Dispersion Quantification and Mechanical Properties of MWCNT/Epoxy Nanocomposite for Different Processing Conditions

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by

Aditya Bhardwaj
(801382001)

Under the guidance of

Mr. Bikramjit Sharma	**Dr. Rajeev Mehta**
Assistant Professor, MED	Professor, CHED
Thapar University, Patiala	Thapar University, Patiala

MECHANICAL ENGINEERING DEPARTMENT

THAPAR UNIVERSITY, PATIALA

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CERTIFICATE

I hereby declare that the thesis entitled **"Dispersion quantification and mechanical properties of MWCNT/epoxy nanocomposite for different processing conditions"** is an authentic record of my work carried out as requirements for the award of the degree of **Master of Engineering** in **Production Engineering** at **Thapar University, Patiala** under the supervision of **Bikramjit Sharma**, Assistant Professor, Mechanical Engineering Department, and **Dr. Rajeev Mehta**, Professor, Chemical Engineering Department, Thapar University, Patiala. The matter embodied in this report has not been submitted to any other university or institute for the award of any degree.

Aditya
ADITYA BHARDWAJ

Date: 15/07/15

It is certified that the above statement made by the student is correct to the best of my/our knowledge and belief.

Dr. RAJEEV MEHTA
Chemical Engineering Department
Thapar University, Patiala – 147004

15/7/15
BIKRAMJIT SHARMA
Mechanical Engineering Department
Thapar University, Patiala - 147004

Countersigned by

Dr. S.K. MOHAPATRA
Senior Professor & Head
Mechanical Engineering Department
Thapar University, Patiala - 147004

Dr. S.S. BHATIA
Dean of Academic Affairs
Thapar University, Patiala - 147004

Dedicated to

My Mother

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Abstract

In this work, multiwalled carbon nanotubes were dispersed in epoxy resin using high shear homogenizer. Two parameters were varied: homogenizing speed (7,500 rpm or 15,000 rpm) and homogenization time (5 min or 10 min). The effect of these varying parameters on the dispersion of MWCNTs in epoxy matrix and mechanical properties of nanocomposites has been quantified. The results indicate that the nanocomposite samples fabricated at 15,000 rpm for 5 min. exhibit highest Young’s modulus and tensile strength values, which is attributed to good dispersion of MWCNT as is shown by value of high composite index. However, the values of Young’s modulus and tensile strength decrease with a further increase in homogenization time due to possible nanotube damage. The flexural modulus and bending strength remain unaffected with the homogenization conditions. SEM studies and dispersion quantification indicated that nanocomposite samples prepared at 15,000 rpm and 5 min. as well as that prepared at 7,500 rpm and 10 min., showed higher compIndex values i.e. good dispersion. Hence, composite index values indicated good dispersion both at “high homogenizing speed, short duration” and “low homogenizing speed, long duration”.

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List of Acronyms

1. CNT ≡ Carbon nanotube
2. SWCNT ≡ Singlewalled carbon nanotube
3. MWCNT ≡ Multiwalled carbon nanotube
4. SEM ≡ Scanning electron microscopy
5. TEM ≡ Transmission electron microscopy
6. AFM ≡ Atomic force microscopy
7. XRD ≡ X-ray diffraction
8. PC/MWCNT ≡ Polycarbonate treated multiwalled carbon nanotube
9. PVA/GO ≡ Poly (vinyl alcohol)/graphene oxide nanocomposite
10. DP ≡ Dispersion parameter
11. ASTM ≡ American society for testing and materials
12. compIndex ≡ Composite index
13. dIndex ≡ Dispersion distribution index
14. sIndex ≡ Size distribution index
15. UTM ≡ Universal testing machine
16. HEX ≡ Hexagonal pattern
17. CP ≡ Clustering parameter
18. EMI SE ≡ Electromagnetic interference shielding efficiency
19. CNF ≡ Carbon nanofillers
20. f-MWCNT ≡ Functionalized multiwalled carbon nanotube
21. TGA ≡ Thermogravimetric analysis
22. DMA ≡ Dynamic mechanical analysis
23. APTES ≡ 3-Aminopropyl)triethoxysilane
24. p-MWCNT ≡ Pristine multiwalled carbon nanotube
25. XPS ≡ X-ray photoelectron spectroscopy
26. FTIR ≡ Fourier transform infrared spectroscopy
27. US ≡ Ultrasonicator
28. MF ≡ Micro fluidizer
29. PSM ≡ Planetary shear mixer

30.	DGEBA	≡	Di-glycidyl ether of bisphenol A
31.	CVD	≡	Chemical vapor deposition
32.	AC	≡	Alternating current
33.	NE	≡	Neat epoxy composite
34.	PC	≡	Polymer nanocomposite

Chapter 1

Introduction

1.1 Nanocomposites

Composites are multiphase material with a significant proportion of each phase. Materials are combined with an aim of getting more attractive properties. Principle of combined action is that a concoction which provides us “averaged” properties.

Constitutional phases are chemically different and alienated by a dissimilar interface. The matrix is a constant phase whose function is to transmit stresses to other phases and to defend them from surroundings. Matrix can be divided into ceramic matrix, metal matrix, and polymer matrix. The composite properties are function of the properties their relative amounts, geometry of the dispersed phase and constitutional phases. The purpose of dispersed phase is to enhance the matrix properties, such as:

(a) Metal matrix improves yield strength, creep resistance and tensile strength.

(b) Ceramic matrix enhances fracture toughness.

(c) Polymer matrix improves, yield strength and tensile strength as well as modulus and creep resistance.

Nanocomposites are the type of substances in which one or more phases having nano dimensions are entrenched in a ceramic, polymer matrix or metal matrix. The properties of nanocomposites depend on the matrix system, loading, dispersion, orientation and shape of the nano phase and synergy among the nano phase and the matrix. Nanostructured materials have exceptional physical and chemical properties as a result of their extremely small size and large surface area.

1.2 Types of Nanocomposites

Nanocomposites can be divided into inorganic–inorganic nanocomposites, organic–organic nanocomposites, and hybrid nanocomposites. Another classification is based on the dimensional morphology; nanocomposites are classified as 1-dimensional, 2-dimensional and 3-dimensional nanostructures. Also, based on the shape, they can be classified as: tube like and non-tube like nanocomposites. Based on the type of filler material used, they can be classified as:

(1) Metal oxide based nanocomposites

(2) Polymer based nanocomposites

(3) Carbon based nanocomposites and

(4) Noble-metal based nanocomposites.

1.2.1 Metal oxide based nanocomposites

Nanocomposites can be based on a metal oxide matrix in which the filler is metal oxide. As is by now, it is well known that metal oxides are important semiconductors which can be used as sensing materials in the chemical sensors. Metal oxide based nanocomposites can also be prepared by sol-gel processes. Aerogels, because of their porous structure, can be used as an ideal starting material in nanocomposites.

1.2.2 Polymer based nanocomposites

Polymer nanocomposites can be defined as an interacting mixture of two phases, a polymer matrix and a solid phase, which is in the size range of nanometre in at least one dimension. A polymer-matrix nanocomposite consists of a medium which is prepared from a polymer. The second phase is a reinforcing filler material which is dispersed within the matrix and has nanoscale dimensions. This phase of nano scale dimensions leads to exceptional properties when mixed with matrix. Because the reinforcing filler has nanoscale size, the surface area to volume ratio is exceptionally more than that from conventional nanocomposites.

1.2.3 Carbon nanotube based Nanocomposites

Carbon nanotubes have been of a huge concern, both from the basic point of view and for impending functions. Their mechanical and distinguishing electronic properties open up a wide range of functions, i.e. manufacturing of nanoelectronic devices, biosensors, nanocomposites, chemical sensors, etc. They also provide enormous opportunities in the design of multifunctional material systems. In particular, they assure to give results to many rasping problems encountered during the application of traditional composite materials. For example, because of their good electrical conductivity, they are appropriate for applications which necessitate the facility to discharge electrostatic potentials. Carbon nanotubes (CNTs) can be classified into two types, i.e. single-walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs).

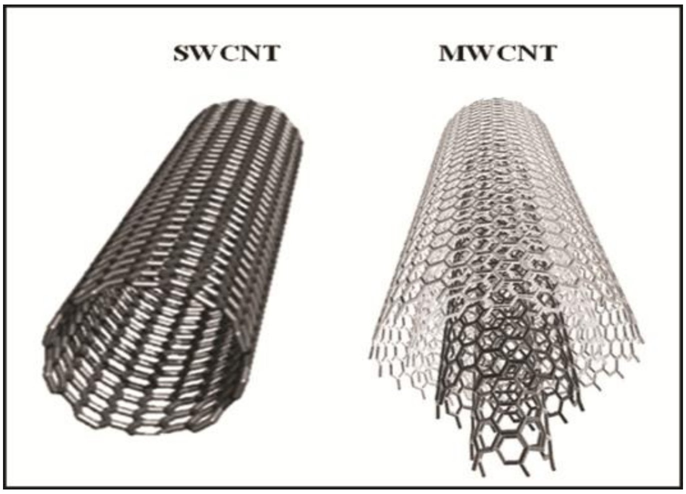

Figure 1.1: Single walled CNT and multiwalled CNT [1]

1.3 Dispersion

More payloads, lower cost, stronger and lighter components can be made using multiwalled carbon nanotubes. Besides having strength and stiffness of about 63 GPa and 970 GPa respectively [2], it is difficult to harness them in manufacturing nanocomposites. Nanotubes consist of carbon bonds, which linked so tightly with each another that it makes them inert. As a result, it is difficult to disperse raw nanotubes in resins. MWCNTs that remain undispersed get aggregated and form clumps. Those clumps become places in composites under mechanical loads where stresses concentrate and initiate cracks. Dispersion is one of the major problems when incorporating MWCNTs as reinforcement in nanocomposites [3]. Due to strong van der Waals forces, it is difficult to achieve better dispersion of MWCNTs

[5]. To overcome these van der Waals forces, the energy should be sufficiently high to disperse the MWCNTs, but not so high that it breaks them [6]. Moreover, long, thin shape and high surface area of MWCNTs also make them jam up and form bundles or agglomerates. But in recent years, researchers have been figuring out various ways of incorporating MWCNTs into resins, by providing various dispersion techniques, to increase the durability and strength of MWCNT/epoxy nanocomposite.

Some of these techniques that are used to achieve dispersion are high shear homogenizing, solution mixing, ultrasonication, non-covalent polymer wrapping, covalent carbon nanotube functionalization [7], high speed stirring [8], surfactant-assisted mixing [9], and melt or shear mixing [10]. Typically, a combination of these methods is employed to further enhance dispersion [11].

Qualitative and quantitative analysis of dispersion is a major challenge. Qualitative methods for evaluating dispersion are scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), confocal optical microscopy and X-Ray diffraction (XRD). Quantitative methods for measuring the dispersion are more important because qualitative methods based on visual observation undergoes subjective judgment and thus, do not result in a metric which can be used for comparing the dispersion of nanocomposites having same constituents of matrix and filler but with different distribution of the filler in the matrix system. Also, a quantitative measure of dispersion can be used as a measure for correlating the constitutional properties of the nanocomposites [12]. Quantitative methods for evaluating dispersion are image analysis and delaunay triangulation method [13], uniform dispersion method [14], inter-particle distance method [14], method of free space length [14], morisita index method [15], ASTM index method (Type A, B & C) [16] and composite index method [11].

1.4 Qualitative Methods for evaluating Dispersion

1.4.1 Scanning electron microscopy

A scanning electron microscope (SEM) an electron microscope which generates images of a specimen with a fixed beam of electrons through scanning. The electrons intermingle with atoms of the specimen, and generate signals which can be sensed and which also hold information about the fractured surface composition and topography of the specimen. The beam of electrons is usually scanned on a model of raster scan. Position of beam is joined with the signal and an image is generated. Resolution more than 1 nm can be achieved through SEM. Specimens are examined at high and low vacuum and at a broad range of low or high temperatures. The general manner of indication is by release of secondary electrons by the atoms which are agitated by the electron beam. The amount of secondary electrons which are released is directly proportional to the angle between the beam and the surface. The plume of secondary electrons is mainly acquired by the specimen. However, on a fractured surface, it is exposed up to some extent and a large amount of electrons are released. An image indicating the fracture of the surface can thus be formed by scanning the specimen and determining the secondary electrons. The SEMs of the fractured surfaces of composites are shown in Figure 1.2 (a), (b), (c) and (d); which represent neat epoxy resin, pristine-MWCNTs/epoxy nanocomposites, acid treated-MWCNTs/epoxy nanocomposites, and functionalized MWCNTs/epoxy nanocomposites, respectively.

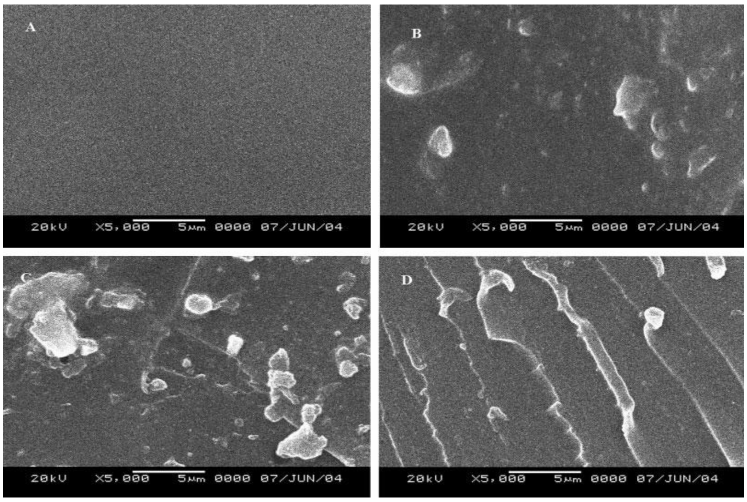

Figure 1.2: SEM images of fractured surfaces of; (a) neat epoxy resin, (b) pristine-MWCNTs/epoxy nanocomposites, (c) acid treated-MWCNTs/epoxy nanocomposites, and (d) functionalized MWCNTs/epoxy nanocomposites [4].

1.4.2 Transmission Electron Microscopy

Transmission electron microscopy (TEM) is a method for measuring the dispersion qualitatively in a manner such that a beam of electrons is passed on through a thin specimen, and as it passes through it, the electrons interact with the specimen. An image is generated at the place where electrons interact with each other, which is passed through the sample. The generated image is then engorged and is resolute onto a device of imaging. TEMs have the ability of producing the images at relatively higher resolution, because they have short de Broglie wavelength. TEM is capable of deducing an analysis method for both the physical and biological sciences. TEMs have their applications in the area of research of virology, cancer, materials semiconductor, pollution, nanotechnology and materials science. The resolution of TEM image is due to the reason that electrons are absorbed in the material at relatively lower magnifications. It happens because of the sample's thickness and its composition. On the other hand, wave signals attenuate the contrasting feature of the image, which necessitate the analysis of experimentally obtained images by an expert, at higher magnifications. TEM is able to recognize the attenuations in chemical characteristics, electronic configuration and crystal direction, electron phase transfer and standard absorption by the use of alternate modes. TEMs of the PC/MWCNT (95/5 wt %) nanocomposites with solution mixing method are shown in Figure 1.3(a) and (b) show the untreated PC/MWCNT nanocomposites and PC/MWCNT nanocomposites with H_2O_2 treatment, respectively. From the result of Figure 4(a), it is seen that the MWCNTs form an entangled structure in the PC matrix. In Figure 4(b), the entanglement of the MWCNTs loosens after H_2O_2 treatment and freeze-drying.

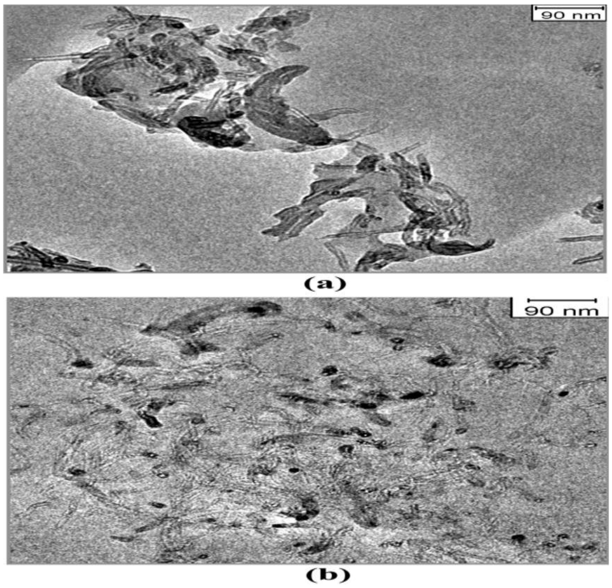

Figure 1.3: Transmission electron micrographs (TEM) showing PC/MWCNT nanocomposites attained with solution mixing: (a) untreated MWCNT; (b) MWCNT after H_2O_2 treatment [7].

1.4.3 Atomic Force Microscopy

Atomic force microscopy (AFM) or scanning force microscopy (SFM) is a measure of qualitative dispersion with a degree of resolution of the fractions of nm, and thus its resolution value is even 1000 times better than the limit of optical diffraction. The AFM is one of the best tools for calculating, imaging and controlling the issue at the nanoscale dimensions. The results are obtained by sensing the fractured surface with the probe used in this microscopy. The sample that shows small but accurate movements on electronic media, results in perfect scanning. It is to be noted here that the electric potentials obtained can also be scanned through a conducting cantilever. The AFMs of the PC/MWCNT (95/5 wt %) nanocomposites are shown in Figure 5(a) and (b) which represent PC/MWCNT nanocomposites without H_2O_2 treatment and PC/MWCNT nanocomposites with H_2O_2 treatment, respectively.

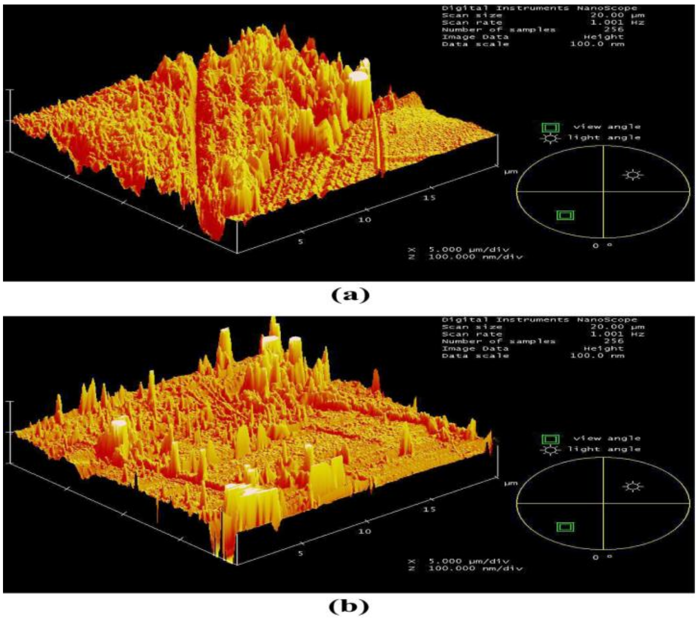

Figure 1.4: Atomic force micrographs of PC/MWCNT nanocomposites fabricated by solution mixing showing (a) untreated MWCNT; (b) MWCNT after H_2O_2 treatment [7].

