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Influence of dispersion states of carbon nanotubes on mechanical and electrical properties of epoxy nanocomposites

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Multiwalled carbon nanotubes (MWCNTs)/ epoxy resin composites have been fabricated by dispersing very low content (0.2%) of MWCNTs in the epoxy matrix using ethanol. To analyze dispersion of CNTs, optical microscope is used. Further ductile nanocomposites (NCs) are prepared by setting samples at low temperature. With a little wt% of CNTs, composite samples yield higher mechanical and electrical properties than pure resin samples. Improvement in flexural modulus and electrical conductivity are observed in NCs containing well dispersed CNTs than the ones with poorly dispersed CNTs. Lower values are due to inhomogeneous dispersion of nanotubes in polymer matrix. Moreover, ductile samples having better dispersion state exhibit significant improvement in mechanical and electrical properties.

Keywords: Carbon nanotubes, Dispersion, Electrical properties, Epoxy nanocomposites, Mechanical properties

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Introduction

Carbon nanotubes (CNTs), since the discovery in 1991 by Iijima[1] have been extensively studied in chemistry, physics, materials science and electrical engineering. Investigators have endeavored to fabricate advanced CNT composite materials that exhibit one or more of mechanical, thermal and electrical properties[2]. Industry recognizes these advanced nanocomposites (NCs) for electrostatically dissipative materials and aerospace structural materials[3-8]. Currently, one of the major obstacles of using nanotubes as a polymer filler is their cost; however, advances in the synthesis of CNTs continue to rapidly improve both their quantity and quality[9], though growing structurally perfect nanotubes at large scales is not yet at hand[10]. In order to disperse CNTs in polymer homogeneously, entanglement of CNTs produced by synthesis and agglomerates of CNTs caused by the intermolecular van der Waals force must be broken. Multiwalled carbon nanobutes (MWCNTs) are generally entangled in the form of curved agglomerates. Singlewalled carbon nanotubes (SWCNTs) are produced as bundles. Aggregation problems have been usually solved by using melt mixing, bulk polymerization, and sonication during the CNTs dispersion process[11].

In a number of studies[12-18] conducted, expected potential of CNTs as reinforcement has not yet been fully realized. Several groups[12-14] observed only marginal improvement or even a decrease in nanocomposite tensile moduli after small additions of nanotubes into an epoxy resin matrix. Lau *et al*[15,16] showed the reduction in flexural strength of a CNT-epoxy NC relative to pure epoxy, probably a result of a weak interface. Electrical conductivity (>10^{-8} S/cm) is needed in order to avoid the electrostatic charging of insulating matrix. Sandler *et al*[17] showed that CNTs/epoxy NCs have electrical conductivity of about10^{-4} S/cm with the filler volume fractions as low as 0.1 wt.%. Alloui *et al*[4] have prepared NCs using overaged hardener by incorporating CNTs (1-4 wt %) in epoxy matrix.

In this work, the NCs have been prepared using sonication method with very low content (0.2 wt %) of CNTs in the epoxy matrix to study the effect of CNTs dispersion on various properties of the CNTs filled composites. Usually MWCNTs consist of agglomerates that would be an obstacle to the uniform dispersion into the epoxy matrix. In order to mitigate such a situation in this investigation, two different specimens (well dispersed and poorly dispersed) are prepared depending upon whether

CNTs are dispersed in ethanol or not. Additionally, ductile NCs are prepared at low temperature in refrigeration process. Mechanical and electrical properties of NCs are examined and variations in different properties between the respective cases are observed. Dispersion state of CNTs in epoxy NCs are morphologically characterized by the optical microscope images.

