INFLUENCE OF COMPATIBILIZER AND FILLER FUNCTIONALIZATION ON THE NANOMECHANICAL PROPERTIES OF PP/MWCNT AND EPOXY/MWCNT COMPOSITES

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Abstract - In last decades experimental mechanics gained increasing importance in nano materials characterization. Nanoindentation is a new method to characterize material mechanical properties on a very small scale. In this study we investigate structure and nano mechanical properties of two types of nanocomposites – thermosetting (on the base of epoxy resin) and thermoplastic (on the base of polypropylene) filled with multi walled carbon nanotubes. The influence of using of compatibilizer for polypropylene and functio nalization of multiwalled carbon nanotubes in epoxy resin are analyzed in order to obtain better dispersion of multiwalled carbon nanotubes and hence improved nanoindentation hardness and modulus.

Keywords - Polypropylene Nanocomposites, Epoxy Nanocomposites, MWCNT, Nanoindentation.

I. INTRODUCTION

Thermosetting and thermoplastic nanocomposites filled with carbon nanotubes (CNT) are being subjected to enhanced studies as advanced multifunctional materials in view of CNT exceptional physical and mechanical properties in the recent years [1-13].A unique feature of polymer nano composites is that the improved performance is reached at low filler content, resulting in light weight materials [3,5-13]. In order to attain optimal performance of the polymernanocomposites, there are several key issues to be resolved, i.e. improved dispersion of CNT, alignment of CNT in the polymer, and functionalization of the CNT surface for good adhesion. MWCNT are mostly dispersed in small aggregates than in single nanotubesin the polymer. The presence of aggregates decreases the surface areaand disturbs the formation network structure, which is essential to improve mechanical properties; thus, the main task of processing is to disperse such aggregates as much as possible. Therefore, uniform dispersion of the nanotubesis required to realize the potentiality of the nanotubes as reinforcingfillers.

In last decades experimental mechanics gained increasing importance in nanomaterials characterization. Hence, novel methods and experimental techniques havebeen recently proposed for use in micro- and nanomechanical characterization of nano structured materials. Recently, the nanoindentation method has widely been adopted and used in the characterization of mechanical behaviour of materials atsmall scales, so called nanoindentation [4,14,15]. The attractiveness of this method stemslargely from the possibility to determine the mechanical properties directly from indentation load and displacement measurements without the need to image the hardness impression.

In the present paper, we discuss the effect of the influence of compatibilizer in polypropylene/multiwalled carbon nanotubes nanocomposites (PP/MWCNT) and functionalization of nanotubes in epoxy/MWCNT nanocomposites on the dispersion and nano mechanical properties.

II. DETAILS EXPERIMENTAL

2.1. Materials and Methods

The materials used in this study is PP supplied by LukoilNeftochim Co, Bulgaria, as Buplen 6231 with MFI (230/2.16) of 12.2 g/10 min. The master batch of 20 wt% MWCNTs in polypropylene was obtained in pellet form from Hyperion Catalysis International, the United States. Typical outside diameter range of the MWCNTs was from 10 to 15 nm, the lengths between 1 and 10 microns, and density approximately 1.75 g/cm^3. The chemical compatibilizer used was MA-g-PP chains, Licomont AR504, produced by Clariant International Ltd. The composites were produced by melt compounding of the MWCNT/PP masterbatch [6].

Epoxy resin D.E.R.™ 321 (ortho-cresyl glycidyl ether diluted standard bisphenol A based liquid epoxy resin), production of Dow Chemical Company was used as polymer matrix for preparation of epoxy/MWCNT composites. Polyethylene polyamine hardener (PEPA) was used as a curing agent. Multiwall carbon nanotubes (MWCNTs) produced by CVD method, having external diameter ~ 30±10 nm, approximate length 10-20 μm, supplied by IFW Dresden were used as a filler. Two different processing modes were applied for the preparation of nanodispersions. First, the MWCNTs were functionalized with amino groups bypremixing with the amine hardener. Second, the MWCNTs were not functionalized withamine, as premixed directly with the epoxy oligomer [3].

