

Structure, Vibrational Order and Thermal Stability of Polyethylene Oxide Membrane with ZrO₂ Filler

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Abstract: Poly (Ethylene) Oxide/Zirconium dioxide (PEO+xZrO₂) (x = 0, 5, 10, 25 and 50% wt.) membranes were obtained using 2.5% wt. acetonitrile solution. Room temperature X-Ray diffraction (XRD) showed the presence of a mixture of phases for the whole range of ZrO₂ content. Raman measurements (Raman Spectroscopy (RS)) at room temperature revealed the presence of a mixture of vibrational states for the two phases PEO and ZrO₂, respectively. The two techniques XRD and SR confirmed an exponential trend of the increase in the relative volume of ZrO₂ on the basis of the content of ZrO₂. The thermal stability of the (PEO+xZrO₂) membranes was corroborated using DSC measurements. The presence of ZrO₂ in the host matrix promoted the reduction of the energy needed to obtain the fusion of the complex polymer and with it an implicit increase of the disorder, coinciding with the two XRD and RS measurements.

Key words: Poly (ethylene) oxide, zirconium dioxide, micro-Raman, thermal stability, RS measurements, implicit

INTRODUCTION

The integration of polymers with organic and/or inorganic materials (complex polymer) is a challenge for researchers seeking to improve properties: mechanical, optical, dielectric, electric, among others. Among the complex polymers, we highlight those known as Solid Polymer Electrolytes (SPEs) which involve metal ions. Their importance lies in the development of rechargeable batteries, given their low level of environmental pollution (Armand and Tarascon, 2001; Zhang *et al.*, 2015). Among the many applications of SPEs, they may be used as good electrical insulators (Kazmiruk, 2012; Yap *et al.*, 2013) which means that they can be used in the development of fuel cells, supercapacitors electronic sources, among other things. Within the group of SPEs, one of the most broadly studied is Poly (Ethylene) Oxide (PEO)/proton salts, for example, 2 PEO with alkaline salts sodium perchlorate (NaClO₄) and Nb₂O₅ (Kumar and Aparna, 2016), PEO with LiCF₃SO₃, PEO with NaIO₄ and Polyvinylpyrrolidone (PVP), among others (Caruso *et al.*, 2002; Zhang *et al.*, 2005; Turkovic *et al.*, 2005). The results presented in the studies point to discerning the correlation between the conductivity of the composite with the free ions in the polymer. An increased presence of organic and/or inorganic material in the polymer matrix leads to a reduction in the disassociation of ions, implying a reduction of the semi-crystalline order which correlates with the ionic conductivity and its mechanic stability.

The substantial conductivity of SPEs is associated to the interaction of the OH polymer groups with inorganic filler and the probability that the filler may act as reticular sites which increases the amorphous phase of the complex. This topic has not yet been clarified and continues to be the subject of discussion. We present the results of structural ordering, Raman response and ionic conductivity of SPEs (PEO+xZrO₂) for, x = 0, 5, 10, 25 and 50% wt. in the shape of membranes, prepared with acetonitrile 2.5% wt.

MATERIALS AND METHODS

Experimental details: Complex polymer PEO+xZrO₂, (x = 0, 5, 10, 25 and 50% wt.) membranes were obtained based on: poly (ethylene) oxide (Mw = 8×10⁶) from the Aldrich trading house and acetonitrile (99% purity) and zirconium dioxide (99% purity) from Merck. PEO is dissolved in acetonitrile in 2.5% wt. ratio. ZrO₂ was dissolved separately in acetonitrile in a 5% wt. ratio with respect to the PEO. The two solutions are shaken separately using room temperature ultra sound for approximately 40 min. They are then placed in a magnetic stirrer at room temperature for 150 min. The two solutions are mixed and stirred constantly for 24 h. The resulting gel is spread on Teflon substrates and stored in a controlled environment for 24 h to evaporate the solvent, repeating the procedure for 10, 25 and 50% wt., respectively.

The thickness of the SPE membranes oscillated between 200 and 700 μ . The membranes were white, slightly opaque and elastic. The opacity is associated to the membrane's high degree of semi-crystallinity. The crystalline structure was determined using A8 Advance Buker AXS equipment at room temperature. Raman scattering at room temperature was measured using a LabRam HR800 Horiba Jovin Yvon in a 200-1900 cm^{-1} range. The thermal stability of the SPE membrane was characterized using TA3 Instruments Q100 DSC; the samples were hermetically sealed in aluminum caps. Each sample was subjected to a heating cycle of $10^\circ\text{C min}^{-1}$ in a temperature range of 25-100 $^\circ\text{C}$ in a nitrogen flow of 50 ml. min^{-1} .

