Carbon nanotubes modified with octylthiophene derivatives for improved performance of ethylene-octene copolymer composites

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Abstract. The effects of poly-3-octylthiophene (P3OT) functionalized multiwalled carbon nanotubes (MWCNTs) on the structure as well as stress-strain characteristics and electrical conductivity of ethylene-octene copolymer with 17% of octene comonomer content (EOC17) are investigated. According to Raman spectroscopy and TEM analysis, thiophene groups have been successfully grafted onto the surface of MWCNTs. EOC17 nanocomposites with P3OT functionalized MWCNTs show simultaneously high values of stress at break and strain at break, even at high nanofiller content, being respectively 2.5 and 3.5 times higher than the values determined for the systems containing pristine MWCNTs. It is also demonstrated that at functionalized filler content of 10 wt%, twofold increment of the modulus of elasticity is observed. In addition to that, P3OT functionalized MWCNTs containing EOC nanocomposites possess up to 279 times greater electrical conductivity in comparison to the systems with pristine MWCNTs.

Key words: ethylene-octene nanocomposites, thiophene derivative, carbon nanotubes, functionalization.

1. INTRODUCTION

In recent years use of polymer materials in our everyday life has greatly increased, largely due to rapid developments in electronics and energetics. High deformability in addition to remarkable electrical conductivity is one of the most important requirements in developing specific polymer materials for rising markets in electronics and energetics. Achievement of this task is often challenging because the properties needed for high carrier mobilities, like rigid chains in π-conjugated polymers and high degrees of crystallinity in the solid state, are antithetic to deformability [1]. Largely, two approaches can be used to overcome this issue: 1) development of conductive filler containing systems based on highly deformable elastomers, allowing incorporation of comparatively great amounts of conductive fillers without considerable loss in deformability; and 2) development of formulations of compositions on the basis of intrinsically conducting polymers such as polythiophene, polyaniline, polypyrole, polyacetylene and its derivatives.

In respect to the first approach, carbon allotropes, including carbon black, carbon nanotubes, graphene and fullerenes, have probably gained the greatest interest. Carbon allotropes have been successfully incorporated into polyurethane [2,3], polyethylene copolymers [4,5] as well as other highly deformable materials to increase not only electrical conductivity, but also mechanical stiffness, thermal conductivity, heat resistivity, solvent vapor and gas permeation resistance and other properties,

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allowing to use the developed polymer composites for numerous smart material applications like sensors [4,6], thermoelectric devices [7] and shape memory elements [3,6,8].

There are also numerous researches about the use of intrinsically conductive polymers for smart material applications, from which the systems based on thiophene derivatives and its composites, such as alkylthiophenes and poly(3,4-ethylenedioxythiophene) polystyrene sulphonate, respectively, seem to be most promising [9]. To increase processability and also to extend application range of the systems based on polythiophene derivatives, various conventional polymers have been combined with some limited success (for example, ethylene-vinyl acetate copolymer and polymethylmethacrylate [10]).

The main goals of the current research relay on the development of novel polymer filler based on the laboratory synthesized poly-3-octylthiophene (P3OT) functionalized multiwalled carbon nanotubes, which show reliable improvement of the structure as well as deformation characteristics and electrical conductivity of highly deformable ethylene-octene copolymer composites due to increased interfacial compatibility and improved overall performance.

2. MATERIALS AND METHODS

2.1. Materials used in research

Ethylene-octene copolymer with octene comonomer content of 17% (EOC17, *Engage 8540*, The Dow Chemical Company, Michigan, USA) is used as a matrix. Multiwalled carbon nanotubes (MWCNTs, *Baytubes® C150P*, Bayer AG, Germany), kindly donated by the company, are used as a conductive filler. Purification

