Characterization of electron beam cross-linked ethylene–octene copolymer composites with carbon nanotubes

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Received 17 May 2017, revised 29 June 2017, accepted 13 July 2017, available online 30 October 2017

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Abstract. The effect of radiation cross-linking on the properties of Engage® 8200 ethylene–octene copolymer (EOC) with multi-walled carbon nanotube (CNT) nanocomposites was evaluated. An ultra-sound assisted technique combined with thermoplastic mixing was used to make EOC/CNT composites with a wide ratio of CNT concentrations (0 to 15 wt%). Composite films were irradiated by 5 MeV accelerated electrons at relatively high doses (150 and 300 kGy), and their structure and mechanical and dielectric properties were compared. Gel fraction measurements indicated dominant cross-linking of EOC with the rise of the absorbed dose. Cross-linking as well as chain scission of macromolecules in the presence of CNTs caused a certain change in mechanical properties. Dielectric measurements indicated a decrease in ac conductivity and a change in dielectric permittivity, mainly associated with prevented charge movements between CNTs incorporated in the spatially cross-linked macromolecular structure of EOC compared to that of unirradiated EOC/CNT composites.

Key words: ionizing radiation, ethylene–octene copolymer, carbon nanotubes, mechanical and thermal properties, dielectric characteristics.

1. INTRODUCTION

Studies of the effects of ionizing radiation (gamma rays, accelerated electrons, and even neutrons) on nanocomposites reinforced with carbon nanotubes (CNTs) and graphene affecting high strength and stiffness, thermal and electrical conductivities have expanded in the last decade due to the potential use of thermoplastic nanocomposites with carbon nanofillers such as radiation sensors, reinforced elements, or even radiation protection devices [1–3]. Conventional polyolefin based polymers (high and low density polyethylene and ultra-high molecular weight polyethylene) have been recently studied for the development of composites with CNTs due to their low cost, good processability, and cross-linking efficiency. However, the effects of radiation treatment may induce undesired effects of polymers such as chain scission and oxidation [4,5], leading to deterioration of properties and a shorter service life. These may be successfully prevented by carbon nanofillers acting as radical scavengers [6,7]. However, studies of gamma irradiated CNTs have shown a decrease of their scavenging capacity due to radiation-induced defects [8]; thus, studies in this area are of high importance. Improvement of thermal stability and mechanical properties has been also recently detected in polyolefins radiation crosslinked with CNTs [8,9].
Recently much interest has been applied to carbon nanofiller reinforced Engage trademark (Dow) ethylene–octene copolymers (EOCs), made by selective catalysts causing regular distribution of 1-octene comonomers, and leading to good dispersion of CNTs in their matrices of thermoplastic elastomer behaviour [10]. Such composites have shown applications in gas and vapour separation [11] as well as force sensors due to conductive pathways in elastic matrices depending on their comonomer content [12,13]. The toughening effect to improve the durability of other polymers has been also determined for EOCs in CNT nanocomposites with other polymers [14]. Compared to polyethylenes, EOCs have enhanced macromolecular cross-linking due to their high content of tertiary radicals formed within irradiation as well established by several authors [15,16].

Considering the increasing interest in radiation treatment on cross-linkable conductive thermoplastic composites, the effect of CNT nanofillers on the structure and physico-chemical characteristics of electron beam cross-linked EOCs is evaluated in this paper. The goal of the study was to investigate the potential impact of CNT filler particles on the mechanical and dielectric properties of EOC/CNT films irradiated at high doses (150 and 300 kGy). In order to achieve good CNT dispersion in the EOC matrix, an ultrasound assisted procedure was used to prepare masterbatches followed by thermoplastic mixing to make the final EOC/CNT composites with a wide ratio of CNT filler concentrations. To our best knowledge, the effect of the electron beam irradiation on the dielectric properties of EOC/CNT composites has not been previously evaluated.