The morphology of the bulk polymer/carbon nanotube composites at micro- and nanoscale was studied by scanning electron microscopy (SEM). Samples were cut in liquid nitrogen and coated with vacuum evaporated chromium.

2.2. Nanoindentation Test

Nanoindentation test was carried out using a Nanoindentation Tester (UNMT) with inline imaging by atomic force microscopy (AFM), produced by Bruker Co. The sample surface was polished by means of Leica RM2245 microtome with stereo microscope Leica A60S and a diamond knife, Leica Microsystems, Germany. The hardness and elastic modulus were calculated from the recorded load-displacement curves using Oliver and Pharr methods [14,15]. The indentation imprints were inline imaged using Q-Scope™ 250/400 AFM (Ambios Technology Inc.). Indenter type Berkovich Diamond with tip radius of 70 nm was used for indentations in force control mode of 5 mN. A series of 48 (4x12; spacing between indents 80 um) nanoindentations were performed for each sample. A typical indentation experiment consists of the subsequent steps: (1) approaching the surface, (2) loading to the peak load of 5 mN for 15 s, (3) holding the indenter at peak load for 10 s, (4) unloading from maximum force of 5 mNto 10% for 15 s, (5) holding at 10% of max force for 15 s, and (6) final complete unloading for 1 s (load function 15s-10s-15s trapezoid).The hold step was included to avoid the influence of the creep on the unloading characteristics since the unloading curve was used to obtain the elastic modulus of the material.Figure 1 shows the AFM image of a print made on 0.5 wt% PP/MWCNT composite with Berkovich nanoindenter at a load of 5 mN. No discontinuities or steps are found on the loading curves, indicating that no cracks have been formed during indentation.

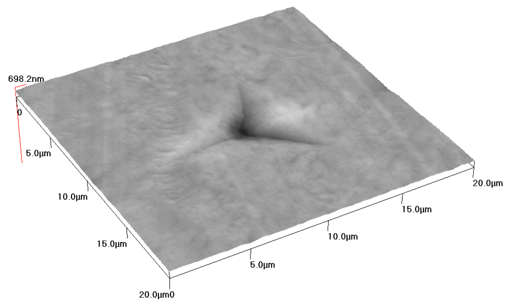

Fig.1. AFM image of a print, made on 0.5 wt% PP/MWCNT composite with Berkovich nanoindenter at a load of 5 mN.

III. RESULTS AND DISCUSSION

3.1. Morphology

Figure 2 presents SEM micrograph of epoxy nanocomposites containing 0.3wt% of amino-functionalized carbon nanotubes. The micrograph shows that amino-functionalized carbon nanotube composites demonstrate good dispersion state in the epoxy matrix.Nanotubes are debundled and bridge the cracks, which is determinant for the fracture mechanism of carbon nanotube composites.

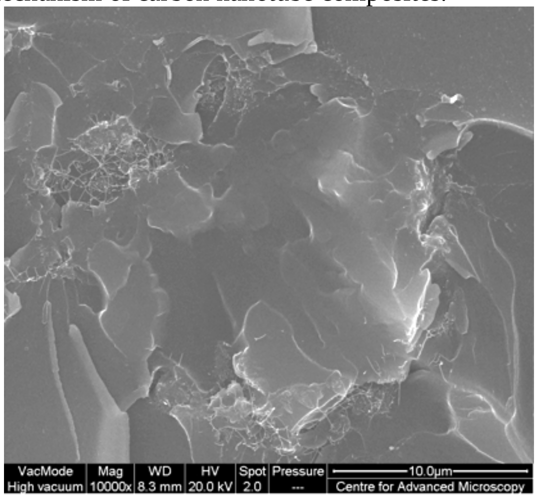

Fig.2. SEM micrograph of epoxy nanocomposites containing0.3wt% of amino-functionalized carbon nanotubes (tests at CfAM, University of Reading, UK).