1.4.4 X-Ray Diffraction

X-ray diffraction is a technique used for qualitatively evaluating the dispersion by analyzing the atomic and molecular structure of a crystal. The atoms of the crystal diffract the beam of X-rays into various directions and calculate the measure of angles and their corresponding intensities. Crystallographer thus has the ability of generating a 3-Dimensional micrograph indicating the density of electrons inside the crystal. Chemical bonds in crystal, disorder, position of atoms and dispersion of atoms in crystal can be evaluated from the known electron density. X-ray crystallography is widely accepted, commonly used and very helpful in the progress of various fields of science. X-ray diffraction is the most important characterization technique for studying the dispersion of nanocomposites. As shown in Figure 1.5, X-ray diffraction profiles of a PVA/GO nanocomposites and GO.

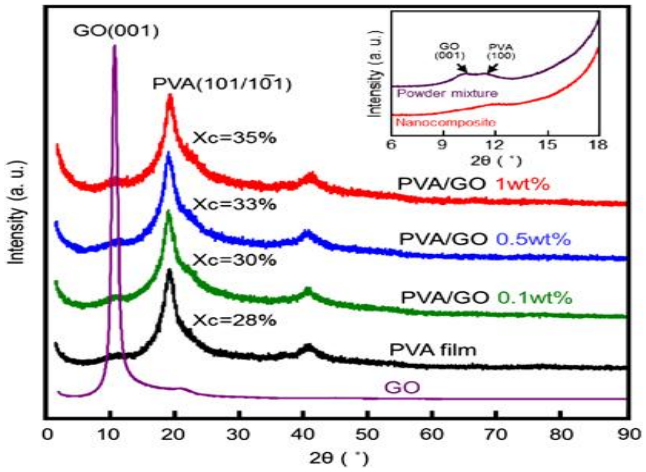

Figure 1.5: X-ray diffraction profiles of a PVA/GO nanocomposites and GO [23].

1.5 Quantitative Methods for evaluating Dispersion

1.5.1 Inter-particle distance method

The distance between the nanoparticles of filler within the matrix gives a measure of dispersion. Khare et al. [14] used mean inter-particle distance which is the mean of distances between each and every particle in the image and are near to one another. The given technique is susceptible to the amount of particles, although it is unsusceptible to the quality of dispersion. This is shown in Figure 1.6, where it can be seen that the image on the right side is relatively more agglomerated than the other one. Then also, inter-particle distance method would yield similar values for both these images. Therefore, this method only identifies the number of particles instead of identifying the distribution of particles in the matrix.

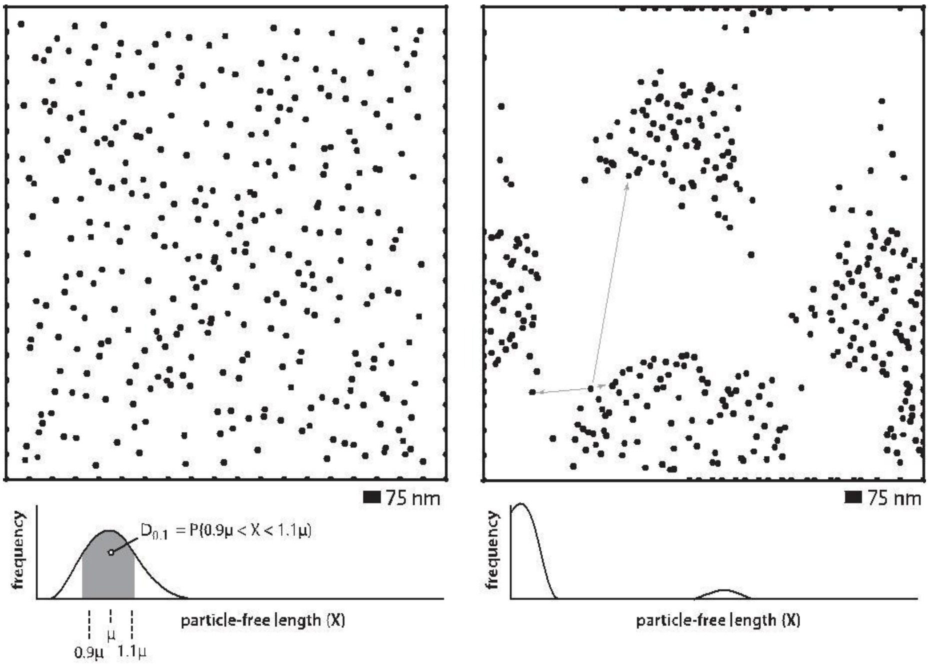

Figure 1.6: Micrograph showing a) a non-agglomerated dispersion; b) an agglomerated dispersion [14].

1.5.2 Quadrat Methodology

Quadrat methodology is a quantifiable measure of dispersion in which an image is divided into a specific number of quadrats and then the technique is applied for dispersion quantification.

A measure, known as free-space length (L_f), is related to the attributed size of the polymer matrix system [14]. Free space length can be defined as the measure of the biggest square which is placed in the matrix system of the image to be analyzed such that there is no intersecting nanoparticles present within that square as shown in Figure 1.7. The limitation of free space length method is that the large value of L_f shows that the presence of nanofillers within the matrix is less.

The Morisita index method [15], for quantifying dispersion of nanofillers within the matrix does not depend on quadrat size at any respect. This method is used for comparing the images with similar constituent of filler material but with different distribution. As a result, this method is proved to be insufficient for nanocomposites with similar distribution of filler mixing.

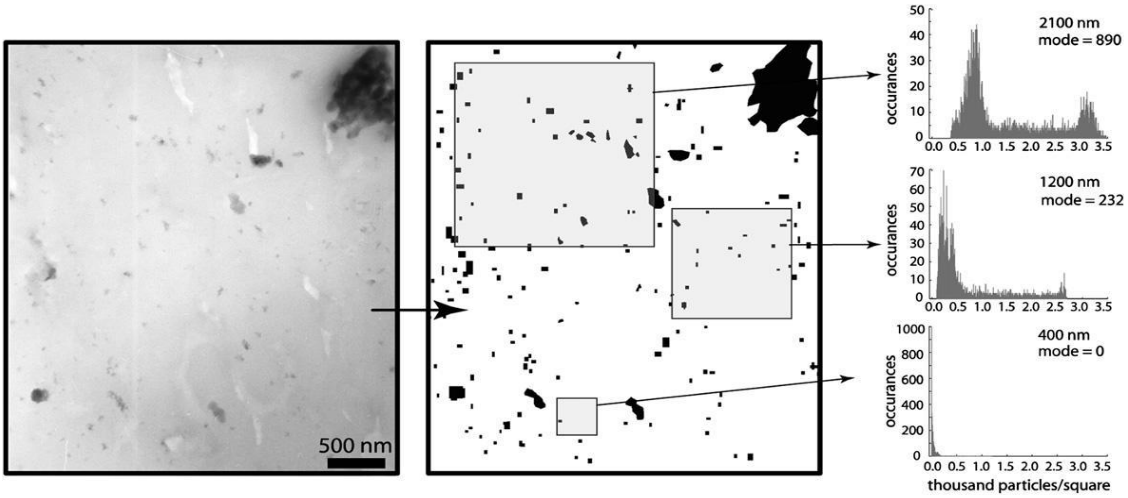

Figure 1.7: Illustration of the technique used for calculating the free-space length [14].

1.5.3 Image analysis method

Image analysis method is the dispersion quantification method used for evaluating distribution of CNT in an image. Size of CNT cluster is indicated by an order up to which an image is divided into quadrats such that one or more than one quadrat shows the CNT fraction of more than 0.9. More the divisions of micrograph more will be the number of cells and smaller is the cell size and CNT cluster size better will be the CNT dispersion. The degree of dispersion can be calculated by a dispersion parameter (DP), which is shown below:

$$\mathrm{DP} = \frac{N}{\text{Cell size} \times \text{Overall CNT fraction}} \tag{1.1}$$

Here N is the number of divisions. The values of dispersion parameter is calculated to be 1.07, 0.74 and 1.20 for the given three micrographs (Figs. 1.8a, 1.9a and 1.10a) respectively. Thus it can be summarized that that Fig. 1.10a shows best degree of dispersion of all other micrographs and Fig. 1.9a shows the lowest degree of dispersion.

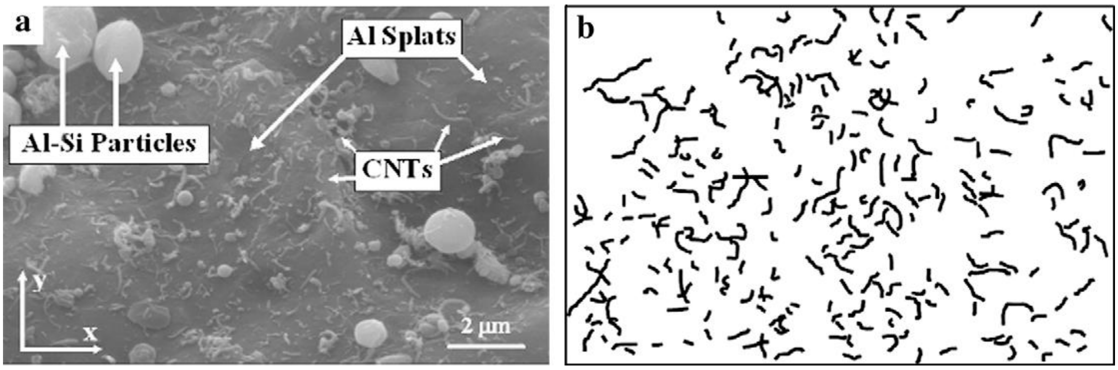

Figure 1.8: (a) SEM micrograph (b) distribution of CNTs in the micrograph [13].

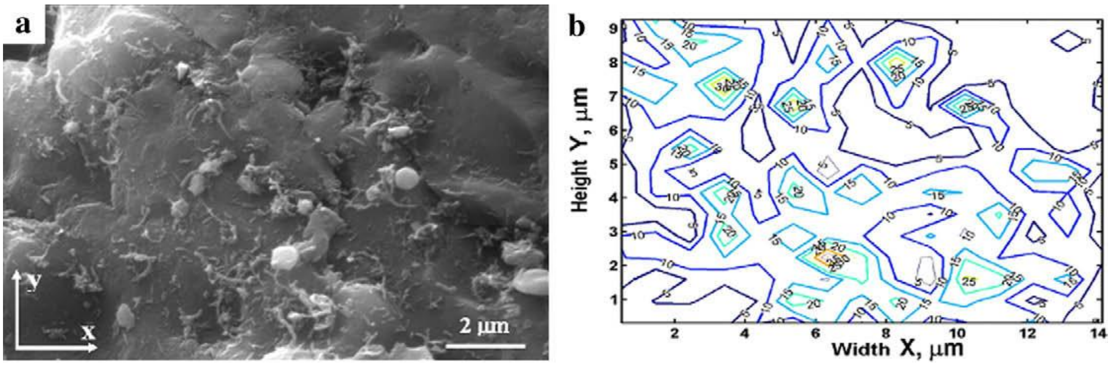

Fig. 1.9: (a) SEM micrograph (b) contour map CNT fraction in the micrograph [13].

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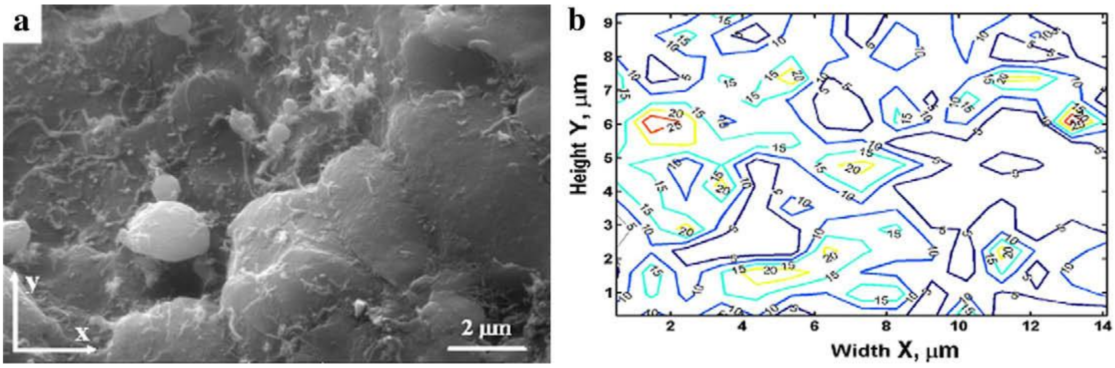


Fig. 1.10: (a) SEM micrograph (b) contour map of distributed CNT fraction in the micrograph [13].

1.5.4 ASTM Index

ASTM (American Society for Testing and Materials) standard constitutes 3 test methods for quantifying the dispersion of CNT fibers in the polymer matrix. First method includes visual inspection in which the degree of dispersion is related to five standards chart ranging from 1 to 5, with 1 indicating poor dispersion and 5 indicating good dispersion. In second test method, a technique based on quadrats is applied in which only those agglomerates whose area is greater is greater than 5µm is identified and subtracted from the known content of reinforcing medium. The quadrats that contain agglomerated area less than 5µm are used for determining the degree of dispersion such that if area is greater than 97%, then it will show good dispersion of that micrograph. If it is between 92% and 97%, then it will show intermediate dispersion and if it is less than 92%, then it indicates poor dispersion of CNTs in micrograph. The third method of ASTM index incorporates the analyzing of fractured surface of a specimen with the stylus and calculating the roughness caused by agglomerates at that place, which is translated and used as a measure of degree of dispersion.

1.5.5 Composite Index Method

Composite index method is a measure for quantifying dispersion which considers two parameters. One is spread of filler particle within matrix system and is computed by dIndex, known as distribution index, whose value ranges between 0 and 1. The second parameter is size of agglomerate or bundles of filler constituent in the matrix and is given by sIndex, known as size index, the value of which ranges between 0 and 1. This method was based on Quadrat methodology. The final degree of dispersion known as composite index (compIndex) is the arithmetic average of these two indices. The value of compIndex varies between zero and one, with zero showing poor dispersion and one shows good dispersion.

The degree of dispersion calculated by dIndex is obtained by dividing the micrograph into quadrats of equal area. While there is a certain amount of uncertainty in choosing the optimum number of quadrats for calculating dIndex, but it is found to be a better method than the others for dispersion quantification.

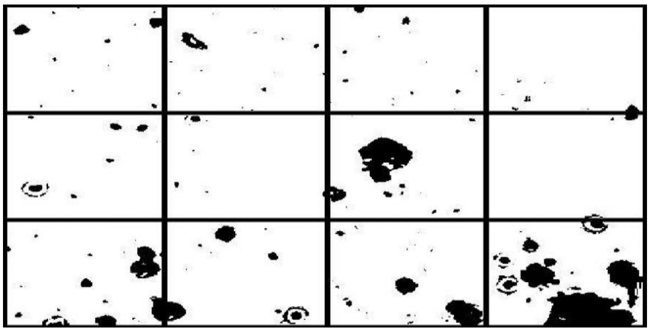


Figure 1.11: Illustration of the 3x4 grid used for calculating dispersion distribution index (dIndex) [11].

1.6 Mechanical Properties

1.6.1 Tensile testing

Tensile testing is the method for testing the specimens of particular dimensions by applying tensile force on them until failure. Depending on the results obtained after tensile test, the material is selected for its correlated application and its is envisaged as how the material will react under other applied forces. Properties that are obtained after incorporating tensile test are Young's modulus, tensile strength, Elongation at brake and various other parameters are attained.

The most commonly used tensile testing machine is the universal testing machine (UTM). This machine consists of two crossheads out of which one is adjusted according to the length of the specimen on which testing is used to be done and the other crosshead is driven by machine itself for applying tension on the specimen during tensile test. These can be divided into two types i.e. hydraulic powered and electromagnetically powered tensile testing machines.

1.6.2 Flexural testing

Flexural strength is the property of material examined through flexural testing and is defined as the ability of brittle material to resist bending, when a force is applied. Flexural testing also known as transverse bending test commonly applied for a sample having area of crossection of eighther a rectangular or circular shape is twisted until rupture. Properties determined by applying flexural testing on a given specimen are Flexural modulus, bending strength, interlaminar shear strength and many more. The flexural strength evaluated through flexural testing is the maximum strength experienced by the brittle specimen at its moment of rupture. It is calculated in the unit of strength, and is denoted by σ.

Fig. 1.12: Universal Testing Machine

(Photo courtesy: Chemical Engineering Department, Thapar University, Patiala)

Chapter 2

Literature Review

2.1 General

In this chapter, the work done by various researchers has been summarized which includes methods of quantifying dispersion in nanocomposites, their properties and applications etc. In the last section, gaps in the present literature has been discussed which present the scope of the proposed study.

2.2 Literature Summary

Pfeifera et al. (2013) studied a method for quantifying the dispersion of nanofillers in polymer matrices. The method is based on the quadrat methodology and an algorithm was proposed. A measure given by d(P||Q) was used for determining the distribution of nanoparticles. The ‘given distribution’ (P) was related to the ‘required distribution’ (Q) of nanofillers and a quantitative measure was developed based on the relation of both these distributions. The d-metric-based approach is applied to Figure 2.1, with the results indicated in Table 2.1. The comparison was again to a hexagonal pattern distribution. The steadily increasing d-metric values from the top to the bottom, for both columns, indicate definitive and well-founded values for the degree of dispersion.

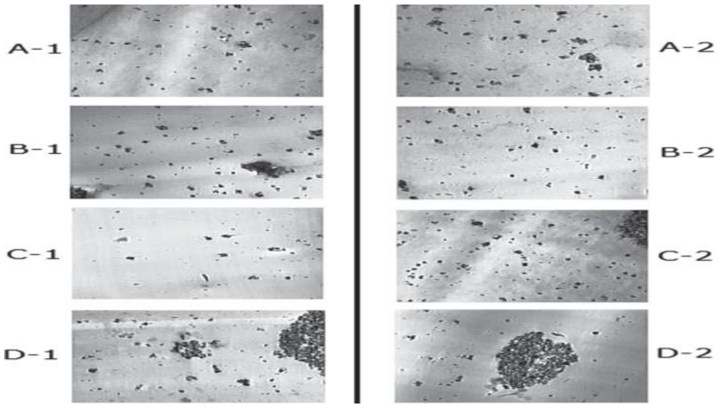


Figure 2.1: TEM images showing the decrease of degree of dispersion from A1 to D1 and A2 to D2. The dispersion metric proposed in this work shown in Table 2.1 [17].