Materials and Methods

Nanotubes and Polymer Matrix

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MWCNTs, obtained from MER corporation, USA, are produced by chemical vapor deposition (CVD) method (purity 95%, length 10-50 μm, diam 6-20 nm). SEM morphology of CVD products (Fig. 1) was carried out with a "JEOL JSM-5800 Scanning Microscope, OXFORD". Epoxy polymer matrix was prepared by mixing epoxy resin (Ciba-Geigy, araldite LY-556 based on bisphenol A) and hardener HY-951 (aliphatic primary amine) in wt ratio 100/12. Epoxy resin (5.3-5.4 equiv/kg) was of low processing viscosity and good overall mechanical properties.

Nanocomposite Preparation

Preparation of Pure Resin Specimens

Epoxy resin (150 g) and hardener (18 g) were mixed using ultrasonic vibrator to obtain one batch of pure epoxy specimens. The mixture was poured into a mold (12 cm×14 cm×2 cm). One sample (0) was set at room temperature and another (D0) was allowed to set at low temperature in a refrigerator. Both samples were then cured for 5 h at 80°C in an oven.

Preparation of Nanocomposites

Well-dispersed NCs (2 types) were prepared by dispersing 300 mg MWCNTs (0.2 wt% of 150 g epoxy) in 10 ml ethanol. After evaporation of ethanol, MWCNTs were added to 150 g epoxy resin and mixture was sonicated for 1 h. Then 18 g hardener (12% of epoxy) was added and mixture was kept for 15 min under sonication. Samples allowed to set at room temperature were named as sample-1 and those in a refrigerator were named as sample-D1. Poorly dispersed NCs were prepared by adding MWCNTs (300 mg) in epoxy resin (150 g) under sonication for 3 h. Then hardener was added and sonicated for 15 min. Samples set at room temperature were named as sample-2 and those set in refrigerator were named as sample-D2. Mold (12 cm×14 cm×2 cm) has been used for obtaining one batch of samples. All composite samples were cured for 5 h at 80°C in an oven.

Mechanical Measurements

After taking out of the mold, samples were cut using a saw and specimens of pure resin as well as MWCNTs/epoxy composites were made for mechanical measurement. From each sample, five rectangular specimens were taken for three-point bend test as per ASTM D790 (width=2.7 cm, thickness=0.7 cm, span=11.2 cm, length=12 cm). Flexural tests were carried out at ambient temperature using Instron 1195 keeping the cross-head speed 2 mm/min. Flexural modulus of each sample was determined from the average value of five specimens.

Electrical Measurements

The dc electrical conductivity values of pure resin and MWCNT reinforced epoxy composites of (4 cm×0.5 cm×0.4 cm) have been obtained. Electrical resistance was measured at room temperature (25°C) by two probe method using Keithley Electrometer–617 having maximum input resistance $\sim 10^{17}\ \Omega$. Two-probe method has been chosen instead of four-probe method because the sample shows relatively high resistance. Silver paints were used at the electrode point for ohmic contact. Respective resistivities of samples were determined taking the cross-sectional areas (0.2 cm^2) and length (4 cm) of the sample into account. From this information, conductivities of respective sample are calculated.

Morphological Measurements

Morphology of poorly dispersed and well-dispersed MWCNTs/epoxy composites have been analyzed. All SEM micrographs were taken at x200 resolutions by using optical microscope *(Verasmet-II, Union 7685).*

Results and Discussion

Mechanical Measurements

Flexural modulus of samples (Fig. 2) are found to be: 0, 24.52; 1, 64.61; 2, 136.86; D0, 44.15; D1, 92.34 and D2, 176.30 Mpa. All the composite samples show greater modulus than pure resin samples. Moreover, increase in flexural modulus is more pronounced in well-dispersed samples (2 and D2) than poorly dispersed samples (1 and D1) because MWCNTs are easier to disperse and/or to be impregnated when ethanol is used. Ductile sample-D2 has more (29%) flexural modulus value than sample-2 that implies variation in polymerization process under the action of low temperature. This may be due to contraction of matrix that increases frictional force between nanotubes and matrix.

