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FUNCTIONAL
MATERIALS

Fabrication and characterization of ethylene–octene copolymer composites with ionic liquid functionalized carbon nanotubes

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Abstract. Modification of multi-walled carbon nanotubes (MWCNTs) by means of imidazolium ionic liquid (IL) was performed. Structural characterization of funtionalized nanofillers (IL-f-MWCNTs) was made by means of Raman spectroscopy and transmission electron microscopy. MWCNTs and IL-f-MWCNTs were introduced within ethylene octane copolymer (EOC) with octene co-monomer content of 17% by using the masterbatch approach. The efficiency of the carbonaceous nanofiller distribution within the polymer matrix was characterized by means of scanning electron microscopy. It was shown that MWCNTs and IL-f-MWCNTs were both effective in rising storage modulus, tensile modulus, stress-at break, and electrical conductivity of EOC-based nanocomposites along with the increasing nanofiller content. Besides, it was observed that the modification efficiency of the investigated EOC matrix composites by IL-f-MWCNTs was greater in comparison to pristine MWCNTs.

Key words: material science, carbon nanotubes, polyethylene copolymer, nanocomposites

1. INTRODUCTION

Purposeful modification of polymers with nanostructured functional additives has been an issue of intensive research already for more than 20 years. Although various materials of nanolevel dimensions have been considered for the modification of polymers, carbon-based nanofillers probably have gained the greatest interest largely due to intrinsic properties of carbon itself as well as because of the broad spectrum of allotropic forms in which the filler is available: diamond, graphite, fullerenes, nanotubes, graphene, etc. This has initiated development of polymer–carbon nanocomposites for a broad range of applications: energy storage and transformation [1,2], electronics [2,3], environmental remediation [4], structural engineering [5] and industrial coating [6], transport [7], medicine [8], etc. Practical application of polymer–carbon nanocomposites, however, is mainly limited to niche markets being considerably restricted due to price considerations (generally carbon nanofiller) and insufficient compatibility between the polymer matrix and carbon nanofiller. Aspects of this insufficient compatibility are addressed in many scientific researches starting since first attempts to develop polymer nanocomposites [9] and including the most recent investigations in this research area [10], hence demonstrating the limited practical applicability of such systems. Several approaches have been used [11] with greater or smaller success to overcome this issue,

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including (i) functionalization using cationic, anionic, and radical polymerization; (ii) covalent functionalization using click chemistry; (iii) functionalization using electrochemical polymerization; (iv) non-covalent functionalization using H-bonding and π–π stacking; (v) electrosteric stabilization; and (vi) hydrophilic to hydrophobic phase transfer.

Recently Kim et al. [12] demonstrated poly(1-vinyl-3-ethylimidazolium) ionic liquid to be suitable for the functionalization of graphene sheets for the fabrication of high-performance supercapacitors. Ionic liquids have been also successfully used for the solubilization of carbon nanotubes [13], which is an important prerequisite for development of perspective polymer nanocomposites via masterbatch routes. In recent years also successful use of ionic liquids for the development of diene elastomer nanocomposites with CNTs was reported [14,15]. In our previous work [16] it was shown that functionalization of multi-walled carbon nanotubes with imidazolium ionic liquids allows greater increment of mechanical stiffness and thermal stability of ethylene–octene copolymer with high octene co-monomer content (38%) based composites in comparison to systems containing neat multi-walled carbon nanotubes.

Consequently, by considering the actualities in the field of carbon nanofiller surface modification for improving compatibility with polymer matrices, this research is devoted to the functionalization of carbon nanotubes by means of ionic liquids and characterization of the structure, as well as elastic, dielectric, and thermal properties of respective polymer nanocomposites based on ethylene-octene copolymer for many possible applications, some of which include, but are not limited to, shape memory devices as well as gas and solvent vapour barriers.

