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Application of a mathematical model to the study of the glass transition temperature in polymer electrolyte precursor systems

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Abstract

To the purpose of studying the effect of composition on the glass transition temperature (Tg) of a series of polymer electrolytes based on blends of polyethylene oxide (PEO), poly (octafluoropentoxytrifluoroethoxy)phosphazene (PPz) and poly(epichlorhydrine), a mathematical model was applied to results obtained through DSC determination using seven ternary blends selected by an experimental design. The parameters of the model were chosen by means of stepwise linear regression method. The final model proved to be appropriate (R^2=0.997; s=0.99 K) to predict the Tg values. From a structural point of view it was found that the lowest Tg values were obtained for the blends containing the smallest PECH portion.

Introduction

The use of polymeric electrolytes in advanced rechargeable solid state batteries has gained considerable scientific and technological interest, due to the fact that these devices may, in the near future, constitute an alternate energy source to the conventional petrochemical sources of today, thus combining attractive economic perspectives with environmental benefits (1-4). Our research group has been developing since some time new polymer electrolytes based on polyether blends (PEO, PECH) and polyphosphazenes (PPz) with the aim of obtaining ion membranes possessing high conductivity and good dimensional stability at ambient temperature. One of the objectives pursued through blending the different components was to reduce the glass transition temperature (Tg) and the crystallinity of PEO through its thermodynamic compatibilization with PECH and/or PPz. Pursuing these lines further, in this work the effect of composition of the blends on Tg is examined, applying the reduced cubic model to the observed Tg data for an experimentally designed blends (5). The Tg values were obtained by differential scanning calorimetry.

Experimental

Materials and Analytic Techniques

The following commercial polymers were used: Polyethylene oxide (PEO) (Mw = 5.10^6) from Aldrich; poly (octafluoropentoxytrifluoroethoxy)phosphazene supplied by Firestone under the trade name PNF-200; and poly(epichlorhydrine) (PECH) (Mw = 7.10^5), also supplied by Aldrich.

Seven samples were prepared varying their composition according to the experimental design, as compiled in Table I. The blends were obtained by dissolving the appropriate amounts of the three components in acetonitrile and chloroform. The solutions were dried by evaporating the solvent and maintaining the samples under vacuum conditions until their weights remained constant. The compositions of the seven samples chosen for this study are shown in the ternary diagram in Fig. 1. As can be observed the experimental sites are well distributed over the whole experimental range.

The glass transition temperatures (Tg) were obtained with a Mettler TA4000 differential scanning calorimeter. The samples were heated to 220°C and held at that temperature for 5 minutes in order to delete their thermal history. Then they were cooled to -100°C at the maximum rate of the calorimeter (100°C/min.) and subesequently re-heated to 100°C at a rate of 10°C/min., defining the glass transition temperature as the half value of the specific heat increment during the transition.

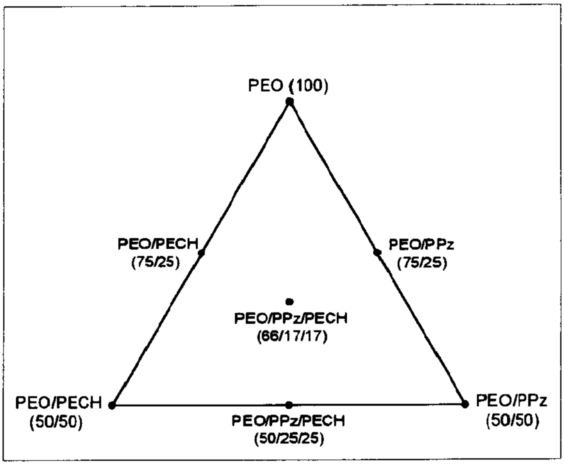

Figure 1.- Composition of the different samples according to the experimental design.

Mathematical Model

In order to determine the influence of composition on the glass transition temperature (Tg), the reduced cubic model which is widely used in the study of blends was accepted as valid. It takes into account the potential interactions between the three polymers, according to the following expression:

$$\mathrm{Tg} = a_1\mathrm{PEO} + a_2\mathrm{PECH} + a_3\mathrm{PPz} + a_{12}\mathrm{PEO{\cdot}PECH} + a_{13}\mathrm{PEO{\cdot}PPz} + a_{23}\mathrm{PECH{\cdot}PPz} + a_{123}\mathrm{PEO{\cdot}PECH{\cdot}PPz} \qquad [1]$$

In order to select the parameters of the model, as well as to calculate the respective regression coefficients (a_i), the stepwise linear regression technique was used.

The BMDP2R program from BMDP package (6) and the SYSTAT program (7) were used for the regressions.

Results and Discussion

Table I shows the blend compositions tested, as well as the experimental glass transition temperatures obtained through DSC determination. Depending on the compatible or incompatible nature of the systems under study and following the general blend theory (8,9), three different cases can be found for binary systems: in the case of compatible systems a unique Tg is obtained which is intermediate between the Tg values of the unblended components; in the case of incompatible systems two Tg values are obtained overlapping with those of the pure components, whereas for a partially compatible system the two Tg's appear to be shifted vis à vis the Tg values of the pure components. If an incompatible binary system is to be compatibilized through the addition of a third polymer which is miscible with one or both of the original components, the same pattern as indicated for binary systems is still valid, i.e. a) the two Tg's of the incompatible components converge to a single Tg positioned between the two Tg's prior to ternary blending, hence indicating compatibilization; b) the two original Tg's approach one another evidencing partial compatibilization; and c) the

Table I.- DSC glass transition temperatures.