of MWCNTs is done by using a mixture of 6M hydrochloric acid and 6M nitric acid (both, obtained from the concentrated chemical purity grade acids, purchased from Ing. Petr Švec – PENTA s.r.o., Czech Republic). Carboxylation of purified MWCNTs is performed by treatment with a mixture of concentrated nitric acid (70%) and sulphuric acid (97%) (both purchased from Ing. Petr Švec – PENTA s.r.o., Czech Republic). Reagent grade chemicals, used in the process of further functionalization of the obtained carboxylated MWCNTs, are methanol (obtained from LabScan, POCH S.A., Poland), chloroform, pyridine, anhydrous tetrahydrofuran (≥99.0%), thionyl chloride (>99%), 2-thiophenemethanol (>99%), 3-octylthiophene (>97%) and anhydrous iron(III)oxide (>97%) (all purchased from Sigma–Aldrich Chemie GmbH, Darmstadt, Germany). Millipore Durapore PVDF membrane filters with pore size 0.1 μ (purchased from Thermo Fisher Scientific, Massachusetts, USA) are used in filtration/separation processes of functionalization of MWCNTs. Reagent grade toluene and acetone (obtained from LabScan – POCH S.A., Poland) are used as solvent and anti-solvent for manufacturing of EOC based masterbatches with acid purified and functionalized MWCNTs. High purity water (15 MΩ cm^{-1}) is generated by Millipore Elix 3 water purification system (Merck Millipore, USA).

2.2. Functionalization of MWCNTs by poly(3-octyl-thiophene) and preparation of EOC based composites

The synthesis of poly(3-octylthiophene) functionalized MWCNTs (P3OT-f-MWCNTs) is done similarly to the procedure described in [11]. The stages of the synthesis are summarized in Fig. 1.
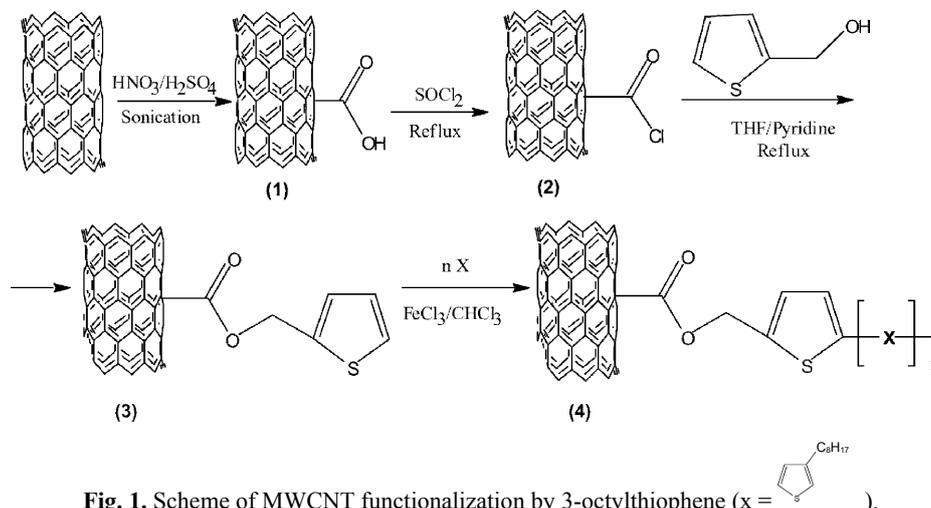

Fig. 1. Scheme of MWCNT functionalization by 3-octylthiophene (x =).

The procedure for fabrication of EOC17 masterbatches with MWCNTs (either acid purified MWCNTs or P3OT-f-MWCNTs) will be described. At first, a solution of 2 wt% of EOC in toluene is prepared and mechanically mixed at 70 °C until clear solution is obtained. Then calculated amounts of MWCNTs or P3OT-f-MWCNTs are added to the EOC solution to yield respective masterbatches containing 0, 0.5, 1, 3, 5, 10, 12 and 15 wt% of MWCNTs or P3OT-f-MWCNTs (in respect to the final melt-mixed compositions). The sonication process is carried out in a thermostatic ultrasound bath *Ultrasons 3000837* (JP Selecta S.A., Spain) for 30 min at 70 °C, allowing to obtain stable dispersions without a tendency of precipitation of the matrix polymer. Although sonication procedure may lead to reduction of molecular mass of the polymer matrix, the effect was not evaluated. EOC based masterbatches are obtained by pouring carbon nanofiller containing mixtures in acetone at room temperature under continuous sonication for 1 minute in the ultrasound bath. As acetone is non-solvent of EOC, its addition to the system leads to precipitation of the EOC/MWCNT and EOC/P3OT-f-MWCNT nanocomposites from the toluene dispersions. The products are separated by filtration using Buchner vacuum filtration system. The crude solid is washed with ether and dried under vacuum at 40 °C.

