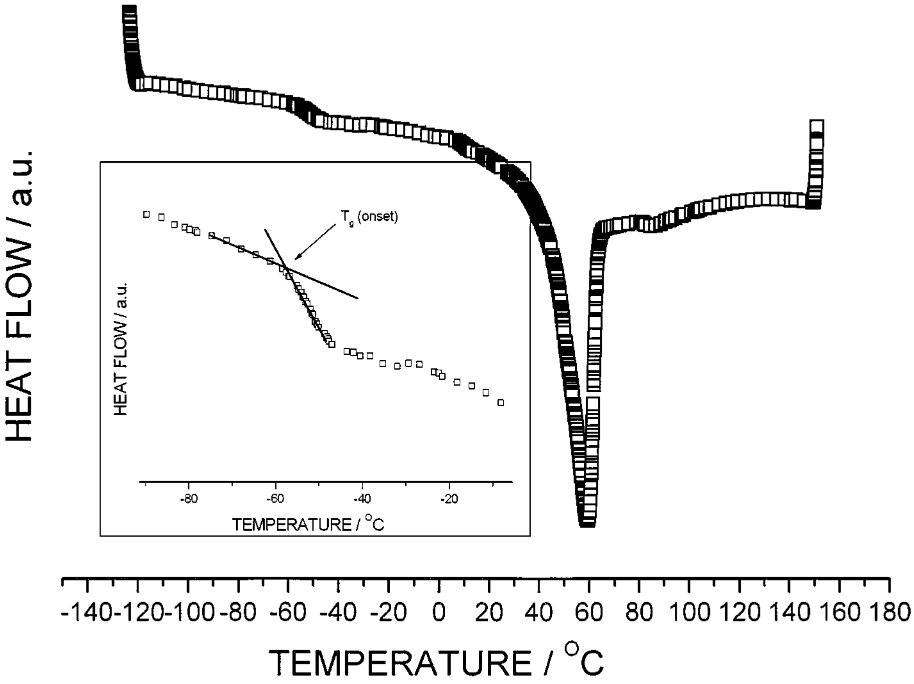

Figure 3 Typical DSC curve obtained for PEO/$LiClO_4$/EC. Sample A.

which should be able to take into account these experimental difficulties.

For statistical modelling the T_g values were corrected for material with crystallinity above 20%, resulting in the T^* values in Table I. This correction is necessary considering the influence of crystals on the properties of interest, such as conductivity and mechanical stability. The correction was calculated in a simple way taking as a base the T_g values of samples K and K_2 with approximately 5 and 57% crystalline phases (using the tabled values of ΔH_m of PEO) respectively. A correction factor that adjusts the T_g of K_2 to the same value of the T_g of K was obtained. This factor, weighted by each degree of crystallinity, was apllied to the T_g values of the other semi-crystalline samples. Crystallinity lower than 20% will produce corrections within the accuracy range of the T_g values. Therefore, this correction was applied to all samples with ΔH values corresponding to more than 20% crystallinity. The correction was calculated considering that the crystalline phase is basically crystalline PEO since EC is present at low concentrations and its T_m is lower than the values observed in Table I [7].

The arbitrary parameter T^* expresses T_g as well as crystallinity variations. The model behind the use of T^*, in a statistical treatment, looks for a unique parameter, representing in a very simple way, the structure of the ternary system and allowing a correlation with the conductivity measurements. When T_g increases, T^* increases, but larger T^* values are also obtained when the concentration of crystals is high. Thus, the overall effect when T^* is raised is a phase arrangement less favourable to ionic conductivity.

A special cubic model [28], given in Equation 2 was adequate for treating the corrected T_g , or T^*, values for the 13 samples (without K and K_2) as a function of polymer, salt and plasticizer proportions:

$$y(T^*) = \underset{(\pm 55)}{-92x_{\mathrm{PEO}}} \underset{(\pm 667)}{- 942x_{\mathrm{salt}}} \underset{(\pm 719)}{- 1005x_{\mathrm{EC}}} \underset{(\pm 1167)}{+ 1415x_{\mathrm{PEO}}x_{\mathrm{salt}}} \underset{(\pm 1240)}{+ 1539x_{\mathrm{PEO}}x_{\mathrm{EC}}} \underset{(\pm 4733)}{+ 6571x_{\mathrm{salt}}x_{\mathrm{EC}}} \underset{(\pm 7527)}{- 9987x_{\mathrm{PEO}}x_{\mathrm{salt}}x_{\mathrm{EC}}} \qquad (2)$$

