

# The effect of additive carbon nano tube on optical properties of epoxy resin

Nadia A. Ali

Department of Physics, College of Science, University of Baghdad

Email: nadia29seb@yahoo.com

## Abstract

In this work, MWCNT in the epoxy can be prepared at room temperature and thickness (1mm) at different concentration of CNTs powder. Optical properties of multi-walled carbon nanotubes (CNTs) reinforced epoxy have been measured in the range of (300-800)nm. The electronic transition in pure epoxy and CNT/epoxy indicated direct allowed transition. Also, it is found that the energy gap of epoxy is 4.1eV and this value decreased within range of (4.1-3.5)eV when the concentration of CNT powder increased from (0.001-0.1)% respectively.

The optical constants which include (the refractive index (n), the extinction coefficient (k), real ( $\epsilon_1$ ) and imaginarily ( $\epsilon_2$ ) part of dielectric constant calculated in the of (300-800)nm at different concentration of CNT powder. It decreased with increasing of CNT and the values take at  $\lambda=550$ nm.

## Key words

Epoxy,  
Carbone nanotube,  
Optical properties.

## Article info

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## تأثير اضافة CNT على الخواص البصرية لراتنج الايبوكسي

نادية عباس علي

قسم الفيزياء، كلية العلوم، جامعة بغداد

## الخلاصة

في هذه الدراسة تم تحضير متراكب من الايبوكسي وكاربون نانوتيوب في درجة حرارة الغرفة بسمك 1 ملم وبتراكيز مختلفة من الكاربون. تم قياس الخواص البصرية بمدى من (300-800 نانومتر). الانتقال الالكتروني في راتنج الايبوكسي والمتراكب يشير الى الانتقال المباشر من النوع المسموح به. كذلك وجد بان فجوة الطاقة للايبوكسي بحدود 4.1 إلكترون فولت والتي قلت من 3.5 – 3.9 إلكترون فولت عند زيادة نسبة المضاف. الثوابت البصرية المتكونة (معامل الانكسار، معامل التوهين، معامل العزل الحقيقي والخيالي والمحسوبة عند مدى الطول الموجي (300-800 نانومتر) باختلاف تراكيز المضاف وجد بانها تقل مع زيادة المضاف عند طول موجي 550 نانومتر.

## Introduction

Epoxy resin is the polymer matrix used most often with reinforcing fibers for advanced composites applications. The resins of this class have good stiffness, specific strength, dimensional stability, and chemical resistance, and show considerable

adhesion to the embedded fiber since the discovery of carbon nanotubes (CNTs) in 1991 by Iijima [1]. CNTs have been looked at extensively by researchers in various fields such as chemistry, physics, materials science and electrical

engineering. CNTs are unique nano structured materials with remarkable physical and mechanical properties [2,3]. These properties have inspired interest in using CNTs as a filler in polymer composite systems to obtain ultra-light structural materials with enhanced mechanical, electrical and thermal characteristics[4]. The prospect of obtaining advanced nanocomposites with multifunctional features, e.g., materials used for structures and electrical conductors, has attracted the efforts of researchers in both academia and industry [5, 6, 7].

Industry in particular recognizes many potential applications such as electro statically dissipative materials and aerospace structural materials [8]. Currently, one of the major obstacles to using nanotubes as a polymer filler is cost; however, advances in the synthesis of CNTs continue to rapidly improve both their quantity and quality, though growing structurally perfect nanotubes at large scales is not yet at hand [9,10].

Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure. Nanotubes have been constructed with length-to-diameter ratio of up to 28,000,000:1 [1] which is significantly larger than any other material. These cylindrical carbon molecules have novel properties that make them potentially useful in many applications in nanotechnology, electronics, optics and other fields of materials science, as well as potential uses in architectural fields[11].

