Multifunctional composites as Solid-Polymer-Electrolytes (SPE) for Lithium Ion Battery (LIB)

Salvatore Mallardo[1,a] *, Gennaro di Mauro[2,b], Michele Guida[2,c], Pietro Russo[1,d], Gabriella Santagata[1,e], Rosa Turco[3,f]

[1]Institute for Polymers, Composites and Biomaterials, National Research Council, Pozzuoli, Italy

[2]Department of Industrial Engineering, University of Naples Federico II, Naples, Italy

[3]Department of Chemical Sciences, University of Naples Federico II, Naples, Italy

[a]salvatore.mallardo@ipcb.cnr.it, [b]gennaro.dimauro@unina.it, [c]michele.guida@unina.it, [d]pietro.russo@ipcb.cnr.it, [e]gabriella.santagata@ipcb.cnr.it, [f]rosa.turco@unina.it

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Abstract. Novel solid-polymer-electrolytes (SPE) have been formulated as key components of structural multifunctional materials to develop Lithium Ion Battery (LIB). To this aim, SPE blends based on polyethylene oxide (PEO), different molecular weights polyethylene glycole (PEG), PEG-modified sepiolite (SEP) and lithium triflate have been prepared by one pot melt mixing. The films were obtained by compression moulding following a method easily scalable to industrial level. The different films have been characterized by structural (FTIR-ATR), thermal (DSC, TGA), morphological (SEM) and mechanical (tensile tests) analysis. The different properties could be mainly addressed to the diverse PEG both amounts and molecular weight and to the specific physical interaction occurring between PEO, PEG sepiolite and lithium ions strongly influencing crystallinity, thermal stability and mechanical response. Thus, SPE2 sample evidenced the highest both crystallinity and mechanical stiffness and toughness, whereas SPE1 and SPE3 film showed the best compromise between molecular crystallinity and mechanical performances, mostly as strain at break are concerned. Finally, SPE4 film, including the highest amount of PEG showed a peculiar increasing of mechanical rigidity in opposition to molecular plasticization effect exploited by PEG. The many features of SPE systems requires special attention and further research when it comes time to design structural multifunctional materials for LIB based batteries of Type-III.

Introduction

The emerging technologies of structural batteries (SBs), i.e., multi-component-based systems able to combine the functions of energy storage and the load-bearing ability in the attempt to improve such performances, are gaining even more attention to solve the environmental sustainability at decarbonizing the transportation sector [1]. SBs are based on solid polymer electrolytes (SPEs), i.e., solid polymeric materials with ability to transport lithium ions. Usually, SPEs consist of polymer matrices and lithium ions obtained after dissolution of polymer with lithium salts and following drying process. The result is the formation of a thin, inflammable, and flexible film of a coordination complex between the polymer and the lithium ions [2]. When a potential difference is applied across the solid electrolyte, the lithium ions move from the anode to the cathode through the polymer matrix, they react with the cathode material to produce a flow of electrons. Among the polymers, polyethylene oxide (PEO) is the most attractive since it shows excellent solubility for lithium salts, is a low cost, non-toxic, biocompatible, water soluble, high conductive material [4] with high energy density, high electrochemical stability, and excellent compatibility with inorganic salts. It is widely accepted that lithium-ion transport occurs at the expense of the flexible amorphous phase [5, 6]. In this paper, PEO as organic electrolyte, lithium triflate (lithium

trifluoromethanesulfonate) $LiCF_3SO_3$ as electrolyte, sepiolite $(Si_{12}O_{30}Mg_8(OH)_4(H_2O)_4 \times_8 H_2O)$ (SEP) as a natural, low cost and abundant fibrous clay mineral enhancing the dissociation of lithium salts, have been used to develop SPEs [7, 8, 9]. To enhance SEP dispersion in PEO thus avoiding fiber aggregation, organic modification of SEP surface has been performed by blending it with water solutions of polyethylene glycol (PEG), a plasticizer able to reduce PEO crystallinity promoting the ion conductivity [10]. All components were melted, composed, and compressed into films in a "one pot solution" avoiding solvents, thus following an environmentally sustainable approach. The SPEs were characterized by thermal, mechanical, and morphological analysis to evaluate their chemical-physical performance.

Experimental: Materials and methods

PEG1000 and PEG1550 by Fluka, polyethylene oxide (PEO) Mw 5.000.000, Sepiolite and Lithium triflate by Sigma Aldrich. Mixtures of PEG and sepiolite (SEP) were prepared by SEP water dispersion and subsequently adding 5% and 10 % w/w of PEG1000 and PEG1550, as detailed in Table 1. The suspension was washed, centrifuged, and dried thus obtaining organo-modified sepiolite (SEPmod). The raw physical blends of SEPmod, Polyethylenoxide (PEO) and Lithium triflate (LiTfr), obtained by their physical mixing, were melt blended, using a Brabender Plasti-Corder mixer kept at 140°C and 80 rpm of screw rate. The resulting SPEs were recovered, cooled at room temperature, roughly powdered, dried and compression molded at 130°C by using a table hydraulic hot-press. FTIR-ATR, DSC, TGA, SEM and tensile tests have been performed on samples. DSC analysis were carried out using a Mettler DSC/822 calorimeter at a nitrogen gas flow of 50 ml/min. Samples were firstly heated from 25 to 150 °C at 10 °C min^{-1}, then cooled up to −80 °C at a rate of 50 °C min^{-1} and newly heated up 250 °C at 10 °C min^{-1}.