Electrical Measurements

It is observed that electrical conductivity values of composite samples are higher compared to that of resin samples (Fig. 3). Pure resin (sample-0) and ductile pure resin (sample-D0) have conductivity values of 0.027 μS/cm and 0.054 μS/cm respectively. Composite samples 1 and D1 offer conductivity values of 0.65 μS/cm and 0.90 μS/cm respectively. This clearly indicates an increase of conductivity by a factor of 16-24. MWCNTs are generally conducting[17] and typically have aspect ratio of around 1000. Due to improvement in dispersion of nanotubes in the epoxy, aggregated phases form a conductive three-dimensional network throughout the whole sample. This may be the reason for conductivity values of sample-2 (2.00 μS/cm) and sample-D2 (2.35 μS/cm), which are almost 3 times compared, to the samples-1 and D1. In addition, increase in conductivity is more significant in case of ductile samples- D0, D1 and D2 compared to samples-0, 1 and 2 indicates the impact of temperature that needs more investigation.

Previous workers[4] have found that with 0.5 wt.% CNT, composite still behaved like an insulator. However, present investigation indicates good results even with 0.2 wt% taking into account the random orientation of MWCNTs. Composite sample conductors (conductivity order of 10^{-6} S/cm) agrees with the earlier report[18] of obtaining a percolation threshold with less than 0.5 wt% of CNTs. Little improvement in conductivity is because measurement has not been taken in the direction of CNT alignment.

Morphological Characterization

Presence of CNTs aggregates (shown by white arrows) and porosities (shown by dotted white arrows) are more prominent in sample-1 and sample-D1 (Fig. 4) as compared to that in sample-2 and sample-D2 (Fig. 5). In well-dispersed sample-D2, there is almost no porosity and relatively homogeneous distribution of MWCNTs is observed though in some places CNT concentration is higher (Fig. 5b). From all the measurements, it is clear that better dispersion and cooling process at refrigeration temperature (4°C) facilitates improvement in electrical conductivity and increase in flexural modulus. Better dispersion is possible because ethanol helps to deagglomerate nanotubes and high-energy sonication action breaks the entanglement, which helps to distribute MWCNTs homogeneously in the polymer matrix. Low temperature offers delay in the settling procedure that ultimately has an impact on the matrix structure and crosslinking ratio and by this way the molecular motions. Further work can be aimed at the alignment of CNTs in the matrix and improvement in interfacial bonding between CNTs and matrix that would still improve the results in terms of electrical and mechanical parameters.

Conclusions

Epoxy composites filled with a little wt% CNTs yield better mechanical and electrical properties than pure resin samples. NCs containing well-dispersed CNTs exhibit higher flexural modulus and electrical conductivity than ones with the poorly dispersed CNTs. Much higher conductivity can be achieved if the alignment of nanotubes would be taken care of. CNTs composites have poor interfacial bonding between CNTs and polymer matrix, which is identified from the presence of CNTs agglomerates in the optical images. Better result of ductile well-dispersed sample as compared to other samples indicates that use of ethanol to disperse CNTs and settling the composite at lower temperature brings improvement in physical properties.

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Figure captions

Fig. 1(a & b). SEM micrographs of CNT at different resolutions

Fig. 2. Flexural modulus of: a) Sample-0, 1 and 2; b) Ductile samples-D0, D1 and D2.

Fig.3. Electrical conductivity of: a) Sample-2, 1and 0; b) Ductile samples-D2, D1 and D0.

