1. Effect Dispersibility of MWCNT on the Mechanical and Tribological Performance of Polymer Nanocomposite Coating

Ammar Al-kawaz
Faculty of Materail Engineering,polymer Department,Babylon University,Iraq
mat.ammaremad@uobabylon.edu.iq, emadammar79@yahoo.com

Abstract

To utilize MWCNTs as influential reinforcement in polymer composites, reasonable dispersion and a satisfactory interfacial bond between the MWCNTs and polymer matrix must be ensured. The chemical modification of carbon nanotube surface (CNTs) could enhance their chemical compatibility and dispersibility with the polymer matrix. In this study, polymer matrix composites reinforced by pristine MWCNT and MWCNT grafted PMMA (CNTPMMA) were prepared. A comparative study executed to analyze the impact of MWCNT dispersion on the mechanical and tribological performance of the resultant polymer nanocomposite coating. The results showed that the dispersion of carbon nanotubes in the base polymeric material was improved after being grafted with polymethyl meth acrylate chains, and thus improved their mechanical and tribological performance in the composite coatings.

Key Words:- Nanotubes, Surface Modification, Friction, Plastic Deformation, Coating.

الخلاصة

للاستخدام الانابيب الكاربونية النانوية كتقويه فعالة للمواد البوليميرية المركبة يجب ضمان التشتيت المناسب والالتصاق البيني القوي بين الانابيب الكاربونية والمادة الاساس البوليميرية. ان التعديل الكيميائي لسطح الانابيب النانوية يمكن ان يحسن انتشارها وتوافقها الكيميائي مع المادة البوليمرية الاساس.

في الدراسة الحالية تم تحضير مادة مركبه بوليمريه وتم تقويتها بالأنابيب النانوية البكر (غير معدلة السطح) وانابيب نانوية مطعمة بسلاسل البولي مثيل ميثا اكريلك وبنسبة وزنية ٢% حيث تم اجراء دراسة مقارنه للتحقق من تأثير التشتت الجيد للأنابيب على الأداء الميكانيكي والسطحي للطلاءات المركبة الناتجة. وقد اثبتت النتائج تحسن قابلية التشتت للأنابيب الكاربونية في المادة البوليمرية الاساس بعد تطعيمها بسلاسل البولي مثيل ميثا اكريليك وبالتالي تحسن اداءها الميكانيكي والسطحي في الطلاء المركب.

الكلمات المفتاحية :- الانابيب النانوية ، معاملة السطح ، الاحتكاك ، التشوه البلاستيكية ، الطلاء .

Introduction

Reinforcement of polymers by way of carbon nanotube fillers is presently a key scientific problem in mechanical engineering especially for tribological applications **(Friedrich *et.al.*, 2005)**. In comparison to classical fibers using nanoparticles especially increases the interface with the polymer matrix (in the case of similar quantity) that could make certain study chemical bonding. Therefore, dispersion of such nanoparticles promotes repartition of mechanical pressure and allows modulating the mechanical performances to the desired applications. However, one disadvantage of carbon nanoparticles is their high interaction with one another because of van der Waals interactions. To take benefit of polymer reinforcement with carbon nanoparticles, these aggregate is a major problem. There are several routes of composite processing to overcome this problem were tested on a wide style of polymers as reviewed via Spitalsky et al **(Spitalsky *et.al.*, 2010)**.

The interfacial interaction between the nanofiller and the polymer matrix can determine the overall mechanical performance of polymer nanocomposites. **(Bhattacharya, 2016)**. It is recognized that an effective improvement of CNT/polymer nanocomposites relies to a great extent on the capacity to disperse carbon nanotubes homogeneously in the polymer matrixes with a strong CNT-polymer interfacial adhesion for appropriate load transfer.(Wang, Pramoda, & Hong, 2005). Chemical functionalization of carbon nanofiller allows the change in their solution properties for facility of dispersion and next information of the chemistry of these nanomaterials **(Liu *et.al.*,2009)**.