COMPOSITION (%)			Tg (K) DSC			
PEO	PPz	PECH	PEO	PPz	PECH	blend
100	0	0	220.3	---	---	---
75	25	0	221.9	211.8	---	---
50	50	0	221.5	212.8	---	---
75	0	25	---	---	---	239.0
50	0	50	---	---	---	245.0
66	17	17	---	209.5	---	234.3
50	25	25	---	210.3	---	241.2
0	100	0	---	211.7	---	---
0	0	100	---	---	250.5	---

two Tg's remain unchanged, as no compatibilization is achieved.

In this research the attempt was made to compatibilize the incompatible system PEO/PPz through PECH addition, which is compatible with PEO. The test data reveal that in the case of binary PEO/PPz blends there appear two Tg's clearly assignable to each of the individual components and which do not vary with composition. In the case of the ternary blends PEO/PPz/PECH, two Tg's are detected. One of these corresponds to PPz, and the other to the compatible blend arising from PEO and PECH, which increases notably as a function of composition. This means that PECH is capable of partially compatibilizing the binary PEO/PPz blend. For statistical fit the Tg values which belong to the common polymer and which are modified through compatibilization were considered, i.e. those assigned to PEO.

After the application of the stepwise linear regression method to these test data, accepting the reduced cubic model expressed in equation [1], the parameters of the model and their corresponding regression coefficients were obtained as well as the statistical data valuating the accuracy of the model, i.e. the determination coefficient (R^2) and residual standard deviation (s). Mention should be made of the fact that the regression models for mixtures differ from ordinary regression models because the independent variables sum to a constant value. The regression model, therefore, does not include a constant and the regression and error sum of squares have one less degree of freedom. Hence the determination coefficient (R^2) of blend models are below those that could be obtained with the general linear regression models.

Relying on the results obtained, the parameter Tg was predicted in terms of the individual blend constituents (PEO, PECH, and PPz), as well as considering the binary products PEO·PECH and PEO·PPz, according to the following final model:

$$Tg = 220.7PEO + 244.9PECH + 221.9PPz + 26.47PEO\cdot PECH + 32.9PECH\cdot PPz \qquad [2]$$

where the determination coefficient (R^2) and residual standard deviation (s) are 0.997 and 0.99 K, respectively. To the purpose of comparing the tested versus the computed Tg values

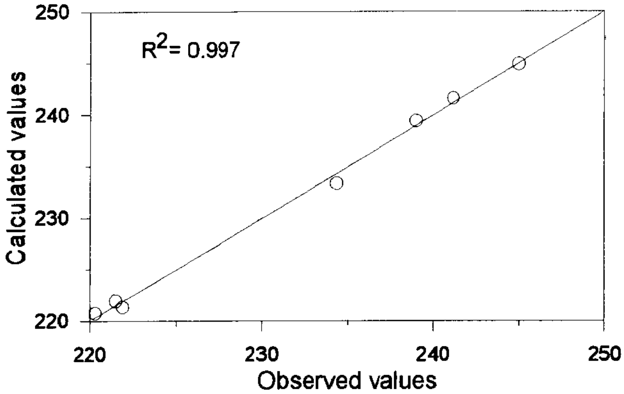

Figure 2.- Calculated Tg values from final model versus observed Tg values.

are plotted in Fig.2; deviation between both being below 1 K in all cases.

In Fig.3 the isoresponse curves for Tg can be seen, which provide information about the Tg behaviour as a function of blend composition. Tg proves to be dependent on PECH and rises proportionate to the PECH content of the blend, irrespective of the amounts of the other two components. In this way the value of the Tg becomes predictable for any composition and, by the same expression taken but inversely, the best suited blend composition to obtain a certain Tg value could also be predicted. To our purpose Tg should be as low as possible which refers us to the samples containing the smallest PECH portion. In any case, Tg constantly remains below room temperature, which encourages our expectation that, once the electrolytes are synthesized by means of lithium salt addition, their conductive behaviour will be such that rechargeable solid state batteries become feasible and operative. The thermal and electrical study of polymer electrolytes based on these precursor systems will be dealt with in forthcoming work.

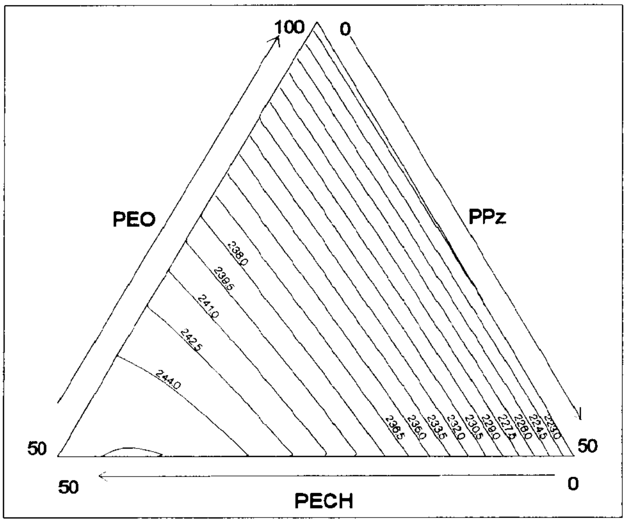

Figure 3.- Isoresponse curves for the parameter Tg as a function of the ternary composition.

Acknowledgements

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