Fig. 4. Optical micrograph of poorly dispersed CNTs: a) Sample-1; b) Sample- DI

Fig. 5. Optical micrograph of well dispersed CNTs: a) Sample- 2; b) Sample- D2

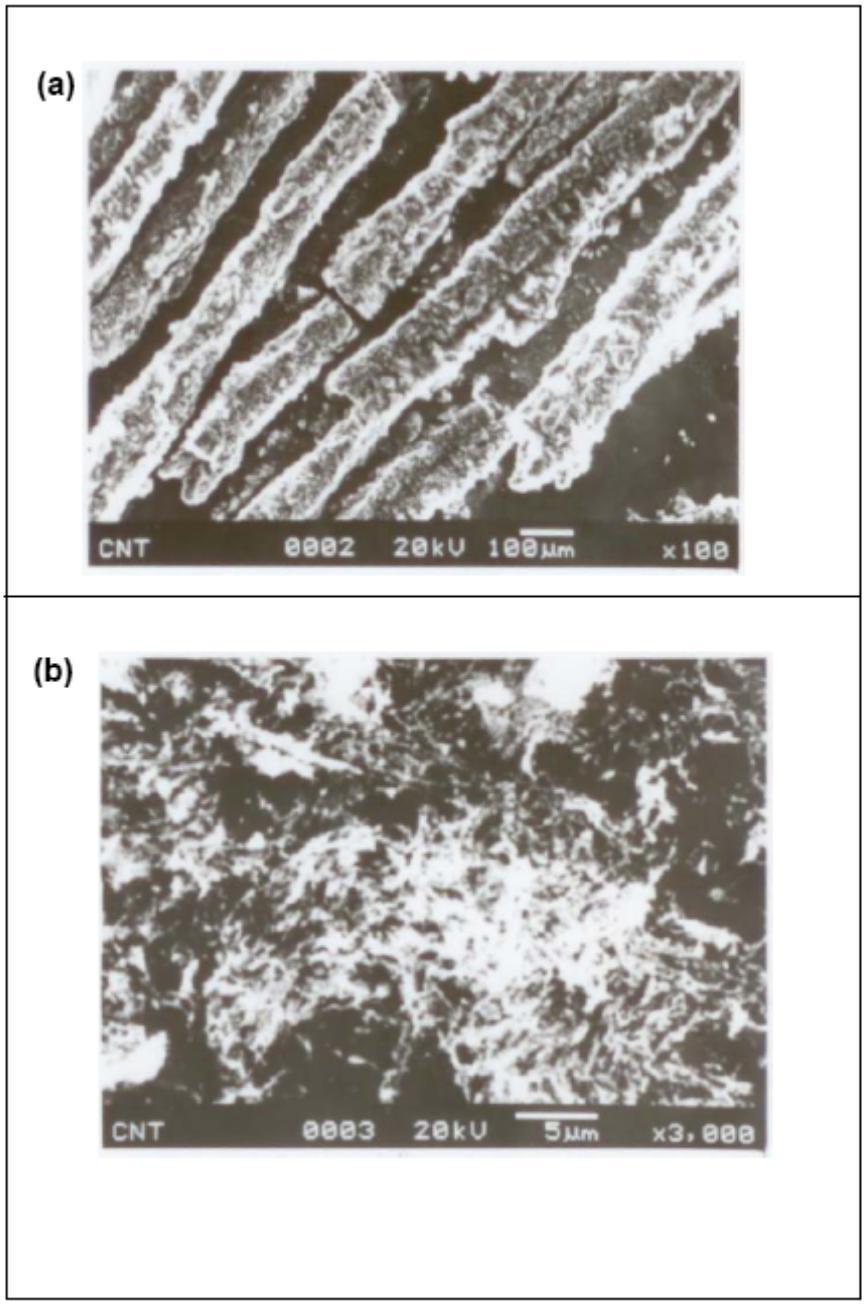