2. MATERIALS AND METHODS

2.1. Materials used

Ethylene–octene copolymer (EOC) with octene co-monomer content of 17% (EOC17, Engage 8540) was provided by The Dow Chemical Company. Multi-walled carbon nanotubes (MWCNTs, Baytubes® C150P) were kindly donated by Bayer AG. Chemical purity grade (>96%) concentrated hydrochloric acid (37%), nitric acid (70%), and sulphuric acid (97%) were purchased from Ing. Petr Švec – PENTA s.r.o. (Chrudim, Czech Republic). Reagent grade methanol, toluene, and acetone were obtained from LabScan – POCH S.A. (Gliwice, Poland). Reagent grade tetrahydrofuran (≥99.0%), 1-(3-aminopropyl)imidazole (>97%), 1-bromohexadecane (>97%), sodium bicarbonate, and sodium hexafluorophosphate (99%) were purchased from Sigma-Aldrich Chemie GmbH. All reagents were used without further purification. High purity water (15 MΩ cm^{-1}), used for MWCNT modification and fabrication of masterbatches, was generated by using the Millipore Elix 3 Water Purification System (Merck Millipore). Millipore Durapore PVDF membrane filters with pore size 0.1 μ were purchased from Thermo Fisher Scientific.

2.2. Functionalization of MWCNTs by ionic liquid

The modified procedure of MWCNT surface carboxylation transforming it to methyl ester and covalent grafting of imidazolium ionic liquid (IL) derivate to modified MWCNTs was performed on the basis of the procedure described by Kim et al. [17]. A principal scheme for MWCNTs functionalization is shown in Fig. 1. The procedures for all stages of MWCNTs modification are described elsewhere [16].

2.3. Composite preparation

Masterbatches of EOC17 and MWCNTs (either acid purified MWCNTs or IL-f-MWCNTs) were prepared as follows: first, a solution of 2 wt% EOC in toluene was prepared and ultra-sonicated at 70 °C until a clear solution was obtained. Then calculated amounts of MWCNTs or IL-f-MWCNTs were added to yield masterbatches of the composites containing 0, 0.5, 1, 3, 5, 10, 12, and 15 wt% of fillers in the final compositions. The sonication process was carried out in a thermostatic ultrasound bath Ultrasons 3000837 (JP Selecta S.A.) for 30 min at 70 °C, which enabled obtaining stable dispersions without a tendency of EOC precipitation. The EOC-based masterbatches were obtained by pouring carbon nanofiller containing mixtures in acetone into the ultrasound bath at room temperature under continuous sonication for 1 min. As non-solvent of EOC, acetone led to the precipitation of the EOC/MWCNT and EOC/IL-f-MWCNT nanocomposites from toluene dispersions. The products were recovered by vacuum filtration and dried under vacuum at 40 °C.

