

NEW APPROACHES FOR SOLID POLYMER ELECTROLYTES

M. Willgert^{1*}, M. H. Kjell², M. Johansson¹

¹Coating division, Department of Fiber & Polymer Technology, KTH Royal Institute of Technology SE-100 44 Stockholm, Sweden

²Applied electrochemistry, Department of Chemical Engineering & Technology, KTH Royal Institute of Technology SE-100 44 Stockholm, Sweden

*markuswi@kth.se

Keywords: Structural batteries, solid polymer electrolyte (SPE), Ionic conductivity, Mechanical properties

Abstract

In the present study, series of solid polymer electrolytes (SPEs) have been manufactured in a solvent free process through UV curing. All electrolytes are based on poly(ethylene oxide) systems, however the study also investigates the ability to involve thio ethers in the structure as well as inorganic reinforcing particles covalently bonded to the matrix. The SPEs are tested with EIS and DMA to establish the ionic conductivity and mechanical properties. Thio-ethers improve the conductivity but makes the material softer, while particle reinforcement increases the T_g although the ionic conductivity is constant.

1 Introduction

1.1 Background.

The rapid progress in development of portable devices such as laptop computers and mobile phones calls for new smart solutions to store electrical energy. One way to lower the weight parasitic nature of a battery is to let it (besides of storing electrical energy) be incorporated in the construction of the device to replace a load bearing part in the structure and reduce the total weight of the item [2,3]. To construct such a battery, the electrolyte needs to both carry mechanical load as well as transport ions (two competing properties in a thermoset electrolyte since higher crosslink density gives lower ionic conductivity due to restricted segmental motion of lithium ion coordinating groups in the polymer [4]) where a balance needs to be established. Since sufficient mechanical properties are wanted, solid polymer electrolytes (SPEs) are in focus, which can be polymeric networks with abilities to transport ions [5]. A consequence of the need for mechanical strength in the material is that polymer electrolytes containing solvents are excluded, which reduces the ionic conductivity vastly. Earlier work has utilized polymer thermoset networks, where ethylene oxide (EO) oligomer segments with methacrylate functionality have been crosslinked into poly(ethylene oxide) (PEO) networks [6]. The EO segments are able to coordinate to a lithium ion with suitable coordination strength [6-8]. Although the ionic conductivities obtained in these materials are rather modest, lower conductivities can be accepted due to the synergetic effects of having a load bearing item in the construction that also performs other tasks. Earlier work has focused on PEO based networks to make SPEs. However, the challenges arising from the difficulties to construct solvent free thermoset electrolytes suggest that new components should be considered in the formulation. The study presented involves two main categories,

- (i) thiol-ene/PEO SPEs with thio ether segments and EO segments (T-PEO).
- (ii) PEO/inorganic particle SPEs with inorganic particles covalently bonded to the PEO matrix (PEO/IPA).

1.2 T-PEO SPEs.

In addition to the conventional free radical polymerization reactions of methacrylates and acrylates to create crosslinked polymer networks, UV induced thiol-ene click reactions have gained increased interest [9,10]. In the design of novel SPEs, incorporation of a thiol compound might have interesting impact on both mechanical properties as well as the ion conducting ability of the SPE. While a free radical polymerization reaction is a chain-growth type reaction with a gel point at low monomer conversions, the thiol-ene click reaction, on the other hand, is a step-growth type reaction (that proceeds through a free radical chain mechanism) with a gelpoint at high monomer conversions. This suggests that by combining the two, the overall gel point is increased, resulting in a more homogeneous network, which may be beneficial when small geometries are to be made. It will also give rise to a more narrow temperature span in which the T_g transition of the network occurs, which increases the ability to tune the performance properties of the electrolyte.