Fig. 1 SEM micrographs of CNT at: a) × 100; b) × 3000

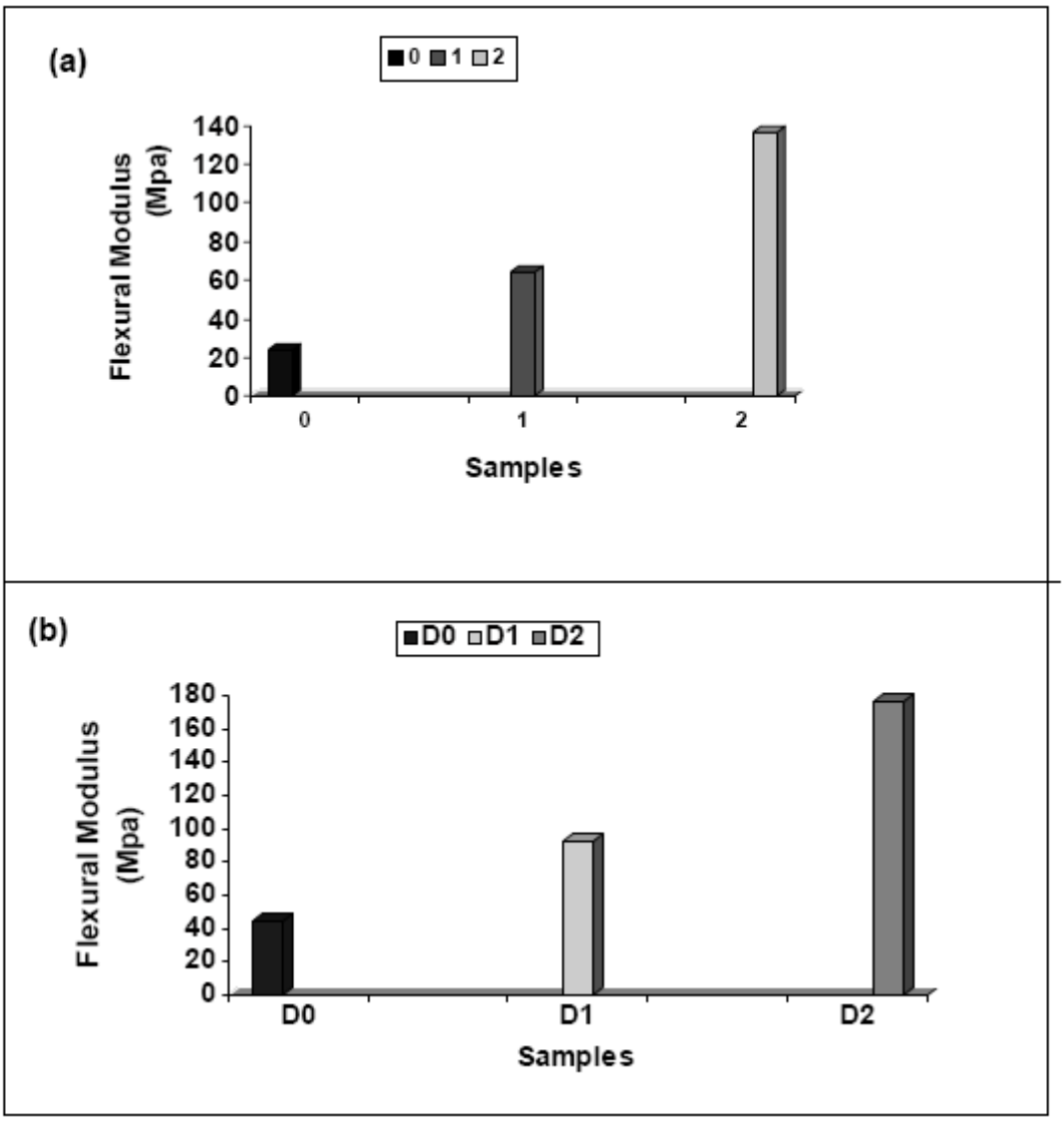

Fig.2 Flexural modulus of: a) Samples-0, 1 and 2; b) Ductile samples-D0, D1 and D2

