Impact of non-functionalized and ionic liquid modified carbon nanotubes on mechanical and thermal properties of ethylene-octene copolymer nanocomposites

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Abstract. In this article the development and characterization of composites made from metallocene based ethylene-octene copolymer (EOC) with 38 % octene content, non-modified or modified multi walled carbon nanotubes (MWCNTs), covalently functionalised with long chain hexadecyl moiety imidazolium ionic liquid (IL-f-MWCNTs), is presented. The procedure of MWCNTs functionalization is discussed. In order to obtain a good dispersion of the filler, composites with MWCNTs and IL-f-MWCNTs in the concentration range of 0.5-12 wt.% were made by ultrasonication / thermoplastic mixing method. The results indicated improvement in mechanical properties with increase of the filler content. The methodology of the development of EOC matrix nanocomposites with IL-f-MWCNTs showed advantages of the conductive material creation with high mechanical stiffness compared to direct melt mixing of EOC with non-modified MWCNTs. A notable enhancement of thermal stability was observed in case of both pristine MWCNTs and IL-f-MWCNTs containing EOC nanocomposites, which was attributed to scavenging action of the nanofiller. Modification of EOC with IL-f-MWCNTs showed somewhat increased efficiency in enhancing overall thermal stability of the composites because of better dispersion of the nanofiller due to compatibilizing effect of IL modifier.
1. Introduction
In last decade, the studies of conductive nanocomposite development have broadened due to increased functionality of several carbon nanofillers, such as carbon black, single and multi-walled carbon nanotubes (SWCNTs, MWCNTs), graphene and others, dispersed in thermoplastic matrices [1-3]. In last decade, ionic liquids (IL) have been widely applied in functionalization of carbon nanomaterials in order to improve specific properties such as ionic and electric conductivity, thermal and mechanical performance of carbon nanofillers and their composites with polymer materials in order to develop advanced materials in engineering, electronics and other needs. Recently, ILs have shown benefits on modifying composites with carbon nanofillers: ILs have been used as plasticizers, coupling-agents or as compatibilizers [4-6].

Thermoplastic-polyolefin elastomers, such as ethylene-octene copolymers (EOCs) have potential in several applications due to their low costs, good processability, regular structure and variable properties, depending on octene content in matrix. Recently several authors have shown benefits of incorporating of MWCNT filler in EOC matrix with potential to develop conductive materials, as well as electronic and sensor devices [7-8].

The present paper deals with functionalizing MWCNTs with ionic liquid and comparing the developed IL-f-MWCNTs with pristine MWCNTs as fillers on improvement of mechanical and thermal properties of EOC.

2. Experimental
2.1. Materials and reagents
ENGAGE™ 8200 ethylene-octene copolymer (EOC) with 38 % of octene, density 0.870 g cm\(^{-3}\) and melt flow index (MFI) 5.0 dg min\(^{-1}\) (at 190 °C/2.16 kg) was supplied by The Dow Chemical Company. MWCNTs of trademark Baytubes® C150P, produced by acetylene chemical vapour deposition (CVD) method (purity \(\geq 95\%\), average outer diameter 13 nm, average inner diameter 4 nm, length \(> 1\) mm, bulk density 1.3-1.5 g cm\(^{-3}\) ), were supplied by Bayer MaterialScience. Chemical purity grade (>96%) concentrated hydrochloric acid (37%), nitric acid (70%), and sulphuric acid (97%) were purchased from Penta (Chrudim, Czech Republic). Reagent grade methanol and acetone were both obtained from LabScan (Gliwice, Poland). Tetrahydrofuran (\(\geq 99.0\%\)), 1-(3-aminopropyl)imidazole (>97%), 1-bromohexadecane (>97%), sodium bicarbonate, and sodium hexafluorophosphate (99%), all of reagent grade, were purchased from Sigma Aldrich. All reagents were used without purification. High purity water (15 M\(\Omega\) cm\(^{-1}\)), used in MWCNT modification and fabrication of masterbatches, was generated by Millipore Elix 3 (Millipore). Ultrasound bath (Ultrasons 3000837) of 40 Hz, 50 W was purchased from JP Selecta (Poland). Millipore Durapore PVDF membrane filters with pore size 0.1 \(\mu\) 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 derivate to modified MWCNTs was performed on basis of procedure described by Kim et al. [9].
The scheme for MWCNTs functionalization is shown in Figure 1. The procedures for all stages of MWCNTs modification are discussed below.