1.3 PEO/IPA SPEs.

In addition to neat polymer thermoset mentioned above, surface modified inorganic particles may be introduced to the network to improve the mechanical strength. The idea is to utilize a polymer matrix with a low T_g , for a higher ionic conductivity. In order to improve the low mechanical strength given by this polymer matrix, inorganic particles, with a large number of functional thiol groups are added and, through thiol-ene chemistry, covalently bonded to the matrix. This would overall increase T_g and modulus of the material, but allow segmental motion of the EO segments, which is crucial for ion transport. Additionally, crystallization of the linear PEO is suppressed, which is of significant importance since crystallization of electrolyte polymer is detrimental to the conductivity of ions.

2 Experimental

2.1 Materials.

The monomers/oligomers used are depicted in **Figure 1**. Tetraethylene glycol dimethacrylate (SR209) (**a**), and methoxy polyethylene glycol (350) monomethacrylate (SR550) (**b**), were kindly supplied by Sartomer Company Europe. Trimethylol-propane-tri(3-mercaptopropionate) (**c**) was kindly supplied by Bruno Bock Chemische Fabrik GmbH & Co (Germany). 2,2-dimethoxy-2-phenylaceto-phenone Irgacure 651 (DMPA) was thankfully received from Ciba Specialty Chemicals (Switzerland). Lithium trifluoromethanesulfonate (lithium triflate) (97%) was purchased from Chemtronica AB (Sweden). SiO₂ particles (40-60 μm) were purchased from Acros. 3-mercaptopropyl(trimethoxy)silane (**MPS**) was purchased from Sigma Aldrich. All reagents were used without further purification.

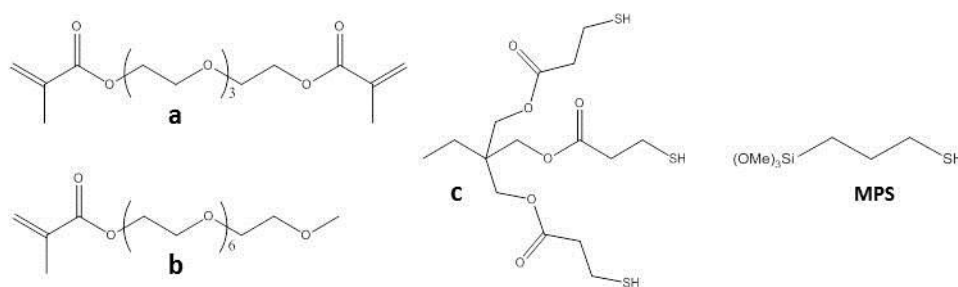


Figure 1. Chemical structure of monomers used in this study.

2.2 Instrumentation.

UV source used for curing was a Blak Ray B-100AP (100 W, 365 nm) UV lamp. Dynamical mechanical analysis (DMA), film tension tests, were performed on a TA instruments DMA, model Q800. To measure the electrochemical performance, the SPEs were placed in a four-electrode test cell with four gold wires (two working electrodes 20 mm apart and two reference electrodes 5 mm apart). The impedance was measured potentiostatically across a frequency range of 1 Hz to 300 kHz, at 10 points per decade, using a Gamry Series G 750 Potentiostat/ Galvanostat/ZRA interface. All impedance measurements were carried out in a glove box under dry argon atmosphere (<0.05 ppm H₂O) at ambient temperature.

2.3 Modification of silica particles.

10 grams of SiO₂ particles was put in a round bottom flask. Distilled water and 37% hydrochloric acid (1:1) was added. The mixture was refluxed for 24 hours. The particles were filtered off and rinsed thoroughly with distilled water. The particles were dried in a vacuum oven overnight at 50 °C. Activated silica particles were added to a solution of **MPS** (10 mmol) in dry toluene and the mixture was refluxed for 24 hours. The modified **Si-SH** particles were filtered off and washed thoroughly with hot, dry toluene. The particles were dried in a vacuum oven for 5 hours at 50 °C.

