Polymer (PEO)-liquid crystal (LC E8) composites: The effect from the LC inclusion

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Abstract. The effect from the inclusion of nematic liquid crystal (LC) E8 into the polymer poly(ethylene oxide) (PEO) was inspected by studying of structural and electrical properties of PEO-E8 composites at weight percentage of E8 ranging from 10 % to 50 %. Flexible PEO-E8 films with a thickness of 0.1 mm were structurally characterized by X-ray diffraction and X-ray photo-electron spectroscopy. The results obtained by our analyses indicate that a polymer-LC intermolecular complex is formed by inclusion of E8 LC molecules in the PEO host at a certain their concentration level. The structural properties of PEO-E8 composites were correlated with their electro-conducting properties as depending on the E8 LC concentration. By the amount of the LC fraction one can achieve a controlled modification of the structural and electro-conducting properties of the PEO-E8 material. As compared to PEO, the inclusion of E8 LC in the PEO polymer matrix can lead to a considerably enhanced electrical conductivity of PEO-E8 composites.

1. Introduction

The doping of organic compounds into matrices of organic polymers is a strategic route to improve the performance of material characteristics like structural, optical, non-linear optical, electro-optical, electrical, dielectric, thermodynamical and mechanical properties. This is well exploited in the very quickly developed field of solid polymer electrolytes [1-5]. During the last decade, there are continuous investigations on multifunctional composite materials produced from polymers and liquid crystals (LCs). Such all-organic composites are a class of high-quality advanced materials with a wide spectrum of applications, e.g., in organic electronics, electro-optics and optoelectronics, in mechatrionic systems and medicine. In particular, they are of practical interest as electrolytes in rechargeable mini-batteries, organic electronics, photovoltaics and mechatronics [6-9]. Due to the improved electrical properties, various electrolytic polymer-LCs systems based on the polymer poly(ethylene oxide) (PEO) [10-12] have been synthesized and investigated [13-15]. Very recently we
have studied PEO-LC composite electrolytes produced of PEO with addition of molecules of the room-temperature nematic cyanophenyl LC with the commercial name E8 [16]. Thin (~ 0.1 mm) films of these flexible blends exhibited enhanced ionic conductivity and dielectric properties. In order to elucidate the effect from the inclusion of E8 LC in PEO, in the present study we have characterized the physico-chemical structure of PEO-E8 composites (with common methods like X-ray diffraction (XRD) and X-ray photo-electron spectroscopy (XPS)). As depending on the concentration of the LC E8, the structural and ion-conducting properties of PEO-E8 composites were interrelated.

2. Experimental

Samples of our poly(ethylene oxide) (PEO)-based polymer-LC blend electrolyte (flexible free-standing films with a thickness of 0.1 mm) were produced by conventional solvent-cast method (in our case, in methanol at room temperature, as described in [17-19]). By this technique, the structure of the composite film can be controlled by solvent evaporation rate. The structure of PEO is commonly expressed as [–H₂C–CH₂O–]ₙ [10] (figure 1a). In the present study, high-molecular-weight PEO (M.W. = 8 × 10⁶ g/mol) was used (purchased from Sigma Aldrich). In order to include LC molecules into the PEO polymer network, the powder of PEO monomers were mechanically mixed with the commercially available multicomponent room-temperature nematic LC with the abbreviation E8 (or BL002), supplied from Merck. This LC is an eutectic blend of five cyanophenylene LCs. It contains 45 wt.% of 4-cyano-4′-n-pentyl-biphenyl (5CB), 16 wt.% of 4-n-propoxy-4′-cyanobiphenyl (3OCB), 12 wt.% of 4-n-pentoxy-4′-cyanobiphenyl (5OCB), 16 wt.% of 4-cyano-4′-n-oxyoctylbiphenyl (8OCB) and 11 wt.% of 4-cyano-4′-n-pentyl-p-biphenyl (5CT) (figure 1b). All these nematic-type LCs have elongated rod-like molecules. The mixture E8 exhibits a single nematic to isotropic transition temperature at ca. 72°C and a glass transition temperature. PEO-E8 blends with 10, 20, 30, 40 and 50 wt.% of E8 were produced. PEO-E8 samples (thin films) were obtained by drying the PEO-E8 blends, and then evaporating the solvent under vacuum. Besides of PEO-E8 composite films, also films of net PEO with the same thickness were prepared by solvent casting.

