Diyala Journal of Engineering Sciences

ISSN 1999-8716
Printed in Iraq

Vol. 07, No. 03, pp. 106-119, September 2014

CHARACTERISTICS AND PROPERTIES OF EPOXY/POLYSULFIDE COMPOSITE MATERIALS REINFORCED BY CARBON NANOTUBES

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(Received: 23/6/2013; Accepted:12 /1/2014)

ABSTRACT: - In this research, multi-walled carbon nanotubes (MWCNTs) were used to enforce the blend of epoxy /polysulfide and then tensile and wear behavior of this reinforcement were evaluated. For achieving this goal, different weight percentages of MWCNT (0.2–0.6 wt %) were dispersed in the epoxy resin then polysulfide resin is added and mixed with two curing agents. Experimental results have shown significant difference between epoxy/polysulfide and CNT /epoxy /polysulfide in mechanical properties. With 0.2–0.6% MWCNTs we observed an increase in Young's modulus from 245 to273 MPa, tensile strength from 30.5 to 38.9 MPa and fracture strain from 12.4% to 14.2%. For understanding the structure and morphology of nanocomposite, the dispersion states were studied using scanning electron microscopy (SEM) and field emission electron microscopy (FESEM).
Keyword: Composite Materials, Carbon Nanotubes, Mechanical Properties, Polysulfide.

1- INTRODUCTION

Polysulfide resins are the first synthetic elastomers which were manufactured on a commercial scale in United State. Liquid polysulfide resins are obtained by splitting preformed high molecular and cross-linked latex into shorter di and tri-functional chains.SH-terminated polysulfide is mainly used as base polymers in elastic sealants for insulating-glass windows and in construction purposes.

The liquid polysulfide is converted to elastomers by chain extension and cross linking. During the curing process the terminal thiol groups react with each other to form disulfide bonds. Polysulfide-based materials are known for their special strength and relaxation properties. Cured polysulfide shows low gas and vapor- diffusion rates, a high chemical resistance especially against fuel and solvents and good weathering stability.

Because of their highly reactive SH-end groups liquid polysulfide can be used as starting materials for other poly-functional macromolecules [1]. Epoxy/polysulfide is a polymer combine the unique properties of polysulfide (softness) with those of epoxies(hardness), it uses in different objects such as producing paint, gum and elastic sealant, flexible anti-corrosion coatings, relieving cracks of broken concretes in building, sewage pipes and surface of streets, producing marine color and two-walled glass [2].

To further strengthen the properties of current polymer materials, the addition of many kinds of inorganic fillers has already been researched and applied extensively. The size and dispersion characteristics of inorganic particles have a great effect on the comprehensive properties of polymer composites. The application of nanometer fillers to polymer materials is a promising channel for property modification.

Some nano-fillers have improved polymer performance remarkably because of their high specific surface area compared to conventional fibers or particles [3]. Since discovery of multi-walled carbon nanotube (MWCNT) in 1991 by Iijima, and synthesis of single-walled carbon nanotube (SWCNT) in 1993 by him and his coworkers [4], CNTs have become one of the most promising fillers for reinforcement and multi-functionality because of their exceptional mechanical (elastic modulus in the range of 500–600 GPa and tensile strength close to 200 GPa) [5, 6] electrical, and thermal properties [7,8] .Many studies have shown significant property enhancement in CNT-filled epoxies [5,9]. For example, a 20% increase in storage modulus at room temperature was achieved in a bisphenol-F type epoxy with only 0.3 wt% of single-walled carbon nanotube (SWNT) [9].

There are a few publications about polysulfide polymer nanocomposite. Guchhait et al. have been modified epoxy resin with polysulfide polymer and then prepared nanocomposites by dispersing the nanosilica in polymeric matrix. The effect of nanosilica on morphology, mechanical, thermo-mechanical and dielectric properties of epoxy/polysulfide has been studied by them [10]. In the similar research Zhang and Shi JH have studied morphology, mechanical and thermal properties of polyurethane/polysulfide reinforced with 1, 3, and 5 wt% nanoclays [11-13]. In this study we considered the effect of addition of MWCNT on properties of epoxy/polysulfide blend. Despite significant need, this topic has not yet been addressed sufficiently and there remain controversies in this area. As polysulfide epoxy is used in industrial and special coatings, mechanical properties are very important in resin which must be investigated. For this mean, three different samples including 0.2%, 0.4% and 0.6% by weight of MWCNT were prepared and a comparison on the properties of these nanocomposites provided preliminary results. Also, tensile, wear resistance of each nanocomposite were determined.

