Comparison of mechanical properties of multi-walled carbon nanotube and graphene nanosheet/polyethylene oxide composites plasticized with lithium triflate

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Abstract. A strong engineering interest in nanostructured conducting polymers and its composite materials have been widely used to build various sensor devices, electronic interconnect devices, fuel cells and batteries. Preparation of polymeric nano-composites with finely controlled structure, especially, at nano-scale, is still one of the most perspective modification ways of the properties of polymeric composites. Multi-walled carbon nanotube (MWCNT)/polyethylene oxide (PEO) and graphene nanosheets (GR)/PEO composites and composite of MWCNT/GR/PEO were prepared by solution casting and hot-pressing method. Composites were plasticized by 5% of Lithium triflate (LiTrifl), which play role of additional ion source in conducting polymer composite. Mechanical tensile tests were performed to evaluate nanoparticles influence on the mechanical strength of the conductive polymer composite materials. Difference of tensile tests of prepared composition can be seen from tensile tests data curves. The results of tensile tests indicated that the nanoparticles can provide PEO/5%LiTrifl composite with stiffening effects at rather low filler content (at least 0.05% by volume).

1. Introduction

The most frequently studied polymer in energy storage and generation devices field is poly(ethylene oxide) (PEO) due to its low glass transition temperature (for PEO with molecular weight more than 20000 Tg ≈ -66°C) and high solvating characteristics for a wide variety of salts [1–4]. The presence of the lone pair electrons at the ether oxygen of PEO enables it to complex with high concentration of wide variety of salt [5–8]. It is known, that Lithium salts are added to polymers composite to increase its conductivity, because of ease transport of Li^+ along intercrystalline amorphous phase [4,9]. Measurements via surface-enhanced Raman scattering confirms that Li^+ ion interacts with the PEO in the complex electrolyte [10].

In our previous scientific paper [8] we concluded that addition of 5% of Lithium triflate (LiTrifl) and small (less than 3% by volume) content of multi-walled carbon nanotubes (MWCNT) and graphene nano-platelets (GR) nanoparticles increase electrical conductivity of prepared PEO nano-composites. MWCNT and GR are added to electrically conductive polymer primarily for the reason of electrical conductivity and stiffness improvement [11–13]. Nevertheless mechanical strength should be determined to evaluate effect of small content of MWCNT and GR nanoparticles on PEO/5%LiTrifl composite material.

GR is a single layer of carbon atoms arranged in a two dimension hexagonal lattice [14,15]. Structurally, CNT is one-dimensional cylinder composed of rolled-up one (if single-walled CNT) or more (if multi-walled CNT) graphene sheets, with aspect ratio between length and width of >1000. Additional GR sheets rolled up around the single-walled CNT with van der Waals attraction between neighboring layers. Because of CNT and GR dimensional structure, electron transport occurs in ballistic transport mode (occurs through a small number of channels with a quantum of conductance, $G_0=2e^2/h$ ($\sim7.748\cdot10^{-5}$ S), for each spin), offer high electrical conductivity properties [16–18]. Composite with MWCNT exhibited charge transfer resistance reduce, with a factor 10 [19]. Mechanically, GR has been shown to be the strongest material ever measured, with a Young's modulus of 1 TPa and yet it can be stretched elastically by up to 20% [20]. Both GR and MWCNT have excellent electric conductivity, thermal conductivity, and mechanical strength, which make them excellent candidates as reinforcing, stiffening and conducting fillers of composites [21].

Although more than half amount of scientific papers describe effect of average statistical (higher than 3%, but lower than 20% by volume) and high (higher than 20%) concentration of MWCNT and GR on semi-crystalline electrical conductive polymers [8,14,15,22,23]. It should be noted, that increase of nanoparticle concentration increase other necessary properties of the matrix polymer such as viscosity, density, appearance, ageing performance and the price of the finished product. Therefore, a composite with improved desirable properties and low nanoparticle content is higher valued. An advantage of nanoparticle is its high surface area with the purpose to create a great interphase in a composite.