The X-ray diffractograms of the samples were recorded using a D8 ADVANCE ECO (Bruker-AXS, Bruker Co.) X-ray diffractometer system with Ni-filtered Cu Kα radiation of wavelength λ = 0.154 nm. Angular scans of diffraction in reflection mode were taken in the 2θ range of 10° – 80° with a constant step of 0.1° and at counting time of 35 s. The XPS studies were performed by apparatus described in [20]. XPS spectra were obtained at 45° take-off angle and were referenced to C 1s peak (binding energy (BE) of 285.0 eV) resulting from small traces of adventitious carbon. The acquisition time was 0.6 s, the accuracy of the measured BE was 0.1 eV. The recorded C1s photoelectron lines were corrected by subtracting a Shirley-type background. Peak identification was performed by reference to a database of XPS. The electrical conductivity of the PEO-E8 thin films were measured by means of complex electrical impedance spectroscopy performed by a impedimeter (SP–200, Biologic) in the frequency range from 0.01 Hz to 2 MHz of the applied electric field. Te PEO-E8 samples were sandwiched between two circular-shaped copper electrodes with diameters of 1 cm. The complex impedance spectra were recorded at a probe voltage of 0.5 V_RMS in the sinusoidal waveform. All measurements in this study were carried out at ambient temperature (in our case, 27 – 28 °C).

3. Results and discussion

Optical microscopy studies on produced PEO-E8 films displayed the successful inclusion of nematic LC E8 in the bulk of the films [16]. The structural changes resulting from the dispersed E8 LC molecules into the PEO polymer network were evidenced by vibrational spectroscopy (micro-Raman and FT-IR absorption). The results (will be reported separately) suggest the increase of relative content of the amorphous phase and the flexibility in the examined polymer-LC composite. In addition, XPS studies can provide information about the surface chemistries of PEO-E8 composites (at the top surface and in the very near-surface region of the samples, in our case, within the depth of ~ 5 – 10 nm). In particular, figure 1c presents the changes in the core level C1s spectra of PEO polymer that reflect its local structural modification due to the addition of E8 LC.
Figure 1. Chemical structures of: (a) PEO monomer; (b) constituents of the LC E8. Deconvoluted XPS spectra (after subtraction of a linear baseline) in the range of the characteristic C1s peak, recorded for pure PEO (c) and for PEO-E8 composite at the 30 wt.% E8 concentration (d) under identical conditions. The resolved components and their envelope (the peak sum) are given with lines, the raw data – with circles. The calculated area percentage of C1s(2) peak is shown in parentheses.

The fit-factors (coefficients of determination) are: \( R^2 = 0.99962028 \) (c); \( R^2 = 0.99963553 \) (d).

The shape of the C1s photoelectron line of PEO (figure 1c) can be deconvoluted with use of two components, labeled as C1s(1) and C1s(2), at BE in vicinity of 285 eV and 286.3 – 286.5 eV, respectively, as referenced to a database of XPS for PEO, e.g. [21,22]. The first one is assigned to the C–C/C–H bonding in the [–CH 2–CH2–O–] repeat unit of PEO polymer (polymer backbone), and the second one is typically attributed to C–O bonds of carbon atoms in C–O–C moieties of PEO (the alcohol/ether C–OH/C–O–C type carbon component). Figure 1(c) presents the deconvolution of the C1s photoelectron line of PEO as fitted with both components. The curve fitting was performed as described in [20] – the XPS C1s data from the experiment were deconvoluted by least-square fitting; each component was taken as a product of Gaussian and Lorentzian functions (80% : 20%). Because very small, the contributions related to other types of C to O bondings (usually at BE > 288 eV) were ignored in the curve fitting.