2. EXPERIMENTAL DETAILS

2.1. Material

MWCNTs with minimum purity of 95%, 3–15 number of walls, outer diameter of 2–6 nm, inner diameter of 2–6 nm, length of1–10 μm and density of 0.15–0.35 g/cm^3 were obtained from Plasma Chem GmbH; epoxy resin type (Quickmast 105® (DCP)), containing epoxide group, which is thermoset resin and manufactured by commercially produce from Quick Mast company .The hardener from the same company are used to achieve curing of the epoxy resin and epoxy properties are shown in table (1). Considering polysulfide resin, one of the most properties that distinguishes this rubber is that it contains sulfur as part of a series of linear polymer whose trademark is (DCP). The polysulfide is supplied in the shape of white dough that changes to elasticity shape by adding PbO2 (black dough) in the ratio 1:16 with density (1.35) gm/cm^{3}as table (2) contains properties of polysulfide polymers.

2.2. Preparation of MWCNT/epoxy polysulfide composite

Three series of composite were prepared with different content of MWCNTs as 0.2, 0.4 and 0.6 wt%. First MWCNTs were mixed in epoxy resin via ultrasonic (Hielscher UP 400S) for 30 min and then polysulfide resin was added and mixing was continued for 1 h by (WiseTis) homogenizer with speed of 15000 rpm with ten minute work and ten minute off to keep the device temperature low. Then samples were placed in vacuum for 30 min at 80°C to remove bubbles and after this stage, aliphatic amine hardener and polysulfide hardener were added to composite while were mixed with low speed. After uniform mixing, the mixture was poured into the prepared mould and left for complete curing to be done.

2.3 Characterization of MWCNT/epoxy polysulfide composite

Fourier transform infrared (FTIR) spectroscopic measurements were done using a FTIR spectrometer (Perkin Elmer; model of SpectraI). The FTIR spectra of pristine MWCNTs were obtained in a transmittance mode by mixing a small amount of the nano tubes in KBr pellets. Raman spectroscopy (Thermo Nicolet Dispersive Raman Spectrometer) was used to investigate the structural changes of MWCNTs .Second harmonic@532 nm of a Nd:YLF laser was used as the light source. Furthermore, morphological characterization of the composites was carried out using scanning electron microscopy (Zeiss; model of LEO 1455VP). For SEM observation, samples were coated with platinum via sputtering for 30 s. FESEM images of nanocomposites were recorded on a field emission scanning electron microscope (Hitachi S-4160) operating at 15 kV to determine particle size of MWCNTs in matrix.

2.4. FTIR spectroscopy

FTIR spectra of the samples are shown in Fig.(1) No obvious vibration of carboxylic groups appears for pristine MWCNTs around 1700 cm^{-1}, but, vibrational modes of 3475 are attributed to the O–H stretching, carboxyl stretching and C–O bending, respectively, as reported previously. The presence of the characteristic peak at 3425 cm^{-1} is attributed to remained moisture in MWCNTs which usually is appears in FTIR; but increase in intensity of this peak is an indication that the above chemical treatment led to the graft of polar functional groups such as (–OH) on the surface of MWCNT [14,15].

2.5. Raman spectroscopy

Raman spectroscopy is a useful method for investigation of the low energy elementary excitations in carbon nanotubes like to characterize their structural, electronic, vibrational and magnetic properties ([16, 17]. The main features of CNTs in the Raman spectrum (Fig. 2) are the radial mode band (100–400 cm^{-1}), irregular induced D-band which appears at around 1350 cm^{-1}, G-band which represent the crystalline graphitic and tangent vibrations of sp2 carbon (1500–1600 cm^{-1}), and D_-band which represents the overtone of the disorder (_2600 cm^{-1}). Osswald et al. [18, 19] reported that in MWCNTs the D-band appears due to defects in the tube walls. The value of the intensity ratio of the D and G-bands ID/IG represents the degree of disorder on the MWCNTs structure. Also, intensity ratio of the D and-bands can determine the degree of disorder on the MWCNTs. A growth in D/G or reduction in ID/IG indicates higher defect concentration or a higher degree of disorder. Observing the functionalized MWCNTs, the G-band is less affected by defects from functionalization as compared to the D-band.