Prior to functionalization, the filler was purified by sonicating in 6M hydrochloric acid / 6M sulphuric acid solution mixture for 1 h at room temperature. The obtained purified MWCNTs were subsequently washed with deionized water, filtered through membrane filters and dried in air.

Carboxylated MWCNTs (1) were obtained by functionalization of purified MWCNTs (24 g) with reflux in 1:3 v/v a mixture of sulfuric acid (300 mL) and nitric acid (900 mL). Prior to the process, purified MWCNTs (16 g) were sonicated in the mixture of acids solution for 2 h to open agglomerates. Thereafter, homogenized carbon solution was oxidized under reflux at 100 °C for 6 h to introduce functional carboxyl acid groups. At the end of this period, five-fold dilution was applied to the mixture by deionized water to stop oxidation reaction. The carboxylated MWCNTs were consecutively washed with deionized water until pH of the filtrate was approximately 7. The obtained powder was finally dried in vacuum oven at 60 °C, reaching 15.5 g of final product.

The methyl ester functionalized MWCNTs (2) were obtained by stirring the carboxylated MWCNTs (15.5 g) in methanol with catalytic content of sulphuric acid at reflux under nitrogen atmosphere for 48 h. The reaction mixture was diluted, washed 4 times with deionized water and finally washed with acetone and dried under vacuum overnight at 40°C to give 23.4 g of the product.

Imidazolium functionalized MWCNTs (3) were obtained by stirring mixture of the methyl ester-functionalized MWCNTs (20.0 g) and 480 mL of 1-(3-aminopropyl)imidazole in the presence of a few drops of sulphuric acid at 120 °C for 4 days. Obtained solid product was separated by filtration through a membrane filter, washed carefully with anhydrous tetrahydrofuran, followed by 1 M HCl solution, saturated sodium bicarbonate solution, distilled water until the filtrate pH 7.0, and finally with acetone. The obtained solid matter was dried overnight under vacuum at 50°C to give 19.9 g of Im-f-MWCNTs.

Ionic liquid-functionalized MWCNTs (4) were prepared by stirring the mixture of Im-f-MWCNTs (19.0 g) and 1-bromohexyldecane (190 g) at 80 °C for 24 h under nitrogen atmosphere.
The solids were separated by filtration and washed several times with anhydrous THF to remove the excess bromoalkane. The resulting solids were dried under vacuum at room temperature for 24 h to give 19.0 g of the final product.

In order to obtain more hydrophobic filler, the anion exchange was performed to obtain the final product (5) by the following procedure: 19 g of product (4) was stirred with excess of sodium hexafluorophosphate salt (52 g) in deionised water in room temperature for 24 h. Then the solids were filtered, washed with deionized water for several times and dried for 24 h to obtain the final product of the ionic liquid grafted MWCNT with PF$_6^-$ (IL-f-MWCNTs) as anion (19 g), which was further used for master-batch preparation.

2.3. Composite preparation

Master batches of EOC and MWCNTs (either purified MWCNTs or IL-f-MWCNTs) were prepared by the following ultrasonication procedure: firstly, a solution of 2 wt.% EOC (5 g) in toluene was prepared and ultra-sonicated at 50 °C until obtainment of clear solution. Then calculated amounts of MWCNT or IL-f-MWCNT fillers were added to yield master-batches of composites containing 0, 0.5, 1, 3, 5, 10, and 12 wt.% of fillers in the final compositions. The sonication process was carried out in a thermostatic ultrasound bath for 30 min at 50°C, which allowed to obtain stable dispersions without a tendency of EOC precipitation. EOC based master-batches were obtained by pouring carbon nanofiller containing mixtures in acetone at room temperature under continuous sonication for 1 minute in ultrasound bath. As non-solvent of EOC, acetone led to 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 master-batches were melt mixed with additional amounts of EOC by using two-roll mills for a total time 5 min (speeds of the rolls - 20/25 rpm; temperatures of the rolls - 120/170 °C). Then rectangular plates (length × width ×thickness = 60 mm ×50 mm ×0.8 mm) from the compositions were obtained by compression molding at 120°C.