2. MATERIALS AND METHODS

2.1. Materials used

Ethylene–octene copolymer of Engage® 8200 trademark with octene content 38 wt% (density 0.870 g/cm³, melt flow index 5.0 dg/min at 190 °C/2.16 kg) was supplied by the Dow Chemicals Company (Midland, Michigan, USA). Agglomerated multi-walled CNTs of Baytubes® C150P trademark with the mean outer diameter 13 nm, median inner diameter 4 nm, length >1 μm, and bulk density 1.3–1.5 g/cm³ were supplied by Bayer AG (Leverkusen, Germany). Reagent grade acetone and toluene were purchased from LabScan – POCH S.A. (Gliwice, Poland). Anhydrous o-xylene supplied by Sigma Aldrich was used for gel content measurements. All the reagents were used without further purification. Medium grade paper filters were used for the filtration of EOC/CNT masterbatches.

2.2. Composite preparation

The EOC–multi-walled CNT (MWCNT) composite film specimens were created as follows: first, the EOC pellets were fully dissolved at 50 °C in 200–300 mL of toluene by a mechanical stirrer (Heidolph RZR 2051, Schwabach, Germany) followed by the addition of calculated amounts of MWCNTs. The obtained mixtures of EOC and CNTs in toluene were sonicated for 30 min in a thermostatic ultrasound bath (Ultrasons 300837, JP Selecta, Poland) until stable dispersions were obtained; these were precipitated in acetone under continuous sonication to yield masterbatches of composites. The obtained masterbatches were recovered by vacuum filtration and dried in a vacuum oven at 40 °C, followed by thermoplastic mixing with the addition of an EOC matrix by the roll-forming at 20/25 rpm at 120/170 °C for a total time of 5 min 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 plate films (length × width × thickness = 60 mm × 50 mm × 0.8 mm) of the final filler concentrations of 0, 0.5, 1.0, 3.0, 5.0, 10, 12, and 15 wt% obtained at 120 °C.

2.3. Composite irradiation

A linear particle accelerator ELU-4 (Thoriy Ltd., Russia) of 5.0 MeV electron flux with 0.1 μA/cm² current was used for the irradiation of the samples. The dose rate was 1200 kGy/h. The films were irradiated at ambient temperature by accelerated electrons until the absorbed doses of 150 and 300 kGy were reached.

2.4. Methods of characterization

The gel content of the radiation cross-linked composites was determined by the extraction of the sol fraction in boiling xylene for 24 h using a soxhlet apparatus. The gel content was calculated as a ratio of the final weight to the initial weight of the sample multiplied by 100. The average measurements were obtained from three replicates.

The tensile stress–strain behaviour of the nano-composite dumbbell shaped specimens (width of the working zone 5 mm; gauge length 20 mm), mechanically cut from the compression moulded plates, was studied at 23 °C. The tests at room temperature were performed by using a universal testing machine H1KS (Tinius Olsen TMC) equipped with a 1 kN load cell. The specimens were pre-stressed to 0.1 MPa before the test. The speed of the upper moving clamp was set at 10 mm/min for the determination of Young’s modulus (E) and
200 mm/min for measuring the stress–strain characteristics at break.

The real part of permittivity ($\varepsilon'$) and the real part of ac conductivity ($\sigma$) for unirradiated and radiation cross-linked EOC/CNT disk-shaped test specimens were determined by using a broadband dielectric spectrometer Concept 50 (Novocontrol Technologies GmbH & Co. KG). The measurements were performed at room temperature (+23 °C) in a broad frequency range (from $10^{-2}$ to $10^7$ Hz).