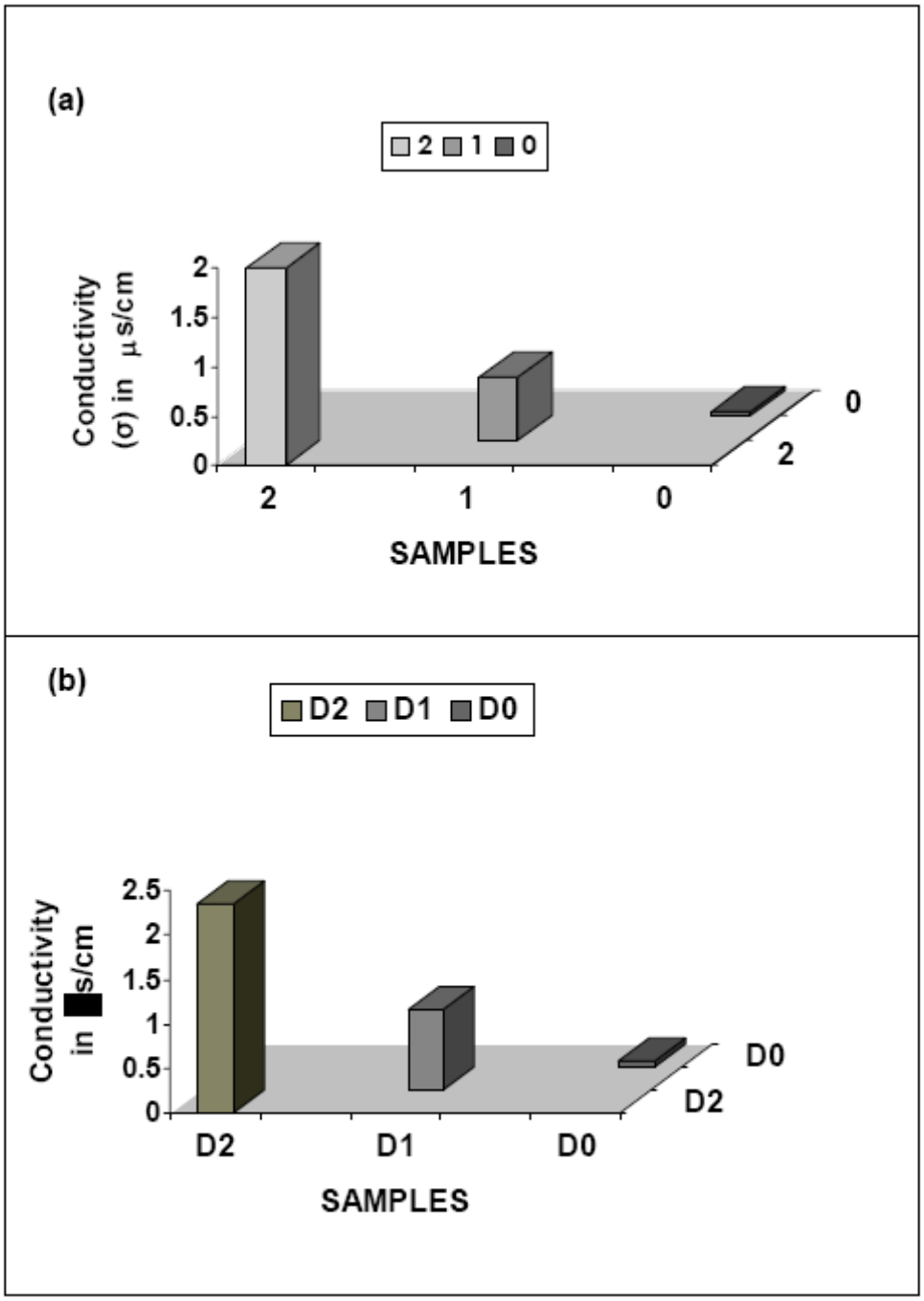

Fig.3 Electrical conductivity of: a) Samples-2, 1 and 0; b) Ductile samples-D2, D1 and D0