Table 2.1: The d-metric values for the TEM images shown in Figure 2.1 [17].

d(HEX‖Pattern)	d(HEX‖Pattern)
d(HEX‖A-1) = **0.293**(0.002)	d(HEX‖A-2) = **0.306**(0.001)
d(HEX‖B-1) = **0.468**(0.002)	d(HEX‖B-2) = **0.322**(0.001)
d(HEX‖C-1) = **0.710**(0.005)	d(HEX‖C-2) = **0.630**(0.002)
d(HEX‖D-1) = **0.717**(0.002)	d(HEX‖D-2) = **1.282**(0.004)

Haslam et al. (2013) proposed a new technique known as composite index method for quantifying the dispersion of CNTs in polymer matrices. The proposed method was compared with ASTM method and the results of both these methods were analyzed for the same micrographs and compared to identify the better method (index) for quantifying dispersion of CNTs. The ASTM index displayed several limitations to measuring the two factors. First, it does not consider the distribution of carbon over the entire sample, because it does not compare the amount of carbon between different sections of the image, but calculates an average over all sections. Second, it does not take into account the size of carbon particles or agglomerates. The compIndex is based on using a two part evaluation that includes the dispersion distribution (dIndex) and the size distribution of carbon (sIndex). The measurement results thus found were accurate and consistent from sample to sample as opposed to evaluating the samples with the ASTM index. It is showed that the composite index method is better method of dispersion quantification than that of ASTM index method.

Khare et al. (2010) studied a method for quantifying the dispersion of nanoparticles within polymer matrix.

1) Makes use of the TEM images;
2) Shows the effect of agglomeration or reinforcement
3) Distinct and physically instinctive metric.

A measure, known as free-space length (L_f), is related to the attributed size of the polymer matrix system. Free space length thus can be defined as the measure of the biggest square which is placed in the matrix system of the image to be analyzed such that there is no intersecting nanoparticles present within that square. The limitation of free space length method is that the large value of L_f shows that the presence of nanofillers within the matrix is less. The Morisita index method, for quantifying dispersion of nanofillers within the matrix does not depend on quadrat size at any respect. This method is used for comparing the images with similar constituent of filler material but with different distribution. As a result, this method is proved to be insufficient for nanocomposites with similar distribution of filler mixing.

Bakshi et al. (2009) developed two methods for quantifying dispersion of carbon nanotubes in matrix nanocomposite. Both these methods used a quantifiable metric or parametric for calculating degree of dispersion. First method known as Image analysis method uses a Dispersion Parameter (DP), while the other method known as Delaunay triangulation method, uses an another parameter i.e. Clustering Parameter (CP). These two methods were analyzed and compared so as to identify better quantifiable measure of dispersion.

Image analysis method

Image analysis method is the dispersion quantification method used for evaluating distribution of CNT in an image. Size of CNT cluster is indicated by an order up to which an image is divided into quadrats such that one or more than one quadrat shows the CNT fraction of more than 0.9. More the divisions of micrograph more will be the number of cells and smaller is the cell size and CNT cluster size and hence, better will be the CNT dispersion. The degree of dispersion can be calculated by a Dispersion Parameter (DP), which is shown below:

$$\text{DP} = \frac{N}{\text{Cell size} \times \text{Overall CNT fraction}} \tag{2.2}$$

Here N is the number of divisions.

Delaunay triangulation method

Delaunay triangulation method is a measure based on the bundling or agglomeration of CNTs within the matrix system and is used as quantification measure of dispersion. The amount of agglomeration in a particular micrograph is analyzed and studied by this method. The degree of dispersion in this method is calculated by the clustering parameter (CP). Hence, CP can be defined as following:

$$\text{C.P.} = \frac{\text{Cumulative fraction of distances less than or equal to } 5 : \text{Dcnt}}{\text{Overall CNT fraction}} \tag{2.3}$$

Where, Dcnt is the average diameter of CNT.

Han et al. (2009) investigated the effect of treated and untreated polycarbonate (PC) multiwalled carbon nanocomposites and its dispersion on the morphological, electrical and rheological properties. The PC/MWCNT nanocomposites were fabricated with and without pretreating the MWCNTs with hydrogen peroxide oxidation. The results showed that untreated MWCNT nanocomposites gave lower values of electrical conductivity than that of treated PC/MWCNT.

The morphological actions showed that H_2O_2 treated polycarbonate nanocomposites had better dispersion of MWCNTs. Moreover, the electromagnetic interference shielding efficiency (EMI SE) of the H_2O_2 treated PC/MWCNT nanocomposites were superior to untreated PC/MWCNT nanocomposites.

Rheological behavior of the nanocomposites indicated that viscosity of H_2O_2 treated PC/MWCNT nanocomposites was greater than untreated PC/MWCNT nanocomposites. It is attributed to better distribution of treated MWCNT nanocomposite. The final results concluded that the improved electrical conductivity and EMI SE of the H_2O_2 treated nanocomposites is due to enhanced dispersion of MWCNTs within the matrix.

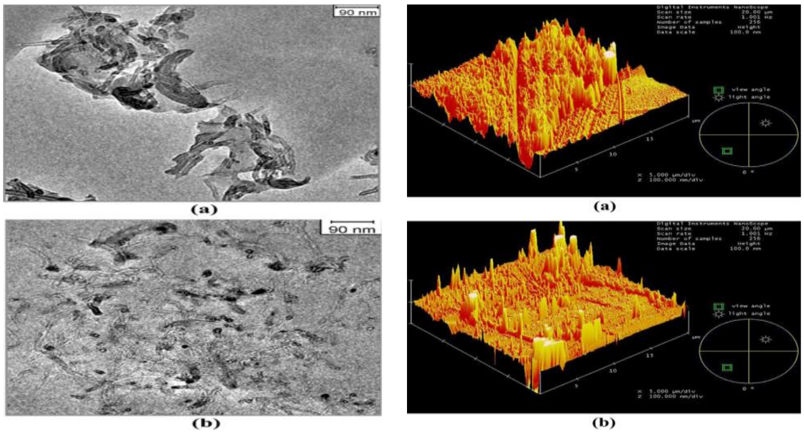


Figure 2.2: Transmission electron micrographs and atomic force micrographs of PC treated MWCNT nanocomposites through solution mixing: (a) untreated MWCNT; (b) H_2O_2 treated MWCNT nanocomposite, respectively [7].

Tyson et al. (2011) developed a general technique for quantifying the dispersion and agglomeration of nanoparticles within nanocomposite. Two parameters are developed based on the amount of distribution and bundling of nanotubes. One metric known as dispersion parameter (D) is developed for measuring the dispersion of nanofillers within matrix system and depends on free space between nanoparticles indicated in the micrograph. Other parameter being the agglomeration metric (A) is based on the calculation of the particle size. In this literature, the proposed method used for the calculation of dispersion and agglomeration of both the carbon nanofillers (CNFs) and carbon nanotubes (CNTs) inside the matrix system. Thus, the values of both these parameters are simultaneously required evaluating the dispersion of the system. A maximum ‘D’ value shows enhanced dispersion; while a lesser ‘A’ value shows a lessening of agglomeration.

Wang et al. (2006) observed that amino-functionalization of MWCNTs enhanced the dispersion of MWCNT in epoxy resin. The mechanical properties of amino-functionalized MWCNT/epoxy nanocomposites were also evaluated. It was seen that amino functionalized MWCNTs greatly improved the decomposing temperature, glass transition temperature and charpy impact strength of the nanocomposite. Moreover, adding pristine MWCNTs in epoxy system dejected the light transmission properties, significantly and this property would positively impound the functionalized-MWCNTs/epoxy nanocomposites applications in the near future.

SEM and TEM are used for qualitatively characterizing the enhanced distribution of the f-MWCNTs in the epoxy system and hence achieving better dispersion of nanocomposite. It is to be noted that 0.05 wt % of functionalized-MWCNTs kept light transmittance of 50% of neat epoxy which was very much superior to pristine-MWCNTs/ epoxy nanocomposites at the same level of loading. Comparatively greater light transmittance of the amino-functionalized MWCNT/epoxy nanocomposites not only showed better dispersal of f-MWCNTs, but also incorporates the increasing use of MWCNTs for various applications in the near future.

Zhou et al. (2007) evaluated the effects of loading rates on mechanical, thermal and flexural properties of MWCNT/epoxy nanocomposite. Thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA) are performed and their respected values are calculated for 0.1, 0.2, 0.3, and 0.4 wt% MWCNT-filled epoxy nanocomposites. The results of DMA seem to found that CNT loading within epoxy system improve the storage modulus by 90 and enhance the value of *T*g by 22 ◦C In the TGA test, for 0.4 wt % CNT/epoxy nanocomposite, a decrease in decomposition temperature by 6 ◦C has been noticed because of lesser agglomeration of CNTs. The flexural results show that with increasing CNT loading rates, flexural modulus also increases. Maximum flexural strength has been noticed for 0.3 wt % CNT loading rate. Ultrasonic cavitation is a proficient technique of incorporating CNTs within epoxy system, when, CNT loading rates are taken to be less than 0.3 wt%. The results of DMA showed an increase of 93 % in storage modulus, and an increase in value of Tg by 17 ◦C, when 0.4 wt% reinforced CNT/epoxy nanocomposite is compared to the corresponding values of neat epoxy. The decomposition temperature decreases with increasing loading of CNTs, which is because of the formation of agglomerates at higher

CNT loading rates. The Flexural modulus values increases with an increase in CNT loading rate.

Pillai et al. (2011) reviewed in this paper that momentous attempt has been specified to the production and dispensation of CNT/epoxy nanocomposites. Modifying the epoxy system with CNTs offered improved properties to nanocomposites such as increase in the values of *T*g, leads to an increase in the mechanical properties and considerable increase in the values of electrical and thermal conductivity. Most of the work is published on improving the dispersion of CNT/ epoxy nanocomposite through CNT functionalization by the use of surfactants. It is also concluded that the uniform dispersion of CNTs in the epoxy system depends on the volume fraction of CNT, CNTs agglomeration, CNT aspect ratio and viscosity of epoxy system. More work is required to be done in this field so as to identify the change in properties of matrix system with the nanoreinforcement.

Kim et al. (2011) examined the effects of CNT modifications on the wear and flexural properties of carbon/CNT/epoxy nanocomposites. Carbon/epoxy nanocomposites and two types of carbon/CNT/epoxy nanocomposites were fabricated by mixing fibers of carbon in epoxy system treated by 2 wt% acid-modified and silane-modified multi-walled carbon nanotubes. Ball-on-disk wear and three-point bending tests were carried out on these three nanocomposites. The results showed that the carbon/CNT/epoxy nanocomposites exhibit superior values of strengths and flexural moduli than that of carbon/epoxy nanocomposites. Particularly, there is an improvement of 10% and 15% in the values of the strength and flexural modulus of the silane-treated MWCNT/epoxy nanocomposite samples respectively, than the respective values of the acid-treated MWCNT/epoxy nanocomposite samples. Also, the wear behaviors of silane-treated MWCNT/epoxy nanocomposite samples were superior to acid-treated MWCNT/epoxy nanocomposite specimens. Scanning electron microscopic (SEM) of fractured surfaces clearly showed that the improvement in the wear and flexural properties of the silane-modified carbon/ CNT/epoxy nanocomposites was accredited to the good dispersion and the superior interfacial properties, which is due to the silanization of CNTs.

Ma et al. (2007) in this work investigated the effects of silane functionalization on the mechanical and thermal properties of MWCNT/epoxy nanocomposites. MWCNT/epoxy nanocomposites are fabricated by silane treatment of MWCNTs and its properties are compared with the relative properties of the nanocomposites fabricated with pristine MWCNTs. The properties of nanocomposites were determined comprehensively through electrical conductivity measurement, thermo-gravimetric analysis (TGA), scanning electronic microscopy (SEM), three-point bending test, dynamic mechanical analysis (DMA) and measurement of fracture toughness. The results showed that silinization of MWCNTs lead to the increase in degree of dispersion which is related to the increase in the thermal and mechanical properties than those nanocomposites fabricated by pristine MWCNTs. These results confirmed that better interfacial properties between epoxy system and f-MWCNTs are developed due to the formation of covalent bonds.

Allaoui et al. (2002) prepared multi-walled carbon nanotube/epoxy resin nanocomposites. By selecting a hardener, matrix system, an elastic epoxy resin has been prepared. The MWCNT/epoxy nanocomposites are fabricated at different weight percentages of MWCNT in epoxy system and their corresponding electrical and mechanical properties are evaluated. It was seen that the values of yield strength and Young’s modulus have been doubled and quadrupled, respectively for MWCNT/epoxy nanocomposites for loading of 1 and 4 wt% CNTs with respect to neat epoxy composite. The study of conductivity values showed that there is a transition from insulator to conductor for CNT loading rate between 0.5 to 1 wt.%. These results have illustrated the inherent potential of MWCNTs. Small quantity addition can alter considerably the electrical and mechanical behavior of a soft polymer matrix. The CNT loading of 1 to 4 wt. % into the epoxy system has a considerable effect on the mechanical properties of MWCNT/epoxy nanocomposite. The results of this paper suggest that it is not supportive to use high concentrations of CNTs for developing the mechanical properties of nanocomposites, if the MWCNTs are dispersed uniformly into the epoxy matrix.

Lavorgna et al. (2013) studied and compared the homogeneous characteristics of both amino (APTES) functionalization and silica enrichment of CNTs on the thermo-mechanical and mechanical properties of CNT/epoxy nanocomposite. Pristine MWCNTs were first functionalized and oxidized with APTES and on the other side p-MWCNTs are modified with silica nanoparticles. The XPS, TGA and FTIR analysis studies the analysis of the silane functionalization and surface silica enhancement. TEM analysis of micrographs indicated the occurrence of bundles due to aggregation of silica nanoparticles. Mechanical, flammability and thermal characteristics of CNT/epoxy nanocomposite having 1 wt% loading of different fillers have been evaluated and compared to the respective values of neat epoxy composite.
Results indicated that there is improvement in the values of storage modulus for silinized enriched and silica enriched CNTs of about 240% and 285% more than the respective values for modulus of neat epoxy composite. There is an improvement in the values of glass transition temperature by about 20 C with silica enhanced CNTs with a considerable improvement in the damping behavior.

Singh et al. (2013) investigated that distribution of high loading CNTs in epoxy resin is a challenging task for the growth of efficient and thin EMI shielding materials. Up to 20 wt% of MWCNTs loading in the nanocomposite was attained by forming CNT prepreg in the epoxy resin. These prepreg laminates were compression molded to form nanocomposites which resulted in EMI shielding efficiency of -19 dB for 0.35 mm thick film and -60 dB for 1.75 mm thick nanocomposites in the X-band (i.e 8.2–12.4 GHz). One of the causes for such high shielding is accredited to the high electrical conductivity of 9 S per cm, which is achieved in these nanocomposites. In addition, an enhancement of 40 % in the tensile stress over the neat epoxy resin is seen. Thermal conductivity of the MWCNT/epoxy nanocomposite is reached to 2.18 W/mK as compared to 0.14 W/mK, which is for cured epoxy.

Gkikas et al. (2012) in this work utilzed MWCNTs disseminated in a polymer matrix to improve the toughness and thermo-mechanical properties of the resulting nanocomposites. The results for tensile tests, 3-point bending tests and dynamic mechanical analysis (DMA) were evaluated on unoccupied, 0.5 and 1 wt% MWCNT in epoxy to show result of amount of MWCNT on abovementioned characteristics. Result of distribution parameters is determined for the sonication energy, CNT content and sonication time. The CNT distribution treatments are of great significance for toughness, mechanical and thermal properties of the customized method. Sonication time of 1 h is highly proficient for glass transition temperature (Tg) and storage modulus improvement for 0.5 and 1 wt% MWCNT loading. The noteworthy enhance of Tg and storage modulus for particular sonication parameters was related to better distribution and interfacial properties of MWCNTs and the epoxy system. Sonication energy is the most persuading condition for improving the mechanical properties. Finest result was achieved, when ultrasonication is done for 50% sonication amplitude and sonication time of 2 hr. It was recommended that at this condition of sonication endorsed suitable distribution of the carbon nanotubes in epoxy systems without destructing structure of MWCNT.

Papanicolaou et al. (2011) investigated the samples of MWCNT-epoxy nanocomposites which were fabricated by using effect of the dispersion degree, high speed shear mixing and sonication methods of MWCNT in epoxy system. It was found after finishing the curing process, by static tests, dynamic tests and SEM. The major results found are as given below:-

- There is an improvement in flexural strength (19.1% - sonication technique and 8.5 - shearing technique) and in flexural modulus (i.e. 26.6% - sonication technique and 3.25% - shearing technique), compared to the relative values of epoxy system.
- The nanocomposites fabricated by the sonication method exhibit improved damping capacity and poorer transition temperatures. This behaviour was partly accredited to the sonication method’s ‘intensity’, that is acknowledged to break the polymer walls as well the CNT chains.

- Apart from glass transition temperature, all dynamic and static characteristics for those nanocomposites which are fabricated by the sonication technique, showed better results when compared to those nanocomposites which are fabricated by the shearing technique.

Jagtap et al. (2013) described a common and new technique of dispersion of MWCNTs in an epoxy system. The MWCNT was treated with half-neutralized dicarboxylic acids, which was procured with epoxy matrix. Distribution of MWCNT in epoxy resin and the improvement in mechanical properties are determined to be superior for nanocomposites fabricated with a dispersing medium. TEM and SEM characterization showed a progress in the distribution of MWCNTs in the epoxy system with the adding up of half neutralized carboxylic acid. Better distribution of the MWCNTs and enhancement in the characteristics are accredited to the cation–p interconnections between the HNAA and MWCNTs. The chemical bonding and cation–p interaction is measured by Raman spectroscopy and Fourier transformations through infrared spectroscopy. The technique described doesn’t devastate the MWCNTs in comparison of the shown functionalization approach.

Huang et al. (2012) studied the progress in modifications and steadiness of CNT/epoxy nanocomposites which necessitate the formulation of fabricating techniques for recognizing the required characteristics. Here, the processes of dispersion of raw CNTs in a dispersing solvent are presented. The appropriate theoretical analysis is briefed and adapted to direct the choosing of best dispersion process, from the techniques of sonication to the application of surfactants, to the final test of nanocomposite properties. Various methods to avoid carbon nanotubes reaggregation post removal of shear stress are illustrated. It comprises a method of using an aqueous solution or a thermodynamic method of choosing a companionable dispersing medium. It is concluded that the carbon nanotube dispersion in epoxy medium as well as the selection of stabilizing agent is accustomed as the requirement of the finishing applications of the CNT/ epoxy nanocomposites. Modification in the dispersion process can direct to significant variations in conductivity i.e from insulting to conducting. Thus, it is concluded from this paper that main discussion is regarding the problems of dispersion of CNT nanofillers in epoxy media or polymer matrix, which is faced by researchers nowadays.