Jooheon Kimet al.(**Kim *et.al.*, 2011)** assumed that the PMMA-grafted MWCNTs displayed unique dispersion potential inside the 6FDA-based polyimide matrix as a compare with the pristine MWCNT composite, that is because of strong interfacial communications between the fluorinated carbon and carboxyl acid of the 6FDA-basically based polyimide grid. They also, avowed that the least coefficient of erosion was gotten for the nanocomposite covering fortified with three distinct rates of MWCNT-grafted to PMMA.

Gil Gonc alves et al **(Gonc *et.al.*, 2010)**, they've efficaciously modified the surface of GO with PMMA chains thru ATRP, and a homogeneous distribution of the fillers inside the PMMA matrix turned into accomplished. Mechanical analysis of the ensuing films affirmed a generous development of the elongation at break, yielding a much extra ductile and, consequently, harder material.

A coating is a common manner of improving the scratch resistance for polymeric glasses. The scratch resistance growth is associated with the polymer microstructure and is equivalent to introduce an elastic contribution into a complete plastic conduct, using nanoparticles as reinforcement fillers. Therefore, a thrilling path: the composite is the association of the large elastic zone of the matrix and the hardness of the nanofillers **(Schottner *et.al.*, 2003)**.

Among all carbon nanoparticles B. Dong et al **(Dong *et.al.*,2005)** showed that MWCNTs substantially increases in wear resistance of the nanocomposites and reduced their friction coefficient, and they confirmed clearly that MWCNTs/Epoxy nanocomposites with 1.5 wt.% MWCNTs exhibited both the smallest wear rate and the minimum friction coefficient.

Therefore, this work is an attempt to study the effect of surface amendment of the MWCNT on the dispersibility of MWCNT in a polymer matrix, also on the mechanical and surface behavior of the resultant composites coating.

2. Materials and experimental

2.1 Materials

The monomer methyl methacrylate (MMA) [- C5H8O2, purity 99% ,M.Wt. 100.12 g/mol] and the initiator 2,2'-azobisisobutyronitrile (AIBN) [$C_5H_{12}N_4$, M.Wt. 164.21 g/mol], were purchased from Sigma-Aldrich.

MWCNT-grafted PMMA (CNTPMMA) were prepared by grafting from method in our previous study **(Al-kawaz *et.al.*, 2016).** Figure(1) shows the transmission electron Microscopy of MWCNT before and after grafted with PMMA chains, which proved the presence of PMMA layer on the MWCNT surface.

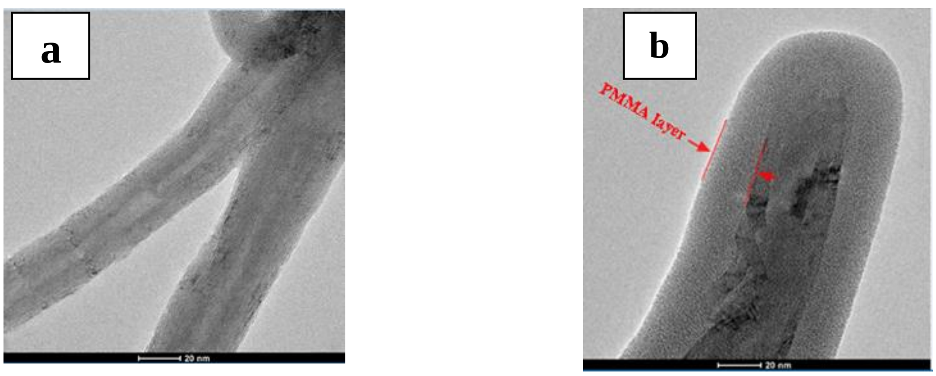


Figure 1 Transmission Electron Microscopy of (a) MWCNT and (b) MWCNT-grafted-PMMA dispersed in THF

2.2 Characterization techniques

Scanning electron microscopy (SEM): SEM micrographs were recorded with a JFOL 2600F magnifying instrument working at an acceleration voltage of 15 KV and an emission current of mA. The samples were covered with a thin layer of sputtered gold.