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

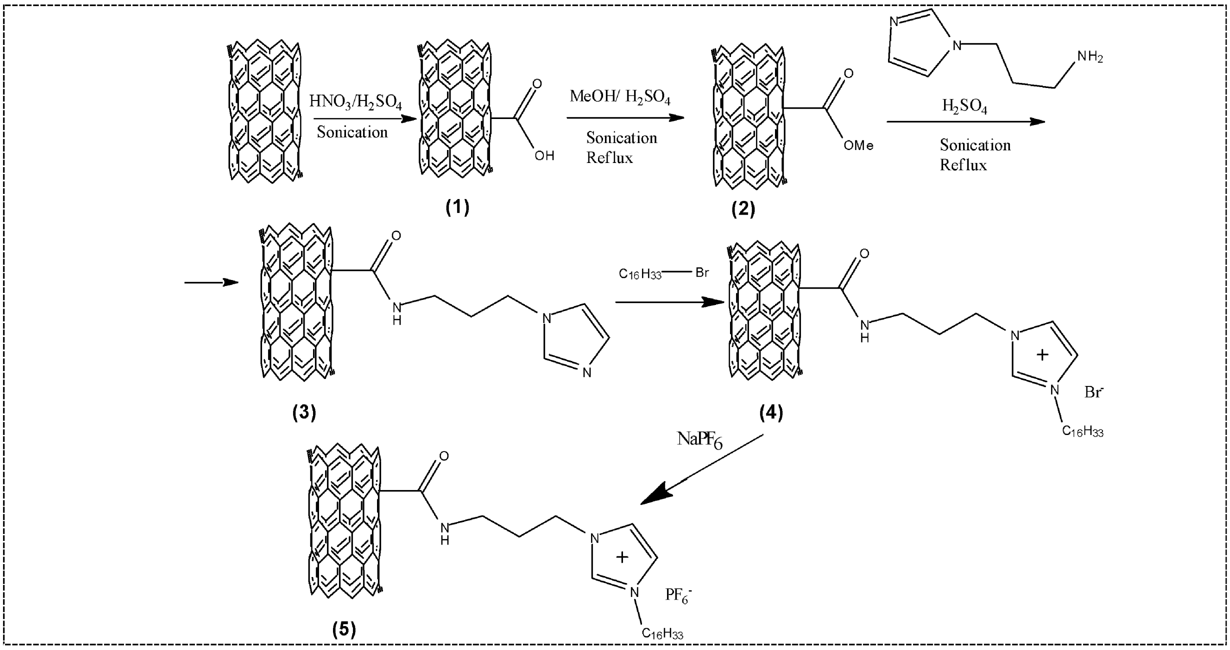

Fig. 1. Scheme of MWCNT functionalization by ionic liquid [16].

2.4. Methods of characterization

The structure of powders of carbonaceous nanofillers was analysed by using a transmission electron microscope Tecnai G20 (FEI Company). The morphology of liquid nitrogen fractured surfaces of compression moulded test specimens was characterized by using a scanning electron microscope ULTRA 55 plus (Carl Zeiss AG).

Raman spectroscopy measurements were performed with an excitation power of 10 mW at 514 nm using an RM 1000-InVia Renishaw Raman spectrometer (United Kingdom). The subsequent analysis of Raman spectra was carried out using Dr. Friedrich Menges Spekwin32 1.720.0 software.

Tensile stress–strain behaviour of the nanocomposite dumbbell-shaped specimens (width of the working zone 5 mm; gauge length 20 mm), mechanically cut from the compression moulded plates, was investigated at 23 ± 2 °C and 50 ± 5 °C. Tests at room temperature were performed by using a universal testing machine H1KS (Tinius Olsen TMC) equipped with a 1 kN load cell. Tests at elevated temperature were performed by using a universal testing machine ST25 (Tinius Olsen TMC) equipped with a 1 kN load cell and an environmental chamber. The specimens were pre-stressed to 0.1 MPa before the test.

The elastic behaviour of the nanocomposite compression moulded films was measured by using a dynamic mechanical thermal analyser DMTA/SDTA 861e (Mettler-Toledo LLC). Measurements were 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 moulded disk-shaped test specimens were determined by using a broadband dielectric spectrometer Concept 50 (Novocontrol Technologies GmbH & Co. KG). Measurements were performed at room temperature (+23 °C) in a broad frequency range (10^{-2} to 10^{6} Hz).

3. MAIN RESULTS

Raman spectral analysis was used to evaluate the change of carbon structures after the modification of pristine MWCNTs (Fig. 2a).

The characteristic spectra bands are assigned to the graphite in-plane vibration of the C–C bond at 1580 cm^{-1} (G band) with a shoulder around 1604 cm^{-1} of the defective graphite-like structure and the band at ~1352 cm^{-1} (disordered carbon D band) activated by the presence of disorder in carbon systems. Graphite (G) and disorder (D) bands as well as the corresponding ID/IG ratio are evaluated with regard to the functionalization of pristine MWCNTs by IL functional groups. From the Raman spectra, the D bands for IL-f-MWCNTs show a sharp increase of band intensity, attributed to the increased structural disorder. The G bands for those nano-fillers also show a notable increase in the intensity, which tends to be shifted from 1583 cm^{-1} to 1572 cm^{-1} for