Nanoparticle distribution in polymer composite depends not only on components theoretical compatibility, but also on composite practical preparation method. It is known, that dispersion of untreated nanoparticles in a polymer is very difficult procedure. From the practical view point composite with nanoparticle agglomerates have tendency to split more easily than without them. It was confirmed that deformation behavior of the polymer matrix remarkably changes with the addition of the treated nanofiller, but crystallization properties do not [24,25].

Still application of tip ultra sound sonication/or shear mixing in nanocomposite dispersion preparation, plasticizer application and additional thermo-pressing can decrease intermolecular forces between filler and matrix, thus reduce nanoparticle agglomeration process [26–28].

Therefore, a commercial PEO was mixed with LiTriflate, MWCNT and GR in the present work. Tensile performance is evaluated as function of filler content to reveal the relationships of the composites, and the mechanical role of the nanoparticles as well.

2. Methodology
PEO (molecular weight 100 000 g/mol) was chosen as matrix of composite polymer electrolyte. Lithium trifluoromethanesulfonate (LiTrifl) were chosen for composite polymer electrolyte as ion source and plasticizer. Properties of substance given above were supplied by manufacturer and are listed in Table 1.

Table 1. Material used in sample preparation.

PEO	*Scientific Polymer Products*	relative density 1.21 g/cm^3; melting temperature 65°C
LiTrifl	*Fluorochem*	molecular weight 156.01 g/mol
MWCNT	*Nanocyl^{TM} NC 7000*	conductivity 10^6-10^7 S/m; average $\varnothing$ 9.5 nm, average length 1.5 μm
GR	*XGnP Sciences*	conductivity 10^2-10^7 S/m; average thickness 7.5 nm

PEO nanocomposites, were prepared by dissolving PEO in dimethylformamide. Nanoparticle distribution was achieved by application of tip ultra sound sonication. Composite solution was casted as film and solvent was allowed to evaporate for 48 h at 45°C with subsequent annealing in vacuum at 45°C for 24 h. Films 270 ± 5 μm thickness were prepared by compression molding method.

The compositions of prepared composite electrolytes are illustrated in Table 2.

Table 2. Filler content in studied PEO composite samples.

SAMPLE Name	LiTrifl (weight %)	MWCNT* (weight %)	GR* (weight %)
PEO	0	0	0
PEO/5Li	5	0	0
PEO/5Li/0.05CNT	5	0.05	0
PEO/5Li/0.25CNT	5	0.25	0
PEO/5Li/0.05CNT	5	0.5	0
PEO/5Li/0.05GR	5	0	0.05
PEO/5Li/0.25GR	5	0	0.25
PEO/5Li/0.5GR	5	0	0.5
PEO/5Li/0.05CNT/0.05GR	5	0.05	0.05
PEO/5Li/0.25CNT/0.25GR	5	0.25	0.25
PEO/5Li/0.5CNT/0.5GR	5	0.5	0.5

* MWCNT and GR weight % further will be written in following form "n", where n = 0; 0.05; 0.25; 0.5.

Material testing machine "Tinius Olsen 25ST" was used for tensile test. Test data was obtained by "Tinius Olsen's Horizon Data Analysis software". Five samples are fabricated and tested for each specimen type and loading rate, respectively, and the results are averaged. Tension speed of 10 mm/min at room temperature was applied. The elastic modulus (E, MPa) and the ultimate tensile strength (σ, MPa) of the composite material specimen is derived from the stress–strain curve for each specimen.