On the other hand, the molecular structures of the constituents of E8 LC (figure 1b) suggest that the corresponding C1s XPS spectra should be deconvoluted by using at least 4 peaks. From them, three are related to aromatic carbon, aliphatic carbons CH 2–CH 3, and C–N species (e.g., for 5CB molecule their assignments are at BE of 284.8 eV, 285 eV and 286.7 eV, respectively [23]). A significant additional peak should be the one corresponding to C–O bonding of the cyanoalkoxybiphenyl (nOCB) constituents of E8 LC. Thus, regarding the C1s line in the XPS spectrum of PEO-E8 composite (figure 1d), besides the C–C/C–H bonding there are strong contributions from C≡C double bonds (in the phenyl rings of the E8 LC molecules) and C≡N triple bonds, related to the functional groups of the compounds belonging to the mixture E8 (figure 1b). However, the XPS signal attributed to C≡C bonds could be hardly distinguished from that associated with hydrocarbon bonds (C–C and C–H), because they are in the same BE region (moreover, for C–C and C≡C bond it is difficult to specify the BE because we would need an independent charging reference). The same problem applies to the BE of the carbon atoms bonded to the N. The contribution of C≡N bond in cyanogroups to the XPS C1s core-level spectra strongly overlaps with that of the C–O bond, and partially with C–C/C–H/C≡C bonds, hence they could not be readily quantified separately and unambiguously analyzed without introducing of a lot of assumptions. Due to the merging of the peaks corresponding to both PEO and E8 LC, the interpretation of the XPS spectral changes in our blend system using these peaks might not be reasonable. Still, the clear diminishing of the shoulder at BE = 286.3 eV (figure 1d) and corresponding decrease of the percent area of C1s(2) peak with respect to the total C1s peak, is indicative of the reducing concentration of C–O bondings in the PEO-E8 composite, even though in the considered case these bondings are associated also with the functional groups of
cyanoalkoxybiphenyl (nOCB) constituents of E8 LC added to PEO. Roughly, one can deconvolute the XPS C1s core-level spectrum of PEO-E8 composite into the same two components C1s(1) and C1s(2) and in the same manner, as the C1s lineshape of pure PEO. The result is shown in figure 1(d). Comparing figures 1(c) and 1(d), one obtains that the area percentage of C1s(2) peak is decreased from 37 % (pure PEO polymerization processing) to 23 % (PEO polymerization in the presence of 30 wt.% nematic LC E8). This, as well as the clear shift of ca. 0.2 eV to the lower BE observed for the composite sample, suggest an appearance of some type LC–(CH$_2$CH$_2$O) molecular complex in the studied PEO-LC blend. The level of concentration of cyanobiphenyls of E8 LC in the composite system ensures their complexation with the ethylene-oxide (CH$_2$–CH$_2$O) units in the host polymer.

Further useful information on the structural modification of the host polymer PEO due to the inclusion of E8 LC in the PEO-E8 composite can be obtained by XRD. The XRD records (figure 2) can be used to determine the phase composition and might be indicative of the influence of E8 LC on the crystalline status of PEO. The XRD pattern obtained for pure PEO (figure 2a) demonstrated two distinct crystalline peaks at diffraction angles (in terms of Bragg angle $2\theta$) of 19.4° and 23.5°. They are attributed to the (120) and (112) crystal planes of the PEO monoclinic crystal structure, as described in the literature. These diffraction peaks of PEO originate from the ordering of polyether side chains and strong intermolecular interaction between PEO chains through the hydrogen bonding [10,12,17,24]. Both characteristic peaks are structural signatures of PEO that exhibit its relatively high degree of crystallinity (the crystallinity is defined as the weight fraction of the crystalline portion of the polymer; as known, the physical properties of polymers are considerably dependent on this parameter). Simultaneously, a broad halo is also present in the XRD pattern (as a hump at the lower angles of XRD) that indicates a partially amorphous phase in the semi-crystalline PEO. As seen from figure 2, this diffraction feature strongly suppresses the weak diffraction peak (doublet) of PEO at 15°.

![Figure 2. XRD pattern of PEO (a) and PEO-E8 films by weight fraction of the E8 nematic LC (wt.%): 10 (b); 20 (c); 30 (d); 40 (e); 50 (f). The insets show the same data on an expanded scale (Bragg angle 20 in the range from 17° to 25°).](image-url)

![Figure 3. Variation of degree of crystallinity ($X_C$%) and electrical resistivity ($\rho$) of the studied PEO-E8 composites at various weight fraction of the LC E8.](image-url)

