Thermoplastic and solid-like electrolytes with liquid-like ionic conductivity based on poly(ethylene oxide) nanocomposites

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ABSTRACT

A series of poly(ethylene oxide) (PEO)/lithium trifluoromethanesulfonate (LiTf)/ethylene carbonate (EC)/sepiolite composite electrolytes have been prepared by melt compounding, using neat sepiolite (Sep), sepiolite coated with polyethylene glycol (PEG-Sep) and with D-α-tocopherol polyethylene glycol 1000 succinate (TPGS-Sep) as fillers. The composites (weight ratio EC:PEO ~ 1) present ionic conductivity close to 10^{-3} S cm^{-1} at 30 °C, i.e. close to liquid electrolytes. Their crystallization and viscoelasticity were investigated evidencing a very complex phase structure and rheological behaviour, both of which dramatically depend on the type of nanofiller introduced in the blend. In the absence of TPGS-Sep as filler, the composites slowly separate into EC-rich and PEO-rich macrophases, what is visually evident in a two month time scale. With TPGS-Sep, the electrolytes are solid-like even at temperatures well above the PEO melting temperature range and do not phase separate in at least two years, constituting a homogeneous and stable blend which keeps its properties for long time periods.

1. Introduction

High diffusivity in mass and ion transport requires microscopically liquid-like membranes, while practical handling of such membranes requires very frequently a solid-like behaviour at the macroscopic scale. Solving this structural contradiction is challenging from fundamental and applied perspectives. In the active field of polymer based electrolytes [1–6], a solution to this issue is the use of gels, which effectively display solid-like behaviour at the macro and liquid-like behaviour at the microlevel, a well-known example of this solution being contact lenses. Highly plasticized polymers can be an alternative to gel electrolytes [7–10] and gainfully compete with them. It is at the frontier between the highly plasticized polymer and the polymer gel that the addition of small amounts of nanofiller, being able to behave as a physical crosslinker, acquires full sense [11–17]. Physical crosslinking has the obvious advantage of being reversible, and thus a physically crosslinked highly plasticized material can behave as a thermoplastic.

In this connection, the pseudo-solid behaviour displayed by certain nanocomposites and particularly by poly(ethylene oxide) (PEO) ones is extremely interesting. When a certain interaction between the filler and the polymer exists, a polymer network can be developed based on physical interactions of polymer chains and filler surface; these networks, not being chemical and permanent in nature, are given the name of transient [18]. From a practical viewpoint, the radical difference between a transient and a permanent polymer network lies on the reversibility of the former and the irreversibility of the latter, being

processing, recycling and reusing straightforward on the first case and very cumbersome or impossible on the second one. Well-known and well-studied composites displaying pseudo-solid behaviour because of the formation of transient networks are PDMS/silica [19] and PEO/silica systems [14,15,20]. This work relies on the hypothesis that it is possible to produce a transient network between sepiolite nanofibres and highly plasticised PEO taking advantage of physical interactions between the polymer and the nanofiller, and that this material can be the basis to produce thermoplastic solid polymer electrolytes (SPEs) behaving microscopically as liquids and thus presenting liquid-like ionic conductivity. Obviously, then, the conditions have been searched to prepare the electrolytes by extrusion and to shape the membranes by simple hot-press moulding, following procedures which can be easily repeated in the laboratory and which are directly applicable at industrial scale.

The formulation of these SPEs has been carefully chosen so as to assure the success of the strategy: ethylene carbonate (EC) has been used as low molecular weight compound, neat and organo-modified sepiolite nanofibres as filler, and lithium triflate (LiTf) as salt. Though aware of EC's flaws, regarding mostly its electrochemical stability and its relatively high melting temperature ($T_m = 37$ °C) [8] this model system may be considered as the most adequate given the large amount of literature found for the system PEO/EC. LiTf has been selected because, as compared to other lithium salts, it is chemically and thermally stable and little sensible to humidity, both a must for extrusion to be employed. Sepiolite nanofibres were chosen because they possess a very high specific surface and a fibre-like geometry, making it very suitable for reinforcement. In fact, nanocomposites of PEO with sepiolite and modified sepiolite have already been prepared in our research group [21], showing among other properties excellent dispersion of the nanofiller.

Being multicomponent and multiphasic, the morphology and structure of EC-plasticised P[EO]$_n$:LiTf electrolytes are complex to characterise. The early works on the structure of the blend P[EO]$_n$:LiTf at different n values [21–25] evidenced the complexity of their semicrystalline morphology [23], and the dramatic effect of the sample preparation on it [24]. A number of crystalline and amorphous P[EO]$_n$:LiTf phases coexist [21,26], and PEO melting endotherms appear in a wide range of temperatures depending on the composition and structure of the electrolyte [27–29].

The addition of low molecular weight compounds such as EC complicates the structure even more, and scarce work is found on the characterization of the phase distribution in PEO/Li salt/EC systems. In some plasticized PEO-based samples both a downward shift of T_m to 40 °C and a splitting into an EC-rich phase (T_m ~ 30 °C) and PEO-rich phase (T_m ~ 50 °C) have been reported [9,30,31]. Likewise, studies on the rheological behaviour of heavily plasticised PEO-based electrolytes are to the best of our knowledge inexistent in the scientific literature, and even the studies on the rheological behaviour of less complex related systems are scarce [17,32–35].