Swager et al. (2012) investigated many processing techniques for dispersing MWCNTs in bisphenol based epoxy which comprises the use of an ultrasonicator (US), micro fluidizer (MF), planetary shear mixer (PSM) and possible combinations. Three methods are used for qualitatively measure the dispersion of MWCNTs in nanocomposite specimens: Raman spectroscopy, optical microscopy and scanning electron microscopy (SEM). The samples produced by using a combination of (MF + PSM) processes shows low bundling of CNTs and better dispersion of MWCNT/epoxy nanocomposite. A differentiating feature of MWCNT/epoxy nanocomposite is that nanocomposites fabricated by applying (MF+ PSM) shows better value of degree of dispersion or uniform distribution of MWCNT than that prepared by using PSM alone or (USM +PSM) processes. Results of tensile testing showed that there is an improvement of 15% in the values of tensile strength, when the MWCNT/epoxy nanocomposites are prepared by using (MF+ PSM) than other processes. Thus, it is concluded that the nanocomposites fabricated by (MF + PSM) processing shows better dispersion of MWCNTs in epoxy system.

Montazeri et al. (2011) described the effect of dispersing medium and sonication time on the dispersion of 0.1 wt % of MWCNT in an epoxy matrix. Hardener, epoxy/solvent and epoxy are being used as dispersing media in this study. The values of strain at failure, Young’s modulus and tensile strength are calculated under distinct dispersion loadings of MWCNTs. The results show that initially there is an increase in the value of tensile strength with the increase in sonication time, followed by decrease in the tensile strength values with an increase in sonication time. The maximum value of Young’s modulus was obtained during epoxy dispersion, and the maximum tensile strength value was obtained, when hardener is used as a dispersing medium. Results indicated that for epoxy dispersion, the consequence of sonication time is highly prominent. The mechanical properties showed least effect, when epoxy/solvent system is used as an MWCNT dispersing medium. Atomic force microscopy

(AFM) and Scanning electron microscopy (SEM) are used for analyzing the distribution of MWCNTs in the epoxy system by analyzing their respective micrographs. A superior degree of dispersion is attained when either the hardener or the solvent is being chosen as the dispersing solvent.

Jacobi et al. (2012) studied that nanofluids show different characteristics, when prepared with different processing methods but keeping the same filler material and base fluids. The size of agglomerates present inside the nanocomposites can affect the mechanical and thermal properties of nanofluids and directed it to different performance of heat transfer. Ultrasonication is most commonly used for breaking the agglomerates that are present inside the nanofluid at the same time increasing the dispersion of nanoparticles inside the base fluids. In this literature, a CNT/ethylene glycol nanocomposite is fabricated at different sonication parameters and their effects are studied on the viscosity and thermal conductivity. The effect of same sonication parameters is also studied on the size of agglomerates inside nanocomposite and the length of CNTs. It is noted that, with an increase in sonication time and energy, there is an increase in the values of thermal conductivity of nanofluids and achieved a maximum value with an improvement of 23%, at the sonication time of 1,355 min. Also, it is found that initially with an increase in sonication time up to 40 min., there was an increase in the viscosity values but it started reducing after that up to the maximum experimental value of sonication time i.e. 1,355 min. Hence it was concluded that with prolonged sonication, there was a large improvement in the thermal conductivity values but the increase in viscosity of nanofluids was very less, which has its impact on the various applications of nanofluids.

2.3 Gaps in the Literature

- Very few reports are there regarding dispersion quantification of functionalised MWCNT/epoxy nanocomposites by any dispersion quantification technique.
- Very few reports on evaluating the effects of homogenizing speed and time on the mechanical properties of MWCNT/ epoxy nanocomposites.

- Not much work has been reported on correlating the results of mechanical properties of MWCNT/ epoxy nanocomposites with their respective quantified values of degree of dispersion.

Chapter 3

METHODOLOGY

3.1 Introduction

This chapter describes the methodology of the present work. It includes the objective of the proposed work, the material selection, information on equipments and instruments required for fabricating and testing the nanocomposites, procedure of fabrication and dispersion quantification.

3.2 Scope of the study

The scope and the requirement for this study could be well explained by understanding the application areas of the MWCNT/epoxy nanocomposites.

1. Improve electrical conductivity**:** For improving the electrical properties, MWNTs have been used, because those Russian dolls like nanotube structures are always conductive. The conductivity of MWCNT is due to the average behavior of the different rolled graphene layers. End-uses include coatings for electromagnetic shielding, composites for automotive fuel systems, and composites amenable to electrostatic painting. Applications include conductive polymers & composites (automobiles and electronics), electromagnetic shielding and semiconducting materials.
2. Improve mechanical properties: High aspect ratio, Young’s modulus, fracture toughness and yield strength are the properties required for achieving for the desired applications of reinforced composite. Applications include sporting goods (tennis and rackets), lithium ion batteries, medical implants, aerospace, textile and fibers.
3. Recent studies have shown exceptional performance in flame retardancy at MWCNT concentrations $\leq 0.5\%$

All the above mentioned applications show that there is a lot of research required in the area of the mechanical properties enhancement of the MWCNT/epoxy nanocomposite. Quantification of dispersion leads to the selection of best process parameters for manufacturing the nanocomposite which has led to the origin of this study.

3.3 Establishing the Objective Function

The reviewed literature shows that several studies are undergoing in the area of MWCNT/epoxy nanocomposite. However, no literature is available on dispersion quantification of MWCNT in epoxy matrix and evaluation of mechanical properties of nanocomposites with respect to changes in speed and duration of homogenizing. The overall objective of the present work is to evaluate **the effect of homogenization treatment conditions on the dispersion of carbon nanotubes and mechanical properties of MWCNT/epoxy nanocomposites.**

The key issues that would be taken up during this study include:

1. Dispersion quantification, tensile and flexural properties of the MWCNT/epoxy nanocomposite.
2. Effect of processing conditions on the dispersion of nanoparticles in the nanocomposite.

3.4 Material Selection

This section deals with the material that would be required for fabricating of the intended nanocomposites.

3.4.1 Epoxy Resin

The epoxy system is a combination of the resin system and the hardener, both belonging to Araldite family. The resin used is the Di-glycidyl ether of bisphenol A (DGEBA) i.e. Araldite 1564 and the hardener used is the Aradur 3486; supplied by Huntsman Advanced Materials, India. It has excellent mechanical properties and chemical resistance, variable within wide limits by using changing hardeners and fillers, very good processing properties and low tendency to crystallize. The mix has density is 1.15 g/cm^3 at 20℃ and mix viscosity is 500–650 mPa s at 25℃. The resin system and hardener are mixed in 100:34 weight ratios (as specified by the supplier).

3.4.2 MWCNT

The multiwalled carbon nanotubes (MWCNTs) produced by the chemical vapor deposition (CVD) were purchased from Intelligent Materials Private Limited., Panchkula. The MWCNTs specifications are: diameter in the range of about 10–70 nm, and a mean length of a few hundred microns with a purity of 99%.

3.5 Experimental Equipments and Facilities

3.5.1 Homogenizer

Homogenization is the method of changing two immiscible liquids into an emulsion. The Homogenizer system (Make: IKA T26 ULTRA-TURRAX, Cole-Parmer, Chicago, US), available at Chemical Engineering Department, Thapar University, Patiala has a digital display that offers a wide range of speed up to 30,000 revolutions per minute, starting softly of course, that allows the user to work at high circumferential speeds and with small diameters of rotor. It is best for physical function, lightweight and has an ability to release quick coupling that makes it easier for changing and cleaning the disperser element. The dispersion incorporated in the solution by homogenizer is based on the rotor-stator principle. The rotor is stirred with lofty circumferential pace which creates suction and draws the solution onto the rotor and then drives it to the outer surface with the assistance from the stator’s teeth. This method resulted in dispersion of the system. It is directed to the rigorous, quick crushing of liquid globules and solid constituent of preferably minute sizes.

Figure 3.1: Homogenizer

(Photo courtesy: Chemical Engineering Department, Thapar University, Patiala)

3.5.2 Probe Sonicator

Probe sonication is highly effective for processing nanomaterials (carbon nanotubes, grapheme, inks, metal oxides, etc.). The ultrasonic generator changes the AC line power to a 20 KHz pointer which moves a piezoelectric convertor/transducer. The electrical signal produced is transformed to mechanical vibrations by transducer owing to the properties of inner piezoelectric crystals. The vibrations produced are modified and passed down to the span of horn/probe where the tip longitudinally inflate and pact. The expanse that the tip moves depends on the amplitude chosen by the user through the amplitude. The probe Sonicator (Make: Q Sonica Sonicators, Newtown, US) is available at Chemical Engineering Department, Thapar University, Patiala.

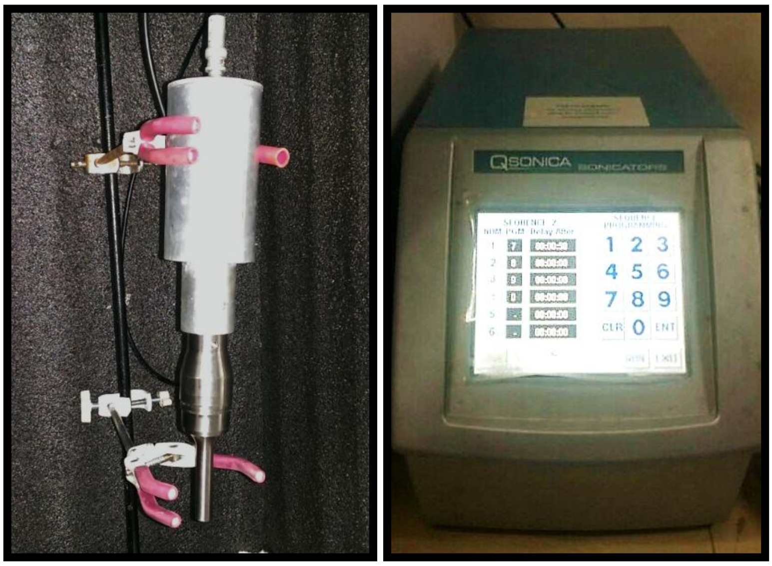


Figure 3.2: Probe Sonicator

(Photo courtesy: Chemical Engineering Department, Thapar University, Patiala)

3.5.3 Mechanical Stirrer

Once the addition of hardener is done in the resin system, the next step would be to add the MWCNTs and finally hardener into the MWCNT/epoxy system and these operations were performed during continuous stirring using a mechanical stirrer. The mechanical stirrer (Make: REMI Laboratory Instruments, Mumbai, India) available has a working speed adjustable to 2400 rpm, shaft diameter (ϕ) of 8 mm and overall length of 400 mm. Its salient features include PMDC motor for powerful stirring, reliable performance even in continuous use and, chuck for easy interchangeability of shaft and stepless electronic speed regulator with digital display.

Figure 3.3: Mechanical Stirrer

(Photo courtesy: Chemical Engineering Department, Thapar University, Patiala)

3.5.4 Vacuum Oven

The vacuum oven (Make: Macro Scientific Works Pvt. Ltd., New Delhi, India) is appropriate for baking, vacuum drying liquids, out-gassing solids, conditioning and curing, vacuum embedding, aging test, plating and moisture testing. It consists of a microprocessor controlled system employing better temperature precision beside the better homogeneity and constancy. Its internal chamber is made up of stainless steel (SS-304).

Figure 3.4: Vacuum Oven

(Photo courtesy: Chemical Engineering Department, Thapar University, Patiala)

3.5.5 Weighing Balance

The analytical weighing balance (Make: Mettler-Toledo, Greifensee, Switzerland) is used for weighing the weight of the epoxy, hardener and the MWCNTs. Available in Chemical Engineering Department, Thapar University, Patiala, this weighing balance has a very high accuracy and precision, with a capacity of 320 g and accuracy of 0.1 mg.

Figure 3.5: Weighing Balance

(Photo courtesy: Chemical Engineering Department, Thapar University, Patiala)

3.5.6 Universal Testing Machine

The universal testing machine (Make: Zwick/Roell, Ulm, Germany), available in Chemical Engineering Department, Thapar University, Patiala, is used to carry out the tensile tests and flexural tests over the samples of the fabricated nanocomposite. It has a capacity of 1 tonne (10 kN), provided with different fixtures for tensile and flexural testing. The tensile testing samples are prepared according to ASTM D638, which is a standard test method for the determination of the tensile properties of reinforced and unreinforced plastics in the shape of standard dumbbell-shaped test specimens. Also, for the flexural testing, the specimen dimensions are selected according to the ASTM D790–02, which is a standard test method for the determination of flexural properties of unreinforced and reinforced plastics in the shape of rectangular or circular crossection. This Universal Testing Machine is available at Chemical Engineering Department, Thapar University, Patiala.

Figure 3.6: Universal Testing Machine

(Photo courtesy: Chemical Engineering Department, Thapar University, Patiala)

3.5.7 Scanning Electron Microscopy (SEM)

The scanning electron microscopy (SEM) is a method of analyzing the fractured surface of tensile specimen. Secondary electrons are emitted from the surface exposed for irradiation by an electron beam. Morphology of the fractured surface can be analyzed by the scanning of electron probe over the fractured surface and attainment of a micrograph from the perceived secondary electrons (Web reference: www.jeol.com). This SEM (Make: JSM-6510LV, JEOL Ltd, Tokyo, Japan) is available at SAI Labs, Thapar Technology Campus, Patiala. SEM analysis is a “non-destructive” test because the fine electron beam doesn’t leads to the loss in the volume from the work piece surface. It is a high performance and low vacuum SEM for fast characterization and imaging of fine structures and has a magnification range 5–300,000 X. Here, it will be used to study the surface topology of the fabricated nanocomposites and the fractured surfaces of the composites.

Figure 3.7: Scanning Electron Microscope

(Photo courtesy: SAI Labs, Thapar Technology Campus, Patiala)

3.6 Experimental Procedure

This section covers the experimental procedure followed for the fabrication of the pure epoxy sample as well as the nanocomposite.

3.6.1 Calculations

1. The very first step towards the fabrication of the composite would be to decide the number of samples required for performing each of the mechanical tests (tensile and flexural tests), and on the basis of this decision, select the mould size. In this study, 4 samples each for tensile and flexural tests were selected. The aluminium mould size is selected as having 27cm in length, 20cm by width and 1.5 cm by height.
2. The next step would be to determine the volume of the epoxy required. As specified by the manufacturer, the density of the epoxy is 1.15 g/cm^3 whereas, the density of the hardener is equivalent to that of water i.e. 1 g/cm^3. Now, if the mixing ratio of the resin and hardener has been defined 100:34 then, converting the same weight ratio into volume ratio, whose calculation is shown below,

$$\text{Volume of Resin System} = \frac{\text{Mass of Resin System}}{\text{Density of Resin System}} = \frac{100}{1.15} = 86.95\ \text{cm}^3.$$

$$\text{Volume of Hardener} = \frac{\text{Mass of the Hardener}}{\text{Density of the Hardener}} = \frac{34}{1} = 34\ \text{cm}^3.$$

Hence it means that if the mixing ratio of resin and hardener is 100:34 by weight then the same mixing ratio would become 86.95:34 by volume. Now, using the mass balance equation for the epoxy system,

Mass of Epoxy = (Mass of Resin System + Mass of Hardener),

Density of Epoxy (ρ_e) × Volume of Epoxy = (100 + 34),

Density of Epoxy (ρ_e) × (86.95 + 34) = 134.

Hence, Density of Epoxy (ρ_e) = 1.1078 g/ cm^3.

Hence from this density calculation, we can determine the mass of the epoxy required in the mould, for the fabrication of a pure epoxy sample, which is given as follows.

Mass of the Epoxy Required = Density of Epoxy (ρ_e) × Volume of sample fabricated,

i.e., Mass of the Epoxy required = $(1.1078 \times 27 \times 20 \times 0.32)$

Hence, the Mass of Epoxy required to fabricate a pristine sample = 191.42 g.

Now using the weight ratio, if 134 g of epoxy system contains 34 g of hardener,

The 191.42 g of epoxy system will contain $\frac{34}{134} \times 191.42 = 48.569$ g of hardener.

So, the weight of resin required for the pristine sample = (191.42 – 48.569) = 142.851 g.

3. Weigh the 142.851 g of resin system and 48.569 g of hardener in separate beakers.
4. Place the aluminium mould over a levelled surface and justify the levelling using a spirit level. Some packing has also been used to ensure approximately perfect level conditions.

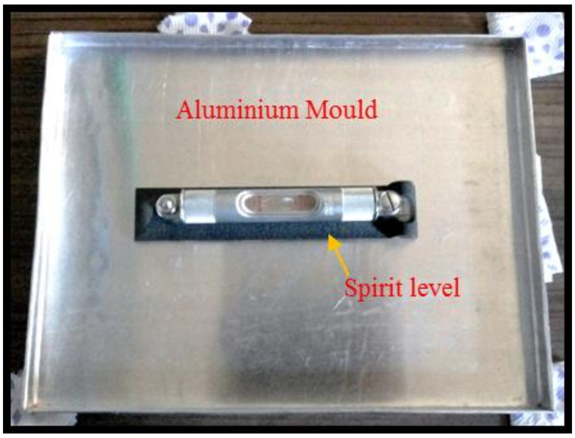


Figure 3.8: Mould Leveling Using a Spirit Level

5. Even before performing the levelling operation, make sure that the mould is properly coated with a layer of mould cleaner and a mould releasing agent (Suppliers: Frekote, Mexico City, Mexico). In the absence of this coating, the release of the composite from

the mould will become an uphill task, even leading to the breaking of the composite or its disfiguring during removal owing to the brittle nature of epoxy.

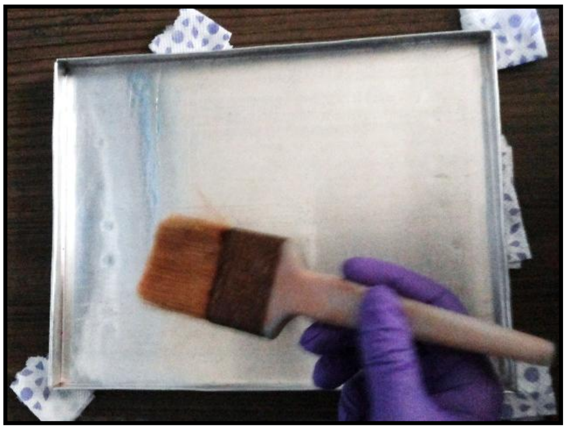


Figure 3.9: Mould Coating with Releasing Agent

3.6.2 Fabrication of Neat Epoxy composite

(a) Add the hardener into the epoxy, with a continuous mechanical stirring at 500 rpm for 5 min. The stirrer must be dipped completely into the liquid. Even during the stirring, before and after the addition of hardener, the stirrer must be completely dipped into the epoxy and any up-down motion of the stirrer must be avoided. All these precautions have been listed to avoid any entrapment of air, as it can affect the quality of sample.