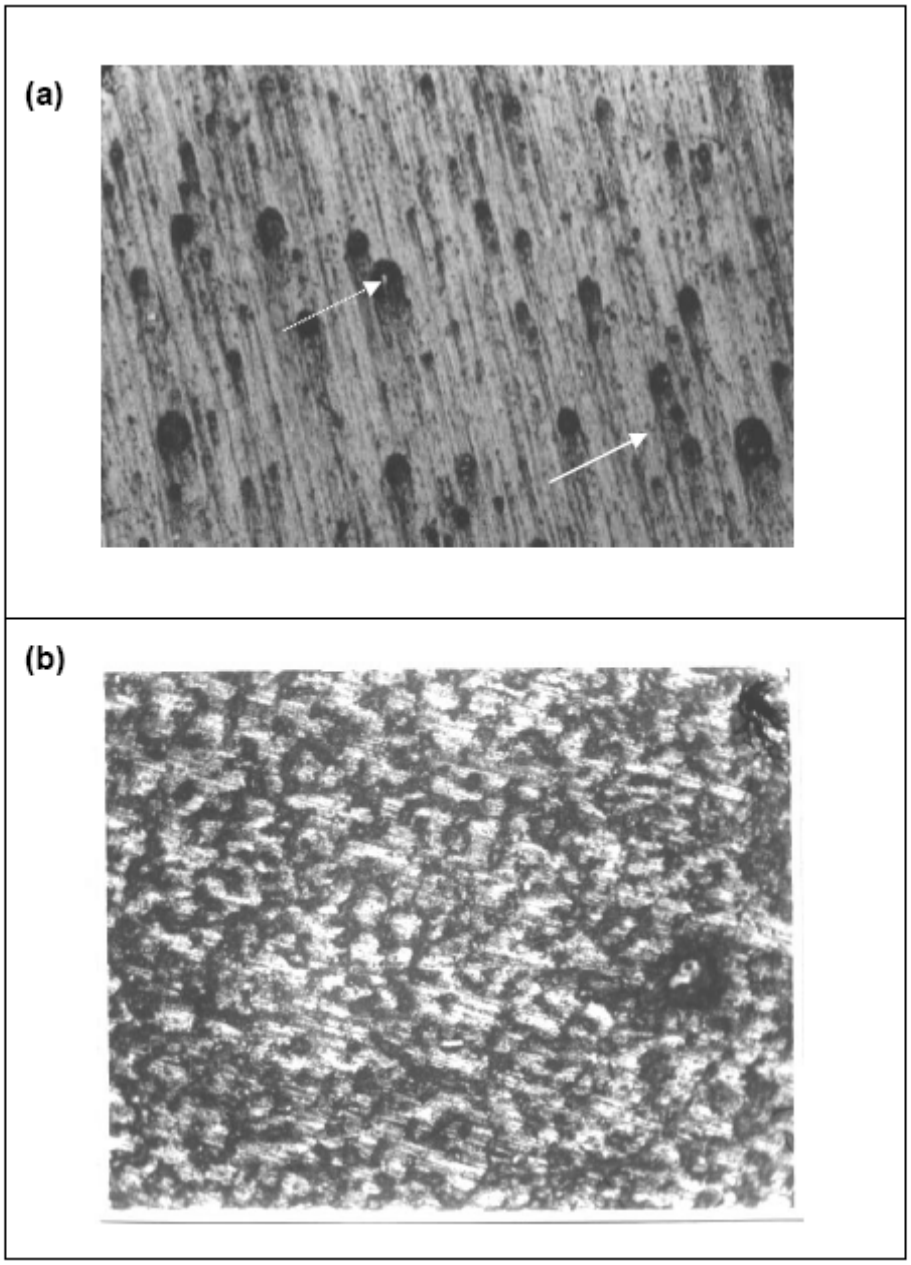

Fig. 4 Optical micrographs of poorly dispersed CNTs: a) Sample 1; b) Sample D1