The obtained masterbatches are melt mixed for a total time of 5 min (speed of the rolls 20/25 rpm; temperatures of the rolls 120/170 °C) with necessary additional amounts of EOC17 by using two-roll mills *LRM-S-110/3E* (Labtech Engineering Co., Ltd, Thailand). Then hydraulic laboratory press *LP-S-50/S.ASTM* (Labtech Engineering Co., Ltd, Thailand) is used to obtain rectangular plates (length × width × thickness = 60 mm × 50 mm × 0.8 mm) at temperature of 140 °C, in the future used for preparation of test specimens.

2.3. Methods of characterization

Structural features of the pristine and functionalized carbonaceous nanofillers are analysed by using transmission electron microscope *Tecnai G20* (FEI Company, USA).

Raman spectroscopy measurements of the pristine and functionalized carbonaceous nanofillers are performed with an excitation power of 10 mW at 514 nm using the *RM 1000-InVia* Raman spectrometer (Renishaw Group, UK). Subsequent analysis of Raman spectra is carried out using Dr Friedrich Menges *Spekwin32 1.720.0* software. Linear baseline correction is made using Origin 7 software [12].

Calorimetric properties of the fabricated EOC nanocomposite powders (ca 10 mg) are measured by using differential scanning calorimeter *DSC1/200W*

(Mettler–Toledo LLC, Switzerland). Measurements are performed under nitrogen flow as follows: 1) heating from 0 °C to 150 °C at the rate of 10 °C/min; 2) cooling from 150 °C to –80 °C at the rate of 10 °C/min; 3) heating from –80 °C to 150 °C at the rate of 10 °C/min.

Tensile stress-strain tests of the fabricated EOC17 nanocomposite dumbbell-shaped specimens (width of the working zone: 5 mm; gauge length: 20 mm) are performed at 23±2 °C by using universal testing machine *H1KS* (Tinius Olsen TMC, USA) equipped with a 1 kN load cell. The specimens are pre-stressed to 0.1 MPa before the test.

Elastic behaviour of the fabricated EOC17 nanocomposite rectangular film shaped specimens (length between clamps: 8.5 mm) is measured by using dynamic mechanical thermal analyzer *DMTA/SDTA 861e* (Mettler–Toledo LLC, Switzerland). Measurements are performed at 1 Hz frequency in a temperature interval from –100 °C to +60 °C at a heating rate of 3 °C/min.

Dielectric properties of the nanocomposite compression molded disk-shaped test specimens are determined by using broadband dielectric spectrometer *Concept 50* (Novocontrol Technologies GmbH & Co. KG, Germany). Measurements are performed at +23 °C in a frequency range between 10^{-2} and 10^6 Hz.

3. MAIN RESULTS

Raman spectra of pristine and poly-3-octylthiophene modified MWCNTs are shown in Fig. 2a. The characteristic spectra bands of MWCNTs are attributed to the graphite in-plane vibration of the C–C bond (G band) at 1580 cm^{-1} with a shoulder around 1604 cm^{-1} due to defective structures and the band at ~1352 cm^{-1} (D band) activated by the presence of disorder in carbon systems. For P3OT-f-MWCNTs the D band is shifted to 1356 cm^{-1} and the G band – to 1577 cm^{-1}. For P3OT-f-MWCNTs a shoulder was determined at 1406 cm^{-1} by Lorentzian fitting, which corresponds to thiophene moieties belonging to P3OT-f-MWCNTs. The change in ID/IG intensity ratio from 1.28 for pristine MWCNTs to 0.66 for P3OT-f-MWCNTs evidently is due to the grafting of the P3OT chain on the surface of MWCNTs. Similar results have been reported in case of graphene/carbon nanotube/polystyrene materials [13].

Successful functionalization of carbonaceous nanofillers by polymer grafting can be confirmed also by TEM measurements. Representative TEM image of P3OT-f-MWCNTs is shown in Fig. 2b, from which one can learn that certain layer of the polymer has been attached on the surface of MWCNTs.