Transmission Electron Microscopy (TEM): A solution or suspensions of nanocarbon filler in tetrahydrofuran (THF) was Ultra-sonicated throughout 10 min. 5µl of the solution have been deposited onto a Lacey-Formvar/carbon-covered copper grid (300 mesh). The suspension was left for 2 min and sooner or later blotted with filter paper. The grids were observed with a Technai G2 microscope (FEI) at 200 kV. Images were gained with an Eagle2K ssCCD camera (FEI).

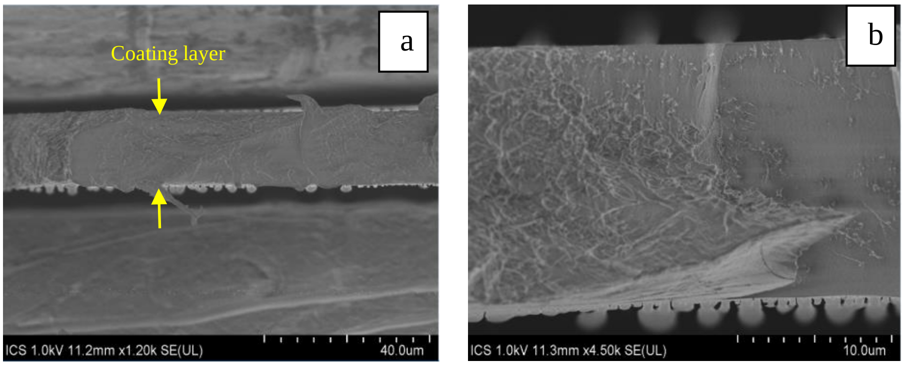
Nano-indentation tests: Nanoindentation testing is a technique to measure the mechanical properties of a material inclusive of hardness and young's modulus were measured by nanoindentation technique on the microscopic scale. The usage of Ultra Nano Hardness Tester (UNHT), synthetic by using CSM devices (Switzerland), with a potential of 30 µN to a hundred mN is having a load decision of 5 µN.The indentation technique becomes evolved by way of Oliver and Pharr (Oliver & Pharr, 2004).

Scratch tests: The tribological performance had been analyzed from a homemade sclerometer, the micro-visio-scratch (MVS) apparatus. It consists of a industrial servomechanism bearing a small transparent field with temperature control, which contains the specimen and the scratching tip, it is geared up with an integrated microscope, permitting in situ studying the contact region and the groove left on the surface. The perpendicular load Fn, tip geometry, temperature and the sliding velocity are the input parameters, whereas the tangential pressure, groove geometry and the real contact region are the output parameters.

3. Results and Discussion

3.1. The dispersibility of MWCNT in the polymer matrix

Figure (2) shows the dispersibility of MWCNT in SEM images of the fracture surface of the polymer composites made with pristine carbon nanotubes, which revailed the agglomerates of carbon nanotubes in the composites of the composite caoting, also the adhesion between the polymer matrix and the nanotube was weak as shown in Figure (2-d).



