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1st International Electronic Conference on Materials
26 May - 10 June 2014

http://sciforum.net/conference/ecm-1

Proceedings Paper

Improvement of Carbon Nanotubes Dispersivity in Poly(Styrene/Methacrylate) Composites by Chemical Functionalization

Fabio Faraguna, Elvira Vidović * and Ante Jukić

University of Zagreb - Faculty of Chemical Engineering and Technology, Marulićev trg 19, HR-10000 Zagreb; ffaragun@fkit.hr; evidov@fkit.hr; ajukic@fkit.hr

* Author to whom correspondence should be addressed; E-Mail: evidov@fkit.hr;
Tel.: +385-1-45 97 128; Fax: +385-1-45 97 142.

Received:18 April 2014 / Accepted: 23 May 2014 / Published: 27 May 2014

Abstract: In this work the composite materials of improved properties based on styrene and methacrylate (co)polymers with differently functionalized multiwalled carbon nanotubes (CNT) were prepared. In order to obtain a fine dispersion and to enhance the interfacial interaction of CNT with surrounding polimer matrix a chemical modification of the surface of carbon nanotubes was performed. Functionalization of CNTs was confirmed by FTIR, Raman and X-ray photoelectron spectroscopy as well as by contact angle method. Dodecyl and ethylbenzene ester modified carbon nanotubes showed contact angle for water 150 and 141 degrees, while the oxidized and methyl ester modified CNT displayed seepage. Dispersibility of all modified carbon nanotubes in methanol and toluene was quantified by UV-Vis spectroscopy and differs considerably in both solvents for all systems, due to the significant change in chemistry of surface of CNTs. Mixtures of styrene/methacrylate monomer with 1 wt % of CNT in toluene were reacted in a radical in-situ polymerization reaction. The synthesized composites were characterized by the SEC, TGA, DMA, SEM. The improvement of the properties of polymer/CNT composite can be attributed to better interaction between nanotubes and the polymer matrix.

Keywords: carbon nanotubes; functionalization; dispersivity; polymer composites

1. Introduction

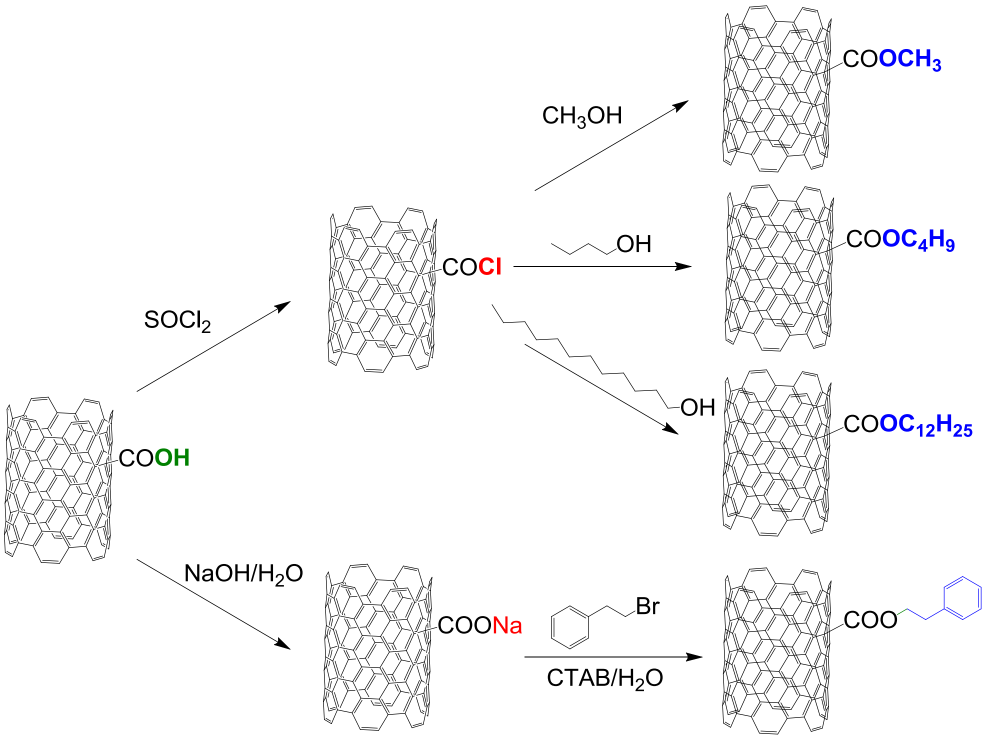
In order to obtain a fine dispersion and enhance the interfacial interaction of CNT with surrounding polymer matrix a chemical modification of the surface of carbon nanotubes was performed. Various types of functionalized multiwall carbon nanotubes were used: oxidized (CNT-COOH) and their ester analogues (methyl, butyl, dodecyl and ethylbenzene). The reaction of covalent functionalization of CNT-COOH with NaOH and further with (2-bromethyl)-benzene and hexadecyl-trimethylammonium bromide into CNT-COOEtBz was successfully performed. Also, oxidized multiwall carbon nanotubes were reacted with thionyl chloride and further in esterification reaction with given alcohols transformed into corresponding methyl or n-dodecyl ester.