2.4 Photoinduced polymerizations.

Following general route was utilized for producing the SPEs. The samples were prepared in a glove box under dry conditions, (<0,5 ppm H₂O), under argon atmosphere. Monomers **a** and **b** were mixed in a vial and the lithium triflate salt (8 wt% to the monomers **a** and **b**) was added. The vial was then sealed with parafilm, taken out of the glove box and left on a shaking table overnight so that all lithium salt was dissolved. The vial was once again entered into the glove box, and the photoinitiator was added to the sample and dissolved. (2 wt%, relative monomers **a** and **b**). For the samples were thiol resin was to be used, monomer **c** was added and the mixture was stirred. Finally, for the samples with silica particles, these particles (**Si-SH**) were added in various amounts to each sample and mixed. The mixtures were poured in a teflon mold and cured under UV irradiation for 4 minutes, and then ejected from the mold for further characterization. The ratios of monomers and particles added are displayed in **Table 1, 2**.

3 Results and discussion

3.1 T-PEO SPEs

Sample no.	a	b	c	T _g ^a	σ
	[wt% of a+b]				[S × cm ⁻¹]
T1:1	30	70	-	23	5×10 ⁻⁷
T1:2	40	60	-	38	2×10 ⁻⁷
T1:3	50	50	-	59	3×10 ⁻⁸
T1:4	60	40	-	75	5×10 ⁻⁹
T1:5	70	30	-	92	6×10 ⁻¹⁰
T1:6	80	20	-	110	-∞
T2:1	30	70	10	3	1×10 ⁻⁶
T2:2	40	60	10	12	4×10 ⁻⁷
T2:3	50	50	10	14	2×10 ⁻⁷
T2:4	60	40	10	27	4×10 ⁻⁸
T2:5	70	30	10	42	7×10 ⁻⁹
T2:6	80	20	10	56	6×10 ⁻¹⁰

Table 1. The electrolyte composition and some results of the T-PEO series. ^aT°C at tanδ_{max}.

Addition of thio ethers to the methacrylate system widely affects the mechanical properties. The influence that addition of **c** has on the T_g of the material (**Figure 2, Table 1**) is explained by the incorporation of this softening segment. In **Figure 2**, a clear shift in T_g between series T1 and T2 can be observed, and this shift is more pronounced as **a** (thus the crosslink density) is increased. The series with no thiol compound added (T1:1-T1:6) has almost a direct correlation in increase of the T_g to the amount of crosslinker **a** added.

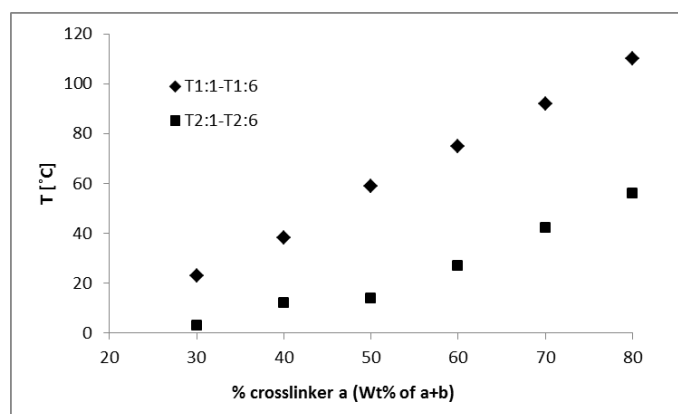


Figure 2. T_g for series T1 and T2 vs. the amount of crosslinker **a** added. The T_g discrepancy between the two series is larger at higher crosslink densities.

However, the overall trend in series (T2:1-T2:6) is more complex especially at low crosslink densities. The T_g of this series does not exceed room temperature until 60 % crosslinker **a** is added. This is interesting information since the material in the present application probably will need to be exceeding its T_g at the given work temperature. It can also clearly be seen that a more crosslinked thermoset is more affected by introduction of the thiol compared to the material with a lower degree of crosslink. This is expected since the latter material already consists of free volume at a large extent. Furthermore, the incorporation of the thiol compound gives a material with a more narrow temperature window in which the glass transition occurs, **Figure 3**.