3. Results and discussions

Examples of obtained data curves of tensile test of pure PEO, PEO/5Li, PEO/5Li/nCNT and PEO/5Li/nGR and PEO/5Li/nCNT/nGR are illustrated in Figure 1a, 1b and 1c.
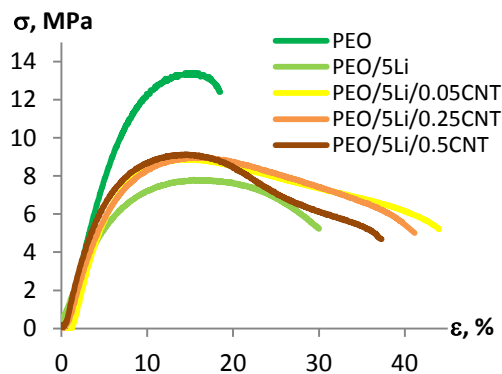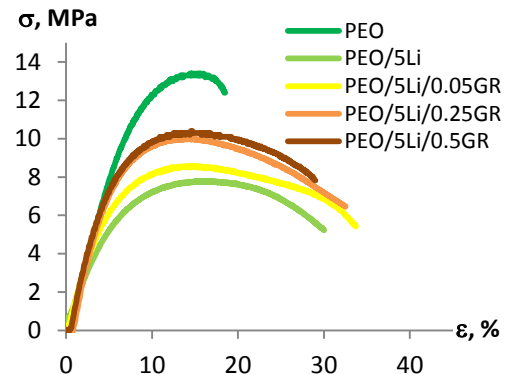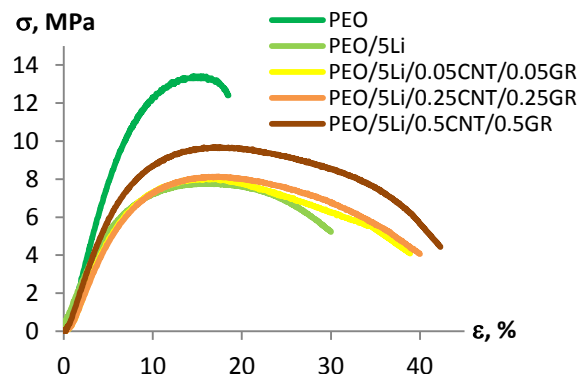

Figure 1a. Tensile test data curves of PEO, PEO/5Li, PEO/5Li/nCNT.

Figure 1b. Tensile test data curves of PEO, PEO/5Li, PEO/5Li/nGR.

Figure 1c. Tensile test data curves of PEO, PEO/5Li, PEO/5Li/nCNT/nGR.

Figure 1a, 1b and 1c show dependence of tensile test stress from strain. Young's module, strain and stress of the PEO composite material specimens with randomly oriented MWCNTs and/or GR specimens are compared to PEO with 5% LiTrifl. From Figure 1a, 1b, 1c can be concluded, that addition of 5% LitTrifl and low content (less or equal to weight 0.5%) of MWCNT and GR effect on PEO tensile test mechanical behaviour. Considerable changes in tensile test curve behaviour occur after adding of LiTrifl salt to pure PEO; due to LiTrifl plasticizer effect. As a result of Li-plasticizing agent addition, intermolecular linkage decreased, therefore ultimate stress decreased too, but strain at break increased. At the same time it is known that LiTrifl contributed greatly to the improvement of electrical conductivity of PEO and its nanocomposites. Figure 1a and 1b show, that addition of at least 0.05% MWCNT or 0.05% GR nanoparticles to PEO/5Li composite increase an ultimate stress and decrease strain at break.

From recorded tensile test data: Yung model (E, MPa), ultimate stress (σ_U, MPa) and strain (ε_U, %), stress (σ_B, MPa) and strain (ε_B, %) at break diagrams with dependence from nanoparticle content were plotted.

Young's module, ultimate strain and ultimate stress results for pure PEO, PEO/5Li and for nanocomposites PEO/5Li/nCNT and PEO/5Li/nGR are illustrated in Figure 2a, 2b and 2c.
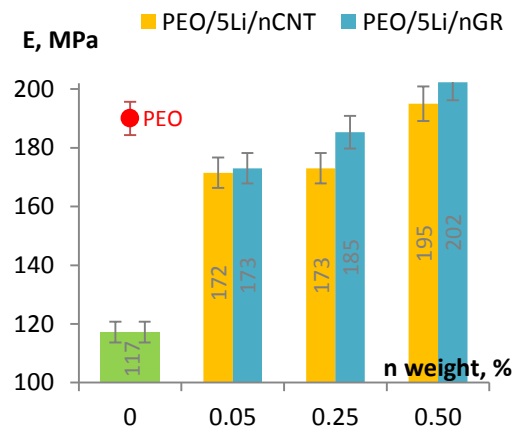