RESULTS AND DISCUSSION

X-Ray Diffraction (XRD): Figure 1 shows the XRD measurements at room temperature, revealing the presence of a single monoclinic semi-crystalline phase for the PEO-membrane, a single monoclinic phase P21/c space group for ZrO_2 -powder and a mixture of phases for the $\text{PEO}+x\text{ZrO}_2$ -membrane. Considering a monoclinic structural order for the $(\text{PEO}+x\text{ZrO}_2)$ -membrane and initial crystalline parameters given by Takahashi and Tadokoro (1973) and Smith and Newkirk (1965) and using the software Gsas (Toby and Dreele, 2013), the values for the crystallographic parameters for $x = 0, 5, 10, 25$ and 50% wt., respectively were determined (Table 1). The values of the crystallographic parameters calculated coincide with those reported by Takahashi and Tadokoro (1973), Smith and Newkirk (1965) and Liang *et al.* (2003). The trend of relative increase of the monoclinic phase of the zirconium dioxide (V_m) was monitored using the expression proposed by Garvie and Nicholson (1972) and Schrader (1995):

$$V_m = \left\{ \frac{I_{z1} + I_{z2}}{I_{z1} + I_{z2} + I_{\text{peo}}} \right\}$$

where, I_{PEO} is the intensity of the peak located in $2\theta \approx 23.46$ for PEO, I_{z1} the intensity of the peak in $2\theta \approx 31.45$ for ZrO_2 (Fig. 1). The XRD results conclude that the incorporation of ZrO_2 to the PEO-membrane at these percentages is not enough to change the semi-crystalline structure of the PEO-membrane. A good semi-crystalline stability of the PEO-membrane with the presence of ZrO_2 is maintained by the fact that the size of the PEO crystalline cell is big enough to leave gaps in which ZrO_2 can fit.

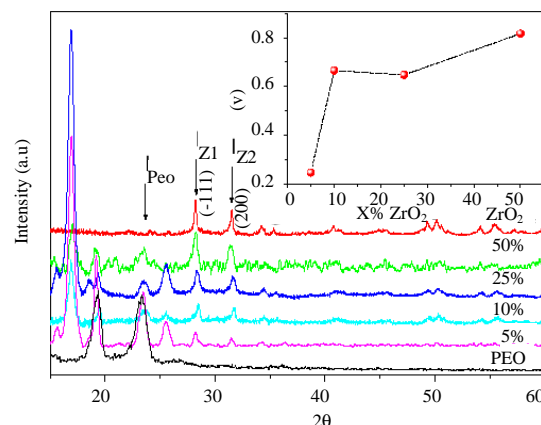


Fig. 1: XRD patterns at room temperature of PEO-membrane, ZrO_2 -powder and $\text{PEO}+x\text{ZrO}_2$ ($x = 5, 10, 25$ and 50%). The Miller indices were assigned to a monoclinic structure. Inset show the trend of the relative increase oh the phase ZrO_2 with the $x\%\text{ZrO}_2$. The line is visual guide

Table 1: Crystallographic parameters and relative increase of phase $\text{PEO}+x\text{ZrO}_2$

x (%)	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	V_m DRX	V'_m RS
0	8.022 ± 0.002	13.040 ± 0.007	19.444 ± 0.007		
5	8.052 ± 0.007	13.030 ± 0.005	19.484 ± 0.002	0.25	0.24
10	8.049 ± 0.008	13.040 ± 0.005	19.778 ± 0.002	0.67	0.69
25	8.054 ± 0.002	13.040 ± 0.005	19.489 ± 0.004	0.65	0.61
50	8.050 ± 0.002	13.191 ± 0.004	19.484 ± 0.007	0.82	0.77
100	5.131 ± 0.005	5.22 ± 0.01	5.277 ± 0.003		

Raman Spectroscopy (RS): Raman measurements at room temperature for PEO-membranes, revealed a presence of the active modes typical of the material's monoclinic phase (Fig. 2). The localization and characteristics of each of the modes are discriminated in Table 1. The position of each of the peaks corresponds to the data presented in reference (Brodin and Jacobsson, 2009). Raman measurements for ZrO_2 -powder (Fig. 2) at room-temperature, reveal the presence of 14 Raman bands whose positions correspond with (Liang *et al.*, 2003), confirming that at room temperature the crystalline structure falls into monoclinic space group P21/b (C_2H) (four molecules per cell unit) and a symmetry of $9Ag+9Bg$ according to reference (Sekulic *et al.*, 1997). Raman measurements for $\text{PEO}+x\text{ZrO}_2$ -membrane reveal the presence of a mixture of active modes for the two phases PEO and ZrO_2 , respectively.

To assess the trend of the relative increase of the monoclinic phase of zirconium dioxide (V'_m) with $x\%\text{-ZrO}_2$, we consider the intensity and position of the peaks denoted with I_{PEO} , I_{Zr1} and I_{Zr2} (Fig. 2) and with the help of Eq. 1. This trend of relative increase is shown in the inset of Fig. 2. The results of the Raman