In the current study, the radial breathing mode (RBM) in the Raman spectra which is a direct measurement of the core nanotube diameter [20] was not evident. Since MWCNTs used in the current study contained a minimum average of about 3–15 shells, in height the Raman spectra of these MWCNTs would correspond to a radial mode band with very low frequency and weak intensity.

2.6. SEM and FESEM

SEM images from fracture surfaces were used to observe the morphology of the neat resin and nanocomposites in detail. As it has been shown in Fig. (3), the morphology of the all MWCNT-nanocomposite samples is considerably changed in comparison with the respective neat epoxy polysulfide resin (Fig. 3a and b). The smooth fracture surfaces of the neat epoxy polysulfide matrices became rough after the attendance of the nanotubes due to agglomeration of CNTs. These results are in good agreement with previous reports [21, 22]. In this work, both pure nanotubes seem to be well impregnated by the epoxy polysulfide

matrices and aggregates are under 100 nm. No micrometric aggregates are observable in the images from surface and fracture surface of nanocomposites. However, the pure MWCNT aggregates are concentrated in small areas, as shown in the composite surface.

3-TENSILE TEST

Tensile testing was carried out on samples by ASTM D-638 using a testing machine (SANTAM; STM – 5). The measurements were carried out at 25 ± 1C using an extension rate of1mm/ min. The tensile stress–strain curve is a tool to provide data on toughness, ultimate tensile strength, ultimate elongation at break and Young's modulus.

Tensile test was done to evaluate the effect of MWCNT on the mechanical properties of composite samples. The results of ultimate tensile properties are presented in Fig. (4) and Fig. (5). as indicated in this Figs., the addition of MWCNT led to an increase in both Young's modulus and the ultimate tensile strength values. due to increasing in value of 0.4% MWCNTs and then reduced at 0.6% MWCNT .This result may be explained by the fact that the agglomerates in the nanocomposites with higher content of MWCNT act as large particles and cause to higher apparent filler loading. These agglomerates confine polymer in the void space between MWCNT and effectively reduce the volume fraction of the epoxy polysulfide matrix. .Similar results have been reported in the last literature [15, 23-25]. An explanation for this behavior may be offered by considering the presence of a weak Van der Waals force between individual graphen shells of the carbon nanotubes, causes easy trip between the shells. Therefore, by higher content of MWCNTs, the nanotubes in the epoxy polysulfide matrices can be drawn layer by layer providing toughness to the sample. Also, pure MWCNT are pulled out more easily when the specimen subjected to tensile or fracture [26]. Good dispersion of MWCNT in the polymer matrices reduces the stress centralization and causes uniform stress distribution fracture strain of untreated MWCNTs/epoxy polysulfide nanocomposites reduced by adding MWCNT value which this indicates tendency to brittle epoxy polysulfide nanocomposites These experimental[27] results are in agreement with the available data in a previous work [15].

4-WEAR RATE TEST

Wear is the progressive loss of substance from the surface of the body brought about by mechanical action. A pin-on-disk test setup was used for slide wear experiments. All experimental data on the slide wear rate of blends and composites is divided into two parts:

First part: gives the results obtained from the polymeric blends before adding the reinforcement.

Second part**:** gives the results obtained from the polymeric blends and additives. Wear debris can be measured either as a weight loss or as a change in volume or size of one or both of the rubbing members. Research results indicate the use of both of these measures of wear, and the following three distinct wear criteria have been proposed [28]:

1. Linear wear rate:-

$k_l=\frac{thickness\ of\ layer\ removed}{sliding\ distance}=\frac{h}{l}$

2. Volumetric wear rate

$kv=volume\ of\ layer\frac{removed}{sliding}distance*apparanet\ area=\Delta v/lAa$

3. Energetic wear rate:-

$ke=volume\ of\ layer\ removed/work\ of\ friction=\Delta v/FL$

The linear and volumetric wear rates are less dimensions and also identical since $\Delta v = Aah$. The energetic and linear wear rates are related by:-

$k_e=k_l(A_a/F)$

Where F is the force of friction, k_E is also referred to as the energy index of abrasion. The mass change of the specimen is measured as the difference in mass of the specimen recorded before and after test, for mass loss measurements, the wear rate is calculated from:-

Wear rate$=\Delta W/S_D$ (gm/cm).