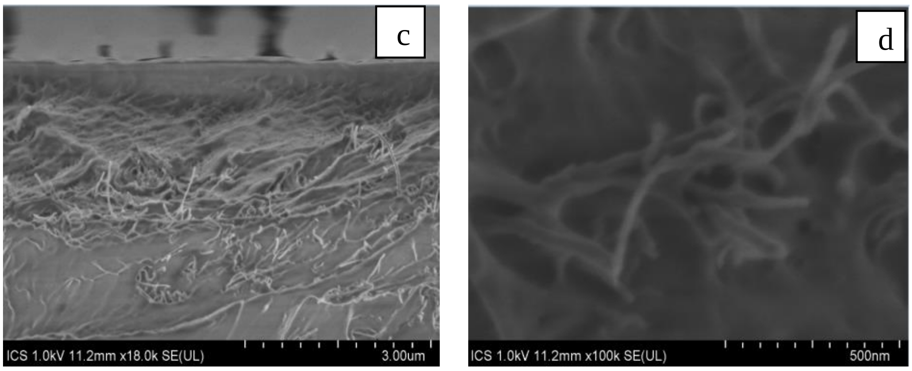


Figure 2 SEM images of a fracture surface of PMMA / MWCNT coating sample

Figures (3) show the fracture surface of composites made with carbon nanotubes grafted with a polymer layer. Micrographs show the very good dispersion of carbon nanotubes in the polymer matrix. A better dispersion not only makes more filler surface area available for bonding with the polymer matrix, but also prevents the aggregate filler from acting as stress concentrator, which is detrimental to the mechanical performance of composites.