The changes in intensity of the two sharp crystalline characteristic peaks of PEO upon the addition of nematic LC E8 should reveal the structural modification of the host polymer PEO, as an indication of the effect from inclusion of E8 LC. In fact, the decrease of their intensity by addition of E8 LC at concentrations 10, 20 and 30 wt.% (figure 2(b-d)) suggests an increase of amorphous content and flexibility in the considered polymer-LC composites, as previously discussed for XRD data for other PEO-based solid-type polymer electrolyte systems with flexibility [17-19]. It is interesting to
inspect the change in the XRD pattern of PEO-E8 as depending on E8 LC concentration. XRD study reveals that all the films measured show semicrystalline structure. As seen in figure 2, the mixture of crystalline/semicrystalline phase in which PEO exists is significantly modified upon addition of the LC. Firstly, by increasing percentage of E8 LC (in our case, in the range 10 wt.%–50 wt.%) gradually occurs a slight transformation from a structure mostly characterized by (120) crystal plane to structure in which the (112) crystal plane of the PEO monoclinic crystal is more pronounced, implying another preferred structural orientation of PEO. Secondly, the addition of E8 LC at higher concentration, e.g., as high as 40 wt.%, leads to appearance of a sharp XRD peak at 2θ near to 18°. This peak arises as a doublet at 2θ = 17.8°/18.25° (figure 2e) and becomes single (2θ = 17.8°), sharp and intense at 50 wt.% of E8 (figure 2f). Its relative intensity increases with increasing E8 weight fraction, whereas the intensity of the PEO diffraction peak at 19.4° declines. The observed additional peak can not be assigned to a crystallographic site of PEO in the pure state and was absent for E8 nematic LCs. For instance, a broad (FWHM ~ 10°) and rather diffuse XRD peak symmetrically centered at 20 ~ 21° takes place for 5CB LC in its nematic state (the peak for the nematic phase) and reflects the absence of ordering in the system. Also, the additional peak in question can not be associated with a hypothetical LC phase induced by polymer, because usually such induced crystalline phases by nematic LCs exhibit XRD peaks at much lower 2θ values. Therefore, the XRD pattern observed for PEO-E8 composite can be attributed to a crystal modification in PEO. Similarly, additional peak (at 2θ ~ 16°) has been found by XRD analyses of molecular complexes prepared from PEO with inclusion of ionic liquid [25], where, in general, such a diffraction peak evidences a change in PEO structural geometry due to interaction/complexation with the ionic liquid.

Based on the results from XRD measurements, one can suppose that by PEO:E8 compositions equal to 60:40 wt.% and 50:50 wt.% arises intermolecular crystalline complex promoted from cyanophenyle molecules of E8 LC being in confined volume within the host matrix of the polymer, and anchored, at least to some extent, to segments of PEO chains. According to XRD data in figure 2(e,f), such a structural formation is characterized with an average intercrystallite separation R that is larger than R for undoped PEO (R ~ 1/sinθ). Most probably such a complex occurs due to electric dipole-dipole intermolecular interactions induced by cyanocompounds in E8 having highly polarized cyanogroups and easily polarizable biphenyl groups. For instance, the longitudinal permanent electric dipole moment of 5CB molecule is ~ 3 D due to the triple –C≡N bond. The dipole moment of PEO molecule mostly due to the charge-polarized group –O– present in PEO is relatively small (~ 1 D, at 25° C), but the PEO ether oxygens are capable of forming hydrogen bonds. Thus, weak hydrogen bonds between the PEO hydroxyl groups and the π-electrons of benzene rings of cyanophenyles in the E8 LCs are rather possible, because the –OH group of PEO can act as a hydrogen-bond donor, and the –CN group of cyanophenyles acts as a hydrogen-bond acceptor. A third type of molecular interaction could be also considered – electronic charge-transfer PEO-LCs interactions because the cyano group is strongly electron-withdrawing, and the oxygen atoms in the [C–C–O]n backbone structure of PEO are electron-donating. The question is about the strength of the contribution of each from these three possible kinds of intramolecular interactions, which are, actually, LC-matrix surface interactions. In fact, each of them should assist the intermolecular coupling and formation of PEO-LC complex. The dipole-dipole interaction between cyanophenyl core, well known for cyanobiphenyle molecules [26,27], can play a weaker role in the mechanism of formation of PEO-LC complex.