Where ΔW is the mass loss (gm) and S_D is the sliding distance (cm) because wear is a surface effect, surface treatments and coatings play an important role in improving wear resistance. Lubrication can be considered to be a way of keeping surfaces apart and so reducing wear [28]. Different kinds of polymer blends have been studied by some researchers, and it is found that the friction and wear behaviors of polymers vary continuously with compositions, the friction coefficient and wear resistance of blends are superior to those of component polymers and reach optimum at certain compositions. The wear process involves a number of complex interactions, but it can be considered to be caused by the energy created by the frictional work and released during sliding within the contact zone. The mode in which the frictional energy is dissipated depend on the contact configuration, which therefore, should be considered as an important factor in friction and wear behavior of polymer. in this research wear rate is calculated for different samples with different percentage of CNT as shown in the Fig.(6) and fig.(7) .as can be observed the wear rate of 0.2%MWCNTs is higher than that of .4% and 0.6%MWCNT because CNT reinforcement enhance resistant of material to wear. The wear rate of blend at loads (5, 10, 15) N is lower than the epoxy resin, blend (0.6% MWCNT) has lower wear rate than other blends. The presence of plasticizer additives increase the free volume and convert it from a rigid to more flexible matrix as can

be observed from samples surface before test which is smooth and homogenous and after wear where the surface become not homogenous and the wear direction is obvious as in Fig.(8).

5. CONCLUSION

In this research. The blend of epoxy polysulfide resin has been reinforced by pure MWCNTs. tensile tests were done on prepared samples to evaluate the effect of presence MWCNTs in epoxy / polysulfide matrices. Results showed tensile strength and Young's module increase by adding MWCNTs, but this improvement decreased when MWCNTs increased in their content. Wear rate showed to be lower for samples with MWCNTs reinforcement than that of epoxy/polysulfide blend. Increasing MWCNTs content cause an increase in wear rate.

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Table (1): epoxy mechanical properties [1].

Test method	Typical results
Compressive strength	70.0 MPa at 20 ˚C
Tensile strength	26.0 MPa at 35 ˚C
Flexural strength	63.0 MPaat 35 ˚C
Young modulus in compression	16 GPa
Pot life	90 minutes at 20 ˚C 40 minutes at 35 ˚C
Specific gravity	1.04
Mixed viscosity	1.0 poise at 35 ˚C

Tabel.(2): properties of polysulfide [1].

Property	Typical value or description
General chemical structure	~~~[R—S]$_x$~~~ R = $(CH_2Cl)_2$ or $(CH_2(OCH_2CH_2Cl)_2$
Service temperature (°C)	–50 to 95
Cold resistance	Fair
Ageing resistance	Excellent
Sunlight resistance	Medium
Ozone resistance	Excellent
Heat resistance	Poor
Flame resistance	Poor
Fluid resistance:	
Aliphatic	Excellent
Aromatic	Excellent
Mineral resistance	Excellent
Animal or vegetable resistance	Excellent
Water resistance	Good to excellent[a]
Electrical resistance	Moderate
Optimum properties	Maximum oil or solvent resistance

[a] Depends upon the percentage of polymer and curing agent used.

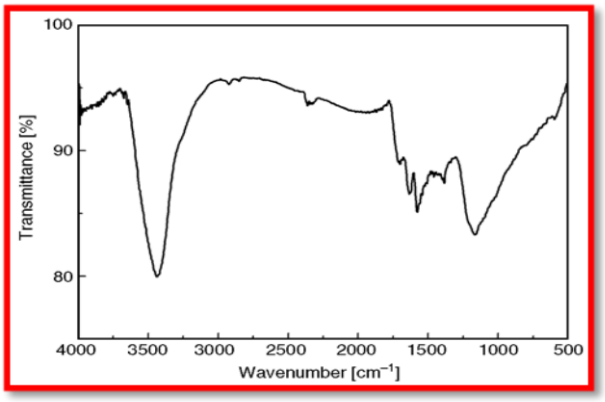


Fig. (1): FTIR of pristine CNT.

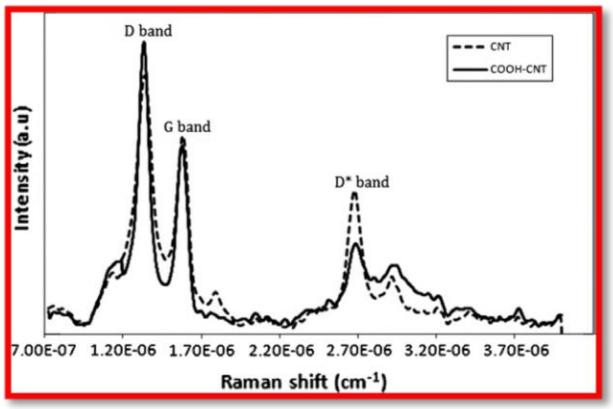


Fig. (2): Raman spectrum of CNT.