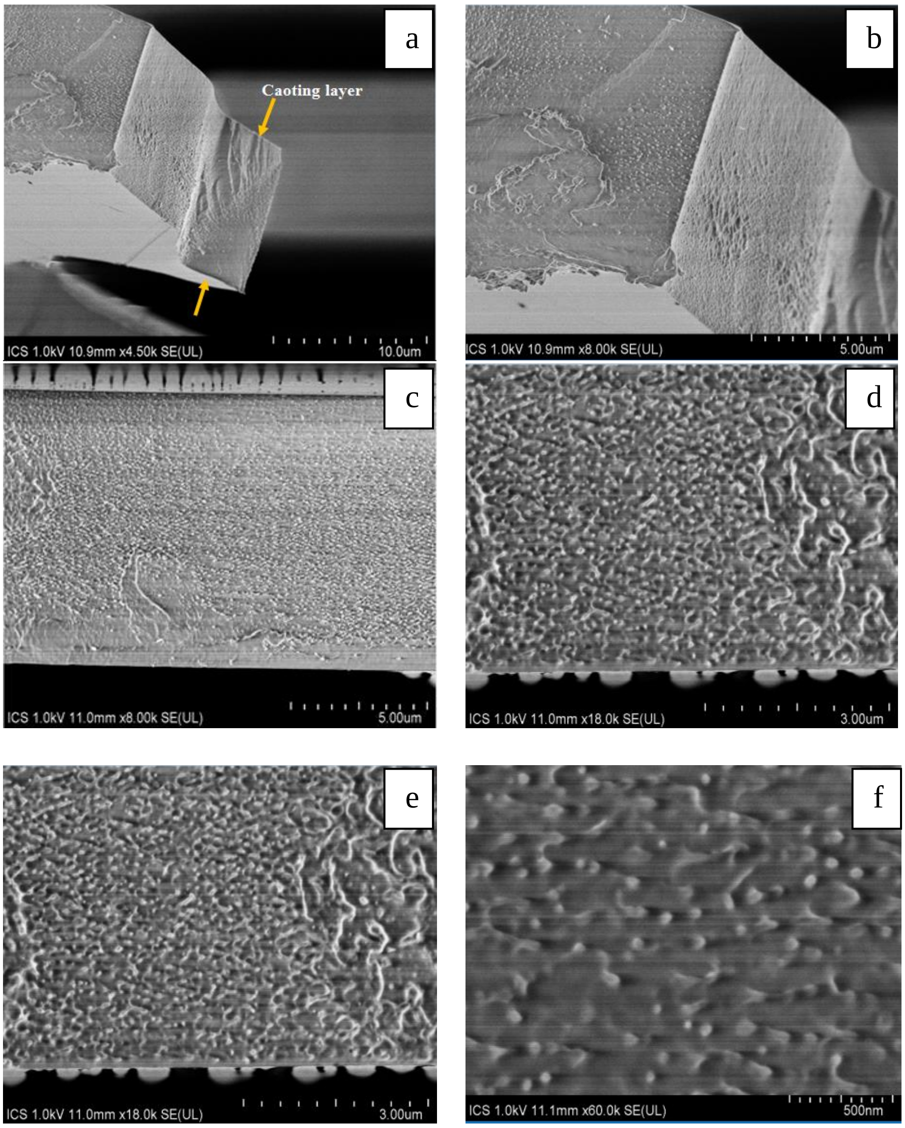


Figure 3 SEM images of a fracture surface of PMMA/CNTPMMA sample

Hardness & Elastic Modulus

The nano-indentation experiments were carried out on three glass slide substrate by pure PMMA coating, MWCNT reinforced PMMA and PMMA reinforced CNTPMMA composites. The results that have been adopted were at a penetration depth of 1µm to avoid the effect of the substrate. Young's modulus and hardness were detected by the nano-indenture for sample coated with a pure PMMA coating and for samples coated with composites of PMMA. Composite films were deposited on a clean glass plate. After the last drying step, the coating thickness is 12-15 µm, which entails that we can probe the coating up to 1.5 µm to get its own mechanical response.

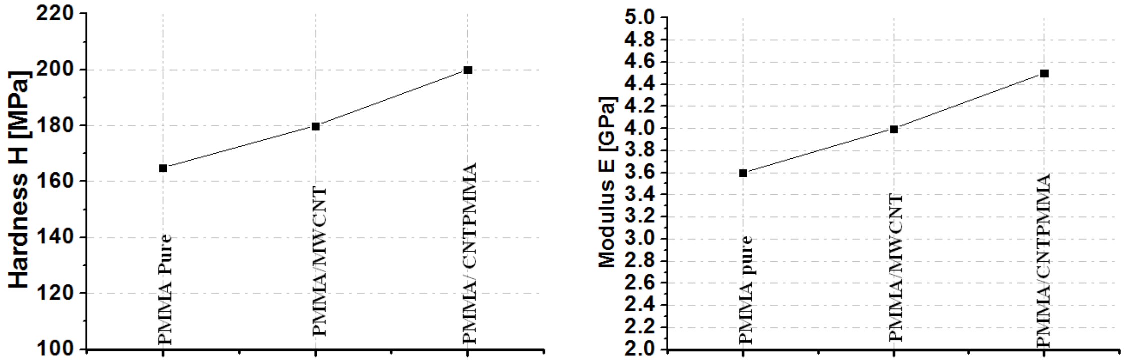


Figure 4 Young's modulus (on the right) and of hardness (on the left)

The experimental results presented that the Young's modulus and hardness, increased by 12% and 11% respectively for PMMA reinforced MWCNT composite compared with pure coating while for PMMA reinforced CNTPMMA increased by 25% and 21% compared with pure coating (Figure 4), which reviled the role of grafting the surface of carbon nanotubes with PMMA layer in developing the dispersibility and compatibility of MWCNT in polymer matrix.

When the external load was applied to MWCNT/polymer composites, the fiber reinforced polymer matrix should transfer the load to the MWCNTs, let them transfer the critical proportion of the load. The interfacial bonding between the filler and the matrix material has a great impact on the performance of load transfer. A tough interfacial adhesion relates to excessive mechanical properties of composites.

Coefficient of Friction

Figure (5) shows the friction coefficient for three coating samples (pure PMMA, PMMA reinforced with MWCNT and PMMA reinforced with MWCNT grafted PMMA). The results obtained by scratch test with tip radius 98 µm at ambient temperature.