The nature of the bonding of a nanotube is described by applied quantum chemistry, specifically, orbital hybridization. The chemical bonding of nanotubes is composed entirely of  $sp^2$  bonds, similar to those of graphite. This bonding structure, which is stronger than the  $sp^3$  bonds found in diamonds,

provides the molecules with their unique strength. Nanotubes naturally align themselves into "ropes" held together by Van der Waals forces .The use of carbon nanotubes (CNT) as

nanofillers in polymer matrices is one of their most promising applications, especially regarding epoxy resin. Multiple enhanced properties at low loadings are the major advantage of CNT over other fillers. Epoxy resin is a widely used polymer as adhesive, coating or as matrix in structural composites. The choice of given application for epoxy is often based on the glass transition temperature, noted as  $T_g$ . This is the temperature at which the mechanical properties of polymer drop and corresponds to a second-order phase transition. There has been an increasing need of an accurate knowledge of the optical constant ( $n$ ) and ( $k$ ) of thin absorbing films over a wide wavelength range for example the photo thermal conversion of solar cell need a selective absorbing films[12].

The optical properties of carbon nanotubes refer specifically to the absorption, photoluminescence, and Raman spectroscopy of carbon nanotubes. Spectroscopic methods offer the possibility of quick and non-destructive characterization of relatively large amounts of carbon nanotubes. There is a strong demand for such characterization from the industrial point of view: numerous parameters of the nanotube synthesis can be changed, intentionally or unintentionally, to alter the nanotube quality. As shown below, optical absorption, photoluminescence and Raman spectroscopes allow quick and reliable characterization of this "nanotube quality" in terms of non-tubular carbon content, structure (chirality) of the produced

nanotubes, and structural defects. Those features determine nearly any other properties such as optical, mechanical, and electrical properties [10,11,12].

**Optical Energy Gap**

Study of the optical absorption spectra provides a very useful tool for the investigation of optically induced transition and insight in the energy gap and band structure of crystalline and non crystalline materials .The experimental results on optical absorption in glassy materials have been reported by Mott and Davis [6].

One important difference between amorphous and crystalline solids is that; in the crystalline nonmetallic solids, there is a sharp well defined lattice absorption edge and energy gap (Eg) given by the relation[7]:

$$E_g = hc/\lambda \tag{1}$$

where: Eg=energy gap, h= Plank's constant, c=velocity of light, λ=wavelength.

While in the amorphous materials, the absorption edge is less sharp and is not well defined.

The absorption coefficient (α) which is defined as the decrement ratio of incident radiation relative to unit length in the direction of wave propagation inside the medium is relating with the absorbance (A) through the Eq.5:

$$\alpha = \frac{2.303A}{t} \tag{2}$$

where t is the thickness of sample.

Many researchers put the empirical equation between the optical energy gap (Eg) and energy of the incident photon which is [8]:

$$(\alpha hv) = A(hv - E_g)^r \tag{3}$$

where A is proportion with the inverse of amorphousity, (hv) is the energy of incident photon, which can be calculated using the equation [7,8]:

$$hv = \frac{1240}{\lambda(nm)} \tag{4}$$

r is the order of the optical transition depending on the nature of electronic transition. The transition is called direct if the extremities of V.B and C.B lie at the same K-space, while the transition is called indirect if the transition possible only with phonon assisted (Δκ ≠ 0) [6]. Thus the value of (r) may be 1/2, 2, 3/2, and 3 corresponding to the allowed direct, allowed indirect, forbidden direct and forbidden indirect transition respectively. The extinction coefficient (imaginary part of the refractive index) can be calculated by the relation [6]:

$$k = \lambda\alpha/4\pi \tag{5}$$

The refractive index (n) can be measured (when the reflectance (R) and (k) are known) by using the Eq.6, where (n) is the refractive index given by:

$$n = \left[ \frac{(1+R)^2}{(1-R)^2} - (k^2 - 1) \right]^{1/2} + \frac{1+R}{1-R} \tag{6}$$