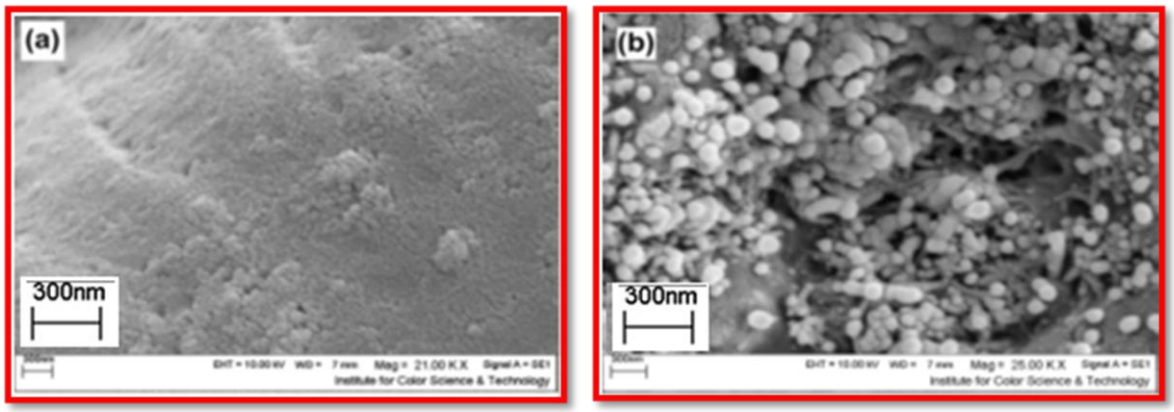


Fig. (3): SEM images from fracture surfaces of (a) the neat epoxy polysulfide resin and (b) the 0.2 wt% MWNT/epoxy polysulfide nanocomposite.

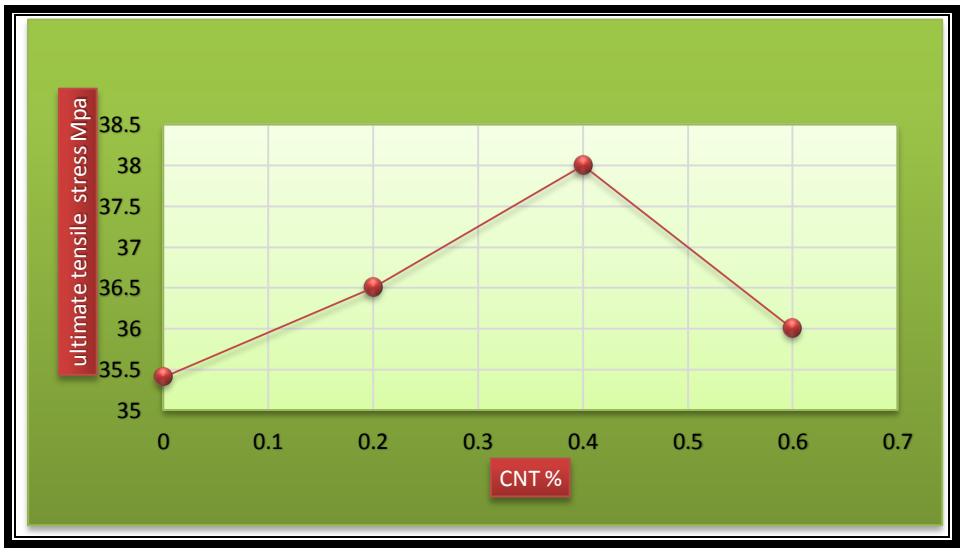


Fig. (4): carbon nano tube effect on stress of 2%polysulfide/epoxy blend.