2. Results and Discussion

2.1. Carbon Nanotubes Chemical Functionalization and Characterization

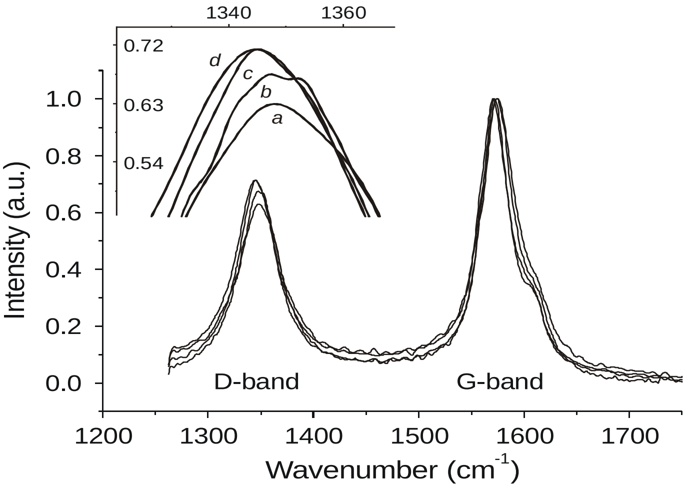
In order to influence their dispersivity in styrene and methacrylate (co)polymer matrices the oxidized multiwalled carbon nanotubes were modified with various functional groups (Fig. 1)[1,2].

Figure 1. Functionalization of CNT-COOH with **(i)** $SOCl_2$ and further reaction with methanol, butanol and dodecanol, **(ii)** NaOH and further functionalization with (2-bromoethyl)benzene into CNT-COOEtBz descriptive label of the figure here.



Functionalization of CNTs was confirmed by FTIR, Raman and X-ray photoelectron spectroscopy as well as by contact angle measurements. The change of the disorder extent due to modification of CNT was determined by Raman spectroscopy by fallowing two specific bands: D band around 1345 cm^{-1} (disorder-induced modes, vibration of sp^3-bonded carbon atoms at the defects) and G band around 1570 cm^{-1} (in-plane stretching tangential mode, vibration of sp^2-bonded carbon atoms). The intensity increase of D-band in normalized Raman spectra of methyl-, butyl- and dodecyl-ester functionalized CNT, in comparison to oxidized CNT is shown in Fig. 2.

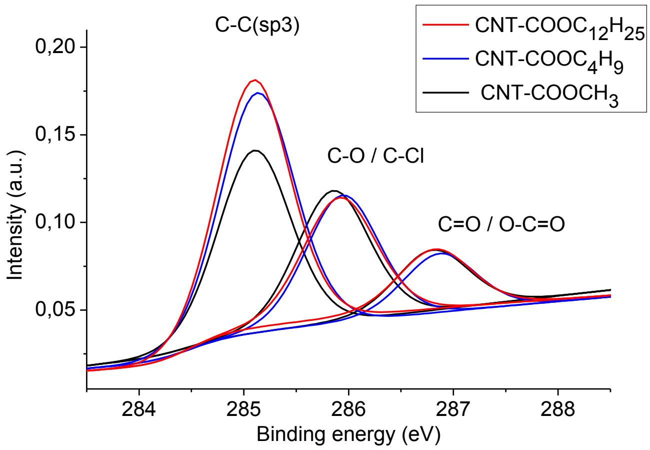
Figure 2. Part of normalized Raman spectra showing changes in D-band caused by different functional groups COOR attached to CNT; R = H **(a)**, CH_3 **(b)**, C_4H_9 **(c)** and $C_{12}H_{25}$ **(d)** and ntensity ratio of D – and G – band for different CNT.