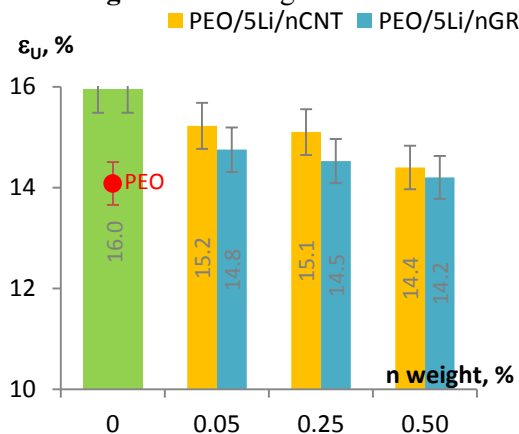**Figure 2a**. Young module results for PEO, PEO/5Li, PEO/5Li/nCNT, PEO/5Li/nGR.

Figure 2b. Ultimate strain results for PEO, PEO/5Li, PEO/5Li/nCNT, PEO/5Li/nGR.
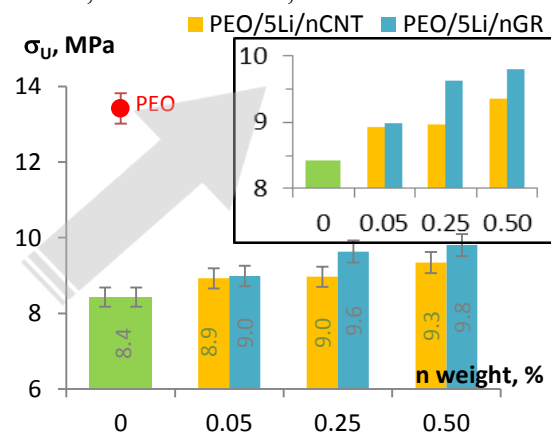

Figure 2c. Ultimate stress results for PEO, PEO/5Li, PEO/5Li/nCNT and PEO/5Li/nGR.

Figure 2a, 2b and 2c show, that addition of 5% of LiTrifl to PEO decrease its Young module and ultimate stress decrease by 38% and 37% respectively, but ultimate strain increased by 13%. It was expected, that of Lithium salt as additional ion source, which at the same time plays plasticizer role, will decrease intermolecular force, thus will decrease stiffness of prepared PEO/5Li composite.

Addition of 0.05% of MWCNT or GR increase Young's module and ultimate stress approximately by 47% and 7%, but decrease ultimate strain approximately by 6%. Following increase of MWCNT or GR, increase Young's module and ultimate stress, but decrease ultimate strain. Concluded, that prepared compositions with GR show higher Young's module and ultimate stress results. This occur due to GR's higher Young's module (1 TPa) in tensile loading tests (Young module for MWCNT is in range from 270 to 950 GPa) [29]. Addition of 0.5% MWCNT or GR increase nanocomposites Young's modules by approximately 70% in both cases (by 66% if MWCNT added and by 73% if GR added).

Young module, ultimate strain and ultimate stress results for pure PEO, PEO/5Li and for hybrid-nanocomposites PEO/5Li/nCNT/nGR are illustrated in Figure 3a, 3b and 3c.
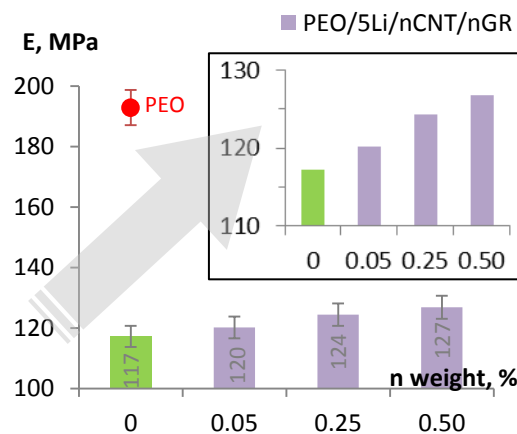

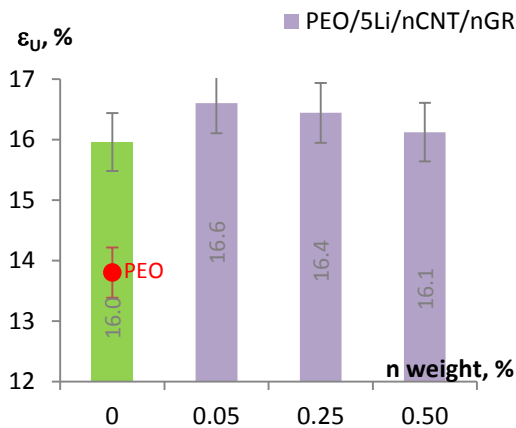**Figure 3a**. Young module results for PEO, PEO/5Li, PEO/5Li/nCNT/nGR.