Functionalization of nanostructured carbon allotropes by high-molecular compounds usually leads to the
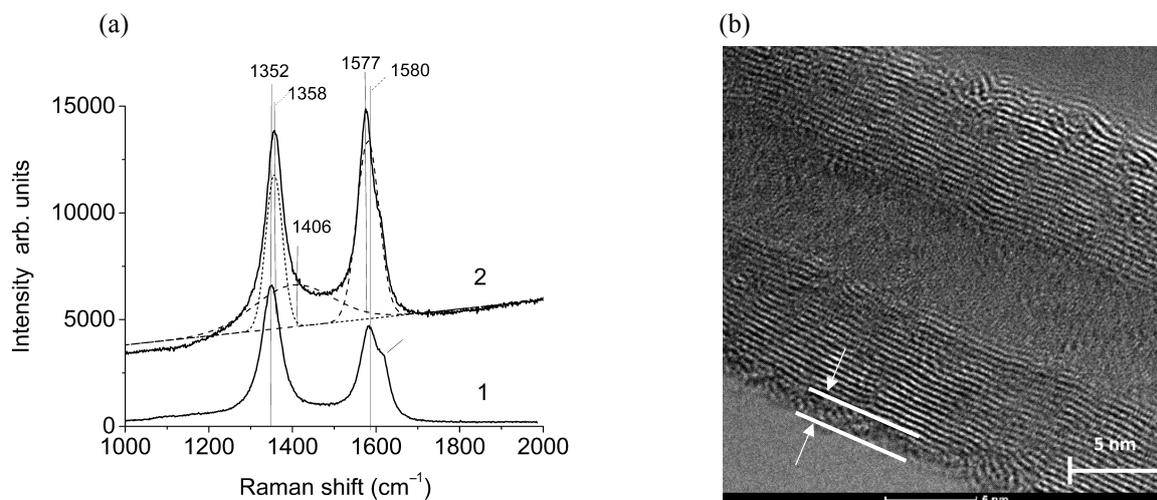
Fig. 2. Base-line corrected Raman spectra (a) of pristine MWCNTs (1) and P3OT-f-MWCNTs (2); and representative TEM image (b) of P3OT-f-MWCNTs.

increased interaction between the nanofiller and the polymer matrix, ensuring considerable improvement of exploitation properties in comparison to neat polymer matrix. The effect P3OT-f-MWCNTs on the crystallization behaviour of EOC17 is shown in Fig. 3. It is seen that by increasing P3OT-f-MWCNTs concentration in the EOC17, crystallization onset temperature and crystallization maximum temperature, both are increased in comparison to the neat polymer matrix. Relatively greater increment in crystallization maximum temperature, however, is observed in the case of the nanocomposite, containing 3 wt% of P3OT-f-MWCNTs. The effect of P3OT-f-MWCNTs on the crystallization temperature of EOC17 is much greater than that of pristine MWCNTs, which hardly affect maximum crystallization temperature of the polymer matrix even at the highest nanofiller content (i.e. 91 °C for neat EOC and 90 °C for EOC nanocomposite with 10 wt% of MWCNTs).
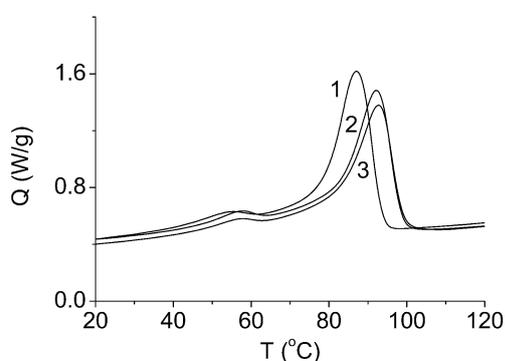

Fig. 3. DSC cooling traces of neat EOC17 (1) and EOC17 nanocomposites with 3 wt% of P3OT-f-MWCNTs (2) and 10 wt% of P3OT-f-MWCNTs (3).

The effect of P3OT-f-MWCNTs on the dynamic mechanical behaviour of EOC17 based nanocomposites is shown in Fig. 4.

Results of the investigation clearly demonstrate that introduction of P3OT-f-MWCNTs within the thermoplastic polymer matrix considerably affects its crystalline phase as confirmed by the shift of the corresponding relaxation peak of EOC 17 by ca 30 °C to the direction of higher temperatures, i.e., from ca 7 °C (at 0 wt% of P3OT-f-MWCNTs) to almost 40 °C (at 10 wt% of P3OT-f-MWCNTs), which is approximately 10 °C higher in comparison to the systems with pristine MWCNTs. Concomitantly, addition of P3OT-f-MWCNTs to EOC17 considerably affects its storage modulus E' along the whole investigated temperature range, as clearly demonstrated in Fig. 4a. Besides, in comparison to pristine MWCNTs, P3OT-f-MWCNTs addition, especially at higher concentrations, has greater effect on the values of E' of the nanocomposites in respect to neat EOC17 matrix, evidently because of improved matrix-filler interaction due to the octyl branches of P3OT, grafted on the surface of MWCNTs.