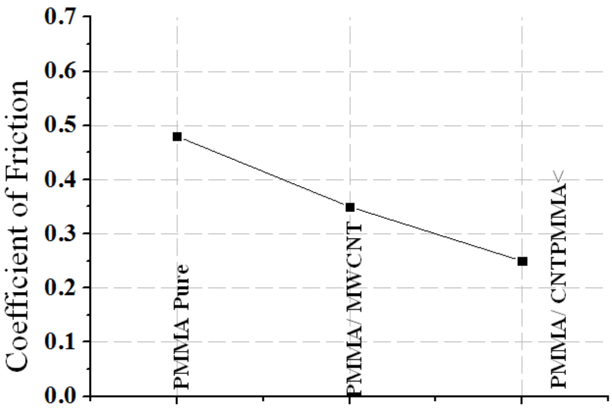


Figure 5 coefficient of friction for PMMA reinforced with pristine MWCNT and MWCNT grafted PMMA.

The experimental results for the samples coated with pure PMMA and composite containing 2% of MWCNT and 2% CNTPMMA respectively indicate that composite coating reinforced with MWCNT grafted PMMA have a lower value of the coefficient of friction. This behaviour is due to the strong interfacial interaction between nanotube grafted PMMA (CNTPMMA) and polymer matrix, which makes them more compatible with both polymer host and solvent, thereby, improving the tribological performance.

Morphology of composite films

The residual grooves from scratching the surface of all samples by the same normal load were studied. The images showed early appearance cracking in the case of pure coating, while in the case of composite coatings, the surface of the groove was smooth and without cracks. Consequently, it can be noted that the coating film reinforced with MWCNT grafted PMMA has a better ability to elastic recovery and this due to homogenous dispersion of nanotube, which leads to improving coating resistance to deformation caused by scratching (Figure 6).

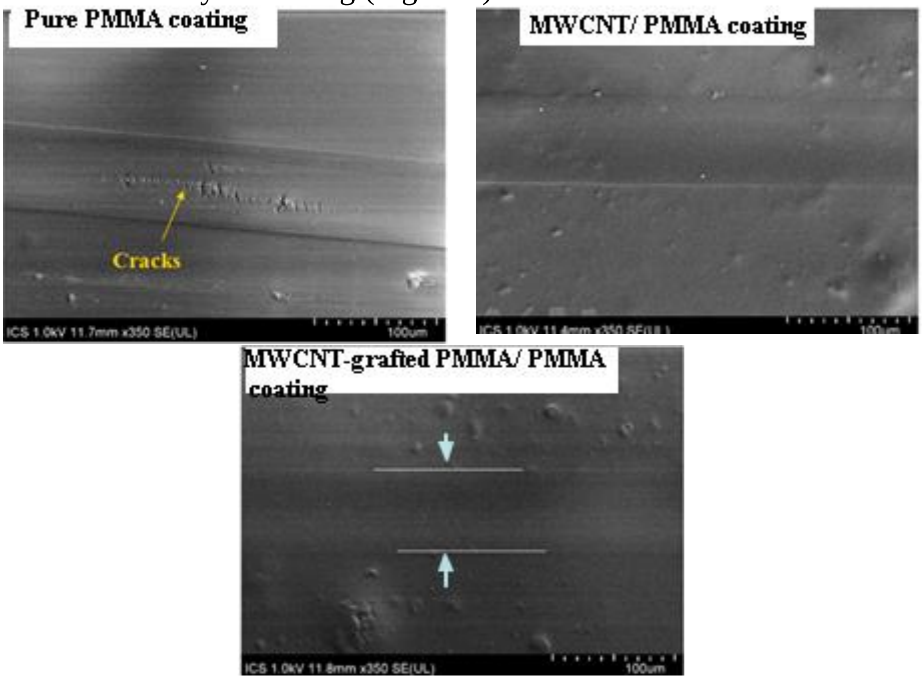


Figure 6 SEM micrographs of the worn surface

Conclusions

The dispersion of the nanotubes and their interplay with the polymer matrix play a vital role in their mechanical and tribological performance.

The robust interfacial interaction with the polymer matrix can be enhanced by means of functionalized MWCNTs.

Nanocomposite coating with an excellent dispersion of nanotube has better mechanical and tribological properties.

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