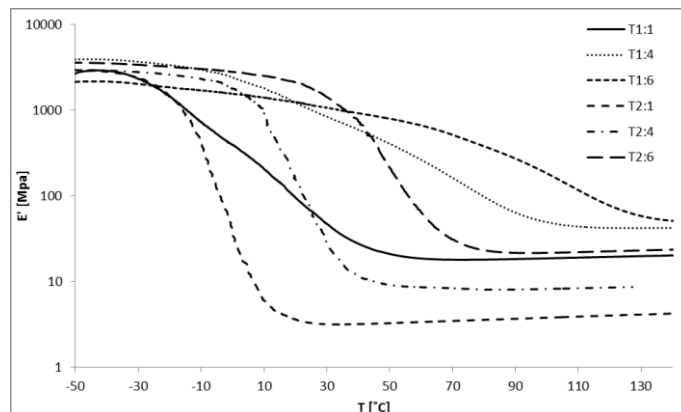


Figure 3. The storage modulus, E' vs. temperature of some samples from both series T1 and T2 is depicted. Samples from series 2, with c added, has a more distinct glass transition.

This is expected since the network is now more homogenous, a consequence of incorporating a compound that will undergo a step-wise polymerization to the network. This action delays the gelpoint so that it will occur at a much higher monomer conversion, making it possible for the microgels to adopt a more suitable conformation with respect to conformation energy thus resulting in a more homogenous network. This can be both advantageous and disadvantageous in the current application. However, having the ability to tune more in detail where the glass transition will occur can be of significant value since the SPE pronounces rapidly decreased ion conductivity when the current temperature is below the T_g , of the SPE. (Table 1, Figure 4). Additionally, when used in small geometries, a homogenous network is more favorable.

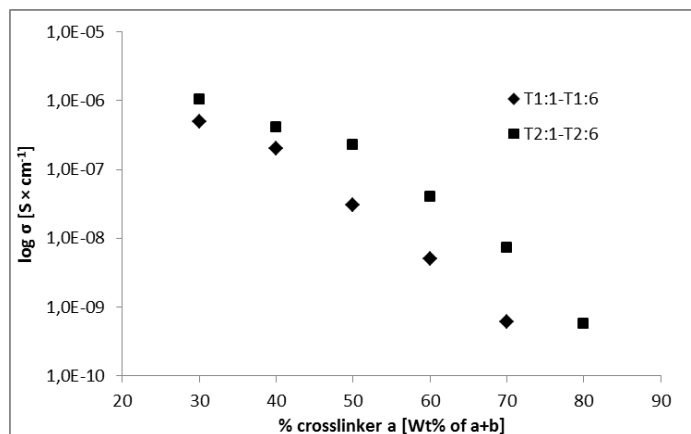


Figure 4. Ionic conductivity, σ , for series 1 and 2 vs. the amount of crosslinker a added. The difference of σ between the two series is larger at higher crosslink densities. Sample 1:6 shows no ionic conductivity at all.

3.2 PEO/IPA SPEs

Sample no.	a	b	c	Si-SH ^a	T _g ^b	σ [S × cm ⁻¹]
	[wt % of a+b]					
IPA:1	30	70	-	0	15	5.0×10 ⁻⁷
IPA:2	30	70	-	2	17	5.3×10 ⁻⁷
IPA:3	30	70	-	4	19	4.8×10 ⁻⁷
IPA:4	30	70	-	8		5.0×10 ⁻⁷
IPA:5	30	70	-	16	21	4.8×10 ⁻⁷

Table 2. The electrolyte composition and some results of the PEO/IPA series. ^awt% of a+b. ^bT°C at tanδ_{max}.