This work describes the preparation of a set of highly plasticised electrolytes with ionic conductivity similar to that reported for viscous liquids, in which attempts to induce a solid-like performance have been done by introducing three differently modified sepiolite nanofibres. It has been found that the nature of the sepiolite affects little the conductivity values, but changes dramatically the rheology of the electrolytes, and depending on the nanofiller they behave as viscous liquids or as solid thermoplastics. Because of the lack of background on the structure of highly plasticised PEO-based electrolytes, together with the rheology and conductivity of the electrolytes, the work has required a serious effort to characterise their structure.

2. Experimental section

2.1. Materials

PEO $M_w = 5 \times 10^6$ g mol^{-1} from Aldrich was used to prepare the nanocomposites. LiTf, from Aldrich, and neat sepiolite (Sep), kindly supplied by TOLSA S.A., were dried under vacuum for 24 h. EC, Polyethylene glycol (PEG, $M_w = 1000$ g mol^{-1}) and D-α-tocopherol polyethylene glycol 1000 succinate (TPGS), both from Aldrich, were used as received.

2.2. Surface modification reactions

Sepiolite was modified according to a variation of a reported procedure [36–38]. Basically, 3 g of sepiolite was mixed with a PEG or TPGS water solution by means of a lab dissolver (Dispermat LC2) operating at 10,000 rpm during 20 min. The resulting suspensions were dried in an oven at 100 °C overnight. The products, which appear in Table 1, were further washed in water, filtered and, finally, isolated by overnight drying at 100 °C. Further details on these modified sepiolites and their properties can be found elsewhere [39].

2.3. Preparation of the nanocomposites

The nanocomposites composition appears in Table 2. The components were physically premixed and then melt-compounded in a

Table 1
Modifier at the feed, final organic loading and specific surface of the sepiolites employed as fillers of the electrolytes.

Sepiolite	Modifier	Feed g/100 g sepiolite	S_{BET} m^2 g^{-1}	Organic loading g/100 g sepiolite
Sep	–	–	354.7	–
PEG-Sep	PEG	219.5	98	11.6
TPGS-Sep	TPGS	21.9	34	20.0

Table 2
Composition in wt.% and conductivity at 30 °C of the electrolytes under study.

Sample	LiTf	EC/PC	Sep	PEG-Sep	TPGS-Sep	$\sigma_{30°C}$ (10^{-4} S cm^{-1})
S17	13.7	40/0	–	–	–	9.0
S18	13.0	38/0	5	–	–	12.0
S19	13.0	38/0	–	5	–	9.9
S20	13.0	38/0	–	–	5	7.8
S23	12.3	36/0	–	–	10	5.7
S24	13.0	19/19	–	–	5	7.0

Haake MiniLab extruder. Processing was carried out at a shear rate of 80 rpm during 25 min and at 120 °C. These conditions were optimised to ensure optimum dispersion of the filler and the blending of the plasticiser with minimum PEO degradation.

2.4. Characterization

2.4.1. Elemental analysis
The carbon and hydrogen contents in the organically modified sepiolite fibres were obtained by a LECO CHNS-932 equipment.

2.4.2. Specific surface area
BET surface area measurements were made by single-point nitrogen adsorption, using a Micromeritics Flowsorb 2300.

2.4.3. Scanning electron microscopy (SEM)
SEM was performed in a Hitachi SU-8000.

2.4.4. Differential scanning calorimetry (DSC)
Differential scanning calorimetry (DSC) studies were performed in a Perkin-Elmer DSC7, on films of controlled thickness (~300 μm) processed by compression moulding at 75 °C during 5 min and quickly cooled down to room temperature. Other conditions used for the melting experiments will be detailed later, but in all cases the heat flow was recorded at 10 °C min^{-1}. For better comparison, the melting endotherms, T_m and crystallinity degree (χ_c) are referred to the polymer fraction in each blend.

2.4.5. Polarized light microscopy (PLM)
PLM images were taken using an Amplival Microscope with an objective 6.3× and a λ-wave compensator plate. The width of the pictures corresponds to real 1.5 mm. Samples were placed between glass supports, heated at 100 °C, spread to produce thin films and cooled down for several days.

2.4.6. Rheological measurements
Rheological measurements were performed using an Advance rheometer AR2000 with a 25 mm steel plate under nitrogen flow to avoid oxidative degradation. 1000 μm thick films were prepared by compression moulding at 75 °C during 5 min and quickly cooled down to room temperature. Prior to the launching of the experiment, samples were annealed in the rheometer for 10 min at the extrusion temperature (120 or 140 °C) and then stabilised at the measurement temperature (usually 75 °C) for 5 min. Oscillatory frequency sweeps were performed in the frequency range of 500–0.01 rad s^{-1} using a stress amplitude from 10 to 100 Pa.

2.4.7. Electrochemical Impedance Spectroscopy (EIS)
The conductivity of the electrolytes was determined by electrochemical impedance, carried out in two equipments: i) in a NOVOCONTROL GmbH Concept 40 broadband dielectric spectrometer in the temperature range −80 °C to 80 °C and in the frequency range between 0.1 and 10^7 Hz, using gold electrodes and ii) in a lab-made device comprising an impedance analyzer Autolab AUT30FRA2 ECOCHEMIE, in the temperature range 20 °C to 90 °C, between 0.1 and