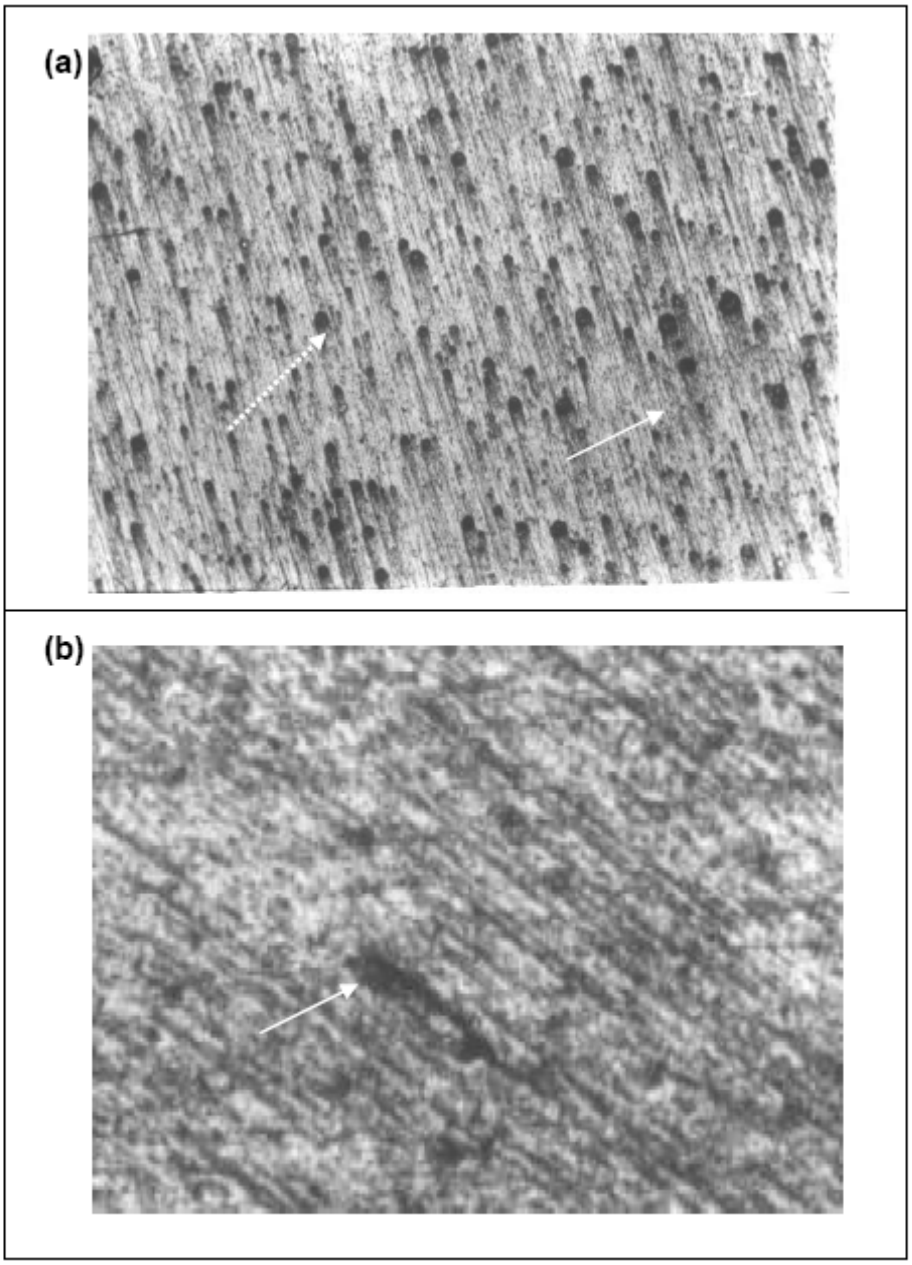

Fig. 5. Optical micrograph of well dispersed CNTs: a) Sample- 2; b) Sample- D2