(b) A degassing period of 30 min. would be more than enough.

(c) Now finally, pour the epoxy system into the aluminium mould. The spatula could be used to remove any of the visible air bubbles over the surface of the epoxy inside mould. Allow the epoxy system to cure for 1 day at room temperature.

3.6.3 Fabrication of MWCNT/epoxy nanocomposite

The above mentioned procedure was for the NE (pure epoxy) composite but for fabricating MWCNT/epoxy nanocomposite (i.e. 1PC, 2PC, 3PC, 4PC), a different procedure is followed. The weight calculations are as follows:

The reinforced nanocomposites (1PC, 2PC, 3PC, 4PC) state that 0.05 wt % MWCNT must be added into the epoxy.

The weight of epoxy = 191.42 g.

So, the weight of the pristine MWCNT required = $\frac{0.05}{100} \times 191.42 = 0.09571$ g.

So, the final weight of the epoxy system = (191.42 – 0.09571) = 191.324 g.

Now using the weight ratio, if 134 g of epoxy system contains 34 g of hardener,

The 189.267 g of epoxy system will contain $\frac{34}{134} \times 191.324 = 48.544$ g of hardener.

So, the weight of resin required = (191.324 – 48.544) = 142.78 g.

The fabrication procedure is as follows:

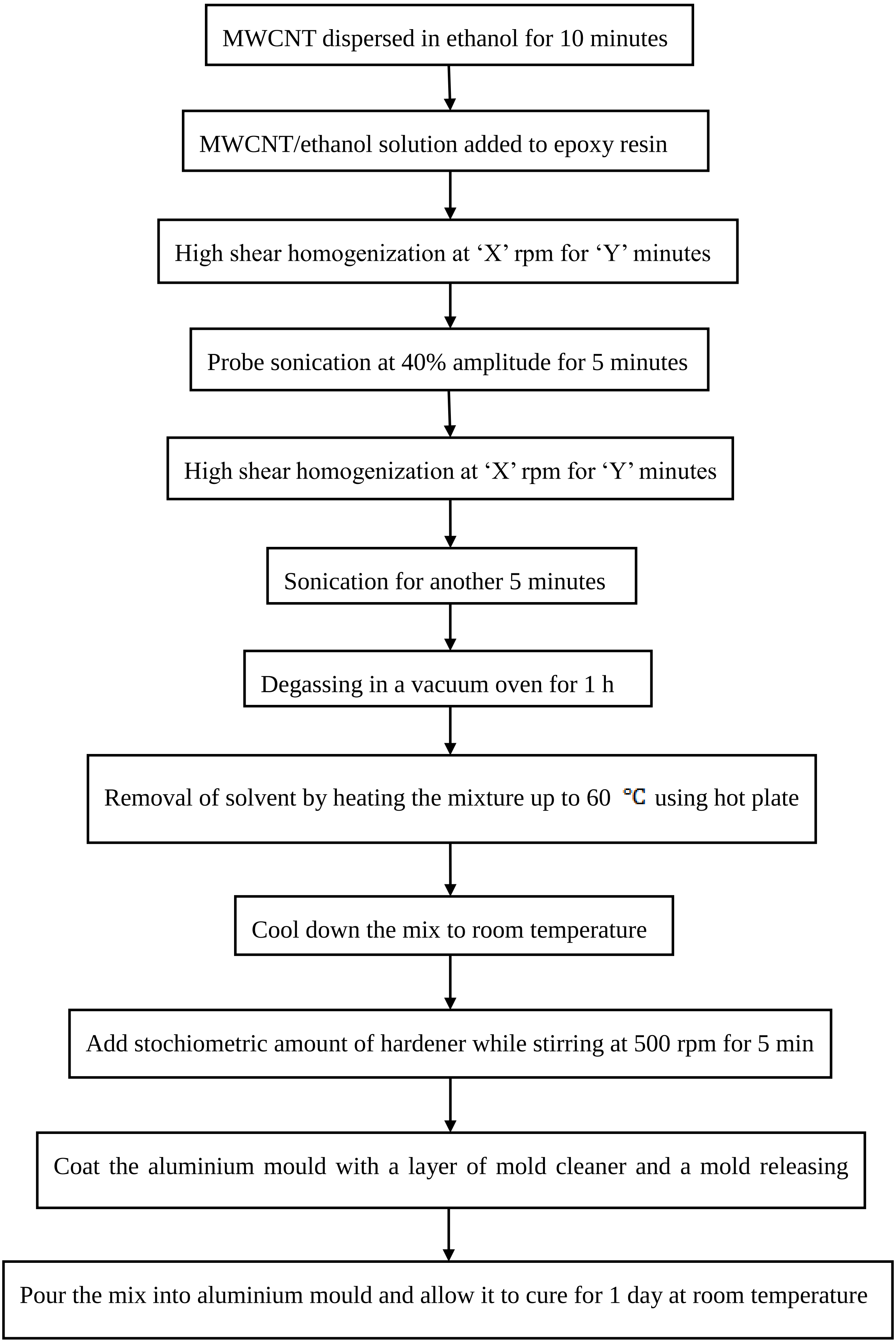


Figure 3.10: Fabrication procedure for MWCNT/Epoxy nanocomposite

Four different nanocomposites (1PC, 2PC, 3PC, 4PC) are fabricated using different homogenizing speeds (X) and different durations (Y). Speeds and times of homogenization are shown in Table 3.1:

Table 3.1: Processing conditions for four different nanocomposites

Nanocomposites Code	Homogenizer Speed (X), rpm	Homogenizer Time (Y), min.
1PC0.05	15,000	5
2PC0.05	7,500	5
3PC0.05	15,000	10
4PC0.05	7,500	10

3.6.4 Characterization and Mechanical Testing

Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was performed with JEOL JSM 6510LV SEM operated at 20kV. The fractured surfaces of all the four nanocomposite samples were examined using SEM. Prior to the SEM analysis; all specimens were coated with a thin layer of gold using a sputter coated to avoid charging effects.

Tensile testing

The samples for the tensile and flexural testing are cut using a circular saw, available at Central Workshop, Thapar University, Patiala. The tensile testing samples are prepared according to ASTM D638, which is a standard test method for the determination of the tensile properties of reinforced and unreinforced plastics in the shape of standard dumbbell-shaped test specimens. Under this test standard, the Type V dimension is selected, which has the specifications: overall length 63.5 mm, overall width 9.53 mm, gauge length 7.62 mm, distance between the grips 25.4 mm, width of narrow section 3.18 mm, length of narrow section 9.53 mm, radius of the fillet 12.7 mm and finally, the thickness of the specimen maintained to be 3.2 mm. The speed of testing selected is 1 mm/min. An average reading was taken for four samples. Four specimens were tested for each sample and the values were averaged.

Flexural testing

For the flexural testing, the specimen dimensions are selected according to the ASTM D790–02, which is a standard test method for flexural properties of unreinforced and reinforced plastics and electrical insulating materials, in the form of rectangular bars molded directly or cut from sheets, plates, or molded shapes. The recommended specimen for molding materials (thermoplastics and thermosets) is 127 × 12.7 × 3.2 mm tested flatwise on a support span-to-depth ratio of 16. The rate of crosshead motion selected is 1.27 mm/min, with a constant span of 47.84 mm. Four samples were atleast tested for each of the composite prepared.

Degree of dispersion

Composite Index method is used for quantifying dispersion in this work. The dispersion quantification of carbon nanotubes of nanocomposite consists of two parameters viz, the distribution of nanoparticles, which tells the spread of carbon in the matrix and the size attribute of nanoparticles, which tells the shape and size of carbon agglomerates or bundles that are present in the whole composite.

The composite dispersion index compIndex used in this work comprises two indexes: the dispersion distribution index i.e. dIndex and the size distribution index i.e. sIndex.

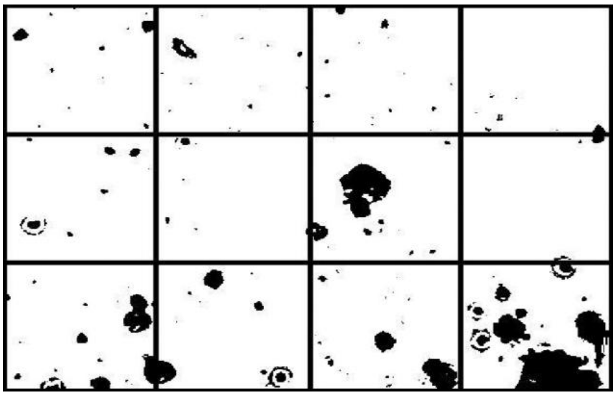


Figure 3.11: Micrograph with 3x4 grid for calculating dispersion distribution index [11].

The dIndex is evaluated by a 3 x 4 grid as shown in Fig. 3.8, selected to overlap the aspect ratio of standard images. The dispersion distribution index is calculated using Eq. (3.1) where 'b' is the set of carbon black percentages for the 12 fields of the grid, s(b) is the standard deviation of b, and b' is the arithmetic average of b. The range of the dispersion distribution index is [0, 1] with 1 indicating perfect dispersion.

$$dIndex = \frac{1}{2}\left[1 - \frac{s(b)}{0.522} + \frac{b'}{\max(b)}\right] \tag{3.1}$$

The size distribution index calculation must be performed without a grid as we know that large number of particles is expected to move across grid margins. The agglomerate areas in the image are evaluated using a computer algorithm by counting the no. of pixels taken by each CNT particle, and sIndex is calculated using Eq. (3.2). For calculating the area of nanoparticles, the pixels that represent the MWCNT nanoparticles are required to be identified. Basically, the digital micrographs are produced by the process of thresholding and sampling process, which represents each pixel in a micrograph by a matrix of real numbers. Every element of the matrix represents the value of the pixel, which is distinguished by its position in the micrograph and this element shows the degree of darkness of that pixel. The value of degree of darkness ranges from 0 to 255, with 0 value showing full dark image and 1 value showing totally white. The pixel representing MWCNTs within micrographs are measured by ImageJ software.

$$sIndex = \frac{1}{2}\left[\frac{L}{N} + 1 - \frac{\max(a)}{\sum a} \right] \qquad (3.2)$$

Here, ‘a’ is the set of area of all particles. N is the total no. of particles and L is the no. of particles whose area is less than a threshold of 100 pixels. The value of sIndex varies between 0 and 1, with 1 showing the absence of any nanoparticles in the micrograph. This suggests that the CNT bundles are too small to be noticed in the micrograph.

The composite index compIndex is calculated as the arithmetic mean of the dIndex and the sIndex.

The results of tensile testing, flexural testing and dispersion quantification of this study have been discussed in the next chapter.

Chapter 4

RESULTS AND DISCUSSION

The prepared specimens were studied for their morphological and mechanical properties, as discussed in the following section.

4.1 Tensile tests

The results obtained by conducting tensile tests on nanocomposites using Zwick/Roell Universal testing machine are shown below:

Table 4.1: Tensile test results

Specimens Name	Specimens Code	Young's Modulus (GPa)	Tensile Strength (MPa)	Elongation (%)
Neat Epoxy Composite	NET1	0.97	51.8	7.9
	NET2	1.48	54.8	5.5
	NET3	1.44	57.1	5.9
	NET4	1.02	57.4	4.6
0.05 wt% MWCNT/epoxy nanocomposite (15,000 rpm & 5 min)	1PCT1	3.0	118	4.9
	1PCT2	2.0	53.9	5.4
	1PCT3	2.0	68.1	5
	1PCT4	2.0	43.6	4.7
0.05 wt% MWCNT/epoxy	2PCT1	2.0	59.9	4.7
	2PCT2	1.33	52.7	6.7

nanocomposite (7,500 rpm & 5 min)	2PCT3	1.0	50	7.3
	2PCT4	1.0	48.2	8.3
0.05 wt% MWCNT/epoxy nanocomposite (15,000 rpm & 10 min)	3PCT1	2.0	88.5	5
	3PCT2	2.0	54.2	4.8
	3PCT3	1.0	40.9	7
	3PCT4	1.0	15.8	6.1
0.05 wt% MWCNT/epoxy nanocomposite (7,500 rpm & 10 min)	4PCT1	1.0	43.4	5.9
	4PCT2	1.0	31.5	5.5
	4PCT3	1.0	31.4	7.7
	4PCT4	1.0	57	6.6

From Fig. 4.1 & 4.2, it is observed that Young’s modulus and tensile strength values are highest for 1PC nanocomposite, which is fabricated using a homogenizing speed of 15,000 rpm for 5 min. The improvement in tensile modulus and strength can be attributed to the good dispersion of MWCNT, which is also quantified in the section 4.4. It is to be noted here that 2PC and 4PC have lower values of tensile modulus and tensile strength, both of which are operated at 7,500 rpm. Thus, it can be concluded here that higher homogenizing speed lead to higher tensile modulus and strength of MWCNT/epoxy nanocomposite and increase in duration has adverse effect on the tensile properties. The considerable homogenizing speed for longer duration (i.e 3PC and 4PC) may also induce unwanted tube breakage, which leads to decrease in tensile modulus and strength of nanocomposite as seen in [21, 22] and shown in section 4.4.

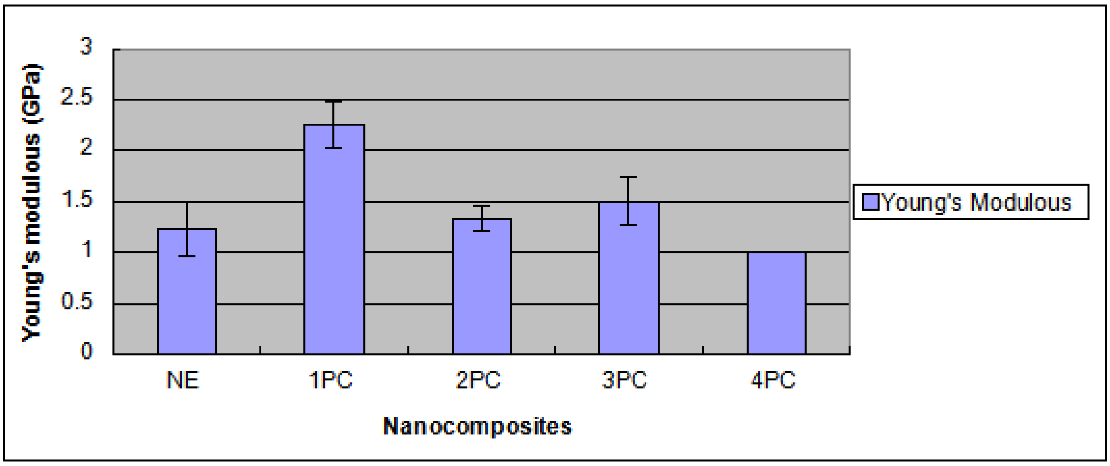


Figure 4.1: Young's modulus of the neat epoxy and the various nanocomposite samples as a function of homogenizing speed and duration.

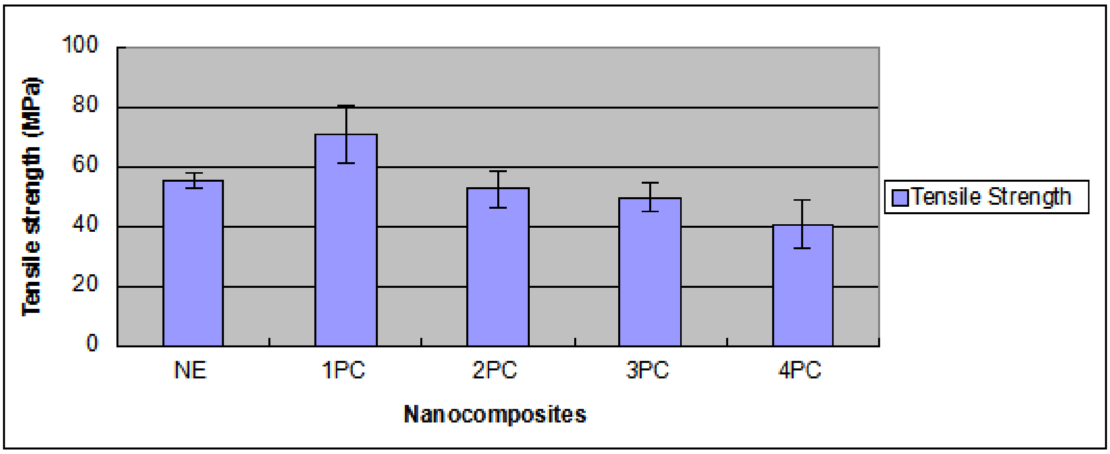


Figure 4.2: Tensile strength of the neat epoxy and the various nanocomposite samples as a function of homogenizing speed and the duration.

From Fig. 4.3, the 2PC and 4PC nanocomposites have higher percentage elongation than other nanocomposites. Thus, it can be said here that nanocomposites prepared at 15,000 rpm undergo less deformation than that operated at 7.500 rpm. Due to which, the former has improved tensile properties when operated for 5 min.

Thus, nanocomposites that are prepared at high homogenizing speed shows improved tensile properties.

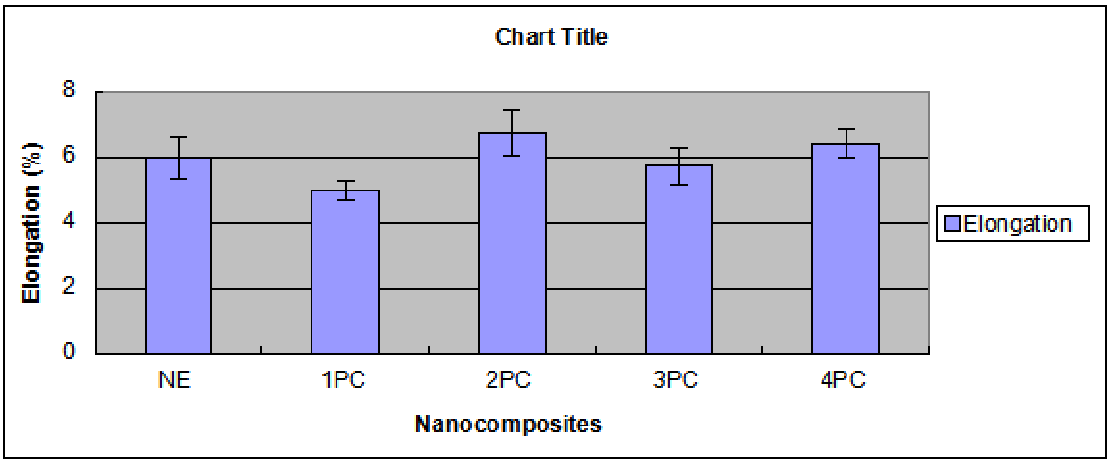


Figure 4.3: Elongation at break of the neat epoxy and the various nanocomposite samples as a function of homogenizing speed and duration.