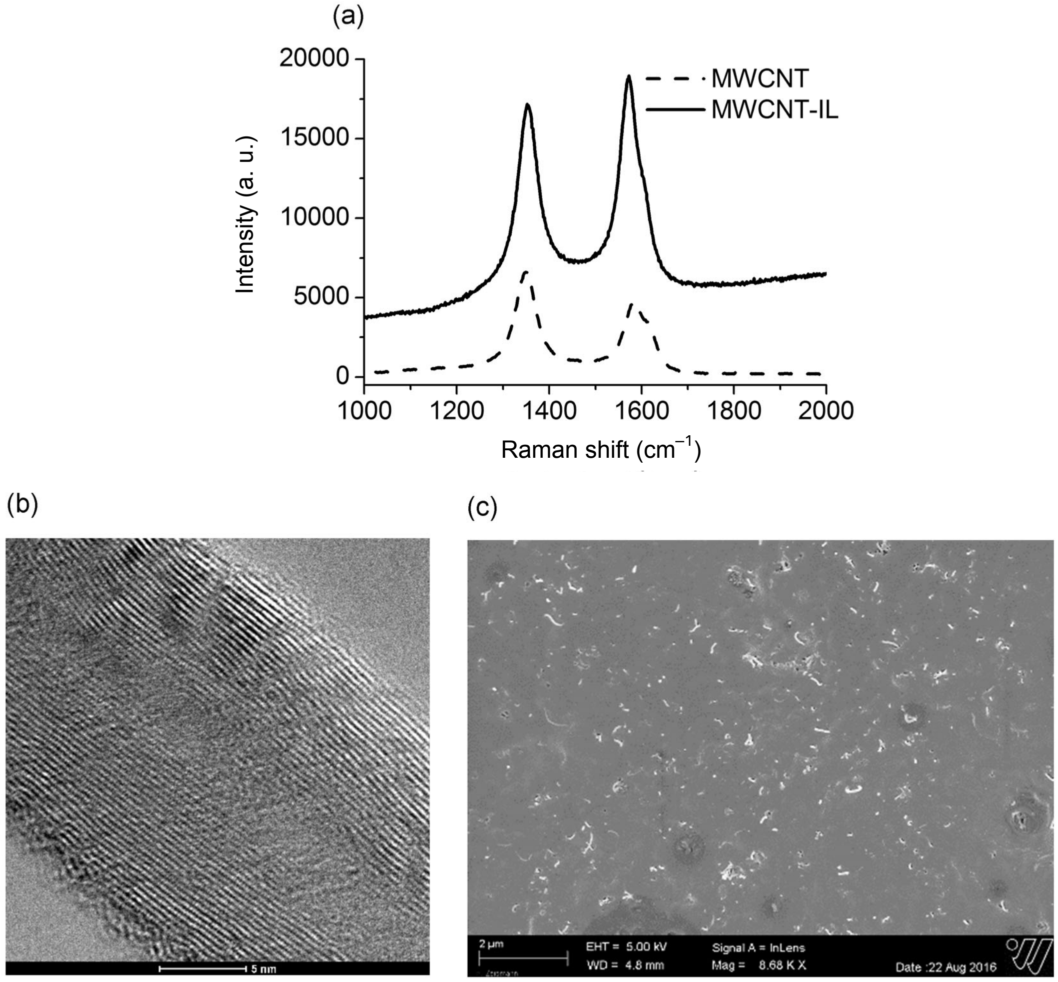

Fig. 2. Raman spectra (a) and representative TEM (b) and SEM (c) images of pristine MWCNTs (a), IL-f-MWCNT (a, b), and the EOC17 nanocomposite with 15 wt% of IL-f-MWCNTs (c).

IL-f-MWCNTs whereas the backbone attributed to defective graphite-like structure disappears due to the attachment of surface-active imidazolium IL functional groups. The ID/IG ratio changes from 1.28 to 0.86 due to the functionalization of CNTs. A TEM image of IL functionalized carbon nanotubes is shown in Fig. 2b. By considering that purification of MWCNTs leads to the removal of impurities, such as amorphous carbon and traces of metal catalysts, it is expected that as a result of functionalization according to the scheme, depicted in Fig. 1, IL has been successfully grafted onto the surface of carbon nanotubes. It is also worth mentioning that the average diameter of IL functionalized carbon nanotubes has increased by ca 5% in respect to non-functionalized CNTs. As demonstrated in Fig. 2c, introduction of IL-f-MWCNTs ensures regular distribution of the nanofiller within the polymer matrix. Good adhesion between the ingredients is also observed, which is a prerequisite for effective reinforcement of the polymer matrices by IL-f-MWCNTs.

The effect of MWCNTs and IL-f-MWCNTs on the mechanical properties of the investigated EOC17 nanocomposites is shown in Fig. 3. As one can see, the modulus of elasticity E and ultimate strength at break σ_b increase but ultimate deformation ε_b decreases along with rising the content of either type of nanofiller in the polymer matrix. Thus E and σ_b increase up to 2.2 and 1.9 times, respectively, concomitant with ε_b decrease 5 times. It is worth mentioning that at the maximum nanofiller content ultimate tensile characteristics of EOC17 nanocomposites with IL-f-MWCNTs prevail over those characteristic for the nanocomposites with unmodified MWCNTs by 1.9 times and 3.6 times in the cases of σ_b and ε_b, respectively. In Fig. 3 changes of E, σ_b, and ε_b as functions of carbon nanofiller weight content are shown also at an elevated temperature. Although