In order to evaluate the effect of P3OT-f-MWCNTs on the stretchability of EOC17 based systems, tensile stress-strain analysis was carried out. Results of tensile stress-strain tests are summarized in Fig. 5.

In accordance with the changes of storage modulus, tensile modulus E also increased along with growing nanofiller content in both composites: at 10 wt% of the nanofiller content almost twofold increment of E was observed for composites with P3Ot-f-MWCNTs compared to that of EOC. Although the $E(w_f)$ relationships for pristine MWCNTs and P3OT-f-MWCNTs containing systems are almost identical, absolute values
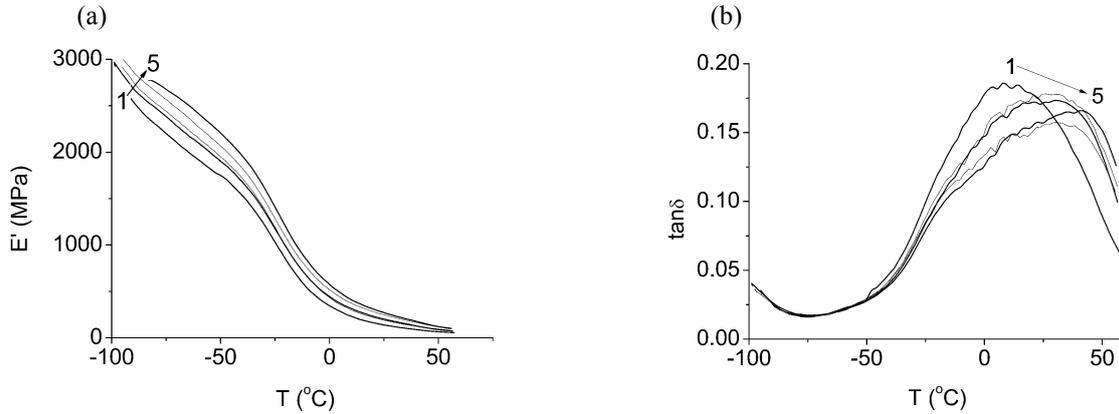
Fig. 4. Storage modulus E' (a) and loss tangent *tanδ* (b) of EOC17 (1) and its nanocomposites with 3 wt% of MWCNTs (2), 3 wt% of P3OT-f-MWCNTs (3), 10 wt% of MWCNTs (4) and 10 wt% of P3OT-f-MWCNTs (5).
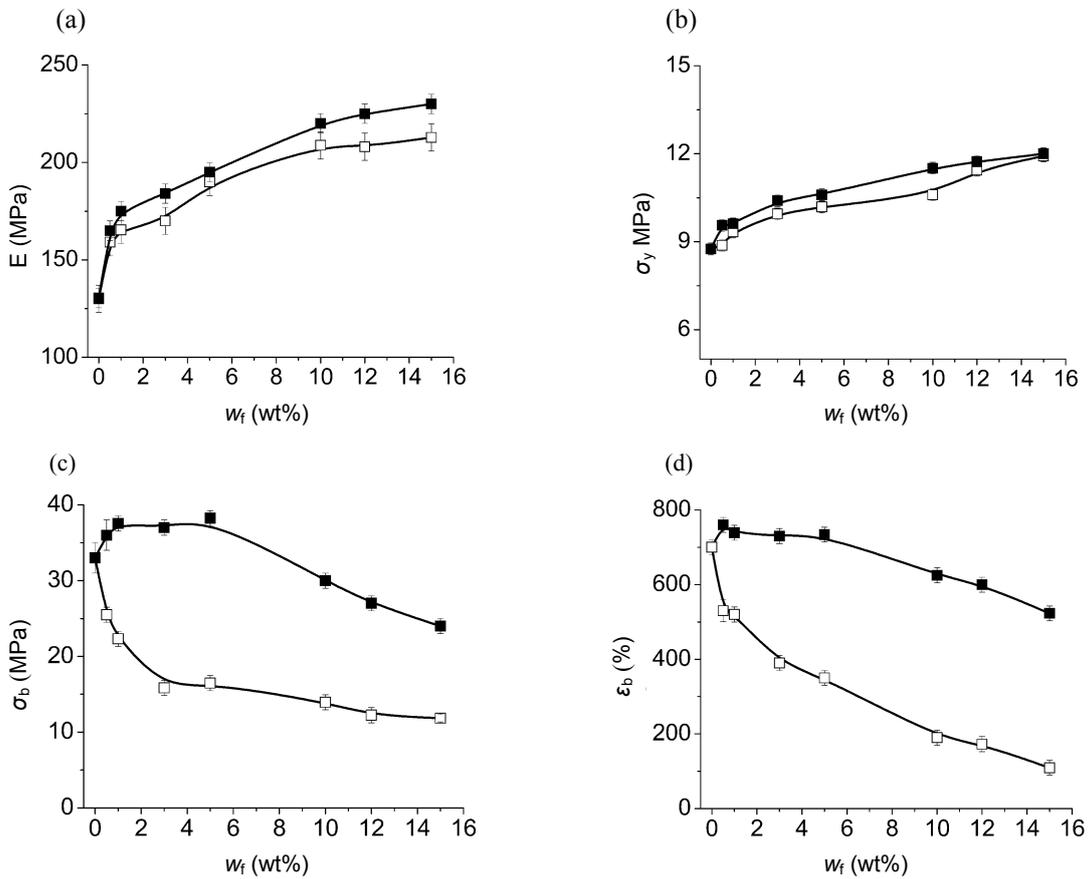
Fig. 5. Tensile modulus E (a), stress at yield σ_y (b), stress at break σ_b (c) and strain at break ε_b (d) of EOC17 nanocomposites with MWCNTs (open symbols) and P3OT-f-MWCNTs (closed symbols).