4.2 Flexural tests

The results obtained by conducting three point flexural tests on nanocomposites using Zwick/Roell universal testing machine are shown below in table 4.2.

Table 4.2: Flexural test results

Specimens Name	Specimens Code	Flexural Modulus (GPa)	Flexural Strength (MPa)
Neat Epoxy Composite	NEF1	0.276	44
	NEF2	0.277	45
	NEF3	0.278	46
	NEF4	0.211	47
0.05 wt% MWCNT/epoxy nanocomposite (15,000 rpm & 5	1PCF1	0.387	46
	1PCF2	0.325	44
	1PCF3	0.363	47

min)	1PCF4	0.412	49
0.05 wt% MWCNT/epoxy nanocomposite (7,500 rpm & 5 min)	2PCF1	0.398	48
	2PCF2	0.221	31
	2PCF3	0.426	51
	2PCF4	0.373	48
0.05 wt% MWCNT/epoxy nanocomposite (15,000 rpm & 10 min)	3PCF1	0.412	45
	3PCF2	0.413	43
	3PCF3	0.414	48
	3PCF4	0.415	47
0.05 wt% MWCNT/epoxy nanocomposite (7,500 rpm & 10 min)	4PCF1	0.379	46
	4PCF2	0.311	40
	4PCF3	0.369	48
	4PCF4	0.368	47

From Fig. 4.4 and 4.5, it is observed that all nanocomposites prepared have relatively small difference in their values of flexural modulus and flexural strength. Thus homogenizing conditions have no significant effect on these properties of MWCNT/epoxy nanocomposites. But, it is to be noted here that neat epoxy composite has lower values of flexural modulus and flexural strength than all other nanocomposites. It is due to the fact that the reinforcement of nanocomposite with MWCNT significantly improves the flexural properties.

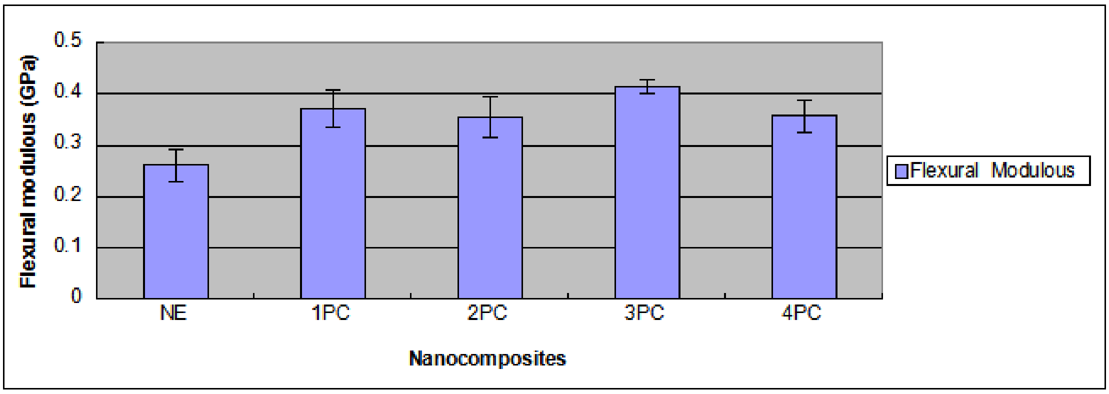


Figure 4.4: Flexural modulus of the neat epoxy and the various nanocomposite samples as a function of homogenizing speed and duration.

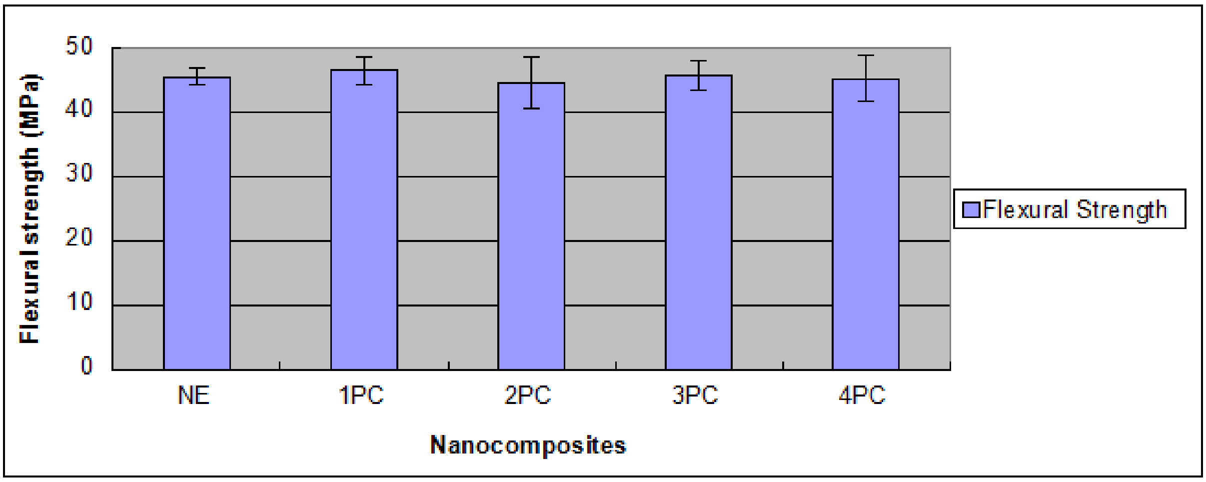
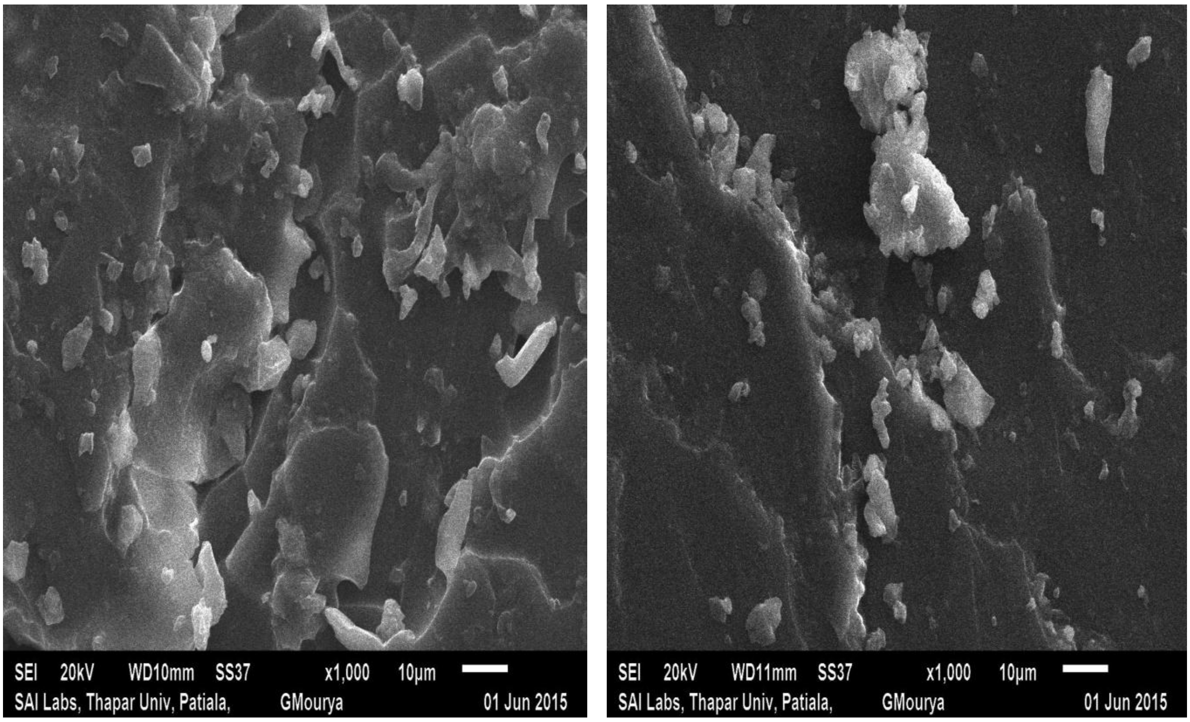


Figure 4.5: Flexural strength of the neat epoxy and the various nanocomposite samples as a function of homogenizing and the duration.

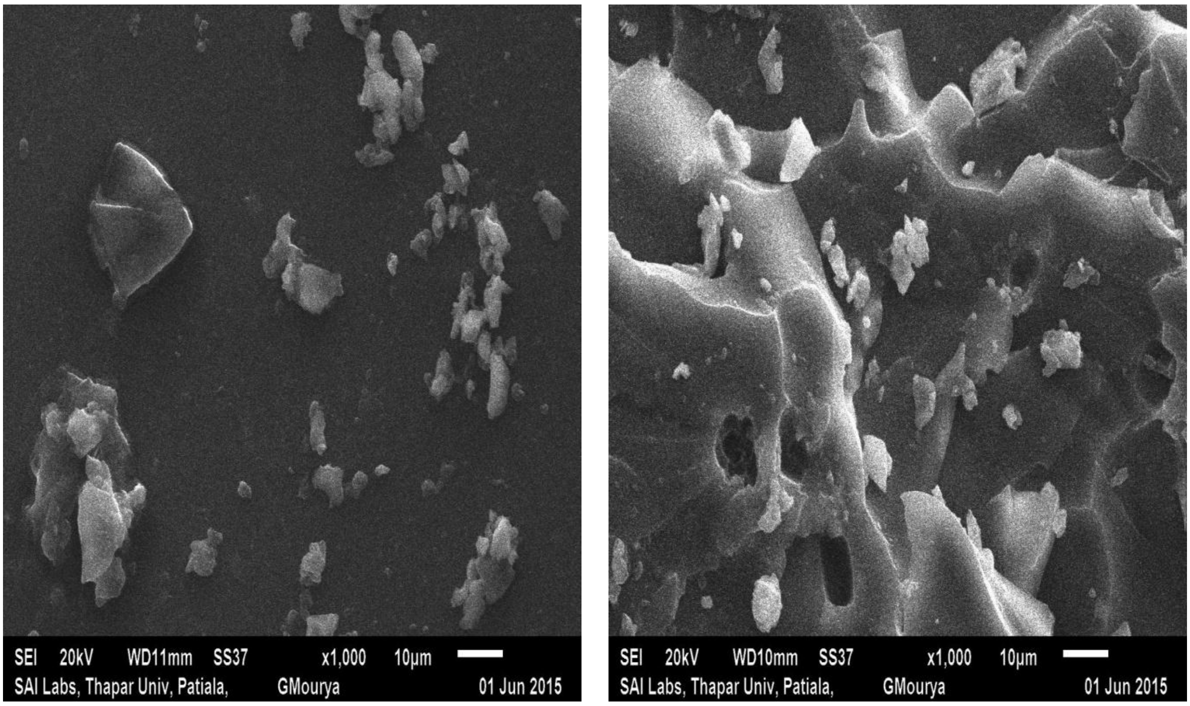
The studied mechanical properties decreased with the increase in homogenizing time. This may be attributed to possible nanotube damage caused by long-time homogenization. The mechanical properties improved with the increase in homogenizing speed.

4.3 Scanning electron microscopy (SEM)

Samples were mounted onto sample holder and fixed with adhesive carbon tape. Fig. 4.6 and fig. 4.7 illustrates the sectional surface morphology of MWCNT/epoxy nanocomposites at two levels of magnification i.e. at 1,000x and 500x respectively. Voids and small holes are observed at some places in these SEM images. Non circular bright regions shows correspond to MWCNT agglomerates or bundles that are observed from SEM micrograph. It is observed that MWCNT is dispersed in the epoxy matrix and the degree of MWCNT distribution in epoxy matrix is calculated by analysing these SEM micrographs in image J application. In image J software, after having set the scale and the threshold (the threshold was set to a uniform value for the whole image), the “Analyse Particles” features was used to generate a table of particles area. This then exported into Microsoft excel, were statistical analysis and histogram plotting were performed.

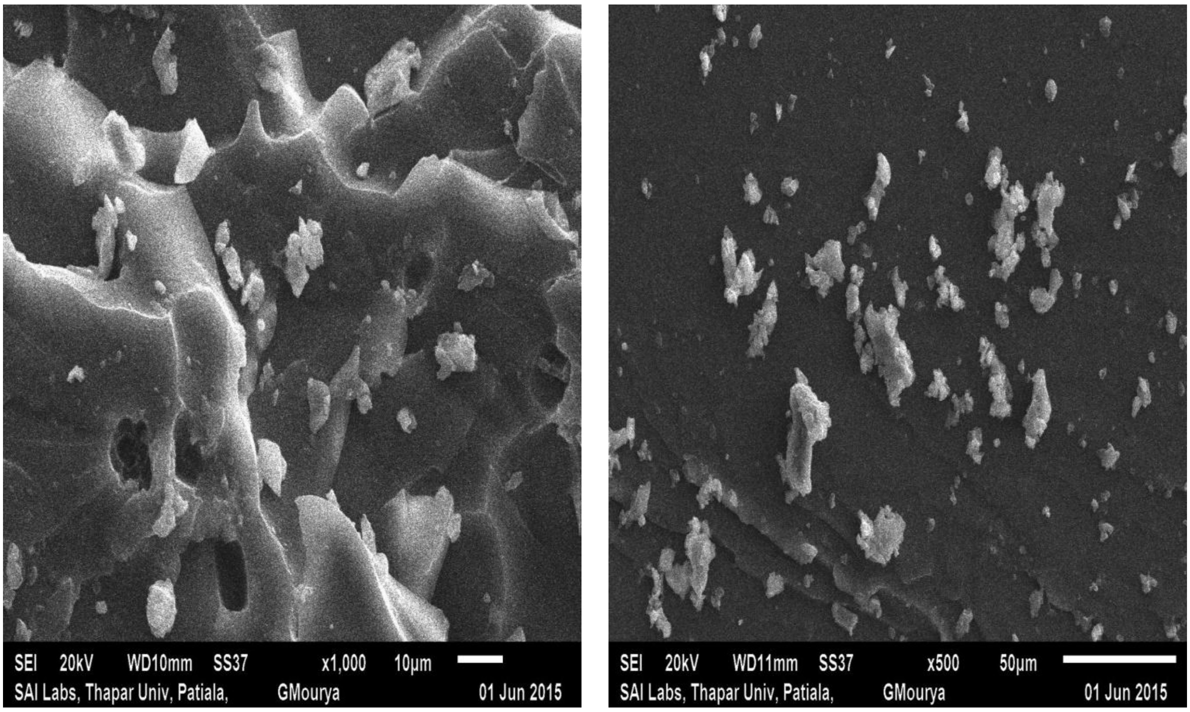


(a) (b)

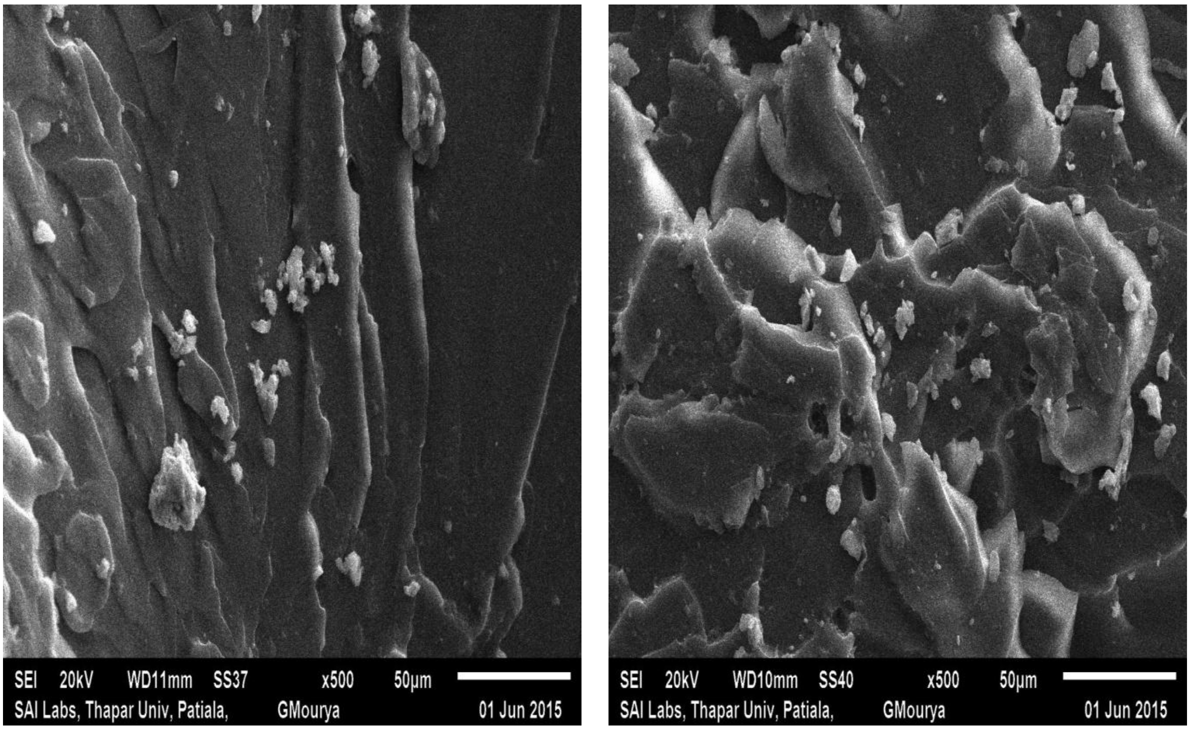


(c) (d)

Figure 4.6: SEM images at magnification of 10µm showing (a) 1PC (15,000 rpm & 5 min); (b) 2PC (7,500 rpm & 5 min); (c) 3PC (15,000 rpm & 10 min); (d) 4PC (7,500 rpm & 10 min)



(a) (b)



(c) (d)

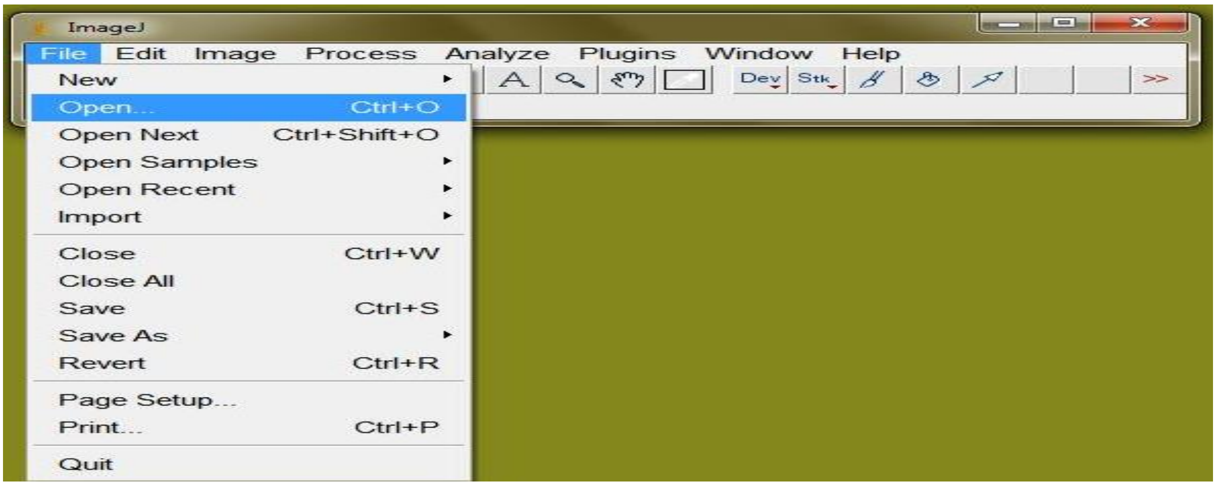
Figure 4.7: SEM images at magnification of 50µm showing (a) 1PC (15,000 rpm & 5 min); (b) 2PC (7,500 rpm & 5 min); (c) 3PC (15,000 rpm & 10 min); (d) 4PC (7,500 rpm & 10 min)