The complex index ( $\bar{N}$ ) of refractive is defined as [6]:

$$N = n - ik \tag{7}$$

The dielectric (ε) is the complex dielectric constant can be introduced from by:

$$\epsilon = \epsilon_1 - i \epsilon_2 \tag{8}$$

The parameter ε<sub>1</sub> is the real part of dielectric constant; ε<sub>2</sub> is the imaginary part of dielectric constant, from Eqs.7 and 8 one can obtain:

$$\epsilon_1 = n^2 - k^2 \tag{9}$$

$$\epsilon_2 = 2nk \tag{10}$$

**Experimental Part**

**Carbon nanotubes prepared**

The catalyst deposited substrates were loaded on a quartz tube representing the

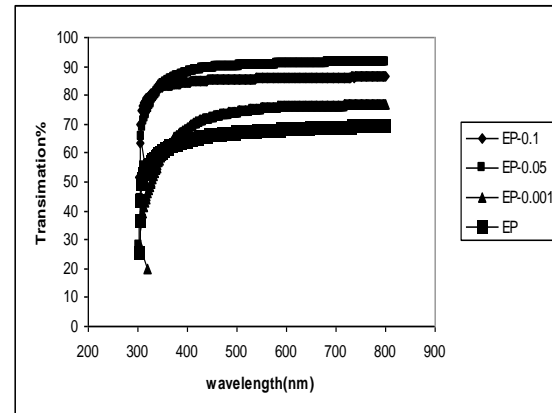
reactor in our CVD system. Argon (Ar) gas was flowed in to a quartz tube CVD oven in order to prevent the oxidation of catalyst film metal while raising the required temperature. For growth CNTs, the temperature was varied between (750-850°C). The fed gas, acetylene ( $C_2H_2$ ) was introduced to the quartz tube after reaching the desired temperature for 10min. The average diameters of the growth CNTs were 7.87nm [13].

In this work Epoxy (EP10) and hardener type (HY-956) were in the ratio of 3:1 for curing of CNT composites with three different concentration of CNTs equal to (0.001%, 0.05% and 0.1%) weight percentage. At first CNT were equal to dispersed in chloroform solution under magnetic agitation to for reducing the maximum size of the aggregates to about 100 nm. After complete evaporation of chloroform, the CNT powder was added directly added to the epoxy resin and hardener mixture. The samples were placed between two metal plates to reduce porosity. Before optical measurements, the surfaces of the specimens were mechanically polished to minimize the influence of surface flaws, mainly the porosity. Finally, they were cast in moulds the specimen were cut at dimensions of 250mm \* 250mm \* 1mm. From the absorption and transmittance spectrum in the region of UV-VISM spectrometer as function of wavelength ( $\lambda$ ) of incident photon in the range 300-800 nm.

### Results and Discussions

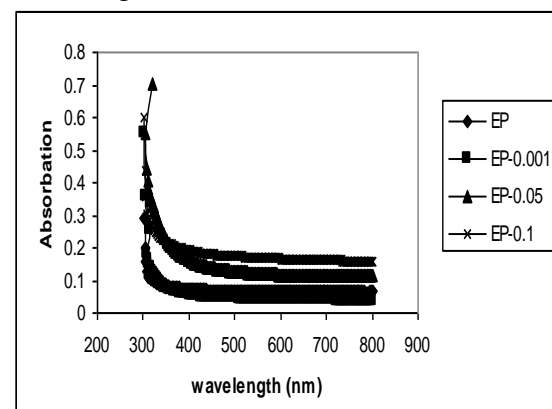
The optical properties of epoxy and epoxy/CNT (0.001, 0.05, and 0.1) at room temperature of thickness (1mm) have been determined by UV-Visible near infrared transmittance spectrum in the region of (300-800) nm. Fig.1 shows the variation of transmittance as a function of wavelength of CNT/epoxy composites at of CNT contact. It can be observed from this fig that the

transmission increase with increasing of  $\lambda$  for all CNT contact. Also, this figure shows that increasing with increase of CNT, this revealed to the smooth reflecting surfaces of the samples and there was not much scattering loss at the surface.



