APPLIED STUDY ON MECHANICS OF NANOCOMPOSITES WITH CARBON NANOFILLERS[*]

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Abstract. The incorporation of small amount of hard and soft carbon nanofillers, such as nanoscale diamond, carbon ash and multiwall carbon nanotubes (MWCNT) have different effect on the surface properties of the neat polyester resin and polypropylene. The soft nanofiller, carbon ash did not influence the wear properties of the polyester resin up to 5 wt% filler content. In contrast, 0.5–5 wt% hard nanodiamond strongly decreased the wear mass loss of the polyester resin. The scratch resistance and the coefficient of friction of the polypropylene is improved significantly while there is 0.1–3 wt% MWCNT. Small amount of MWCNTs change significantly the molecular structure of the polypropylene, producing a nucleation effect. This was found to assist in the changes of surface properties by increasing the hardness, friction and wear of polypropylene.
Key words: polymer nanocomposites, nanodiamond, carbon ash, multiwall carbon nanotubes, wear resistance, scratch, nanohardness, coefficient of friction.

1. Introduction

In our days, application of standard polymer coatings possess some shortcomings such as low wear resistance, poor mechanical properties and high permeability. For this reason, a need arises to create new composite materials

based on polymeric matrix which included nano-sized fillers and due to their mechanical properties to balance the overall sustainability of the final composite material [1]. Several studies have shown that, wear resistance can be increased by the inclusion of solid particles in composite polymer [2]. Polymer-based composites coupled with rigid fillers like diamond and alumina have shown increase of the wear resistance which is strongly dependent on the hardness of the nanoparticles and the degree of dispersion [3].

The advantages of nano-reinforcement over traditional filling materials open new frontiers of polymer nanocomposites in an ever growing range of applications, including surface protection [1]. Recently, the nano-sized particles were found to enable coating surfaces to be more uniformly and completely abrasion resistant protected compared with conventional coating additives. Moreover, the incorporation of nanofillers in surface coatings can provide long-term abrasion resistance without significantly effecting optical clarity, colour, gloss, or physical properties [4].

Few studies have shown that the wear resistance can be increased in polymer composites by incorporation of hard particles, while at the same time the wear of the counterbody decreases and the sliding coefficient of friction decreases [5]. This type of tribological behaviour will have an impact in polymeric bearings and coatings. In order to design composites with the optimum properties and predict performance, several authors [6] discussed the limitations that must be overcome.

In general, the mechanisms contributing understanding to wear performance in filled polymers is poor. This required detailed studying of the role of the filler matrix interface and the effect of particle size, as well as developing appropriate models that consider the interface or size of the filler. The mechanism that lowers the coefficient of friction is unclear for non-lubricious nanoparticles. Moreover, nanoparticle filled polymers have not comprehensively explored for wear applications despite the strong evidence suggesting large improvement of the wear resistance.

The present paper is concentrated on improving of surface properties (hardness, wear resistance, scratch and friction) of bulk polymers and coatings by nano-reinforcement with nanodiamond, multiwall carbon nanotubes and carbon ash. The aim is to study the effect of hard and soft nanofiller on the reinforcement and the surface properties of two types of polymer matrices (a thermoset and a thermoplastic polymer).

2. Materials and methods

A variety formulations of nanocomposites incorporating 0.5–5 vol% of nanodiamond in unsaturated polyester resins was used. Diamond nanoparticles with size of $d \sim 10$ nm, density $\rho = 3.36$ g/cm^3 and specific surface area of 230 m^2/g, as well as the carbon ash were supplied by the Space Research Institute at the Bulgarian Academy of Sciences. Carbon ash is a row mixture of graphite/diamond (67/33) with average particle size $d = 3 \div 6$ nm, density $\rho = 1.86$ g/cm^3 and specific surface $S = 54$ m^2/g, as produced by the shock wave technology, before purification. Nanocomposite preparation was discussed elsewhere [7].