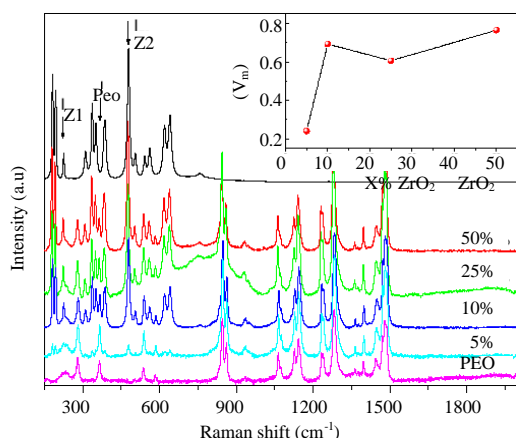


Fig. 2: Room temperature Raman spectra of PEO-membrane, ZrO_2 -powder and $\text{PEO}+x\text{ZrO}_2$ -membrane. The inset show the relative phase tendency whit $x\%$ ZrO_2 . The line is a visual guide

spectroscopy are conclusive enough to assert that the inclusion of ZrO_2 to the PEO-membrane in these percentages is not sufficient to significantly modify the Raman response implicit in the room temperature crystalline order for the PEO-membrane and ZrO_2 separately. There is evidence of the presence of a mixture of active states which coincides with the results shown with XRD. This mixture of active states present in the $\text{PEO}+x\text{ZrO}_2$ -membrane, indicate a slight increase of the disorder given as the ZrO_2 is incorporated but the semi-crystalline monoclinic structure was maintained. This characteristic may help improve the transport of ionic loads.

DSC calorimetry: Figure 3 shows the DSC thermograms for fresh $\text{PEO}+x\text{ZrO}_2$ ($x = 0, 5, 10, 25$ and 50% wt.) membranes in the $25\text{--}100^\circ\text{C}$ temperature range for a heating cycle. All the measurements reveal an endothermic peak at a Fusion Temperature (T_f) for each SPEs. Transition temperature values are not significantly different from the PEO-membrane fusion temperature values (Table 2) and they coincide with the reports in the literature (Jurado *et al.*, 2013; Pielichowski and Flejtuch, 2004). However, it is possible to observe a small decrease in the fusion temperature as $x\text{ZrO}_2$ increases. The associated heat of fusion value (ΔH) for each of the $x\%$ values reveals a slight decrease as ZrO_2 increases. This trend indicates that the presence of ZrO_2 in a highly polar polymer matrix, favors interaction and implies a weakening in the molecular interactions in the polymer chains. That is, the presence of ZrO_2 in the host matrix promotes a reduction in the energy required to obtain a fusion of the complex polymer. The degree of SPE-membrane

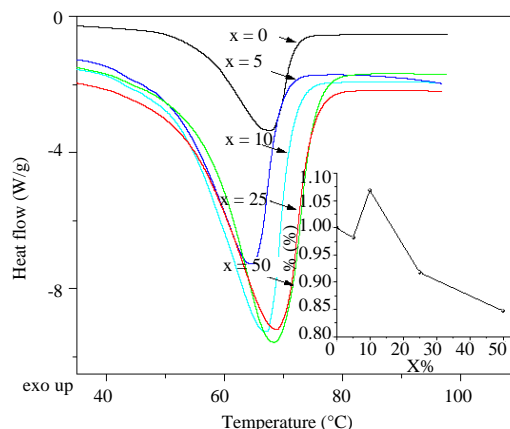


Fig. 3: Heating DSC curves for SPEs-membrane in nitrogen atmosphere. The inset show the degree of crystallinity tendency whit $x\%$ ZrO_2 . The line is a visual guide

Table 2: Raman modes that characterized the groups present in the PEO according to the Garvie and Nicholson (1972)

Molecule	Vibration types	Region (cm^{-1})	Intensity
CH_2	Stretching	1400-1470	Medium
C-O-C	Symmetrical stretch	1060-1150	Weak
C-C-O	Symmetrical stretch	800-970	Medium-strong
C-O-C	Deformed skeletal bounds	200- 600	Highly-strong

Table 3: DSC parameters for SPEs membrane for the heating cycle

Sample	Melting point	Heat of melting	Degree of
$x\%$	T_f (°C)	ΔH (J/g)	crystallinity (χ_c) (%)
0	67.4	115.80	1
5	64.5	113.70	0.98187
10	66.8	123.80	1.06908
25	68.5	106.30	0.91796
50	68.8	98.15	0.84758

crystallinity was calculated using the following formula $\chi_c = \Delta H_x / \Delta H_0 * 100\%$ where ΔH_x ($x = 5, 10, 25$ and 50) and ΔH_0 are the enthalpy of the PEO-membrane (Wang and Alexandridis, 2016). The results lead us to infer that the crystallinity of the SPEs decreases as the ZrO_2 content grows (Table 3) following an exponential trend.

CONCLUSION

The monoclinic semi-crystalline order in the PEO-membrane is invariant to the presence of $x\text{ZrO}_2$ (for $x = 5, 10, 25$ and 50% wt.). Given the size of the semi-crystalline cell of the PEO, the polymer chains leave big enough gaps to accommodate the monoclinic zirconium dioxide cell. The spatial arrangements of PEO and $x\text{ZrO}_2$ leave as invariant the Raman modes associated to the two compounds. The two techniques-XRD and RS-infer a presence of a mixture of phases and the

relative increase shows an exponential-type trend according to the percentage of ZrO_2 . The SPE membranes reveal high thermal stability with a reduction of the degree of crystallinity as ZrO_2 is incorporated into the polymer matrix and this coincides with the XRD and RS measurements, respectively.

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