**Fig.1:** Transmittance as function to wavelength for EP and EP/CNT with different contact.

The absorption spectrum as a function of wavelength of CNT/epoxy at different CNT contact is shown in Fig.2. It is noticed that the absorption decreases with increasing wavelength. In general, and the increased of absorption value with increasing of CNT contact is cleared. The increased in absorption is attributed to this revealed to the smooth reflecting surfaces of the samples and there was not much scattering loss at the surface [14].



**Fig.2:** Absorptions as function to wavelength for EP and EP/CNT with different contact.

The reflectance spectrum of CNT/epoxy in the spectrum range (300-800)nm for different contact of CNT in Fig.3. It is clear from this figure that the spectra charactering are by increasing carbon contact; the reflectance is increased with increasing of CNT contact.

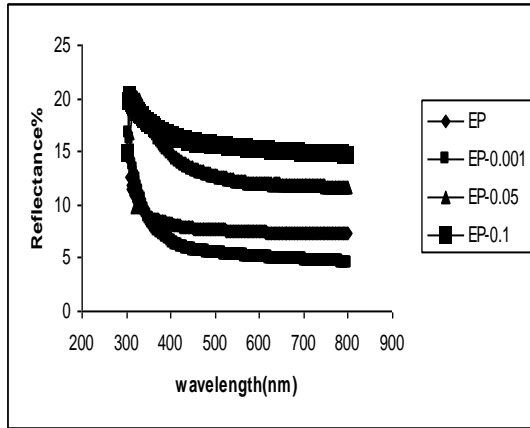


Fig.3: Reflectance as function to wavelength for EP and EP/CNT with different contact.

Fig.4 represents the optical energy gap for pure epoxy and epoxy/CNT composites at different CNT contact, for the pure epoxy the band was in range 4.1-3.6eV, this figure indicated that allowed direct transition is involved which is due to  $\Pi - \Pi^*$  transition while for CNT/epoxy the energy gap is decreased with increasing the contact ratio of CNT at 0.001%, 0.05%, 0.1% of CNT. Also, it can observe that the position of the band edge was shifted towards the lower photon energy than that pure epoxy and it implies that band gap narrow has been occurred by adding the more concentration of CNT material, this lead to change the polymer material from insulator state to semiconductor state. The experimental results to calculate the energy gap according to Tauc relation, indicate that the electronic transition for these polymer equal to  $(r=1/2)$ . The value of the optical energy gap decrease with increase of contact of CNT from (4.1eV-3.5eV) when increase of 0.1 CNT and thickness 1mm, this is can be explained as follows it is well know that

Eg value of bulk material is lower than that of film samples, thus the increase additive causes the reduction of Eg values since the structure will be approach from that of bulk material[5].

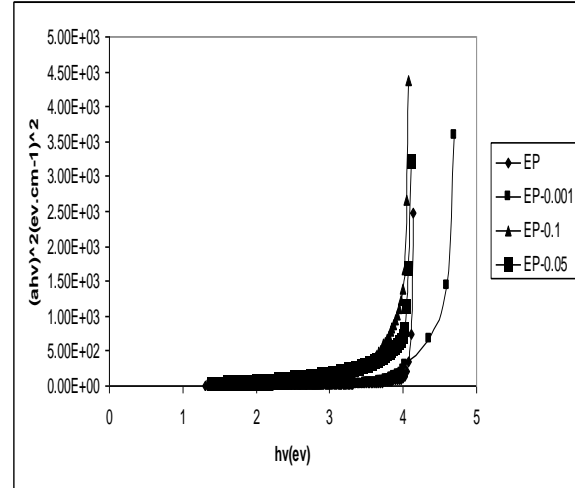


Fig.4: The variation of  $(\alpha hv)^2$  versus photon energy for EP, EP/CNT with different contact.