of E are higher for those EOC nanocomposites, containing functionalized nanofillers, especially at higher weight contents. Addition of carbon nanofillers to EOC17 positively affects also yield strength σ_y of the investigated

nanocomposites. At the maximal nanofiller content increment in σ_y, being almost equal for MWCNTs and P3OT-f-MWCNTs containing systems, is approximately 30%. In respect to ultimate stress-strain characteristics,
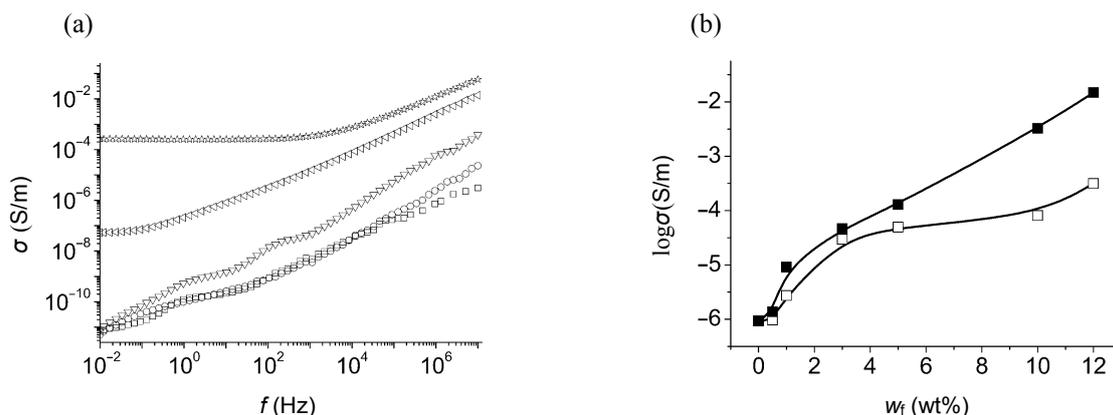
Fig. 6. Electrical conductivity σ of the selected EOC17 composites with various wt% contents of P3OT-f-MWCNTs ($\square$ – 0%, $\circ$ – 0.5%, ∇ – 3%, $\triangleleft$ – 10%, $\star$ – 12%) as a function of frequency (a); and electrical conductivity of the investigated nanocomposites with pristine (open symbols) and functionalized (closed symbols) MWCNTs at 1MHz frequency as function of the nanofiller content (b).