Figure 3 presents a SEM image 0.5 wt% PP/MWCNT with 5 wt% MA composite. As seen in the Figure the agglomerates of nanotubes arevery small and look not so dense; moreover, individually dispersed nanotubes are visible. Obviously, the addition of 5 MA compatibilazer to the PP/MWCNT composites during processing leads to a better dispersion of masterbatch, and a mixed structure is formed consisting of small agglomerates and debundled individual nanotubes in the matrix of polypropylene.

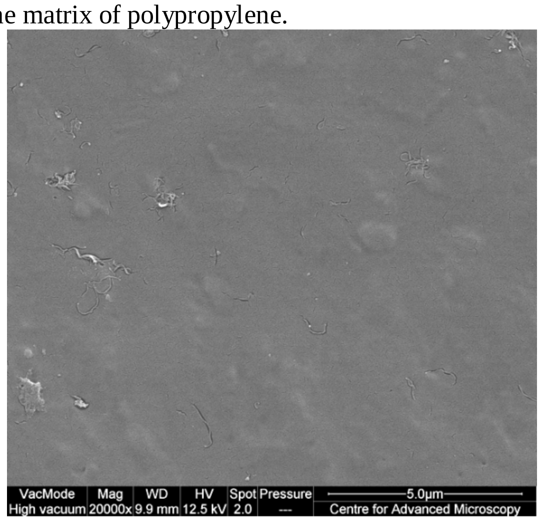

Fig.3. SEM image 0.5 wt% PP/MWCNT with 5 wt% MA composite.

3.2. Nanomechanical properties

Figures 4 and 5 present hardness and Young's modulus versus MWCNT content(in the range from 0 to 0.3 wt%), obtained after nanoindentation tests of non-functionalized and amino-functionalized epoxy/MWCNT composites. The results indicate that with increasing of MWCNT, hardness and modulus also increasing. In general, a very small addition of carbon nanotubes leads to a significant increase of both the elastic modulus and the hardness. The addition of 0.03 - 0.3 wt% MWCNT, shifted the curves to lower penetration depth compared to that of neat epoxy resin, i.e. the nanocomposite material had better resistance to penetration. This evolution evidences that the increase of the reinforcement rate above 0.03 wt% has a hardening effect in the nanocomposites tested. All the values measured show small experimental dispersion. Furthermore, for the amino-functionalized epoxy/MWCNT composites this effect is more pronounced. Thus, functionalization improves not only the degree of dispersion, but it also ensures a strong interfacial interaction, i.e. covalent bonding between the epoxy resin and the amino groups of the hardener absorbed at the nanotube surfaces. This has a significant effect on the nanomechanical properties. Therefore, the properties of the nanoreinforcements are directly linked to the good interfacial polymer-filler interactions, produced by nanotube functionalization, as well as to the ability of nanotubes to be dispersed in epoxy matrix at nanoscale level.

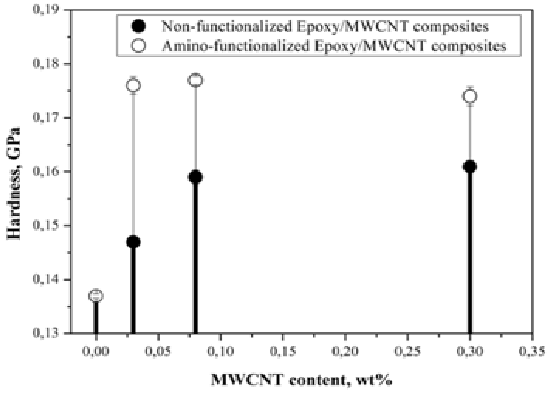

Fig.4. Hardness versus MWCNT content, obtained after nanoindentation tests of non-functionalized and amino-functionalized epoxy/MWCNT composites.

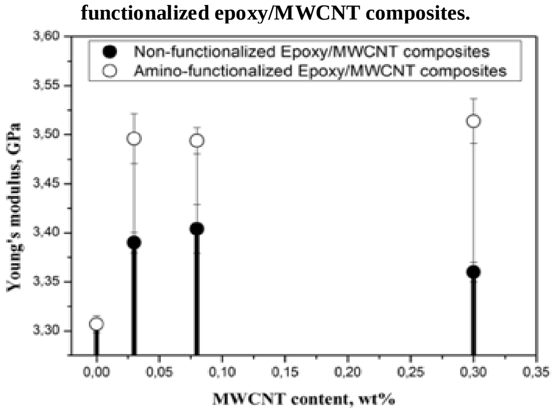

Fig.5. Modulus versus MWCNT content, obtained after nanoindentation tests of non-functionalized and amino-functionalized epoxy/MWCNT composites.