Figure 3b. Ultimate strain results for PEO, PEO/5Li, PEO/5Li/nCNT/nGR.
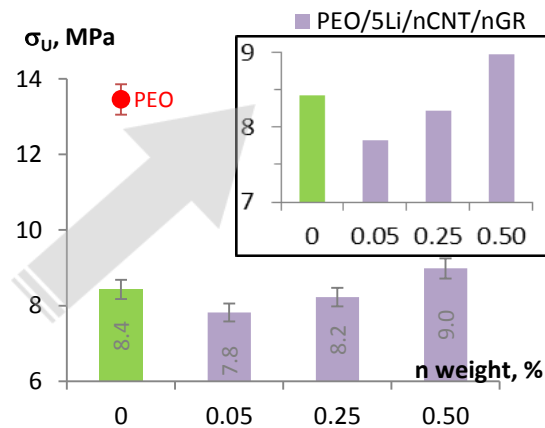

Figure 3c. Ultimate stress results for PEO, PEO/5Li, PEO/5Li/nCNT/nGR.

Addition of MWCNT and GR in the same content and to the same composite increase Young's module and ultimate stress results. Increase of Young's module and ultimate stress results is observed, when concentration of nanofiller is increased. However adding at the same time MWCNT and GR decrease ultimate stress until certain concentration is reached. Concentration for each nanoparticle types above 0.25% increase ultimate stress results. Further possible nanoparticle distribution analysis is necessary to describe this phenomenon. Obtained results show, that highest Young module in hybrid-nanocomposites is equal to 127 MPa (for PEO/5Li/0.5CNT/0.5GR), that is only by 8% higher than PEO with 5%LiTrifl (117 MPa).

Strain and stress at break results for pure PEO, PEO/5Li, PEO/5Li/nCNT and PEO/5Li/nGR are illustrated in 4a and 4b.
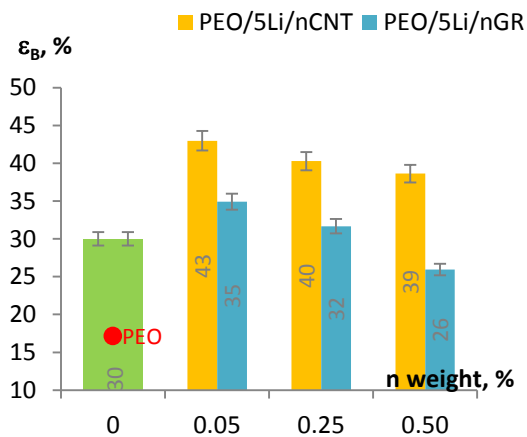
Figure 4a. Strain at break results for PEO, PEO/5Li, PEO/5Li/nCNT, PEO/5Li/nGR.
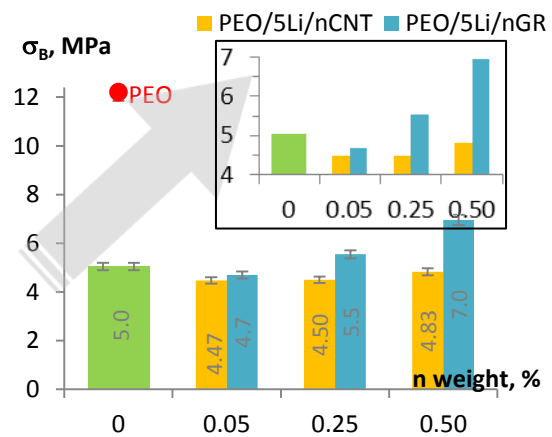
Figure 4b. Stress at break results for PEO, PEO/5Li, PEO/5Li/nCNT, PEO/5Li/nGR.