Type of CNT	I_D / I_G ratio
CNT-COOH	0.629
CNT-COCl	0.600
CNT-$COOCH_3$	0.675
CNT-$COOC_4H_9$	0.713
CNT-$COOC_{12}H_{25}$	0.714

X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical state and electronic state of the elements at the surface of CNTs, in its "as received" oxidized state, intermediate chloride state (1st reaction step) and after functionalization by esterification reaction (2nd reaction step). Carbon and oxygen peaks are present in all functionalized CNTs, but two chlorine peaks, at 200 eV and 270 eV, are only present in CNT-COCl. It is clear evidence that in first reaction step hydroxyl (-OH) group is replaced with chlorine (Cl), which is in the second reaction step entirely replaced by corresponding O-alkyl group. During further examination, deconvolution of C1S peak were performed by using four contributors three of which are common to all CNT, C-C (sp^2) peak at 285.5 eV, C-C (sp^3) peak at 285.1 eV and C=O/O-C=O peak at 286.9 eV. The fourth at binding energy of 286.1 eV corresponds to C-O and/or C-Cl bond. The intensity of C-C (sp^3) signal increases with the increase of the length of the alkyl group (Fig. 3) while the intensity of other signals remains the same. The surface wettability of modified CNTs was quantified by contact angle measurements with water droplets whereas it was found that it changes from 0 ° in CNT-COOH and CNT-$COOCH_3$ to 150.6 ° in CNT-$COOC_{12}H_{25}$. Chemical functionalization of carbon nanotubes influences their dispersibility in solvents, which can be used to indicate other important properties such as manipulation by various processes (mixing, blending, ultrasonic dispersing). Subsequent investigation of nanotubes dispersed using ultrasonic bath during 2 hours in polar methanol and non-polar toluene was performed, where the dispersibility was measured by a UV-Vis spectrophotometer. The quality of dispersion is expressed with the dispersibility index, which has shown a good match between the nature of solvent and functional groups introduced onto CNT. In that way, it indicates indirectly the successfulness of modification[1].

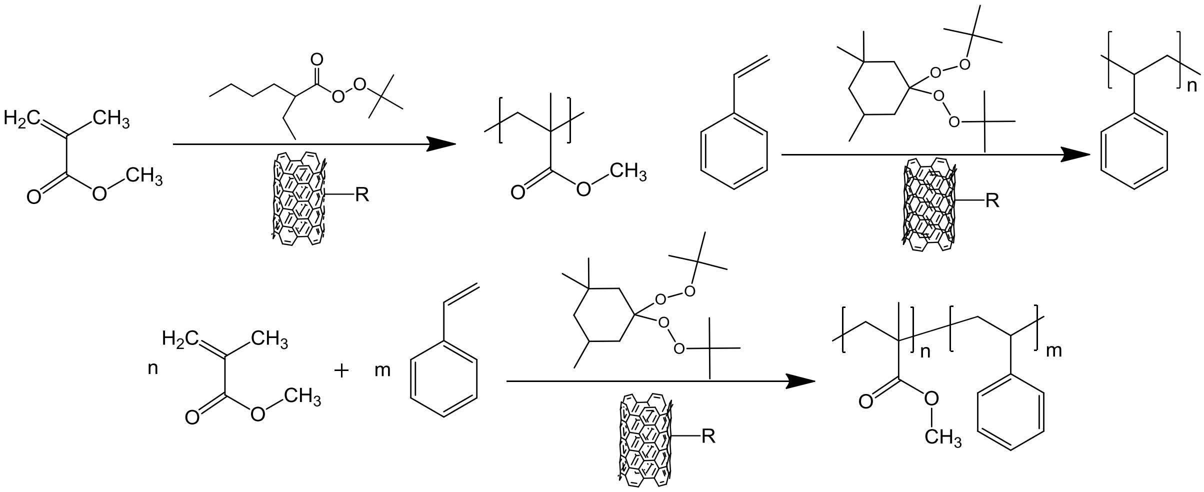
Figure 3. Comparison of intensities of deconvoluted XPS peak of C_{1S} in CNT-$COOCH_3$, CNT-$COOC_4H_9$ and CNT-$COOC_{12}H_{25}$.