Figures 6 and 7 present hardness and Young's modulus versus MWCNT content (in the range from 0 to 1 wt%,) obtained after nanoindentation tests of PP/MWCNT composites without and with MA compatibilizer. It was found that the addition of 0.05-1 wt% MWCNT shifted the curves to lower penetration depth, compared to that of neat PP, that is, the composite material had better resistance to penetration. This evolution evidences a hardening effect in the all tested non-maleinated and maleinated composites. Small addition of MWCNT between 0.05 and 0.1 wt% results in a significant improvement of the nanomechanical properties. This is more pronounced for the maleinated sample, where the improvement of the hardness and elastic modulus is of about 26% and 20%, respectively. Interestingly, the composites modified with 5 wt% MA compatibilizer, showed higher values of hardness and Young's modulus compared with those of non-modified composites. The combined effect of the MA compatibilizer and the MWCNTs on the crystallization structure of PP/MWCNT composites obviously contributes to the enhanced hardness of the maleinated composites.

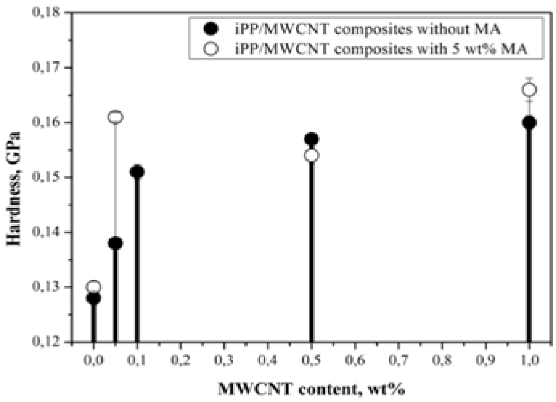

Fig.6. Hardness versus MWCNT content,obtainedafter nanoindentation tests of PP composites without using MA and with addition of 5 wt% MA.

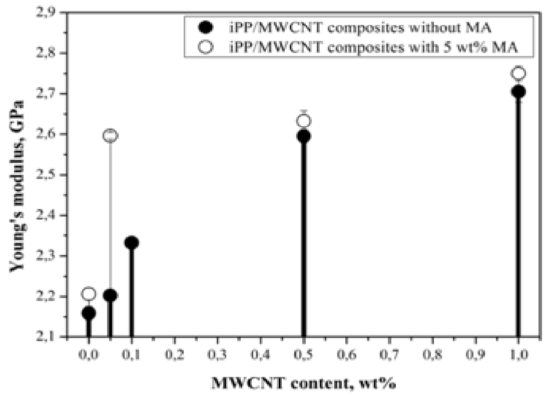

Fig.7. Modulus versus MWCNT content, obtained after nanoindentation tests of PP composites without using MA and with addition of 5 wt% MA.

CONCLUSIONS

Polypropylene nanocomposites containing 0.05 – 1 wt% MWCNT, with and without MA compatibilizer and epoxy nanocomposites containing 0.03 – 0.3 wt% functionalized and non-functionalized MWCNT were studied, and results on nanomechanical properties are characterized and analyzed.It was found that the amino-functionalization of carbon nanotubes results in a significant improvement of the nano-mechanical properties compared to these of non-functionalized samples. The properties of nano-reinforcements are directly linked to the good interfacial polymer-filler interactions, produced by nanotube functionalization, as well as to the ability of nanotubes to be dispersed in epoxy matrix at the nanoscale level.On the other hand, the combined effect of the MA compatibilizer and the MWCNTs on the crystallization structure of PP/MWCNT composites obviously contributes to the enhanced hardness and modulus of the maleinated composites.

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