TGA analysis were performed using a thermogravimetric analyzer TGA/DTG Perkin-Elmer Pyris Diamond. The samples were heated from 25°C to 600°C at 10°C min^{-1}, under nitrogen at 30 mL/min. SEM analysis were carried out using a Quanta 200 FEG, 338 FEI scanning electron device. Prior to the observation, surfaces were coated with a homogeneous layer (18 ± 0.2 nm) of Au and Pd alloy. The micrographs were performed at room temperature and in high vacuum mode. Tensile tests were carried out by using a dynamometer model 4301, Instron equipped with a load cell of 1 kN. The tests were performed on dumbbell-shaped films. Young's modulus, stress and strain at break values were determined and reported data are the average values of six determinations. All the tests were carried out at room temperature and at a crosshead rate of 2mm/min.

Table 1 Film percentage composition and identification codes.

IC	Percentage composition (wt%)				
Sample	PEO	LiCF_3 SO_3	SEP	PEG1000	PEG1550
SPE_Li	91.5	8.5	-	-	-
SPE_0	87.5	8.13	4.36	-	-
SPE_1	87.5	8.13	4.15	-	0.21
SPE_2	87.5	8.13	4.15	0.21	-
SPE_3	87.5	8.13	3.96	-	0.40
SPE_4	87.5	8.13	3.96	0.40	-

Results and Discussion

The thermal parameters of the SPEs samples are showed in Table 2.

Table 2 *Thermal parameters of SPE based films and neat polymers measured by DSC and TGA analysis. The values of crystallization and melting enthalpy in parentheses (ΔH) and the crystallinity (χ) are normalized with respect to the weight fraction of the polymer in the blend.*

	DSC					TGA		Crystallinity
	$\Delta H_c[J/g]$ $\pm 2\%$	$T_{c,onset}[°C]$ $\pm 2\%$	$T_c[°C]$ $\pm 2\%$	$\Delta H_m[J/g]$ $\pm 1\%$	$T_m[°C]$ $\pm 1\%$	$T_{onset}[°C]$ $\pm 2\%$	$T_{peak}[°C]$ $\pm 2\%$	$\chi_c(\%)$
PEO	146.9	-31.7	-40.6	121.8	66.4	366.7	400.2	59.4
SPE_0	118.2	-51.7	-64.0	117.4	62.4	391.9	419.7	65.4
SPE_1	117.4	-21.7	-36.4	118.4	61.3	388.7	419.0	66.0
SPE_2	140.7	-18.3	-30.5	133.5	60.5	383.8	421.3	74.4
SPE_3	119.2	-22.5	-33.8	136.1	61.2	386.	419.8	75.9
SPE_4	134.3	-20.8	-34.4	123.8	60.9	376.1	409.0	69.0

It is worthy to highlight that all the samples began to crystallize at very low temperatures. This result is due to the fast-cooling rate (50°C/min), which decreases the crystallization process as the polymer chains, entangled in the melt, do not have enough time to separate enough to form crystals, so the amorphous nature of the melt is "frozen into" the solid. In the investigated system, all the samples reported in table 1, started to crystallize before than neat PEO and before SPE0 composite and show higher crystallinity percentage (χc). SPE2 systems crystallize before the other systems due to the balanced effects of nucleating effect and plasticizing action of PEG1000. No substantial differences have been detected among SPE1, SPE3, SPE4 samples, except for a slight decrease in Tc compared to SPE2, overall ΔHc and an increase crystallinity. Neat PEO starts to crystallize at lower temperatures, as expected. The absence of PEG in SPE0 sample drastically decreased onset and peak crystallization temperatures. During the second heating run, except for PEO showing the highest melting temperature, all the samples evidenced similar Tm likely associated with the melting of quite regular crystalline pattern developed during the cooling from the melt.

TGA results are reported in table 1 as the onset of temperature degradation, (Tonset), taken as the temperature at which 5% weight loss (WL) of sample occurred, and the peak of DTG thermograms, corresponding to the temperature of maximum degradation rate of the polymer (Tpeak). From the analysis of these data, it emerged that all samples degrade around 419 °C, while at higher temperatures, around 470 °C, lithium triflate begins to degrade.