in the field of composite materials it is commonly accepted that addition of fillers, int. al., nanofillers, especially at high concentrations, cause decrement in the stretchability of the materials. The magnitude of decrement of stretchability in the polymer based nanostructured composites, however, is closely related to the ability to ensure even distribution of the nanofiller within the polymer matrix as well as ensure desirable adhesion between the constituents of the composite. Therefore, it is interesting to see the effect of P3OT-f-MWCNTs on the strain at break ε_b and stress at break σ_b of EOC17 nanocomposites. In the case of σ_b, the parameter is increased until the P3OT-f-MWCNTs content of 5 wt%. At higher P3OT-f-MWCNTs content, increment of σ_b is evidently reduced (even decrease of σ_b is observed) because of reduced strain hardening capacity, caused due to confinement of the rigid nanofiller. Concomitantly, at P3OT-f-MWCNTs content above 5 wt% ε_b of corresponding EOC nanocomposites decreases faster than until this critical concentration. However, in comparison to the systems containing pristine MWCNTs, decrement of ε_b for EOC nanocomposites with P3OT-f-MWCNTs is considerably smaller: at maximal nanofiller content more than 3-fold difference is observed. Considerable difference between σ_b of the systems containing pristine and functionalized MWCNTs is also observed. Thus at maximum nanofiller content σ_b of EOC/P3OT-f-MWCNTs nanocomposite prevails that of EOC/MWCNTs nanocomposite by more than 2 times.

In addition to elastic and stress-strain characteristics, electrical properties of the investigated EOC based composites, containing electrically conductive nanofiller have also been investigated. Electrical conductivity σ of the selected compositions of the investigated

EOC/P3OT-f-MWCNTs nanocomposites as a function of frequency is depicted in Fig. 6a.

In general, σ of the nanocomposites starts considerably increase (predominantly at greater frequencies) if the nanofiller content is increased above 0.5 wt%. Rapid increment in σ of the nanocomposites is evidently connected with development of the electrically continuous network of the conductive nanofiller within the insulating polymer matrix. In order to compare electrical behaviour of pristine and functionalized MWCNTs containing EOC composites, $\sigma(w_f)$ relationships are depicted in Fig. 6b. As shown, functionalization of MWCNTs with electrically conductive compound (P3OT) favours development of electrically conductive network within insulating polymer matrix, especially at higher nanofiller contents. Consequently, at 10 wt% of the nanofiller content σ of EOC/P3OT-f-MWCNTs exceeds that of EOC/MWCNTs by 279 times.

4. CONCLUSIONS

It has been demonstrated that MWCNTs have been successfully modified with thiophene groups. It has also been shown that modification of EOC17 with P3OT functionalized MWCNTs ensures simultaneously high values of stress at break σ_b and strain at break ε_b even at high nanofiller content (10 wt%), which are 2.5 and 3.5 times higher, respectively than the values determined for systems containing pristine MWCNTs. It is also determined that at functionalized filler content of 10 wt%, twofold increment of the modulus of elasticity E is obtained. In addition to that, electrical conductivity σ of functionalized MWCNTs containing EOC nanocomposites is up to 279 times greater than that of

systems containing pristine MWCNTs. In the future, the real conductivities of polythiophene nanofillers will be determined compared to MWCNTs.

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Oktüültiofeeni derivaatidega modifitseeritud süsiniknanotorud etüleen-okteenkopolümeerkomposiitide omaduste parendamiseks

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On käsitletud polü-3-oktüültiofeeniga (P3OT) funktsionaliseeritud mitmeseinaliste süsiniknanotorude (MWCNT) mõju etüleen-okteenkopolümeeri (EOC17) (sisaldab 17% okteenkomonomeeri) struktuurile, pinge-deformatsiooni-omadustele ja elektrijuhtivusele. Tiofeenirühmade seostumine MWCNT pinnale leidis kinnitust ramanspektroskoopia ja TEM-analüüside abil. Võrreldes proovidega, mis sisaldasid modifitseerimata nanotorusid, olid P3OT-ga funktsionaliseeritud MWCNT-lisandiga EOC17 nanokomposiitidel kõrged katkemispinge- ja deformatsiooninäitajad isegi suurtel nanokomposiidisisaldustel, vastavalt 2,5- ning 3,5-kordne tõus pingel ja deformatsioonil. Ühtlasi selgus, et 10% funktsionaliseeritud nanotorulisand suurendas komposiidi elastsusmoodulit kaks korda. Lisaks sellele leiti, et funktsionaliseeritud nanotorulisandiga EOC-nanokomposiitide elektrijuhtivus oli 279 korda suurem kui vastavatel süsteemidel, mis sisaldasid funktsionaliseerimata nanotorusid.