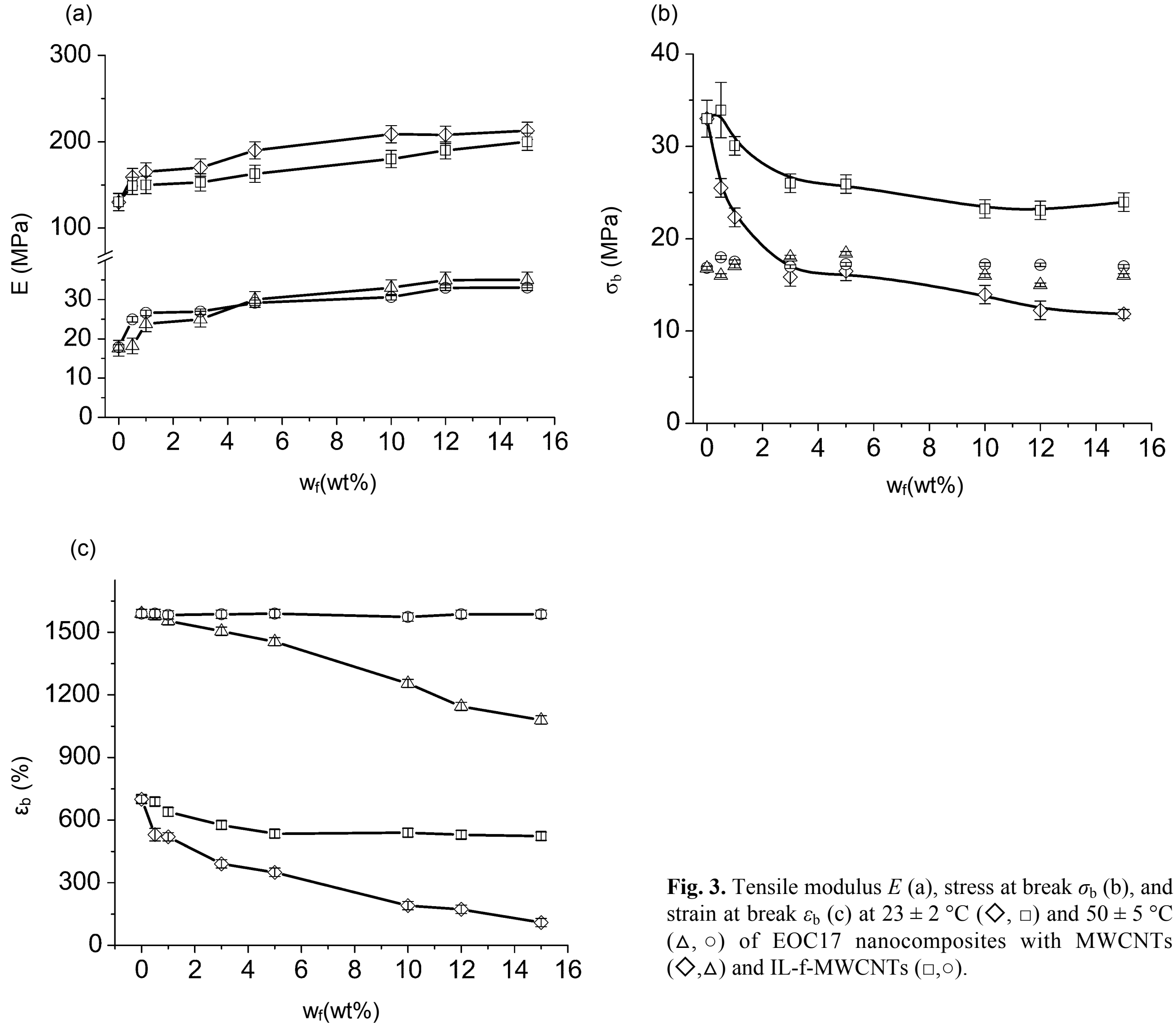

Fig. 3. Tensile modulus *E* (a), stress at break σ_b (b), and strain at break ε_b (c) at 23 ± 2 °C (◇, □) and 50 ± 5 °C (△, ○) of EOC17 nanocomposites with MWCNTs (◇,△) and IL-f-MWCNTs (□,○).

the absolute values of the above-mentioned stress–strain characteristics are lower, in general the same trends in $E(w_f)$, $\sigma_b(w_f)$, and $\varepsilon_b(w_f)$ relationships are observed as in the case of room temperature experiments, i.e. IL-f-MWCNTs modified systems demonstrate higher σ_b and ε_b but lower *E* than EOC17 nanocomposites with MWCNTs. The improved stress–strain behaviour of IL-f-MWCNTs modified EOC17 nanocomposites is evidently connected with the regular distribution of the nanofiller within the polymer matrix as well as the high interfacial adhesion between the ingredients of the system.