A masterbatch of 20% multiwall carbon nanotubes (MWCNT) in polypropylene were commercially manufactured by initially dispersing intertwined agglomerates of nanotubes into the polymer and supplied by Hyperion. Typical outside diameter range of the tube is from 10 to 15 nanometers, the lengths between 1 and 10 microns, and their density is approximately 1.75 g/cm^3. iPP homopolymer "Buplen" 6231 with density $\rho = 0.901$ g/cm^3 and melt flow index MFI (230/2.16) of 12.2 g/10 min, supplied by Lukoil Neftochim Co., Bulgaria, was used as the matrix polymer. The masterbatch was compounded with the iPP for producing of 0.1 to 3 wt% iPP/MWCNTs composites by direct melt mixing in a twin screw extruder according to few step processing. [8]

Nanoindentations were carried out using a Nanoindentation Tester (UNMT) with inline imaging by atomic force microscopy (AFM), produced by Bruker Co. The hardness and elastic modulus were calculated from the recorded load-displacement curves using Oliver and Pharr methods [9]. Mechanical properties are directly determined by indentation load and displacement measurements without the need to image the hardness impression. Load is measured as a function of penetration depth. The test is repeated to have statistical data. Each indentation is performed on a new location on the specimen.

Micromechanical investigations are made using Mechanical and Tribology Tester (UMT-2M) produced by the Center for Tribology (CETR), USA. For the scratch test-micro-cutting blade, composite diamond, tip radius 0.8 mm was used, for pin on plate test 416 stainless steel pin, 6.35 mm × 25.4 mm (dia. x length) was used and for ball on plate – 440-c stainless steel balls, dia. 6.35 mm correspond. Thus, the coefficient of friction was determined in the bulk volume and on the surfaces, respectively. At least two measurements [10] were made for each composition.

3. Results and discussion

3.1. Wear Resistance of Thermoset Nanocomposites

A significant improvement of the wear resistance was found for nanocomposites, which is strongly dependent on the hardness of the nanoparticles and the degree of dispersivity [11, 12]. Figure 1 compares the concentration dependence of the relative weight loss decrease, (Vo-V)/Vo, during the wear of the cross-linked hybrids, which represents the wear resistance improvement. Herewith, Vo is the weight loss during the wear of the neat resin and V is the weight loss for the nanocomposite.
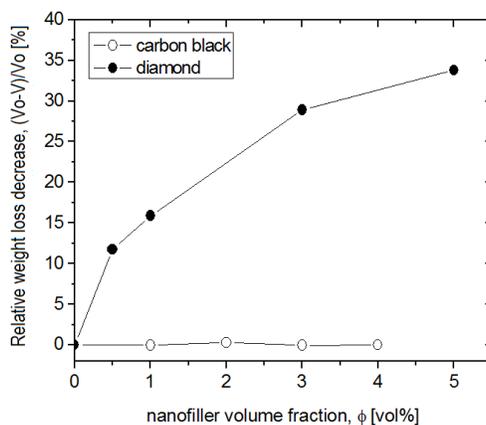

Fig. 1. Relative weight loss Decrease (Vo-V)/Vo (%) vs. volume concentration of diamond (full circles) and graphite/diamond (empty circles) in a polyester resin

Laboratory experiments demonstrate that nanoparticles of diamond incorporated into the polyester resin formulations exhibit very high improvement of the wear resistance. At a relatively low volume fraction (0.5–5%), the diamond nanofiller improves the wear resistance of the matrix polyester resin (Fig. 1) with more than 11–35%. Wear resistance increases rapidly at very low filler content and then, its values tend to a plateau above 4 wt%, which is associated with the mechanical percolation. In contrast, graphite/diamond ash (carbon black), as a soft filler, has no effect on the wear properties of the polymer.