In addition, all SPE based systems showed higher thermal stability than the neat polymer. The neat PEO thermal degradation process is ranged in a shorter space of time than other SPE based samples, as expected, since no reinforcing and stabilizing agents were included inside the polymer matrix. This experimental outcome suggests the formation of tight intermolecular entanglements between the components likely due to their physical compatibility leading to mutual stabilization except for SPE4 sample, strongly influenced by the prevailing effect of high concentrations of PEG1000, significantly affecting PEO thermal stability.

In Figure 1, morphological analysis (SEM) of SPE based films are reported. As for brevity of discussion, only SPE0, SPE1 and SPE2 micrographs have been investigated and discussed. SPE0 sample (Figure 1a), evidenced a quite uneven and highly structured polymer surface with a fine and homogenous distribution of discrete microdomains of rod-like sepiolite filler, visible as white dots on the polymer surface. Moreover, the morphology changed in presence of PEG plasticizers. In SPE1 sample (Figure 1b), a homogeneous, quite smoothed and continuous polymer surface can be observed with the very fine distribution of sepiolite particles between the polymer macromolecular chains. Low concentrations of the higher Mw PEG allow suitable polymer plasticization, improving the physical interactions among the polar residues and the ionic charges of all the components of the biocomposite.

As concerning SPE2 sample, a very different surface topography is found (Figure 1c). A continuous but coarsened polymer surface can be observed characterized by a good interfacial

adhesion between the polymer matrix and the plasticizer, as expected since PEO and PEG show the same polymer network but very different molecular weights. Profuse well dispersed and well embedded sepiolite particles occur confirming that the very close-fitting polymer-based network can deeply entrap these particles to the point of being disguised and no longer visible.
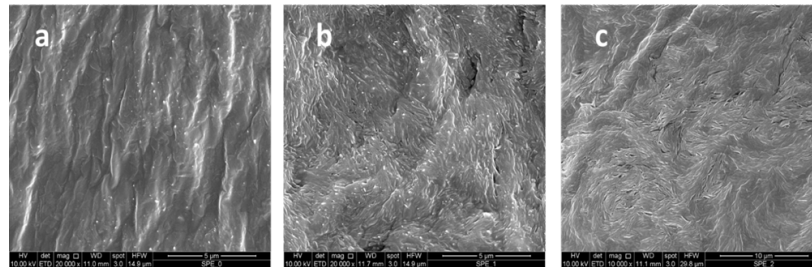

Figure 1 SEM micrographs of SPE0 (a), SPE1 (b) and SPE2 (c) surfaces.

The averaged values of elastic modulus (YM), stress at break (σ_b), strain at break (ε_b) are detailed in Table 3.

Table 3. Tensile test parameters for each adopted formulation

Sample	Thickness (mm)	Young Modulus (YM) [MPa]	Strain at Break (εb) [%]	Stress at Break (σb) [MPa]
SPE_Li	0.092	99.0±13.27	3.5±0.4	1.1±0.2
SPE_0	0.130	331.7 ± 30.0	4.5 ± 07	1.2 ± 0.1
SPE_1	0.145	305.6 ± 13.1	5.9 ± 2.6	1.1 ± 0.4
SPE_2	0.130	343.8 ± 10.8	4.8 ± 0.8	1.2 ± 0.2
SPE_3	0.148	397.9 ± 46.9	6.4 ± 1.5	0.8 ± 0.5
SPE_4	0.103	426.4 ± 65.3	3.8 ± 0.4	1.9 ± 0.1

The addition of lithium salt into the PEO matrix caused a general reduction of mechanical properties with respect to the other PEO based compositions including SEP. Indeed, from the analysis of the results, the system SPE0 evidenced the lowest YM. This finding is not surprising since the lack of inorganic filler is responsible for macromolecular chain mobility restriction and increasing stiffness and rigidity. In addition, also strain at the break of this system evidenced detrimental values. This last outcome could be due to the peculiar PEO Lithium salt interaction occurring between the polar ether groups of PEO and the positive charge of lithium hindering the regular flow of PEO macromolecular chains under tensile test. As concerning the other SPE based composites, the results indicate that usually, except for the SPE1 formulation, the addition of the plasticizer causes an increase in the tensile stiffness of the tested film. This effect is in line with the higher degree of crystallinity of the formulations found in DSC analysis. The crystallization behaviour of polymers the crystallinity, strongly influenced the macroscopic behaviour of polymers, such as the mechanical performances [11]. Both plasticizers induce an increase in this parameter with more marked effects in the case of PEG1000 compared to the PEG1550. This outcome is likely due to different behaviour induced by two PEG molecular weights. The most significant increase in stress for PEG 1000 samples is in line with the greater nucleating effect witnessed by Young's modulus values. Finally, about the strain undergone by the specimens, it seems that all the formulations are characterized by a value usually higher than that of the reference sample (SPE0) without plasticizers. In any case, for the system containing PEG1550, the strain at the peak of the curve seems to increase for a plasticizer content equal to 0.21% by weight and then decrease slightly for higher contents. The results indicate an exactly reversed trend for systems with PEG1000 as the content of this additive increases.

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