2.2. Polymer Nanocomposites Synthesis and Characterization

Mixtures of monomers of styrene, methacrylate or both (ST/MMA = 90/10 mol %) with 1 wt % of modified CNT in toluene were reacted in a radical in-situ polymerization reaction (Fig. 4).

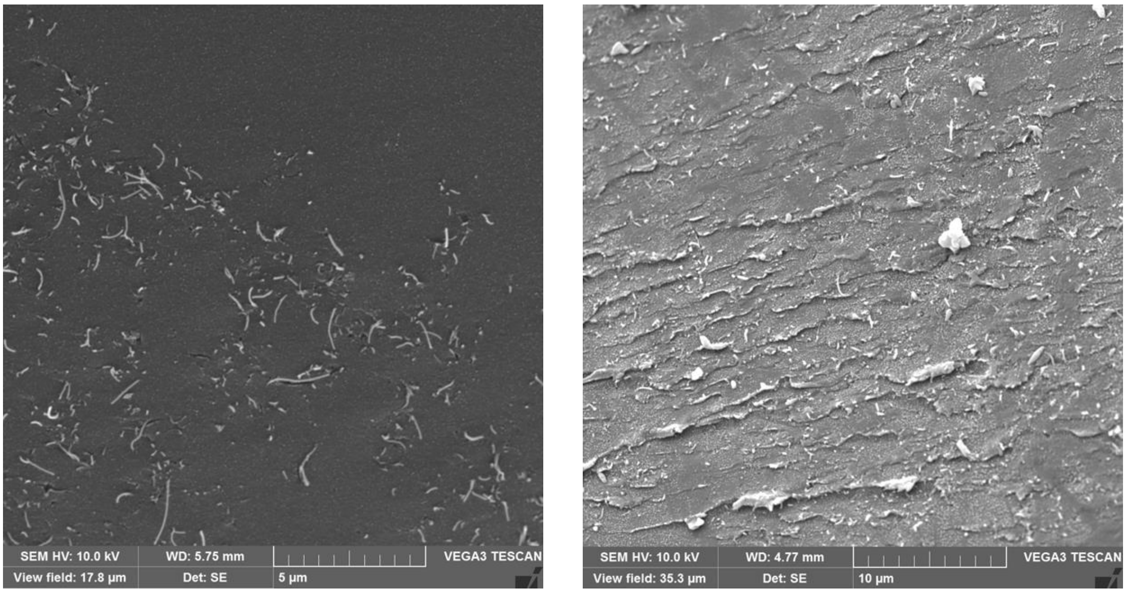
Figure 4. In situ radical polymerization reaction of styrene and methyl methacrylate homopolymers and their copolymer (ST/MMA = 90/10 mol %) nanocomposites with various functionalized multiwalled carbon nanotubes.



The synthesized composites were characterized by the Size Exclusion Chromatography (SEC), Thermogravimetric Analysis (TGA), Dynamic Mechanical Analysis (DMA) and Scanning Electron Microscopy (SEM). The improvement of the properties of the (co)polymer/CNT composite can be attributed to better interaction between nanotubes and the polymer matrix. The SEC measurements have shown that in case of polystyrene (PS) composites nanofillers cause the increase of the molecular mass average (M_n) while in case of poly(methyl methacrylate) (PMMA) and poly(styrene-*co*-methyl methacrylate) (PS/MMA) composites the decrease of the M_n is noticed due to added nanofillers. Furthermore, the TGA measurements have revealed that nanofillers do not have any significant influence on the thermal stability of examined composites in the air.