2.4. Methods of characterization

Infrared spectroscopy was used to confirm the production of ionic liquid grafting to MWCNT surface. The tensile behaviour and thermal properties were characterized to evaluate the influence of ionic liquid grafting to filler surface compared to untreated MWCNTs on the improvement of EOC composite properties as dependence of the filler contents.

2.4.1. Infrared spectroscopy

The Fourier transformation infrared spectrometer (FTIR) Nicolet 6700 (Thermo Fisher Scientifics) was used for confirmation of MWCNTs structure changes during the chemical modification (carboxylation, grafting ionic liquid). The filler powders of non-modified and modified MWCNTs were mixed with KBr. The samples were scanned from 4000 to 400 cm$^{-1}$ at a resolution of 4 cm$^{-1}$, 24 scans per sample.

2.4.2. Mechanical properties

Tensile tests of all composite specimens were performed at 23±2 °C on a Tinius Olsen H1KS Universal Testing machine equipped with a 1 kN load cell. The compression moulded rectangular plates were cut into conventional dumbbell test specimens with 5 mm working width and 20 mm gauge length. The specimens were pre-stressed to 0.1 MPa before the start of stretching.
The crosshead speed, used for the determination of elastic modulus, was 10 mm min\(^{-1}\), and 200 mm min\(^{-1}\) for determination of elongation at break and tensile strength.

2.4.3. Thermogravimetric analysis
Thermogravimetric analysis of obtained composites was carried out by using Mettler Toledo TGA-1/SF equipment at temperature range from 25 to 800 °C at a heating speed of 10 °C min\(^{-1}\) under a flow of nitrogen gas. The average sample mass was 10 mg.

3. Results and discussion
3.1. Characterization of MWCNT functionalization
The synthesis scheme of MWCNT modification was successfully realized in order to functionalize the MWCNTs by ionic liquid. The characterization of changes on MWCNT surface was evaluated by the presence of functional group signals in FTIR spectra of pristine MWCNTs and their functionalized derivatives. The average spectra of pristine MWCNTs, the carboxylated MWCNTs and the final product of MWCNTs grafted with ionic liquid are described in Figure 2. The broad band at 3416 cm\(^{-1}\) for neat MWCNTs is attributed to stretching vibrations of isolated surface –OH moieties, and absorbed water. In Figure 2c the IR spectrum of IL-f-MWCNTs shows a typical broad doublet of amide -NH moieties at 3400-3500 cm\(^{-1}\) range. In all IR spectra the characteristic bands of MWCNTs are shown of C-H covalent and non-covalent vibrations at 3008-2807 cm\(^{-1}\) range as well as the bands of C-C backbone at 1586 cm\(^{-1}\) and at 1460 cm\(^{-1}\) \[10\]. The bands of C-H vibrations for IL functionalized composites become more intense due to the hexadecane moieties of IL. The intensive bands in the 1750–1550 cm\(^{-1}\) range can be assigned to carboxyl groups \[10-11\]. The appearance of band at 1739 cm\(^{-1}\) for carboxylated MWCNTs indicate the oxidation of filler, where the carboxyl group for IL-f-MWCNTs shifts to 1724 cm\(^{-1}\) due to the formation of amide group. The overlapped intensive bands at 1621 and 1590 cm\(^{-1}\) due to C=N moieties of imidazolium and amide groups of linkers confirm the formation of IL-f-MWCNTs \[10-11\]. The backbone band at 822 cm\(^{-1}\) is attributed to imidazolium C-N bounds overlapped with peak of PF\(_6^-\) anion vibrations that also confirm the ionic liquid groups in the filler.

Figure 2. FTIR spectra of neat purified MWCNTs (a), carboxylated MWCNTs (b) and IL-f-MWCNTs (c).
3.2. Stress-strain behavior of composites

The effect of the different MWCNT fillers on the elastic modulus of EOC is plotted in Figure 3. In case of both pristine MWCNTs and IL-f-MWCNTs, the modulus increases steadily with increase of the filler contents until 5 wt.%. The further increase of filler contents from 10 to 12 wt.% show less pronounced growth of modulus, most probably due to fillers agglomeration. As expected, the moduli of EOC composites with ionic liquid grafted MWCNTs are higher compared to pristine MWCNTs containing systems. For example, the modulus increases by 131% to 195%, with increase of pristine MWCNT content up to 3 wt.% and 12 wt.% in comparison to neat EOC, whereas in case of IL-f-MWCNTs the increments reach 152% and 208% at the same filler contents.