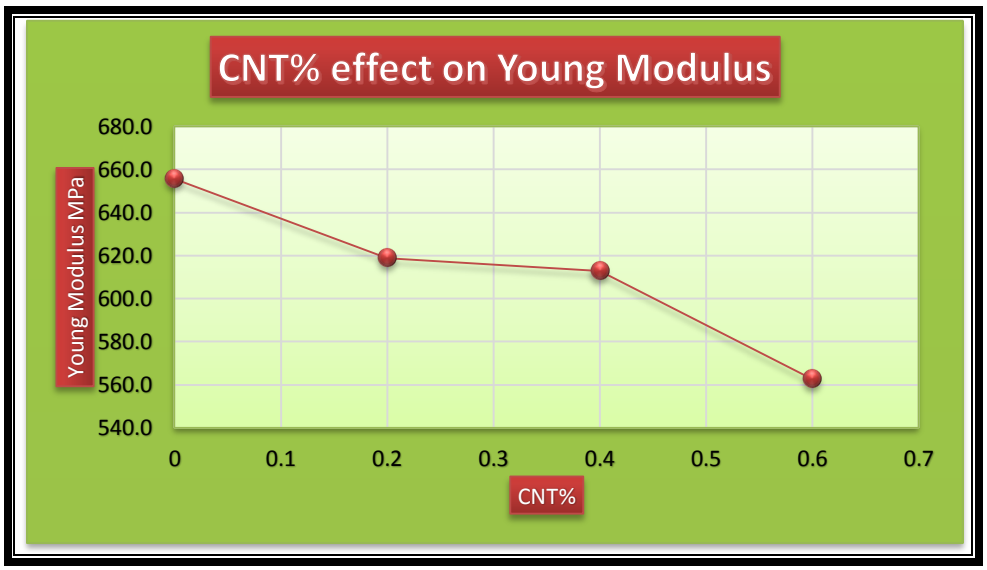


Fig. (5): CNT effect on young modulus.

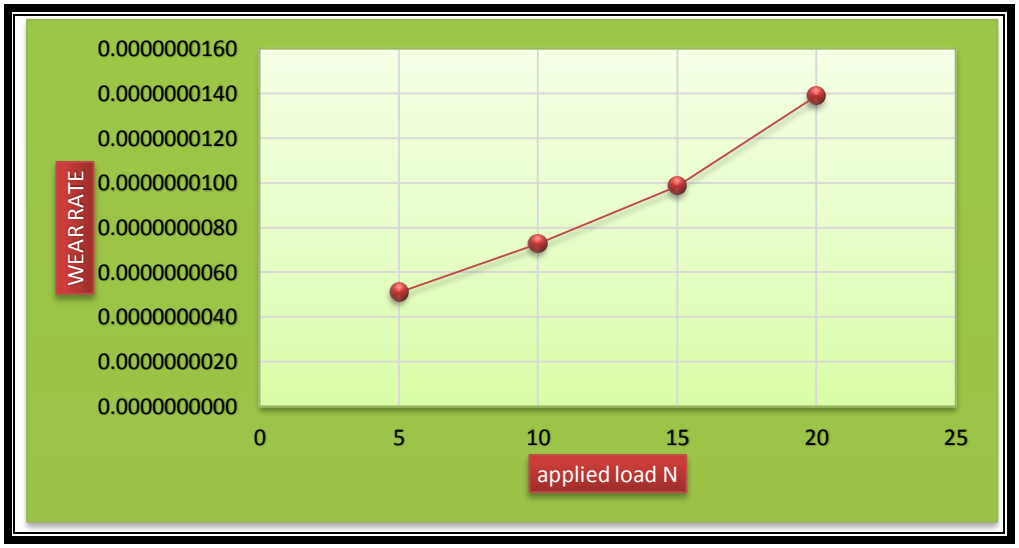


Fig. (6): effect of load on wear rate of epoxy/polysulfide blend.