The salvation role of PEO is to ensure multiple contacts between own electron-donating ether oxygens along the highly flexible PEO backbone and electron-withdrawing cyanogroups of the LC dopants, similarly to the case of complexation of PEO with metal (e.g., Na+) cations in salt-complexed polymer electrolytes [17]. Thus, LC-PEO molecular complex should be formed during the polymerization of PEO, when enough strong chemical interaction between the functional groups of E8 LCs and hydroxyl groups at the ends of PEO chains is realized, enough strong to overcome the coupling effect from the backbone. This happens through the surfaces of both polymer and LC phases. The chains of PEO have no large side-groups, hence can be easily distorted by intramolecular interactions. The chain backbone of PEO is flexible and could adopt other conformations, e.g., as
segments of the entire chain, that can result in clusterization into domains [28]. By that, the originally completely helical conformation may be suppressed. In this context, a calculation by means of the Debye-Scherrer formula gives for the average domain size \( D \sim 35 \text{ nm} \) corresponding to the XRD peak observed at \( 2\theta = 17.8^\circ \). Also, clusterization of LC molecules confined in the PEO polymer matrix is rather possible, and thereby the formation of LC clusters attached to PEO backbone. In such clusters (whose dimensions could be close to the above mentioned size \( D \sim 35 \text{ nm} \)) the rigid rod-like E8 nematic molecules develop spatial and orientational ordering [29].

The reorganization of the crystalline state of the polymer host has a strong impact on the electro-conducting properties of the studied blends of PEO with the nematic LC E8. The situation is much more complicated, since the polymer-LC molecular interactions are accompanied by a redistribution of electron density in the LC molecules that should be reflected in the change of electro-conductivity and dielectric properties of PEO-E8 composite system. As established by electrical impedance measurements, the electrical resistivity of PEO-E8 decreases by the increase of the relative amount of E8 up to \( \sim 30 \text{ wt.\%} \), and after that it increases. Certainly, this effect can be correlated with the degree of crystallinity \( X_c\% \) of the PEO-E8 composites, as calculated from the XRD patterns in figure 2. \( X_c\% \) of the studied PEO-E8 composites can be roughly estimated by the ratio of the total area under the crystalline peaks to the total area under the diffractrogram. The \( X_c\% \) value decreases gradually with increasing concentration of the E8 LC until approximately \( 20 \text{ wt.\%} \) and then increases with further increasing E8 concentration (figure 3). The reduction in the degree of crystallinity can be connected with enhanced flexibility of the polymeric chain, which results in the enhancement of segmental motion in the polymer. When the E8 concentration exceeds \( 20 \text{ wt.\%} \), \( X_c\% \) increases that may be attributed to the reorganization of the polymer matrix.

It is seen from figure 3 that the electrical conductivity of the studied PEO-E8 composites is nearly reciprocal to \( X_c\% \). Thus, by dealing with the blend composition (wt/wt %) of the PEO-E8 PE material one can simultaneously achieve a controlled modification of both its structural and electro-conducting properties. By suppression of polymer crystallinity at a proper blend ratio, one can get the most efficient ion transport. It is worthy to note that our analyses of Raman spectra of the studied PEO-E8 composites clearly confirm the variation of \( X_c\% \) for PEO-E8 composites as depending on the concentration of E8 nematic LC, as well as the conformation of PEO chains (breaking of the intermolecular hydrogen bonds present in the helical configuration of PEO) at higher weight fraction of E8 nematic LC (40 wt.% and more evidently at 50 wt.%).

4. Conclusion

Our claim concerns the preparing of PEO-E8 polymer-LC composites (in form of self-supported, solid-like thin films with a mechanical flexibility) with a good ionic conductivity at room temperature. This was successfully fulfilled by adequate choice of the LC component (the nematic cyanobiphenyl-type LC E8) and its proper concentration. The information obtained from XRD analysis of PEO-E8 composites refers to a transformation of the PEO structure not only to an amorphous state but also to a structural rearrangement and formation of polymer-LC intermolecular complex. The main result of the study reported here is that the inclusion of nematic LC E8 in PEO polymer matrix can lead to a considerable improvement of electrical conductivity of the composed PEO-E8 electrolyte material, as compared to that of the PEO itself. In PEO-E8 composite PE, both components, PEO and nematic LCs, provide effective ion conduction through interactions between PEO oxygen and LC molecules. By that, anchoring effect being induced by interfaces of both PEO and nematic LCs, plays a significant role. On the other side, a negative effect has the conformation of PEO by its molecular complexes with LCs when the LC weight percentage approaches 50 %, that leads to enhanced crystallinity and diminishing ion conductivity. The results reported here will be of interest for engineering of advanced multifunctional polymer-LC flexible composite materials based on interfacial polymer-LC interactions, optimizing the use of LCs as additives to PEs in order to improve their performance aiming their applications in the field of flexible electronics and mechatronics.
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