TABLE III Analysis of the variance for the regression of the corrected T_g (T^*) data as a special cubic function of the mixture proportions

Variance Source	Sum of Squares	Degrees of Freedom	Mean Square	F Test
Regression	1068.30	6	178.05	26.3[a]
Residuals	40.63	6	6.77	
Lack of Fit	13.62	3	4.54	0.50[b]
Pure Error	27.00	3	9.00	
Total	1108.93	12		

Percentage of explained variance = 96.3%.
Percentage of maximum explainable variance = 97.6%.

a) The 95% confidence F value for 6 and 6 degrees of freedom is 4.28. Since this value is smaller than the F test value in the above table the regression model is significant at the 95% confidence level.

b) The 95% confidence F value for 3 and 3 degrees of freedom is 9.3. This value is much larger than the F test value (mean square of lack of fit/mean square of pure error), 0.50, in the table and indicating there does not exist lack of fit at the 95% confidence level.

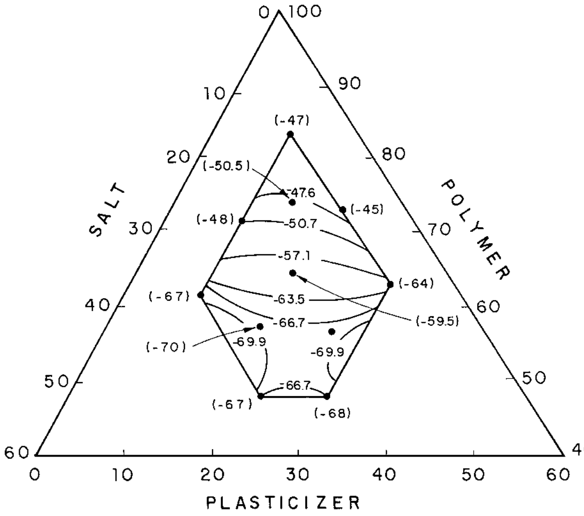

Figure 4 Predicted T^* contour lines for the special cubic model of Equation 2.

The analysis of the variance for this regression is given in Table III. Note that the least squares fit does not show any significant lack of fit at the 95% confidence level, since the mean square of lack of fit/mean square of pure error ratio of 0.50 is much smaller than the 95% confidence level tabled $F_{3,3}$ value of 9.3. The mean square regression/mean square residual ratio is 26.3, and much larger than the 95% confidence level $F_{6,6}$ value of 4.3 indicating a highly significant regression. The model given by Equation 2 explains 96.3% of the 97.6% explainable variance. The 95% confidence intervals given in parentheses below Equation 2 are all smaller than the absolute values of their corresponding coefficients, indicating that all the terms in the special cubic model are significant. All three binary interaction effects are synergetic. The simultaneous presence of any two components tends to increase T^*, in contrast to the linear terms which all tend to decrease T^*. The three component interaction term has a negative sign indicating that the simultaneous presence of all three components lowers T^* from values expected based only on linear and binary interaction effects. Predicted T^* contour lines are shown in Fig. 4, along with the experimental values obtained from the individual samples. Note that the values in the interior of the mixture space are duplicate averages. The good agreement between the contour values and the experimental results is consistent with the analysis of variance results in Table III, which indicates no significant lack of fit. The most striking trend of the T^* contour lines in Fig. 4 is a decrease of T^* values as compositions change vertically from the top of the mixture space (sample A) to the bottom,

TABLE IV VTF parameters for the ternary polymer electrolyte PEO/$LiClO_4$/EC

	weight fraction of			VTF parameters			
Sample	polymer	salt	plasticizer	σ_0/S·cm^{-1} K$^{1/2}$	E^*/K	T_0/K	T_g/K
C	0.64	0.29	0.07	1.3	407	242	206
E	0.50	0.21	0.29	3.2	462	240	205
H_2	0.66	0.17	0.17	1.4	321	256	210

passing through the middle of the line segment connecting samples D and E (See Fig. 1). There is hardly any horizontal dependence of T^* in this graph since the linear terms for salt and plasticizer proportions have almost equivalent magnitudes, as do the polymer-salt and polymer-plasticizer binary interaction terms. This decrease in the T^* values corresponds to decreases in the polymer weight, with consequent increases in the weigth quantities of a 50%–50% salt-plasticizer mixture. Note that the decreasing T^* values roughly correlate with increasing conductivities, as can be seen comparing Figs 2 and 4.