The strong improvement of the wear resistance of diamond-containing nanocomposites may be assigned to the specific physical properties of diamond – extreme hardness and good thermal conductivity, which enhances both hardness and thermal conductivity of the resin. Most of the conventional composites containing micron size fillers possess low thermal conductivity and high

hardness, which produces very high surface friction temperature. While the nanoscale diamond-containing hybrids showed good tribological characteristics, based on the high hardness and high thermal conductivity, leading to a decrease of the surface friction temperature [12–14].

3.2. Relation between Nanohardness, Scratch and Friction in iPP/MWCNT nanocomposites

Nanomechanical properties are studied by instrumented nanoindentation. Representative load–displacement curves for the pristine iPP and MWCNT/iPP composites, obtained from the nanoindentation tests at loading of 5 mN, are shown in Fig. 2 (a) and (b).
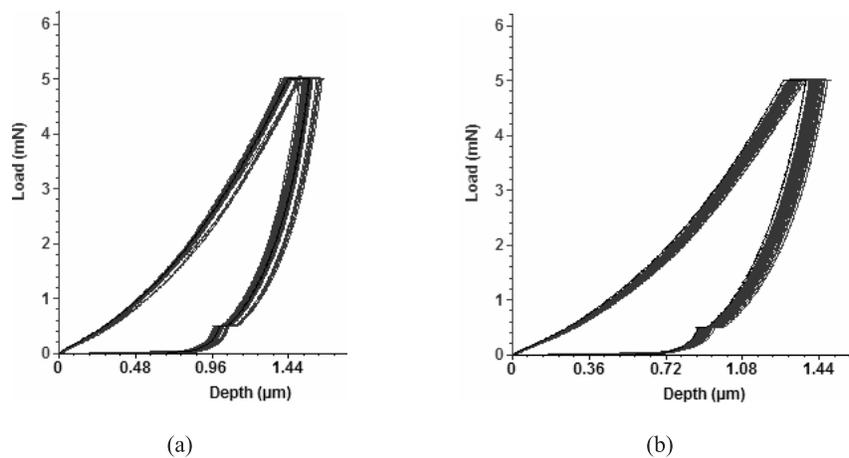

(a)   (b)

Fig. 2. Representative load–displacement curves from nanoindentation tests of (a) pristine iPP and (b) 1 wt% MWCNT/iPP loaded at 5 mN

The addition of a small amount of 0.1% MWCNT displaced the curves to lower penetration depths, i.e., the material had higher resistance to penetration. By adding 0.5–1 wt% of MWCNT, the behaviour was very similar to that of the 0.1% MWCNT/iPP composite, while the sample containing 3 wt% of nanotubes was the one that opposed the highest resistance to the penetration (not shown in the figure). This evolution evidences that increasing the reinforcement rate above 0.1 wt% MWCNT filling has a hardening effect in the nanocomposites tested [15].

From the load–displacement curves, the average values of the hardness were calculated by Oliver-Pharr method [9]. Figure 3 presents the hardness vs. the nanotube filling. Interestingly, nano-hardness is much higher than those
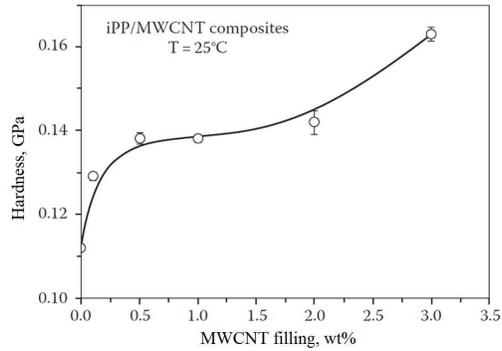
Fig. 3. Average values of hardness from nanoindentation tests of MWCNT/iPP
composites at maximum load of 5 mN

of the neat polymer in the case of a very low addition of 0.1 wt% MWCNT.
At nanofiller content between 0.5 wt%–1 wt%, the values of the modulus and
hardness show a tendency to a plateau, while they increase strongly around
and above 2 wt% filler content which is associated with mechanical percolation
[15].