In the study presented, SiO₂ particles have been surface modified to obtain thiol functionality. The particles have furthermore been reacted with PEO-methacrylates and works as reinforce species of the material. DMA and EIS are techniques employed to quantify the mechanical and -ionic conductive properties respectively. Initial results show that the modulus at room temperature is increased with a factor of 100 when 20 wt% SiO₂ particles are added, **Figure 5**. Furthermore, a higher T_g is observed for composites with more reinforcing SiO₂ particles incorporated, **Figure 6**. When studying the ability to conduct lithium ions, **Figure 7**, the trend of the conductivity is more or less kept constant i.e. the presence of silica particles do not reduce the ionic conductivity.

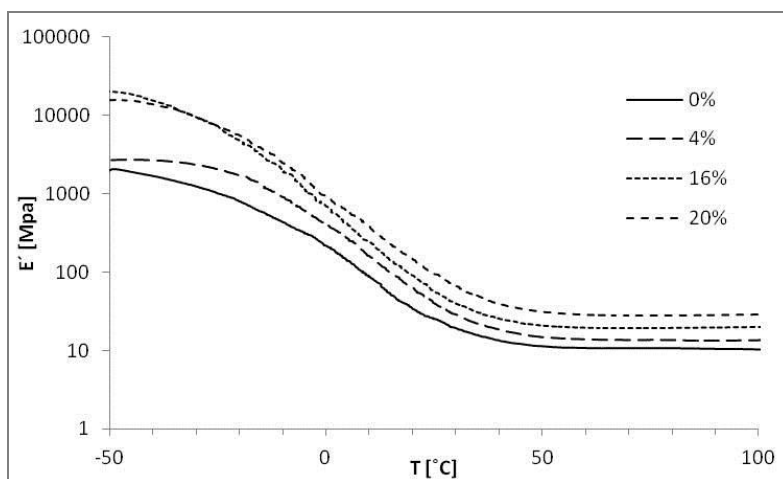


Figure 5. Storage modulus, E'. 0% to 20% SiO₂ particles added.

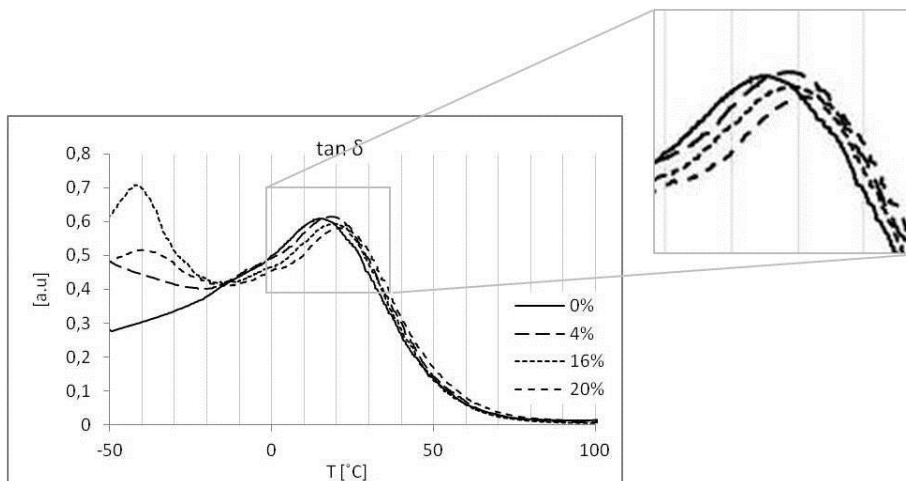


Figure 6. tan δ (E''/E'). 0% to 20% SiO₂ particles added.