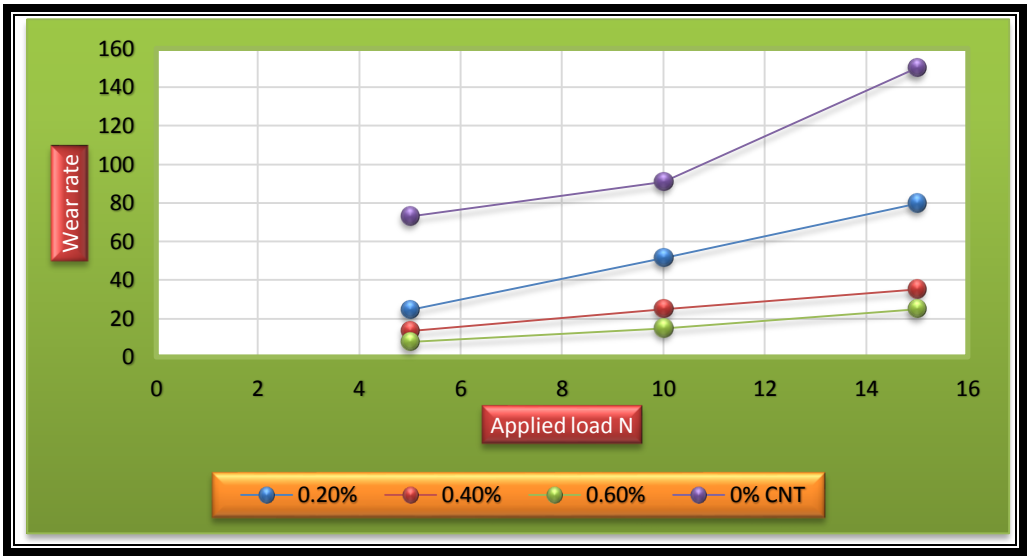
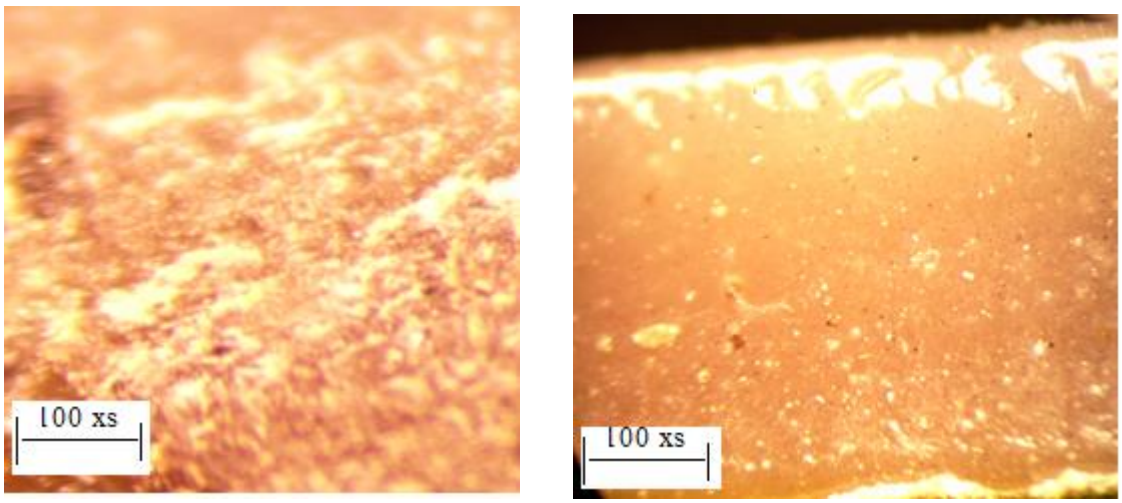


Fig. (7): effect of load on wear rate of carbon nano tube reinforced composite materials.



(a) (b)

Fig. (8): stereo optical microscope samples surface after wear (a) and before wear (b) of epoxy/polysulfide/CNTs.

بعض الخصائص الميكانيكية لمتراكبة خليط الايبوكسى-بولى سلفايد المدعم بانابيب كربونية نانوية

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الخلاصة

فى البحث تم استخدام انابيب الكربون النانوية لتقويةخليط الايبوكسى مع البولو سلفايد وقيمت خواص الشد والبلى. ولغرض الوصول الى تقييم افضل للخواص استخدمت عدة نسب للمادة النانوية وخلطت مع راتنج الايبوكسى ومن ثم اضيف البولى سلفايد واضيف الى الخليط المادة المعالجة للتصلد .النتائج العملية اظهرت اختلاف واضح فى الخواص الميكانيكية للخليط بعد اضافة المادة النانوية .مع اضافة .2%-0.6% من الكربون النانوى ازداد معامل يونك من245-273 ميكا باسكال ومقاومة الشد من 30.5 -38.9 ميكا باسكال واجهاد الكسر من 12.4% الى 14.2%.ولغرض فهم التركيب والية التوزيع للمادة المتراكبة ,حالة انتشار المادة النانوية تم دراستها باستخدام SEM مجهر المسح الالكترونى ,FESEM (مجهر المسح الالكترونى للعناصر المحددة).