Results from Figs 1 and 3, show, that obviously the mechanical perco-
lation of polypropylene containing MWCNTs appears at much lower nanotube
content (2 wt%), if compared with the polyester/diamond nanocomposites (4
vol%).

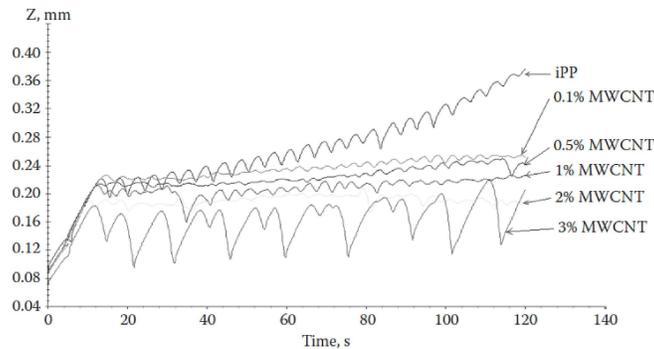Typical surface scratch profiles are shown in Fig. 4, which presents the

Fig. 4. Carriage displacements (Z) vs. time for the iPP and nanocomposites by
varying the nanotube content

depth (displacement)/time curves of iPP and nanocomposites by varying the nanotube content. The increase of the nanotube content from 0.1 wt% to 3 wt% shifts the displacement/time curves to lower values, as well as a tendency to a plateau is observed. Extensive debris and cracking are observed at the bottom of the scratches, and this is mostly evident at high nanotube content of 3 wt%.
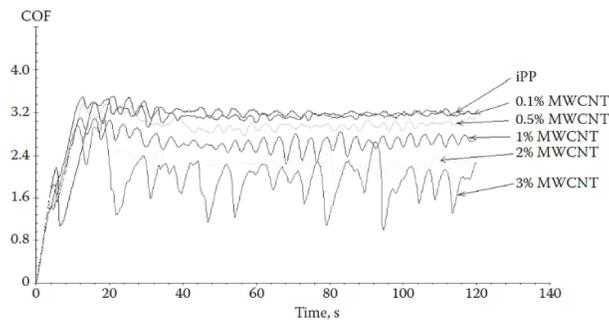

Fig. 5. Surface profiles of the friction coefficient at scratch of iPP and nanocomposites by varying the MWCNT content

Figure 5 shows the variation of the coefficient of friction with the time of lateral displacement of the micro-cutting blade during the scratch test at a constant force of 2 N. Here, the value of the coefficient of friction is defined as the ratio of the lateral force to the normal force. The coefficient of friction depends on several factors including the surface roughness and material properties of the sample. Since the initial part of the data is influenced by surface morphology, the average was calculated using the data from the plateau region of the curves. This value is a measure of the resistance to wear rather than just being a friction parameter. A harder material would impose more resistance to scratch and consequently the blade will experience a larger lateral force.

The computed scratch depth is the average of at least three measurements along the scratch, and the results are shown in Fig. 6 (a). As it can be seen from the plot, the unfilled iPP samples have a relatively deep scratch depth at a time of 120 s. The scratch depths of the MWCNT/PP nanocomposites are significantly lower than those in pristine iPP. A very low nanotube content of 0.1 wt% results in a sharp decrease of the scratch depth, while further increase of the MWCNT content, from 0.1% to 3 wt%, results in a linear decrease of this characteristic. [15]