From Taus Eq.3 and the shape of absorption curve near the band edge, it is possible to evaluate the energy gap by plotting  $(\alpha hv)^{1/r}$  where  $r=(2,1/2,3,3/2)$  versus hv. By plotting  $(\alpha hv)^2$  versus photon energy and taking straight line at high absorption data ( $\alpha > 10^4 \text{ cm}^{-1}$ ), the zero inter kept of  $\alpha=0$  given the value of Eg for direct transition. We observed the energy gap decreases with increase of CNT. The Table1 shows the value of energy gap for pure epoxy and CNT/epoxy composites. Fig.4 shows the variation of  $(\alpha hv)^2$  with photon energy for direct allowed transition to pure epoxy and additives CNT samples therefore the optical energy gap are determined. The CNT additives decreases the optical band gap from 4.1-3.5eV. The reduction in the optical band gap is probably due to the modification of the polymer structure [5,6].

The absorption coefficient ( $\alpha$ ) and energy gap calculated in Eq.2 for all samples revealed by strong absorption at small energies and mobility edge started at small

energies we shows the absorption takes higher values and that shifts to lower energies, this is attributed to the lattice absorption bonds corresponds to the electronic transition through the defect centers such as impurities[8].

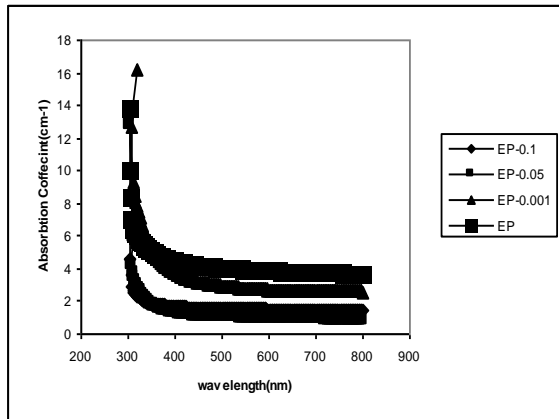


Fig.5: The absorption coefficient as function to wavelength for EP and EP/CNT with different contact.

**Optical Constant**

The optical properties of epoxy /CNT were investigated at room temperature. The optical constants (n, k,  $\epsilon_1$ ,  $\epsilon_2$ ) were determined from both the transmittance (T) and absorbance (A).

Fig.6 shows the variation of reactive index (n) with wave length for epoxy and epoxy/CNT within range (300-800nm)

with variation of CNT content it is found that the values of refractive index decreasing slightly with increase  $\lambda$ . The refractive index decreasing with increase with additives CNT in prepared samples, moreover n decrease from 2.35-1.09 when thickness is 1mm, this behaviour can be explained on the basic of that increasing CNT (lowering the packing density) which in turn increase propagation velocity of light through them which resulting in decreasing of n values since n represent the ratio of light velocity through vacuum to velocity through any medium [9], as shown in Table1.

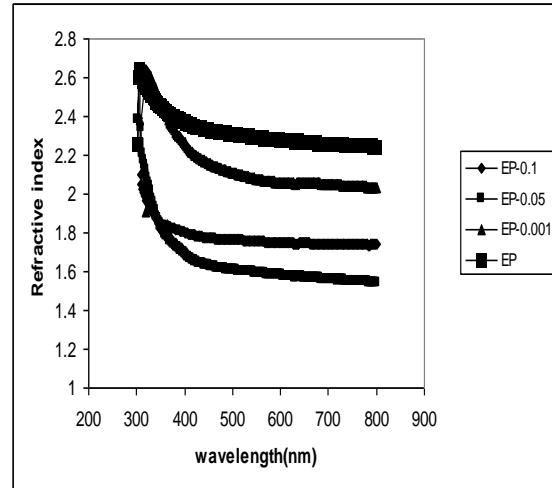


Fig.6: The variation of refractive index (n) versus wavelength for EP, EP/CNT with different contact

The extinction coefficient can be calculated from Eq.5 the behavior of extinction coefficient (k) is corresponding to  $\alpha$  for different  $\lambda$  as shown in Fig.7. In general from this figure can be observed that k decreased within the range 300-500nm and then increasing within the range of 500-800 nm with increasing of  $\lambda$ , it decreases from  $4.5 \times 10^{-5}$  -  $1.3 \times 10^{-3}$  as shown in Table 1. Also, it can be observed that K is decreased with increasing of CNT contact and height value of K is occurred for pure epoxy.