Figure 4a and 4b show, that addition of 5% of LiTrifl to PEO decrease its stress result at break by 59%, but strain at break increased by 75%. Addition of 0.05% MWCNT or 0.05% GR increase strain results at break by 43% and 16% respectively. Additional increase of concentration of MWCNT or GR decrease strain results at break. Concluded, that addition of MWCNT from 0.05% to 0.5% slightly increase PEO nanocomposites stress results at break (from 4.5 MPa to 4.8 MPa).

Strain and stress at break results for pure PEO, PEO/5Li and hybrid-nanocomposites PEO/5Li/nCNT/nGR are illustrated in Figure 5a and 5b.
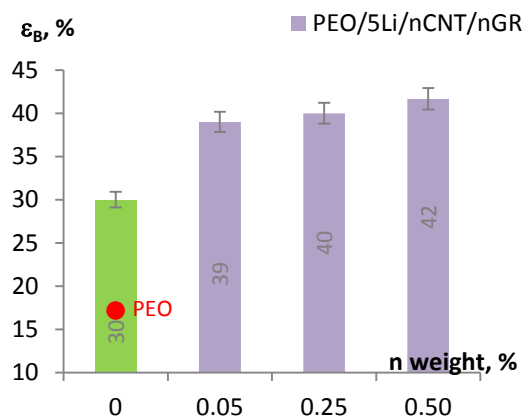

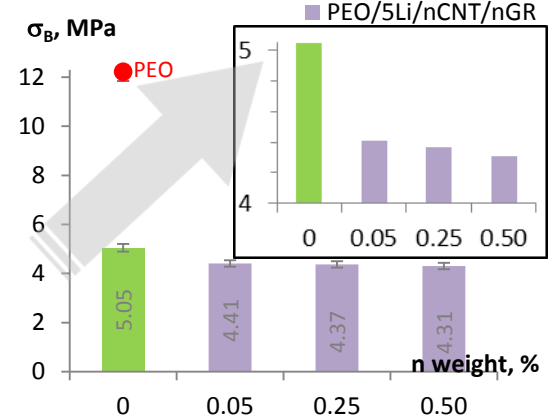**Figure 5a**. Strain at break results for PEO, PEO/5Li, PEO/5Li/nCNT/nGR.

Figure 5b. Stress at break results for PEO, PEO/5Li, PEO/5Li/nCNT/nGR.

Figure 5a and 5b show, that addition of both MWCNT and GR to PEO/5Li increase stain results at break, but decrease stress results at break. Minor changes occur in hybrid-nanocomposites PEO/5Li/nCNT/nGR, when concentration of nanoparticles raised.

From Figure 4a, 4b and 5a, 5b it is observed, that strain and stress results at break of PEO prepared nanocomposites and hybrid-nanocomposites vary within 35 ± 5 MPa. Therefore we can conclude that the amount of MWCNT and GR ranging from 0.05% to 1% (0.5% + 0.5%; if both nanoparticle types are used) and type of nanoparticles has very little effect on strain and stress results at break.

4. Conclusions

PEO nanocomposite and hybrid-nanocomposite material specimens fabricated using described in this paper technique with a MWCNT or/and GR loading rate of 0.05, 0.25, 0.5 weight % demonstrate an increase of the ultimate tensile strength and an increase of the Young modulus compared to the PEO plasticized with 5% LiTrifl specimens without MWCNT and GR. Prepared PEO nanocomposites plasticized with 5% LiTrifl and reinforced by GR show higher Young's module and ultimate stress results, than nanocomposites with MWCNT. Addition of at least 0.05% MWCNT or GR to PEO/5%Litrifl increase Young's module by 46% and 73%. Addition of 0.05% both nanoparticle types (MWCNT and GR) increase Young's module only by 3%. Concluded that the amount of both nanoparticle types in PEO hybrid-nanocomposite plasticized with 5% LiTrifl ranging from 0.05% to 1% (if both nanoparticle types are used) of nanoparticles has very little effect on strain and stress results at break.

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