3. MAIN RESULTS

The average measurements of the gel content for irradiated EOC/CNT composites and their EOC fractions calculated from their weight percentages without CNTs are shown in Fig. 1. The study of unirradiated composites revealed a full dissolution of the EOC matrix during the 24 h period of extraction in boiling o-xylene. Only the presence of CNT remains, increased with their concentration in composites, was detected for the unirradiated CNTs. The values of the gel content for the irradiated pristine EOC increased from 61% to 82% with the rise of irradiation absorbed dose from 150 kGy to 300 kGy. These results are in accordance with the findings of Perraud et al. [17]. The gel content for EOC 8200 reported by Svoboda et al. reached 80% already at 60 kGy dose due to the more effective re-circulated flux of accelerated electrons generated by the toroidal linear accelerator of 10 MeV energy [18]. The lower values could also be due to the lower wt% of the EOC matrix used in the study.

The gel content of the irradiated EOC/CNT composites increased with the CNT concentration. Thus, we recalculated the gel contents attributed to EOC weight contents, which indicated almost no effect of CNTs at 150 kGy dose compared to the pristine EOC. After the dose of 300 kGy was applied, the gel content increased from 80% to 85% at CNT contents reaching 0.5–1% and later decreased up to levels slightly below 80%. The results indicate a slight prevention of chain cross-linking and scission due to the CNTs incorporated in the EOC matrix.

The results of the investigation of tensile stress–strain properties showed the influence of radiation cross-linking compared to those of the unirradiated EOC/CNT specimens (Fig. 2).

However, the processing method may have influenced the aggregation of CNTs in the EOC matrix due to sonication and the low shear rate during the roll-milling procedure compared to the results reported in similar studies [11]. This effect is more obvious for unirradiated blends with the increase of the CNT concentration above 5 wt% causing some agglomeration indicated by a decrease of the elongation at break and the tensile strength below the values of that of the pristine EOC.

As one can see, the modulus of elasticity $E$ increases with the rising content of nanofillers of both types in the polymer matrix for unirradiated as well as radiation cross-linked composites. Thus, the increase of $E$ at 15 wt% content of CNTs for unirradiated and radiation cross-linked composites is respectively up to 2.6 and 2.3 times as high as for the pristine EOC. The effect of radiation cross-linking on the modulus was mostly notable for the pristine EOC, where after the irradiation up to 150 and 300 kGy the value increased by 34% and 43%, respectively. The cross-linking showed a low effect on $E$ for nanocomposites by only 10% to 20% improvement compared to that of unirradiated composites. This may be due to radiation induced defects in CNTs as a result of the radiation treatment. The low effect of radiation on Young’s modulus should be attributed to the low crystallinity of EOC 8200 (19% for the pristine EOC according to a previous study [18]).

The change of tensile properties at break was more pronounced after the radiation treatment (Fig. 2b and 2c). The elongation at break showed a definite decrease with the rise of the CNT content and the increase of the dose of irradiation. The study for unirradiated composites showed a rapid decrease of the elongation due to the agglomeration effect, especially at the CNT content over 10 wt%. We compared the results for the pristine EOC with those reported by Perraud et al. at 150–300 kGy doses [17] and found a full coincidence, which can be attributed to the prevention of chain mobility caused by the increased gel content. The decrease of the elongation at break was attributed to the reduced chain mobility of the spatial cross-linked structure of EOC and the reinforcing effect of the MWCNT filler. Yang et al. reported
a similar effect in the study of low-density polyethylene composites with CNTs [9]. At a CNT content of 5 wt%, the values of elongation decreased 1.3, 1.6, and 2.7 times compared to unirradiated composites and those irradiated up to 150 and 300 kGy, respectively. While reducing the movement of chains, the cross-linking caused a higher stress at a given strain value with an increase of the irradiation dose due to the cross-linking of macromolecular chains.

Dielectric constants (the real part of permittivity) of the investigated compositions are demonstrated in Fig. 3. Based on results of the study of mechanical properties, we predicted a reduced polarization effect for the radiation cross-linked EOC and its composites with CNTs [5]. It was found that at low filler contents (up to 5 wt%) the real part of permittivity decreased with the rise of the irradiation dose up to 300 kGy.