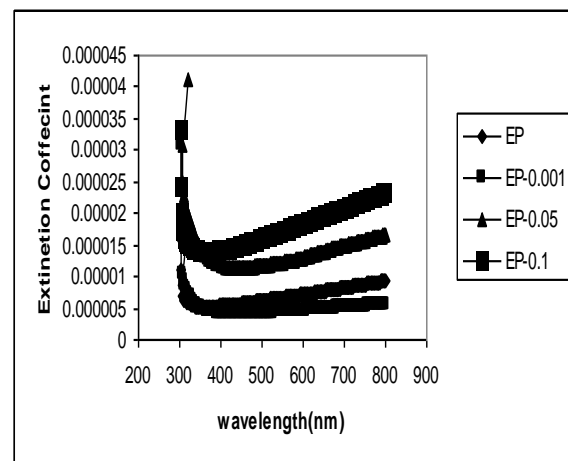
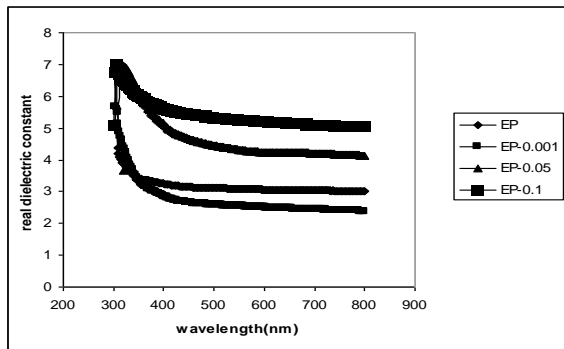
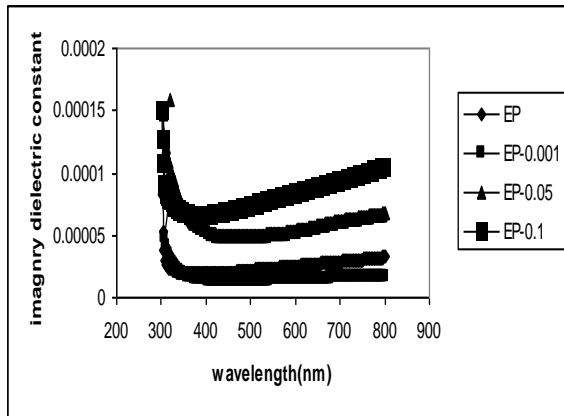


Fig.7: The variation of extinction coefficient (k) versus wavelength for EP, EP/CNT with different contact.

The dielectric constant of real part ( $\epsilon_1$ ) and imaginary part ( $\epsilon_2$ ) which depend on the frequency of the electromagnetic waves, the variation of  $\epsilon_1$  and  $\epsilon_2$  with the wavelength of the incident radiation is due to the change of reflectance and absorbance [11]. The variation of real part and imaginary of dielectric constant as a function of  $\lambda$  for pure epoxy and CNT/epoxy samples were determined and shown in Figs (8 and 9). It can observe that the variation of  $\epsilon$  has similar trend to the variation of  $n$  because of smaller values of  $k^2$  in comparison with  $n^2$ , where  $\epsilon_1=n^2-k^2$  while the variation of  $\epsilon_2$  mainly depends on the variation of  $k$  values which are related to the variation of  $\alpha$ , where  $\epsilon_2=2nk$



**Fig.8:** The variation of real part of dielectric constant ( $\epsilon_1$ ) and imaginary part ( $\epsilon_2$ ) versus wavelength for EP, EP/CNT with different contact.



**Fig.9:** The variation of real part of dielectric constant ( $\epsilon_1$ ) and imaginary part ( $\epsilon_2$ ) versus wavelength for EP, EP/CNT with different contact.