The dynamic mechanical thermal behaviour of the selected EOC17/MWCNT and EOC17/IL-f-MWCNT nanocomposites is depicted in Fig. 4. As demonstrated, modification of the polymer matrix with 10 wt% of the nanofiller causes an increment of the storage modulus in the range between 12% at –100 °C and 80% at +50 °C. Somewhat lower values of *E'* were detected for IL-f-MWCNT modified systems, evidently because of the plasticizing effect of IL. A shift in the relaxation peak of EOC17 towards higher temperatures is also observed along with the rising nanofiller content, testifying about certain interaction between the polymer matrix and nanofiller, most probably leading to an increased stiffness of the nanocomposites in comparison to the neat polymer matrix.

Data on electrical conductivity *σ* of the investigated compositions are demonstrated in Fig. 5. As expected, when a conductive filler is added to the insulative polymer matrix, the electrical conductivity of the system will increase, showing a rapid increment of *σ* at ca 0.5 wt of the carbon nanofiller. At the highest nanofiller content, the electrical conductivity of the investigated systems increased by four orders of magnitude, denoting

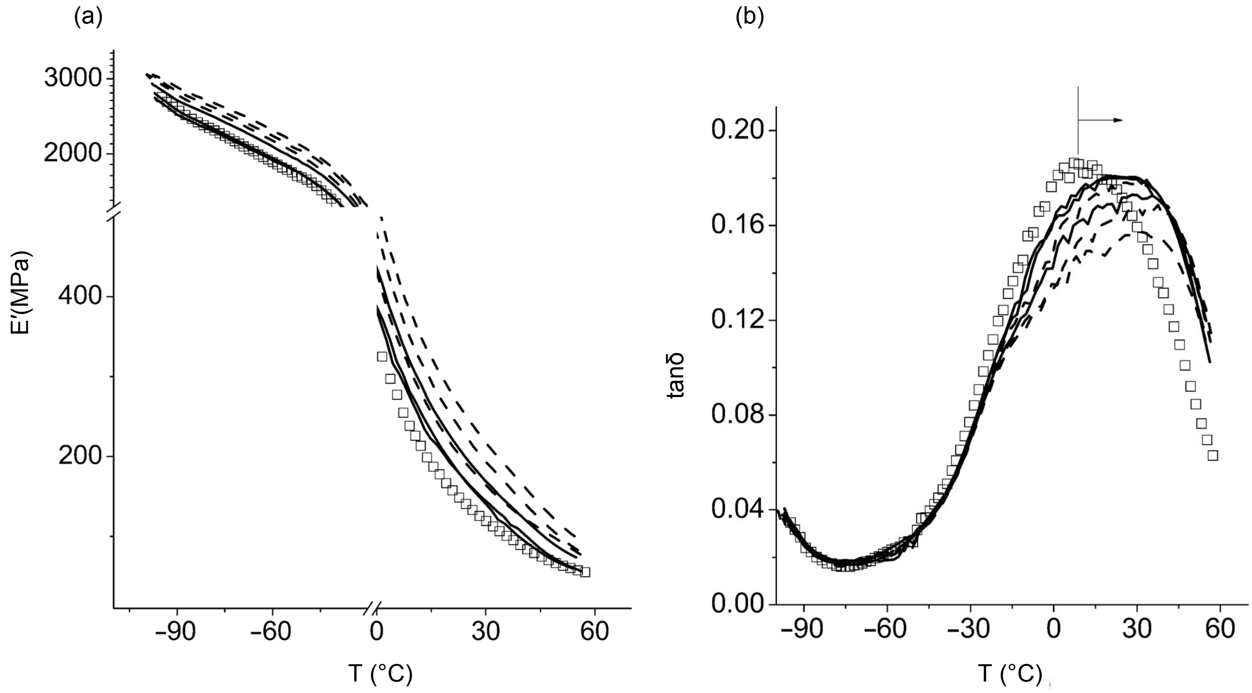

Fig. 4. Storage modulus *E'* (a) and loss tangent tan *δ* (b) of the selected EOC nanocomposites with MWCNTs (dashed lines in the incrementing order of the nanofiller content) and IL-f-MWCNTs (solid lines in the incrementing order of the nanofiller content).