4.4 Degree of Dispersion

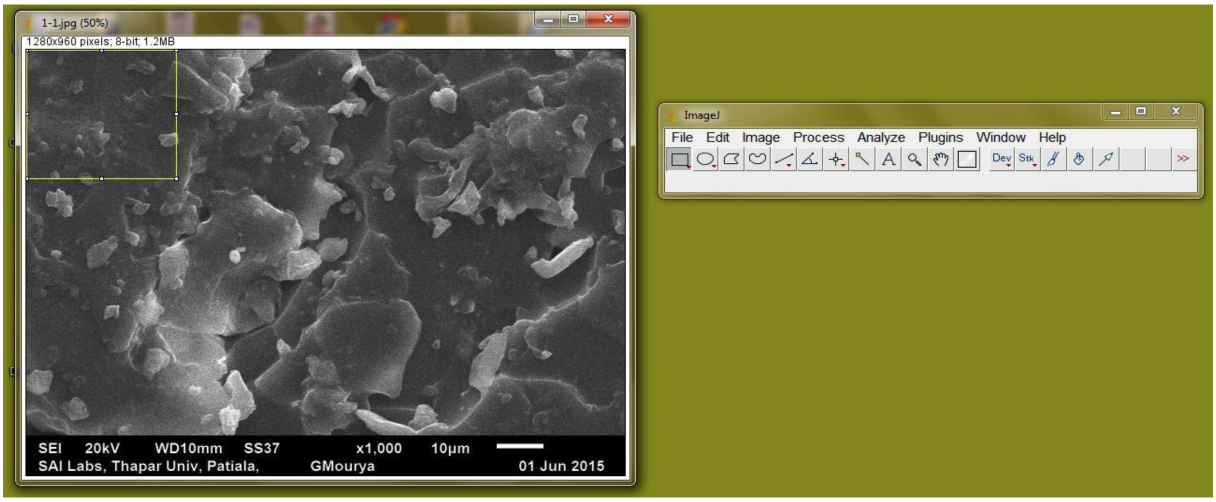
The composite dispersion index compIndex used for quantifying the degree of dispersion of four MWCNT/Epoxy nanocomposites (1PC, 2PC, 3PC, 4PC) with varying homogenizing speed and duration includes two indexes: the dispersion distribution index (dIndex) and the size distribution index (sIndex).

$$dIndex = \frac{1}{2}\left[1 - \frac{s(b)}{0.522} + \frac{b'}{\max{(b)}}\right] \tag{4.1}$$

Image J software is used for calculating dIndex and the procedure is as shown in fig. 4.8 for one particular nanocomposite e.g. 1PC.


ImageJ
File
Edit
Image
Process
Analyze
Plugins
Window
Help
Dev
Stk
New
Open... Ctrl+O
Open Next Ctrl+Shift+O
Open Samples
Open Recent
Import
Close Ctrl+W
Close All
Save Ctrl+S
Save As
Revert Ctrl+R
Page Setup...
Print... Ctrl+P
Quit

(a)


1-1.jpg (50%)
1280x960 pixels; 8-bit; 1.2MB
SEI 20kV WD10mm SS37 x1,000 10µm
SAI Labs, Thapar Univ, Patiala, GMourya 01 Jun 2015
ImageJ
File
Edit
Image
Process
Analyze
Plugins
Window
Help
Dev
Stk

(b)

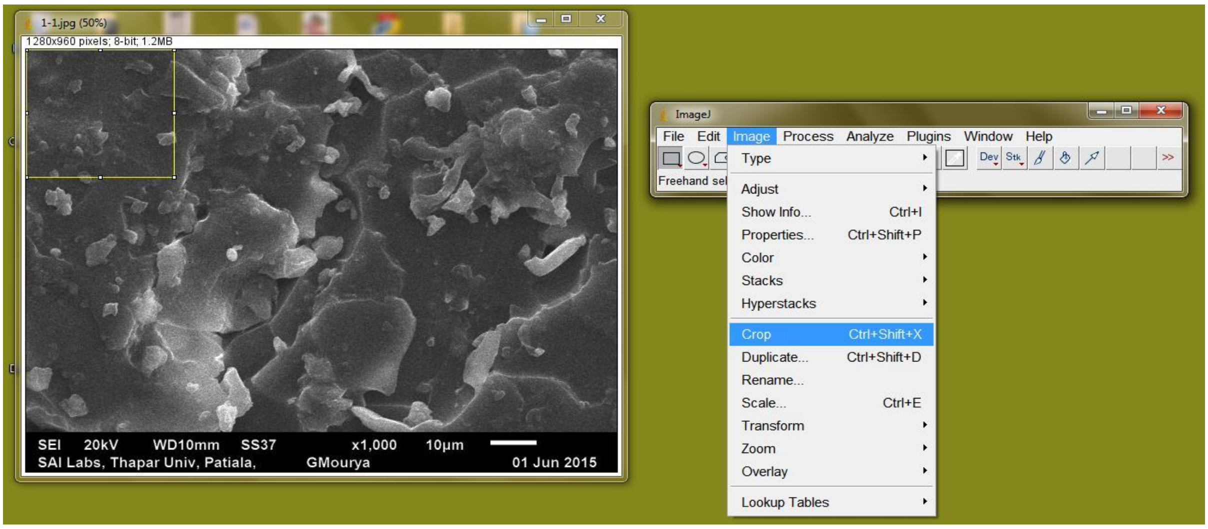

1-1.jpg (50%)
1280x960 pixels; 8-bit; 1.2MB
SEI 20kV WD10mm SS37 x1,000 10µm
SAI Labs, Thapar Univ, Patiala, GMourya 01 Jun 2015
ImageJ
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Image
Process
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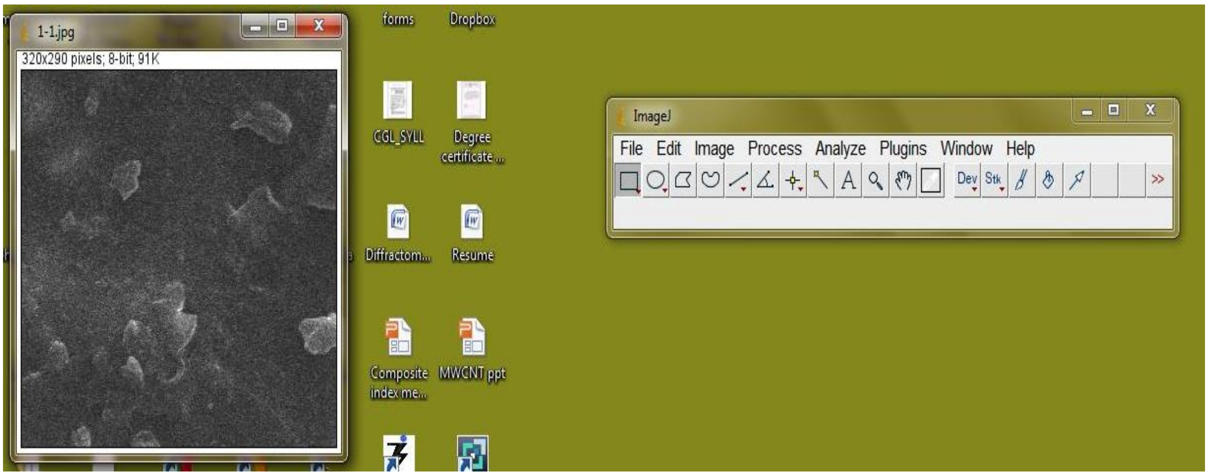
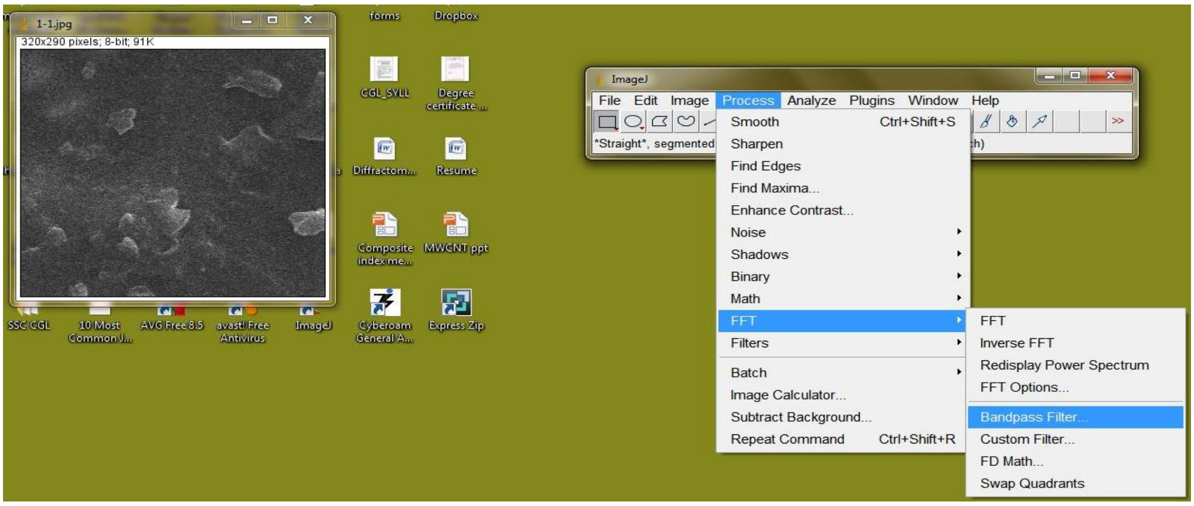
Plugins
Window
Help
Dev
Stk
Freehand sel
Type
Adjust
Show Info... Ctrl+I
Properties... Ctrl+Shift+P
Color
Stacks
Hyperstacks
Crop Ctrl+Shift+X
Duplicate... Ctrl+Shift+D
Rename...
Scale... Ctrl+E
Transform
Zoom
Overlay
Lookup Tables

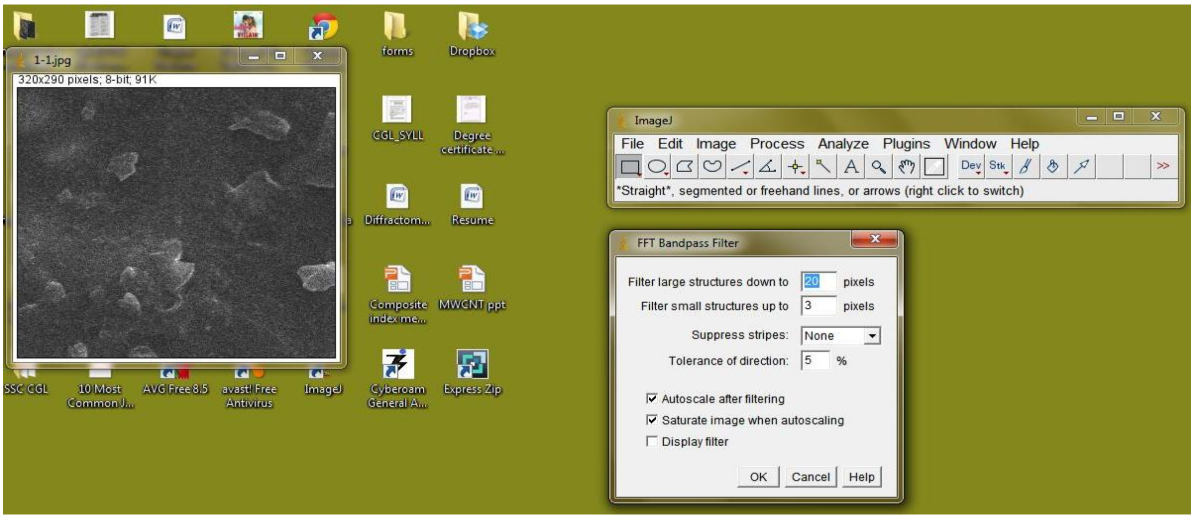
(c)



(d)



(e)


Straight, segmented or freehand lines, or arrows (right click to switch)

FFT Bandpass Filter

Filter large structures down to 20 pixels

Filter small structures up to 3 pixels

Suppress stripes: None

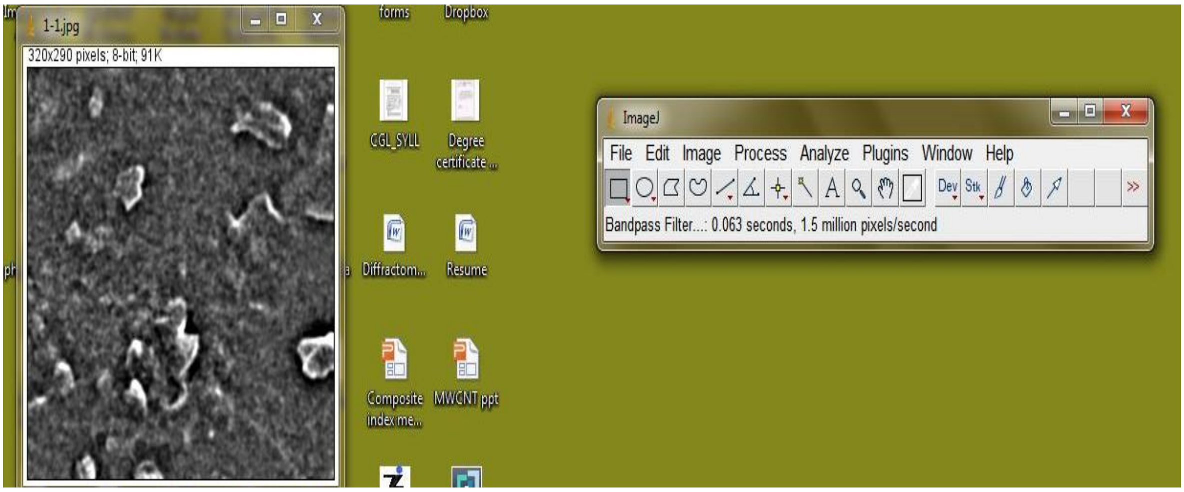
Tolerance of direction: 5 %

☑ Autoscale after filtering

☑ Saturate image when autoscaling

☐ Display filter

(f)



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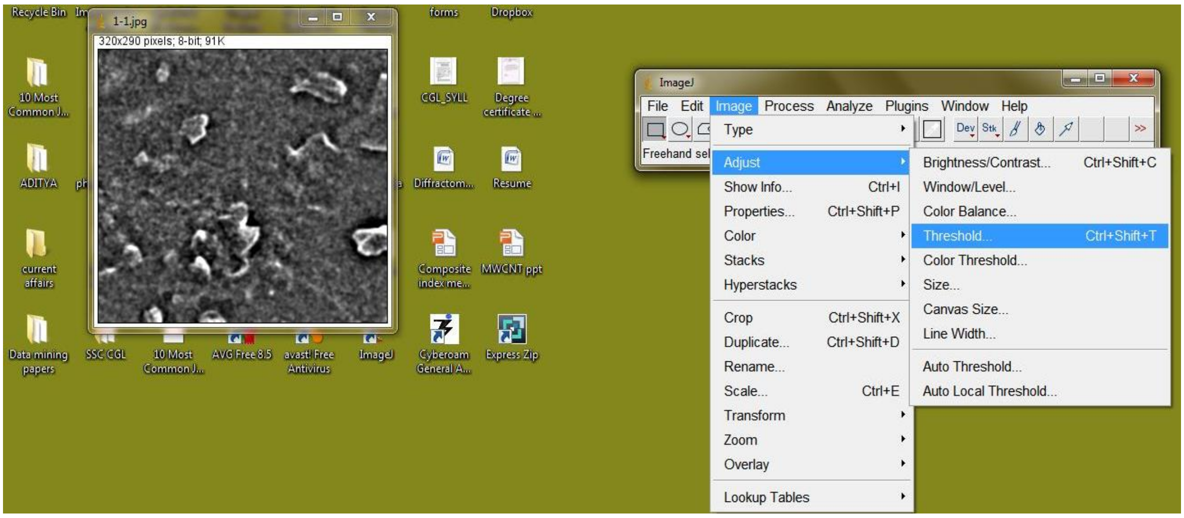
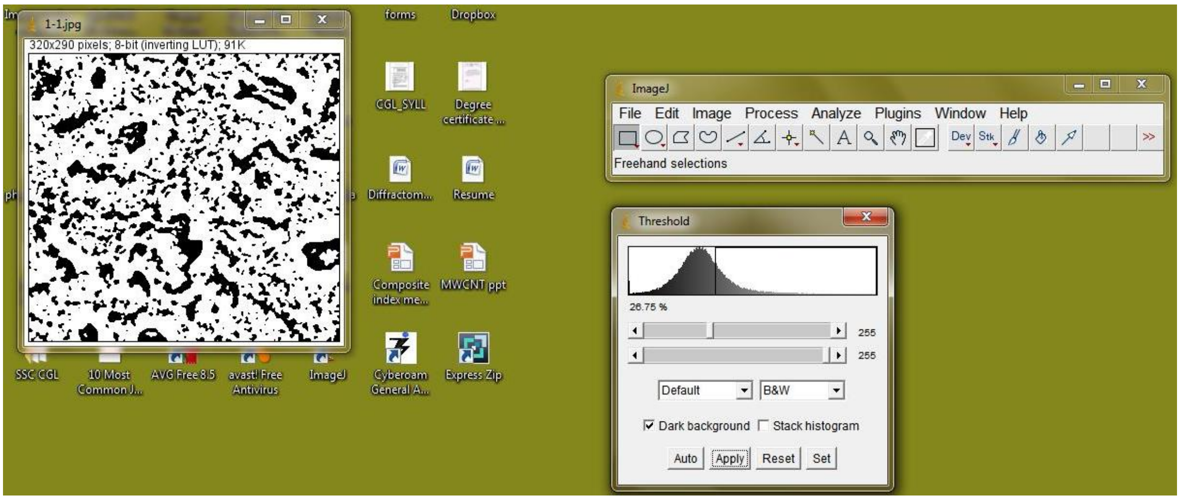
(g)