**Table 1:** The values of  $E_g$  and ( $n, k, \epsilon_1$  and  $\epsilon_2$ ) for epoxy and epoxy/CNT deposited at RT and thickness 1mm at  $\lambda=550$  nm.

Material	$E_g$ (eV)	$n$	$k$	$\epsilon_1$	$\epsilon_2$
EP	4.1	2.35	$6.7 \times 10^{-5}$	3.3	$2.3 \times 10^{-5}$
EP-0.001CNT	3.9	2.13	$4.5 \times 10^{-5}$	2.6	$1.9 \times 10^{-5}$
EP-0.05CNT	3.8	1.09	$1.7 \times 10^{-5}$	2.4	$1.5 \times 10^{-5}$
EP-0.1CNT	3.5	1.27	$1.3 \times 10^{-5}$	2.1	$1.2 \times 10^{-5}$

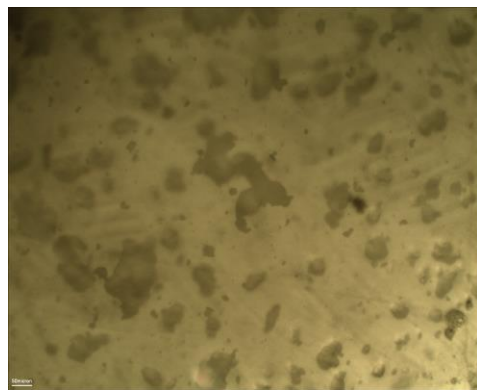
**Morphology of CNT/epoxy composites**

The main purpose of this section is to investigation the structure of CNT/epoxy. Fig.10 shows the optical microscopy image of composites at different contact of CNT at amplification of 50micron.

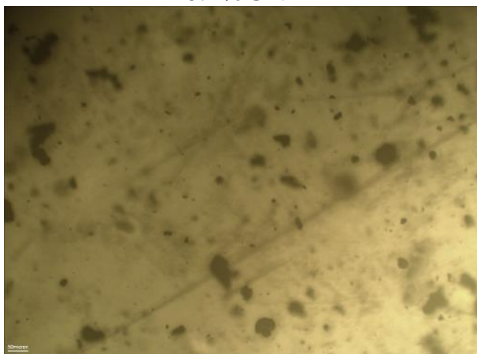
OP images of the composites reveal a structure with dense gains and crystalline structure and clear grain boundaries be comes apparent with increasing contact of CNT in the composites.

Nanotube dispersion in polymers can affect the final nanocomposite properties. To optimize nanotube dispersion, we need to investigate and quantify the dispersion. This can be done by visualizing the nanotubes themselves, the interface, and the effect of the CNTs on the surrounding matrix. It is not surprising that at the nano length scale, characterization, testing and modeling are much more difficult. Optical techniques, typically used for characterizing dispersion, cannot discern between single CNTs.

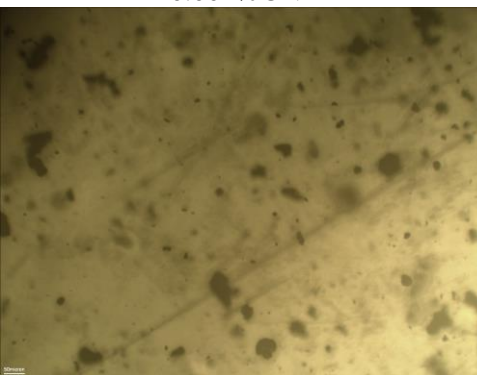
The CNTs nano composites have poor interfacial bonding between the CNTs and the polymer matrix, which is identified in the optical images. The nano composites filled with a little wt% CNTs yield much higher optical properties than neat epoxy samples.



0.1% CNT



0.001% CNT



0.05% CNT

**Fig.10:** The optical microscopy image of composites at different contact of CNT at amplification of 50micron.

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