Ultimate stress-strain characteristics of the investigated EOC based compositions are plotted in Figures 4 and 5.

For composites with pristine MWCNTs the dependence of tensile strength, as well as the deformation at break, show a tendency of decrease with increase of the filler content. Insufficient dispersion and possible defect formation in EOC matrix affect the decrease of tensile strength, especially, in case of pristine MWCNTs. However, ultimate stress and strain values of IL-f-MWCNTs containing composites are constantly by 1.2 times higher if compared to the EOC composites with pristine MWCNTs.
3.3. Thermogravimetric analysis
Degradation of neat EOC and the composites with pristine MWCNTs and ionic liquid functionalized filler were analyzed under inert atmosphere. As MWCNTs possess an antioxidant effect, the increase of thermal stability was predicted with increase of the filler content. It is known that MWCNTs act as radical scavengers within the thermally induced decomposition of EOC chains by breakage of C-H bounds and formation of alkyl and other radicals [12]. In order to investigate the influence of the filler content on EOC composite thermal properties, the values of decomposition temperatures of 10 % mass loss ($T_{\text{ons}}$) as well as the values of decomposition temperatures, at which the greatest mass loss ($T_{\text{max}}$) of the respective decomposition events occur, were obtained from the first derivatives of thermogravimetric curves. The results, compared in Table 1, indicate an increase of $T_{\text{ons}}$ (by 21 $^\circ$C) with increase of filler content from 0 to 3 wt% for EOC compositions with pristine and IL-f-MWCNTs.

| ONC (wt.%) | EOC/MWCNT | EOC/IL-f-MWCNT | EOC/IL-f-MWCNT |
|-----------|------------|----------------|----------------|
|           | $T_{\text{ons}}$ ($^\circ$C) | $T_{\text{max}}$ ($^\circ$C)* | $T_{\text{ons}}$ ($^\circ$C) | $T_{\text{max}}$ ($^\circ$C)* |
| 0         | 404        | 467            | 404            | 467            |
| 0.5       | 405        | 469            | 404            | 467/697        |
| 1         | 407        | 472            | 408            | 466/701        |
| 3         | 425        | 476/620        | 424            | 473/736        |
| 5         | 424        | 481/618        | 422            | 472/743        |
| 10        | 423        | 482/618        | 407            | 462/636        |
| 12        | 407        | 477/618        | 374            | 447/642        |

*value after slash characterizes $T_{\text{max}}$ of secondary minor decomposition event

However, the partial agglomeration of MWCNTs at higher weight contents evidently influence a decrease of $T_{\text{ons}}$ for both compositions. The main $T_{\text{max}}$ value also increases in case of both non-modified MWCNTs and IL-f-MWCNTs containing systems. However, higher values of main $T_{\text{max}}$ is constantly observed for the composites with non-modified MWCNTs, reaching maximum 482 $^\circ$C at filler content 10 wt.%, which is by 14 $^\circ$C higher temperature than that of neat EOC. $T_{\text{max}}$ of secondary peaks are notably higher and emerge at lower filler contents in case of IL-f-MWCNTs in comparison to EOC composites with pristine MWCNTs. That may be attributed to better dispersion of IL-f-MWCNTs due to compatibilizing effect of IL modifier.

4. Conclusions
In the presented studies, commercial MWCNTs were carboxylated and successfully functionalized by grafting surface active imidazolium ionic liquid (IL) with hexadecyl moieties and hydrophobic hexafluorophosphate anion in order to enhance the dispersion of nanofiller in the matrix of ethylene-octene copolymer (EOC). Master-batches of IL-functionalized MWCNTs and EOC were successfully created through the solution casting method followed by melt mixing them into polymer matrix. EOC composites with the content of either MWCNT or MWCNT-IL fillers in the range 0.5-12 wt.% were developed and their mechanical and thermal properties were compared. The results of analysis showed an increase of mechanical stiffness and thermal stability of EOC composites with both types of nanofillers. IL modified MWCNT-EOC composites due to enhanced
interaction of nanofiller particles with polymer matrix showed somewhat improved mechanical and thermal characteristics in comparison to neat MWCNTs containing systems.

5. References

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