Figure 6 (b) plots the coefficient of friction at scratch vs. carbon nan-

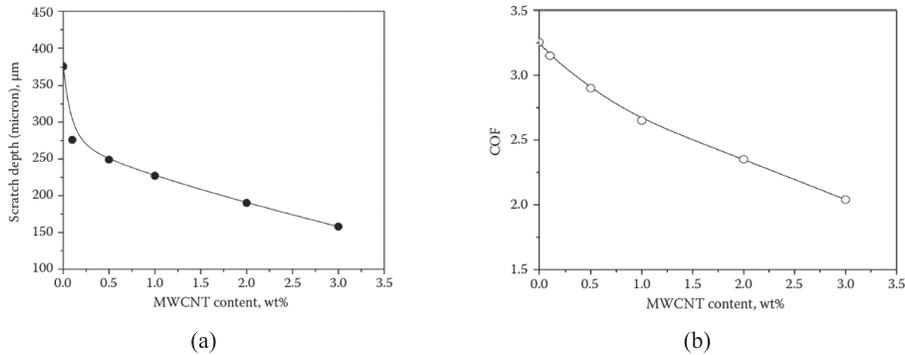(a)   (b)

Fig. 6. The results of (a) Scratch depth of 2 N load scratch vs. the MWCNT
content; and (b) Coefficient of friction at scratch vs. carbon nanotube content

otube content. It is seen that the addition of smaller amounts of MWCNTs
can improve the friction-reduction of polypropylene. Thus, the coefficient of
friction decreases about 40% for the 3 wt% MWCNT-reinforced composites, as
compared to the neat iPP.

3.3. Relation between Hardness, Scratch and Friction of MW-CNT/iPP Nanocomposites as a function of MWCNT

The correlation between the relative changes (%) of the three characteristics: hardness, scratch depth and friction coefficient is shown in Fig. 7.

The increasing of hardness correlates well with the decreasing of scratch
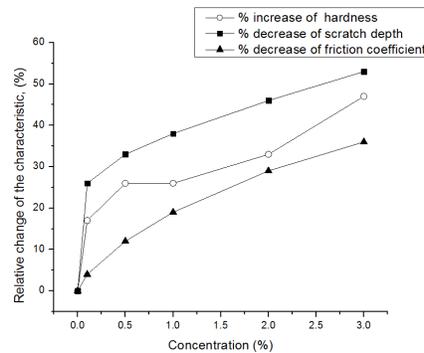

Fig. 7. The correlation between the relative changes (%) of the characteristics
(increase of hardness, decrease of scratch depth and decrease of friction coefficient)
vs. nanotube content

dept, as seen by the shape of both curves. This effect is very strong at low nanotube content and the improvements are relatively smooth at higher concentrations. Thus, at nanotube content of 0.5 wt%, the sharp $\sim 26\%$ increase of the hardness correspond to the $\sim$33% decrease of the scratch depth. The 3 wt% MWCNT content produces significant improvement (47, 53 and 36%, respectively) of the three characteristics (hardness, scratch and friction coefficient) if compared to those of the neat iPP. The friction coefficient is strongly and smoothly improved by increasing the nanotube content.

Therefore, it can be concluded that the MWCNTs are ideal nanofiller for the polypropylene in respect to tribology, producing strong improvement of all surface properties, hardness, scratch and friction.

Conclusions

The addition of a small amount of nanofiller diamond (0.5–5%) as a nanofiller in polyester matrix leads to improving by more than 35% wear resistance of the polyester resin. The addition of hard nanofiller, such as diamond, contributes to a significant enhancement of the hardness of polyester resin nanocomposites. On the other hand, polyester matrix containing soft nanofiller – graphite/diamond ash (carbon black), has no an impact on the wear properties of the polyester resin.

MWCNT/ iPP composites containing low nanotube rate of 0.1 wt% results in a sharp decrease of the scratch depth, while further increase of the MWCNT content, from 0.1% to 3 wt%, results in a linear decrease of this characteristic. The friction coefficient is strongly improved by increasing the nanotube content. The 3 wt% MWCNT content produces significant improvement (47, 53 and 36%, respectively) of the three characteristics (hardness, scratch and friction coefficient) if compared to those of the neat iPP. The mechanical percolation of polypropylene containing MWCNTs appears at much lower nanotube content (2 wt%) compare with the polyester/diamond nanocomposites (4 vol%).

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