A decrease of the real part of permittivity with the rise of irradiation contributes to the prevention of charge movements between molecules in the case of a cross-
linked structure, as observed also in a recent study [19]. It could be predicted that partial cross-linking at the 150 kGy dose may not lead to the prevention of CNT interconnections and partial polarity raised by induced radical defects due to the irradiation of samples in the air atmosphere [5]. A slight increase of the real part of permittivity at an elevated CNT content influenced the dielectric behaviour due to partial interconnections between agglomerated CNTs at filler contents higher than 5 wt%, noted also indirectly in the study of mechanical properties.

The effects of irradiation and the content of the filler on the ac conductivity are compared in Fig. 4. As expected, the rise in the concentration of the conductive filler caused an increase of the unirradiated composite system. At the highest nanofiller content, the electrical conductivity of the unirradiated EOC/CNT systems was increased by 3 orders of magnitude (the value of conductivity was $1.5 \times 10^{-4}$ S/m for unirradiated EOC/CNT with 15 wt% content of CNT), indicating that the percolation threshold had been reached due to the development of a network of the conductive filler. As shown in Fig. 4, the conductivity had a threshold at 1 wt% of CNT for the composite irradiated by 150 kGy due to a potential interaction of CNTs at the partially cross-linked matrix. This may be the reason for the slight increase of conductivity at CNT contents of 0.5–5.0 wt%. However, the increase of the CNT content over 5 wt% resulted in a decrease of conductivity to the level near to that of unirradiated composites due to the potential agglomeration of CNTs. The values of conductivity of EOC/CNT decreased notably at 300 kGy with the increase of the irradiation dose due to the reduced CNT interconnection with the rise of macromolecular cross-linking and production of defects in the CNT structure due to a potential effect of chain scission compared to the results for unirradiated EOC/CNT.

4. CONCLUSIONS

Predomination of radiation cross-linking of EOC composites with multi-walled carbon nanotubes was confirmed by gel fraction measurements. Introduction of CNTs into the matrix of EOC by applying the masterbatch approach made it possible to increase Young’s modulus ($E$), stress at break ($\sigma_b$), and electrical conductivity ($\sigma$) of the material. The effect of radiation cross-linking caused a slight increase of the elastic modulus and a notable reduction in the chain mobility of the spatial cross-linked structure due to the reinforcing effect of the CNT filler. A notable effect of radiation cross-linking was found in the case of increased cross-linking efficiency: a decrease of the real part of permittivity and conductivity with the increase of the radiation dose was observed, contributed to prevented charge movements between molecules due to radiation induced defects during irradiation. Further studies are essential at lower doses to determine the effect more properly as this study showed a slight increase of conductivity at 150 kGy and a notable reduction due to concurring chain cross-linking and scission effects at 300 kGy.

ACKNOWLEDGEMENTS

Financial support from the Latvian National Research Program “Multifunctional Materials and Composites, Photonics and Nanotechnology (IMIS2)” is acknowledged. The publication costs of this article were covered by the Estonian Academy of Sciences.

REFERENCES

Elektronikirega ristsidestatud etüleen-okteeni kopolümeer ja süsiniknanotorude komposition iseloomustamine

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On iseloomustatud kiirguse toimel tekkinud ristsidestatud Engage® 8200 etüleen-okteeni kopolümeeri (EOC) ja nimetsealineist süsiniknanotorudega (CNT) doperitud komposiidit omadusi. EOC/CNT kompositiite valmistamiseks, kus CNT kontsentreeriti varieeriti suures ulatuses (0–15 massprotsenti), kasutati ultrahelga kombineeritud terampilistil segamoodulvit. Komposiitkaaliteki kiirgusest 5 MeV elektronidega suhteliselt suuret doosidega (150 ja 300 kGy) ning analüüsiti kiirgusest mõju nende stрукutuurile ja mehaaniliste ning dielektriliste omadustele. CNT lisamine etüleen-okteeni kopolümeerile maatriksisse võimaldab see nende struktuuri ja mehaaniliste ning dielektriliste omadustele.