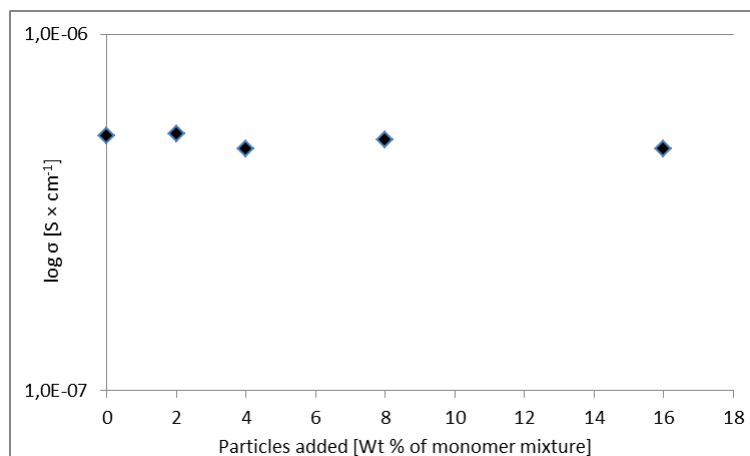


Figure 7. Conductivity vs. amount of SiO₂ particles added.

4 Conclusions

Two studies have been undertaken to investigate whether conventional PEO SPEs can be improved with respect to ionic conductivity, as well as mechanical properties in order to find new formulations for SPEs to work in structural batteries. Study 1 is employing thiol-ene chemistry to create PEO networks with thio ether segments. In study 2, inorganic particles are covalently bonded to a sparsely crosslinked PEO matrix to work as a reinforcing component, but also to suppress crystallization of the polymer. In both studies, SPEs have successfully been manufactured in a solvent free process where the monomers work as active diluent. It has been shown that both actions affect the structural battery SPE properties.

The presence of thio ethers in the structure results in a more flexible material, but also in increased ionic conductivity. At the present, it is not clear whether this is because a more flexible material is created, or if also the introduction of sulfur to the network is affecting, due to its different coordination strength to the lithium ion. However, the study shows that thio ethers are compatible to the system. Furthermore, study 2 indicates that the **Si-SH** particles are compatible with the system. The mechanical properties are enhanced while the conducting ability of the SPE remains quite unaffected. Further work will investigate the system to find advantageous formulations.

To conclude, both routes show potential and represent interesting additions to the toolbox in the future design of SPE for structural battery applications. However, the results are initial and will need to be investigated further.

References

- [1] Ekstedt, S., et al. Structural batteries made from fiber reinforced composites. *Plast., Rubber Compos.*, **39**, pp. 148-150 (2010)
- [2] Snyder, J.F., et al. Improving multifunctional behavior in structural electrolytes through copolymerization of structure- and conductivity-promoting monomers. *Polymer*, **50**(20), pp. 4906-4916 (2009).
- [3] Wetzel, E.D. Reducing weight: Multifunctional composites integrates power, communications, and structure. *AMPTIAC quarterly*. **8**, pp. 91-95 (2004).

- [4] Maccallum J. R., et al. The effects of radiation-induced crosslinking on the conductance of LiClO₄-PEO electrolytes. *Solid State Ionics*, **11**, pp. 307-312 (1984)
- [5] Nair, J.R., et al. Methacrylic-based solid polymer electrolyte membranes for lithium-based batteries by a rapid UV-curing process. *React. Funct. Polym.*, **71**, pp. 409-416 (2011).
- [6] Fenton, D.E., et al. Complexes of alkali metal ions with poly(ethylene oxide). *Polymer*, **14**, pp. 589 (1973)
- [7] Berthier, C., et al. Microscopic investigation of ionic conductivity in alkali metal salts-poly(ethylene oxide) adducts. *Solid State Ionics*, **11**(1), pp. 91-95 (1983)
- [8] Wright, P.V. Electric conductivity in ionic complexes of poly(ethylene oxide). *Br. Polym. J.*, **7**, pp 319-327 (1975).
- [9] Hoyle, C. E., et al. Thiol-enes: Chemistry of the past with promise for the future. *J. Polym. Sci., Part A: Polym. Chem.*, **42**, pp. 5301-5338 (2004).
- [10] Chen, Z., et al. Soy based UV-curable thiol-ene coatings. *J. Coat. Technol. Res.*, **7** pp. 603-613 (2010).