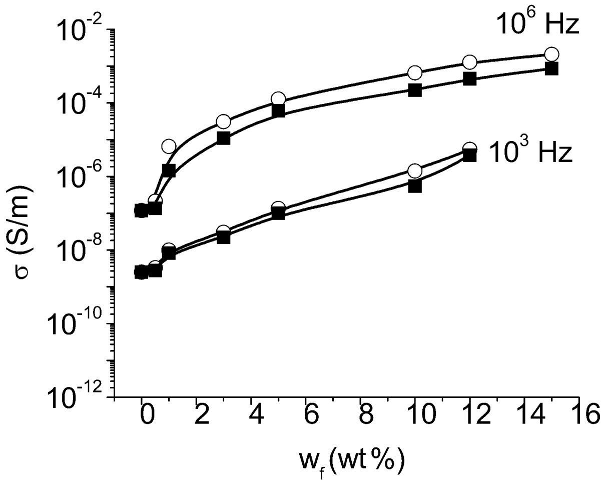

Fig. 5. Electrical conductivity *σ* of EOC composites with MWCNTs (■) and IL-f-MWCNTs (○) as a function of the nanofiller content.

that the percolation threshold was reached due to the development of a network of the electroconductive filler. It is worth mentioning that IL-f-MWCNTs containing systems show somewhat higher *σ* values in comparison to those containing unmodified MWCNTs.

4. CONCLUSIONS

Successful modification of multi-walled carbon nanotubes (MWCNTs) by imidazolium ionic liquid (IL) functional groups was affirmed by Raman spectroscopy and TEM measurements. Introduction of both MWCNTs and IL-f-MWCNTs into the matrix of ethylene–octene copolymer with octene co-monomer content of 17% (EOC) by means of the masterbatch approach allowed increasing the storage modulus (*E'*), tensile modulus (*E*), stress at break (σ_b), and electrical conductivity (*σ*) of the material. In comparison to pristine MWCNTs, modification by means of IL-f-MWCNTs was more efficient in respects to σ_b and *σ*. Besides, the modification of EOC with IL-f-MWCNTs caused a comparatively smaller decrement of strain at break (ε_b) due to a certain plasticizing effect of the functionalized nanofiller.

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Ioonvedelikega funktsionaliseeritud süsiniknanotorudega dopeeritud etüleenokteeni kopolümeerse komposiidi valmistamine ja karakteriseerimine

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Mitmeseinalisi süsiniknanotorusid (MWCNT) modifitseeriti imidasoolium-ioonvedelike (IL) abil. Funktsionaliseeritud nanokompleksi (IL-f-MWCNT-de) struktuuriline karakteriseerimine viidi läbi, kasutades ramanspektroskoopia ja transmissioonelektronmikroskoopia võimalusi. MWCNT-d ja IL-f-MWCNT-d segati etüleenoktaankopolümeeri (EOC), kus okteeni komonomeeride sisaldus oli 17%. Polümeeri maatriksis oleva süsinikku sisaldava nanolisandi jaotuse homogeensust karakteriseeriti skaneeriva elektronmikroskoobi abil. Leiti, et nii MWCNT kui ka IL-f-MWCNT mõjutavad efektiivselt EOC-põhiste nanokomposiitide ajalist vastupidavust, tõmbetugevust, katkevuspiiri ja elektrijuhtivust sõltuvalt nanolisandi sisaldusest. Lisaks tuvastati, et modifitseerimata MWCNT-ga võrreldes oli funktsionaliseeritud IL-f-MWCNT-ga väärindatud EOC maatrikskomposiidi modifitseerimise efektiivsus suurem. Peale selle võimaldab EOC modifitseerimine IL-f-MWCNT-ga tänu funktsionaliseeritud nanolisandile teatud plastifitseeriva toime tõttu suhteliselt väiksemat katkemisristlõike vähenemist (ε_b).