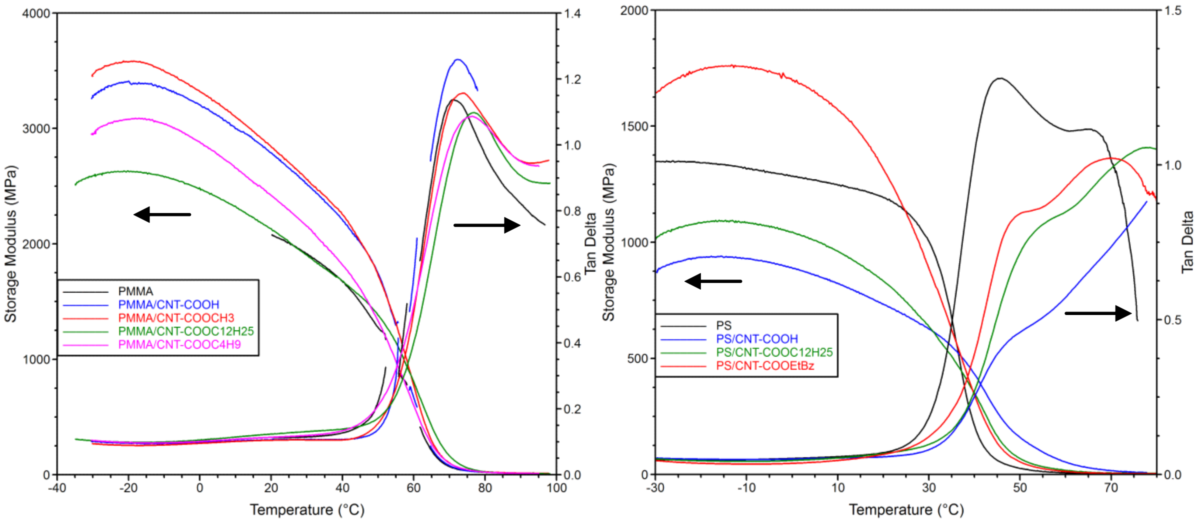
In order to determine the quality of the dispersion and the extent of agglomeration of variously modified nanotubes in polymer matrices SEM images were taken. In case of poly(styrene-*co*-methyl methacrylate) matrix a significant difference regarding the distribution of nanotubes can be seen, which consequently reflects on other properties of the material, as well. As an example, in Fig. 5 a fairly bad distribution with the areas of high and low concentration of nanotubes can be seen in case of 1 wt % CNT-$COOCH_3$, (left) while in case of 1 wt % CNT-COOEtBz (right) a much better homogeneity of nanotubes in poly(styrene-*co*-dodecyl methacrylate) matrix is to be seen. Furthermore, due to bad interactions the former nanotubes are pulled out and can be recognized as a kind of fringe at the site of fracture.

Figure 5. SEM micrographs of poly(styrene-co-dodecyl methacrylate) (ST/MMA = 90/10 mol %) with 1 wt % CNT-$COOCH_3$ (left) and 1 wt % CNT-COOEtBz (right).



In order to estimate the ability of material to store or dissipate energy its DMA analysis was performed. In Fig. 6 the thermograms of homopolymers and their composites measured in a temperature range from -30 °C to 80 °C are shown. In case of PMMA all nanofillers cause the increase of storage modulus (*E*') i.e. higher toughness, elasticity and deformability. However, after comparing with the selected polystyrene composites a big difference in storage modulus (*E*') between the two composites is evident. Thus, PS/CNT-COOEtBz composite shows approximately twice as high storage modulus as PS/CNT-COOH while *E*' modulus of pure PS lies in the middle. In that temperature range CNT-COOEtBz are stronger associated with the polymer matrix due to the similar polarity and possibility of additional π-π interactions between the benzene groups of polystyrene and those on nanotubes, which increases storage modulus. On contrary, the polar COOH groups of oxidized nanotubes display poor interactions with polymer matrix because of different polarity that results in the storage modulus decrease in comparison with pure PS. However, as the temperature rises, these interactions become weaker and consequently the effect of the nanotubes functionalization on the improvement / worsening of storage modulus vanishes.

Figure 6. Storage modulus and angle of phase shift (tan δ) of PMMA with various CNT (left); PS with various CNT (right).



3. Experimental Section

Chemical processes of CNT functionalization, nancomposites synthesis and the characterization methods are described within the *Results and Discussion*, as much as the scope of this work has allowed. For more details, please see the references.

4. Conclusions

A successfully performed modification of oxidized CNT has been proven as a viable mean for the tailoring of properties of styrene and methyl methacrylate (co)polymers based composites.

Conflicts of Interest

The authors declare no conflict of interest.

References and Notes

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