The overall results presented here agree with the most frequently observed effects reported in the literature for the ternary systems. The increase in T_g related to salt concentration increase can be compensated [19] by the additions of plasticizer, keeping the system with a favourable structure to raise the ionic conductivity as a consequence of the increase in charge carriers concentrations. The intricate frame related to effects of crystallinity changes and ionic aggregations seems to be incorporated, in a certain way, in the parameters of the statistical model, permitting a good evaluation of the ultimate properties. Further studies about the charge carrier concentration and free volume features for the ternary mixtures have been carried out.

3.3. Temperature dependence of ionic conductivity

Some of the samples studied by the statistical approach have been tested in relation to their conductivity behaviours with temperature. Fig. 5 exhibits the results in the Arrhenius diagram for the semicrystalline samples A and I_2 and for the amorphous materials C, E and H_2. The compositions and other properties can be checked in Table I. The conductivity differences at room temperature between the Table I values and those in Fig. 5 can be attributed to three different factors; the 12 month interval between the measurements, which can permit slow structural changes in the materials, the different room temperatures which are 25 °C in Table I and 30 °C in the Arrhenius diagram of Fig. 5 and the contact differences between electrolyte/electrode at each measurement.

The semicrystalline samples A and I_2 exhibit a typically high decrease in ionic conductivity below the melting point. At high temperatures these materials show the lowest conductivities in the range associated with the lower salt concentrations.

Sample E that is predicted by the statistical model to be the mixture with maximum conductivity indeed exhibits this behaviour in the whole temperature range.

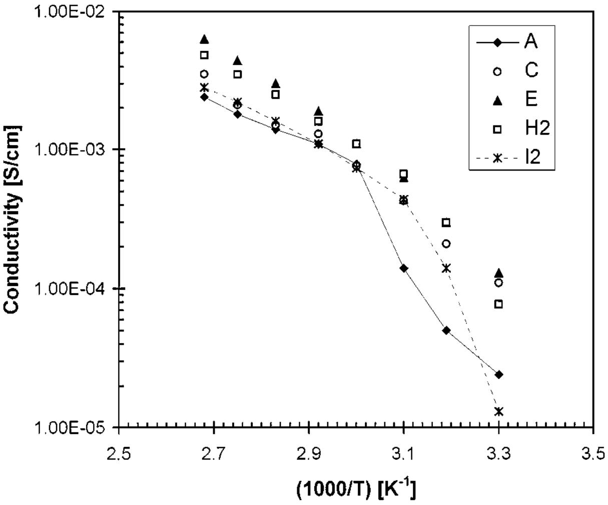

Figure 5 Arrhenius diagram for PEO/$LiClO_4$/EC (samples are especified in the diagram).

The temperature increase does not seem to modify the favourable structure which affords the best conductivity level in the ternary diagram for this material.

The data for the amorphous samples were fitted with the VTF equation, Equation 3 [37–39], which is the usual approach to deal with conductivity versus temperature results in amorphous polymer electrolytes [1–2].

$$\sigma = \sigma_0 T^{-1/2} \exp\left(\frac{-E^*}{T - \mathrm{To}}\right) \qquad (3)$$

In Equation 3, σ is the total ionic conductivity, whose unity is S·cm^{-1}; σ_0 is the pre-exponential factor related to the concentration of charge carriers [40]; E^* is a function of expansivity and can be equationed as proportional to the critical volume of the void required for transport in a free-volume model [41]; and T_0 is the "ideal" glass transition temperature, which was treated as an adjustable parameter in this study.

These parameters, shown in Table IV, are similar to those obtained for binary ethylene oxide systems by Hubbard *et al.* [42]. The pre-exponential factor related to the number of charge carriers, σ_0, exhibits the highest value for sample E (Table IV), which is the electrolyte with maximum conductivity in the whole temperature range. As expected, σ_0 has the same order of magnitude observed for various amorphous PEO materials [42].

4. Conclusions

A quadratic mixture model has been shown to be adequate in explaining how logarithmic conductivity varies as a function of poly(ethylene oxide), $LiClO_4$ and ethylene carbonate proportions. The conductivity increases, owing to increasing salt concentrations are seen to be explained by significant synergetic polymer-salt and plasticizer-salt interactions rather than by a simple salt concentration effect. Higher salt concentrations and high plasticizer/polymer ratios result in higher conductivities. Samples with highest conductivities also exhibit lower values of corrected glass transition temperatures (T^*). The conductivity as a function of temperature study confirmed the sample (0.50, 0.21, 0.29), predicted by the statistical model, as the mixture with the maximum conductivity in the whole temperature range.

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