(h)



320x290 pixels; 8-bit (inverting LUT); 91K

26.75 %

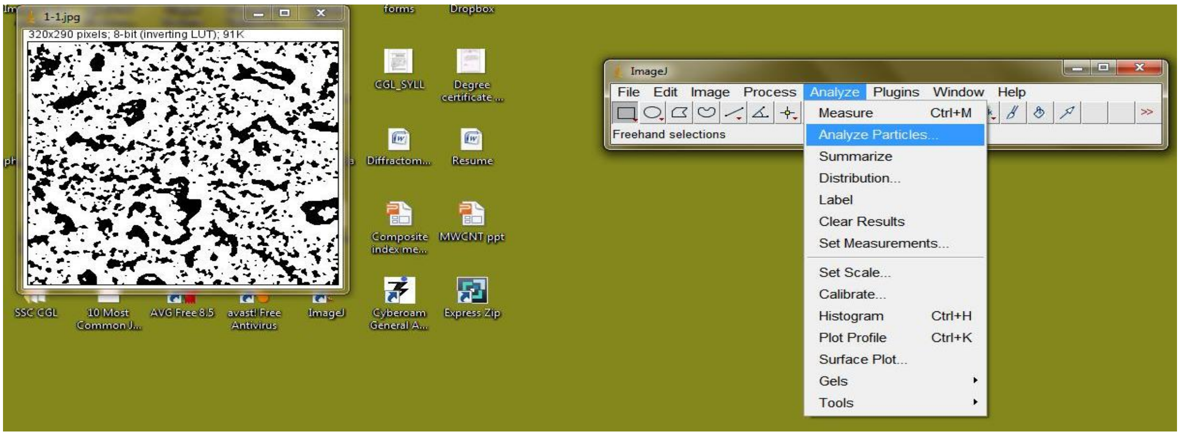
255

255

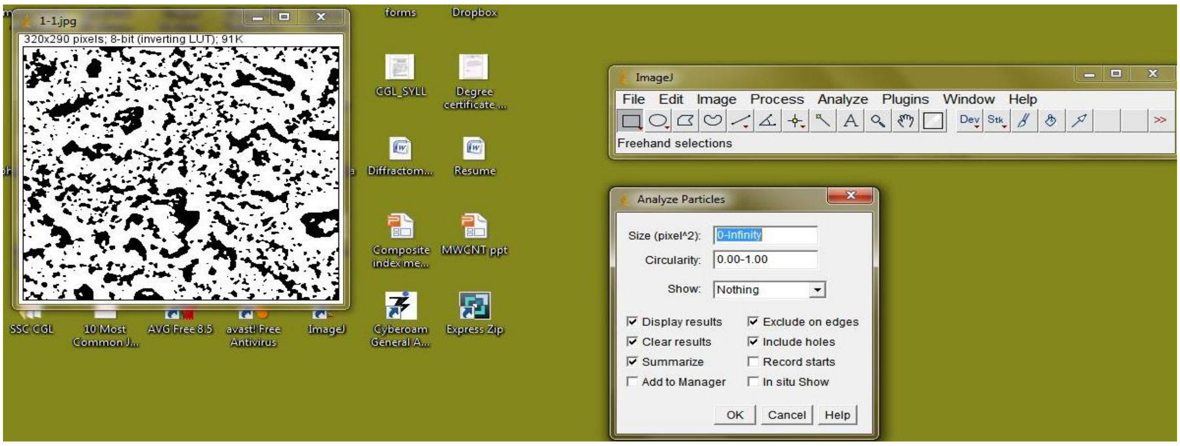
Default B&W

☑ Dark background ☐ Stack histogram

(i)



(j)



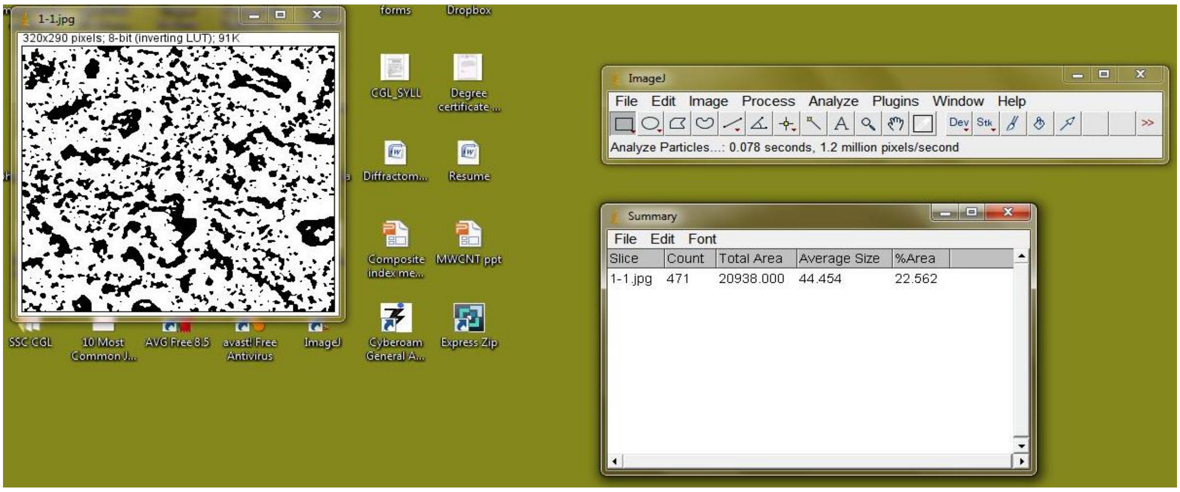
Size (pixel^2): 0-Infinity

Circularity: 0.00-1.00

Show: Nothing

☑ Display results
☑ Clear results
☑ Summarize
☐ Add to Manager
☑ Exclude on edges
☑ Include holes
☐ Record starts
☐ In situ Show

(k)



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Analyze Particles...: 0.078 seconds, 1.2 million pixels/second
```

Slice	Count	Total Area	Average Size	%Area
1-1.jpg	471	20938.000	44.454	22.562

(l)

Figure 4.8: (a)-(l) shows the procedure for calculating dIndex from a small area within the SEM image.

The dIndex values for all the four nanocomposites having different operated homogenizing conditions are calculated as shown in Table 4.3. The nomenclature used is as explained in section 3.6.4.

Table 4.3: Calculations of dIndex for the nanocomposites at two different magnifications in SEM micrographs

Percentage area of MWCNT in Quadrats	SEM of 1,000x				SEM of 500x			
	1PC	2PC	3PC	4PC	1PC	2PC	3PC	4PC
b1	0.26	0.10	0.51	0.30	0.17	0.57	0.11	0.19
b2	0.14	0.77	0.53	0.18	0.11	0.87	0.51	0.18
b3	0.16	0.87	0.77	0.18	0.11	0.91	0.11	0.10
b4	0.16	0.44	0.42	0.19	0.06	0.05	0.47	0.18
b5	0.15	0.37	0.44	0.09	0.15	0.94	0.16	0.18
b6	0.17	0.12	0.45	0.22	0.15	0.69	0.11	0.17
b7	0.15	0.15	0.37	0.20	0.11	0.15	0.11	0.16
b8	0.14	0.07	0.71	0.25	0.13	0.06	0.46	0.22
b9	0.18	0.41	0.14	0.29	0.14	0.14	0.13	0.14
b10	0.17	0.13	0.45	0.22	0.15	0.12	0.09	0.11
b11	0.13	0.32	0.08	0.22	0.07	0.06	0.07	0.14
b12	0.11	0.40	0.52	0.31	0.24	0.05	0.06	0.12
Average (b’)	0.16	0.35	0.45	0.22	0.13	0.38	0.20	0.16
Std. Deviation, s(b)	0.037	0.26	0.19	0.06	0.047	0.37	0.17	0.03

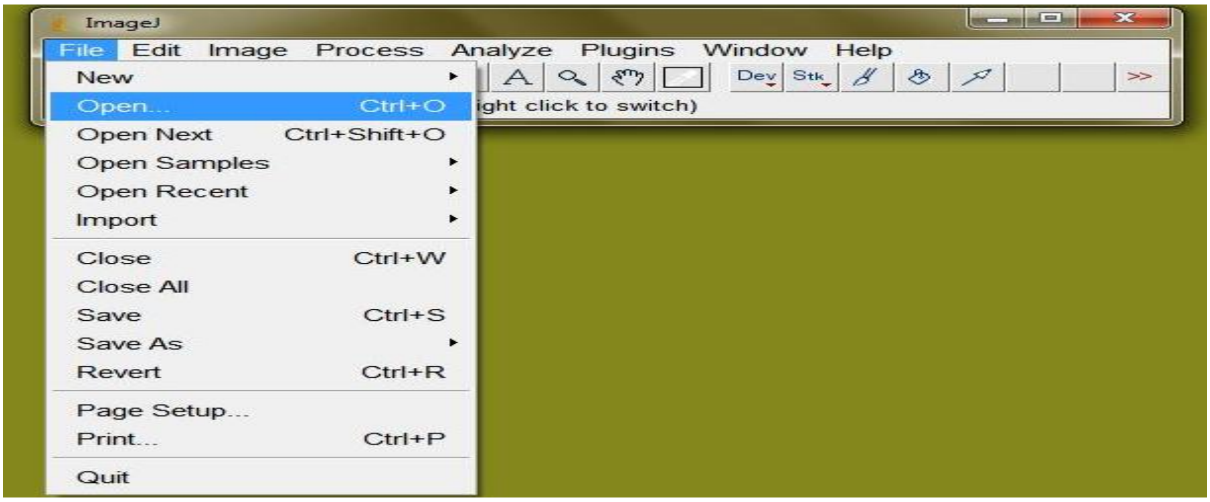
Maximum, max (b)	0.26	0.87	0.77	0.31	0.24	0.94	0.51	0.22
dIndex	0.77	0.45	0.60	0.79	0.73	0.34	0.53	0.83

The results of dIndex show that the spread of carbon in the matrix is better in 1PC and 4PC nanocomposites i.e. the nanoparticles are uniformly distributed, when fabrication is done at “high homogenising speed and short duration” (1PC) or “low homogenizing speed and long duration” (4PC).

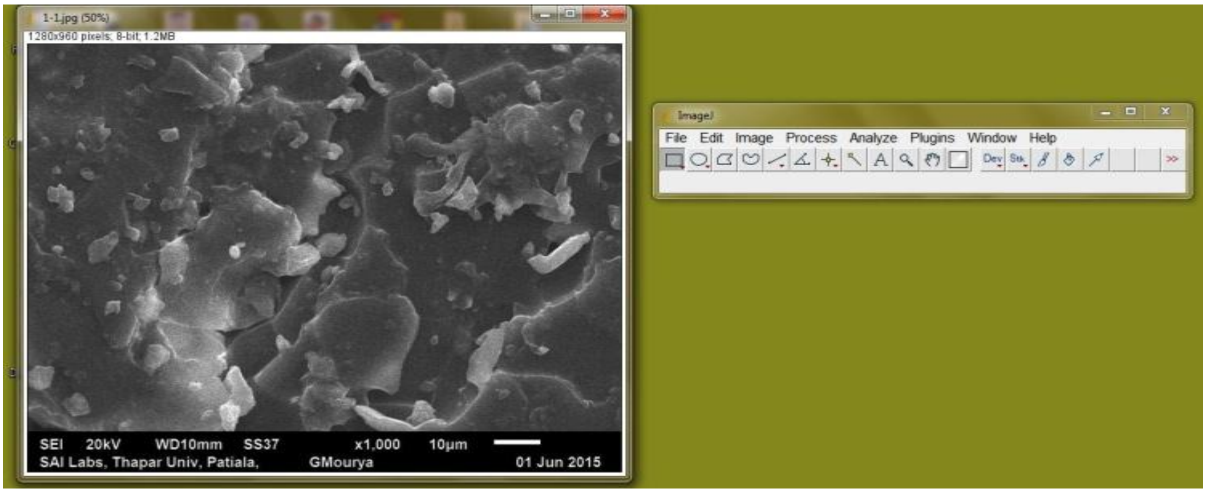
The area of each particle in the image is evaluated using ImageJ application software by counting the number of pixels occupied by each particle, and *sIndex* is calculated using Eq. (4.2).

$$sIndex = \frac{1}{2}\left[\frac{L}{N} + 1 - \frac{\max(a)}{\sum a}\right] \tag{4.2}$$

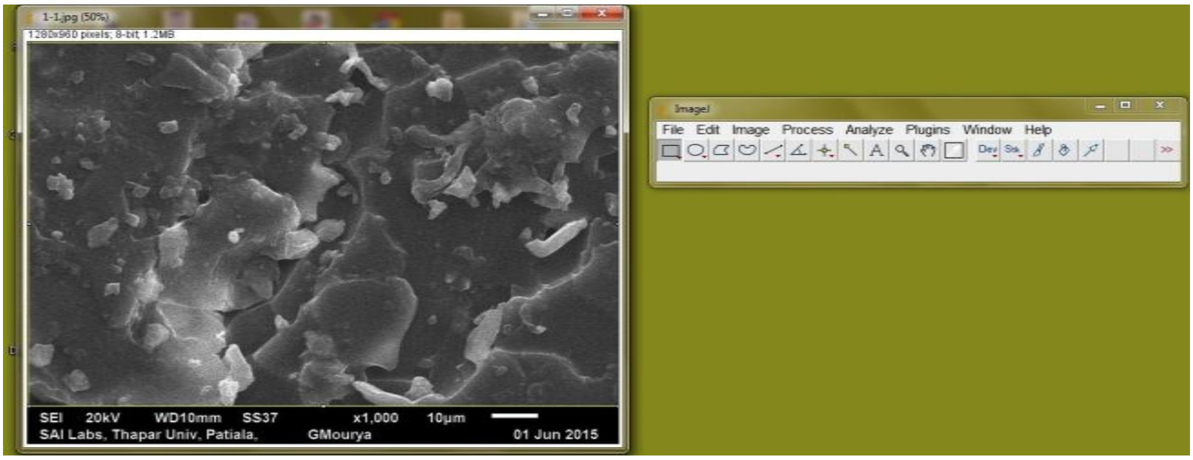
The method of using image J for evaluating sIndex is shown in fig. 4.9 for 1PC nanocomposite whose SEM analysis is done at 10 µm.



(a)


1-1.jpg (50%)
1280x960 pixels; 8-bit; 1.2MB
SEI 20kV WD10mm SS37 x1,000 10µm
SAI Labs, Thapar Univ, Patiala, GMourya 01 Jun 2015
ImageJ
File Edit Image Process Analyze Plugins Window Help

(b)


1-1.jpg (50%)
1280x960 pixels; 8-bit; 1.2MB
SEI 20kV WD10mm SS37 x1,000 10µm
SAI Labs, Thapar Univ, Patiala, GMourya 01 Jun 2015
ImageJ
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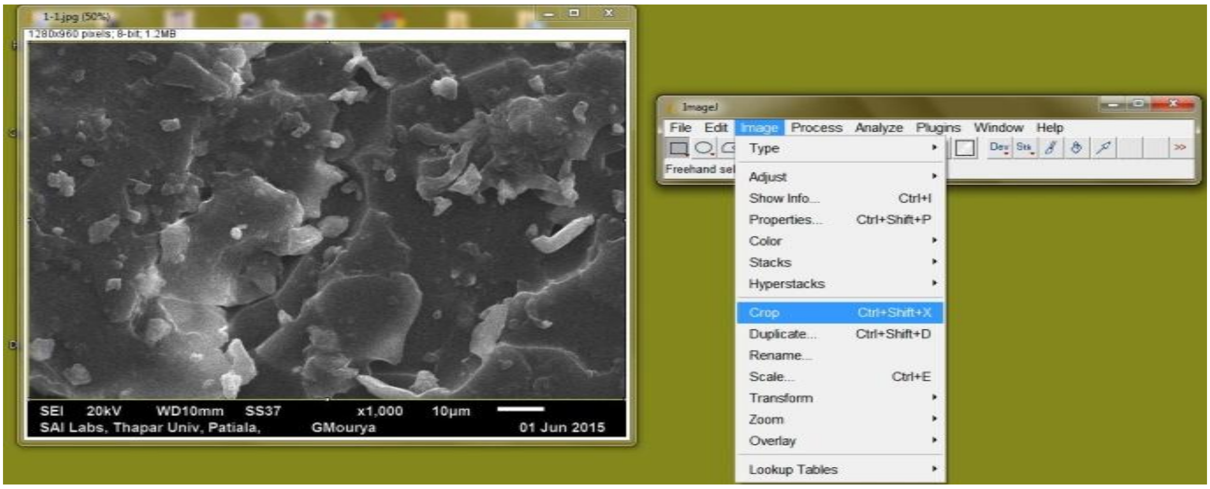
(c)


1-1.jpg (50%)
1280x960 pixels; 8-bit; 1.2MB
SEI 20kV WD10mm SS37 x1,000 10µm
SAI Labs, Thapar Univ, Patiala, GMourya 01 Jun 2015
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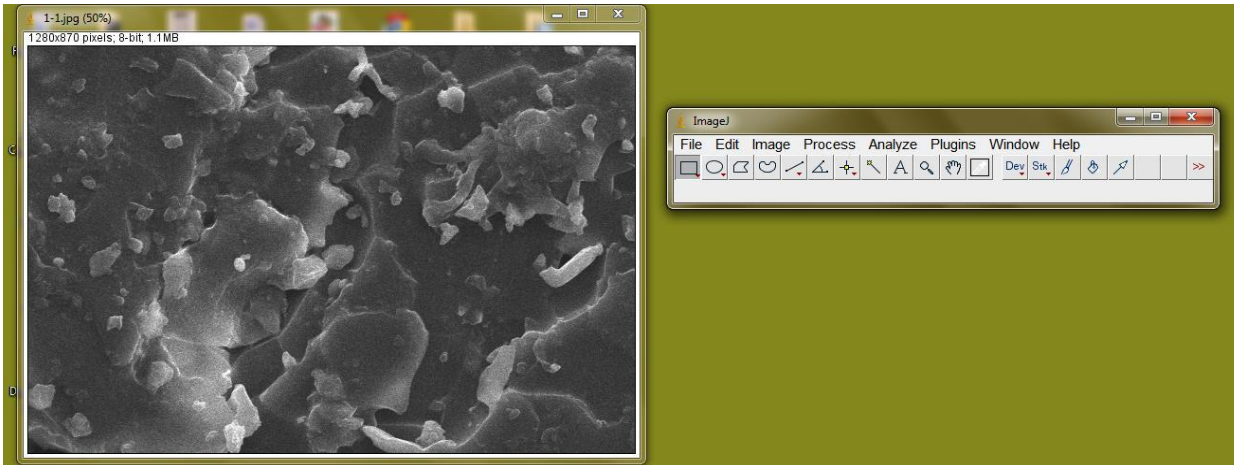
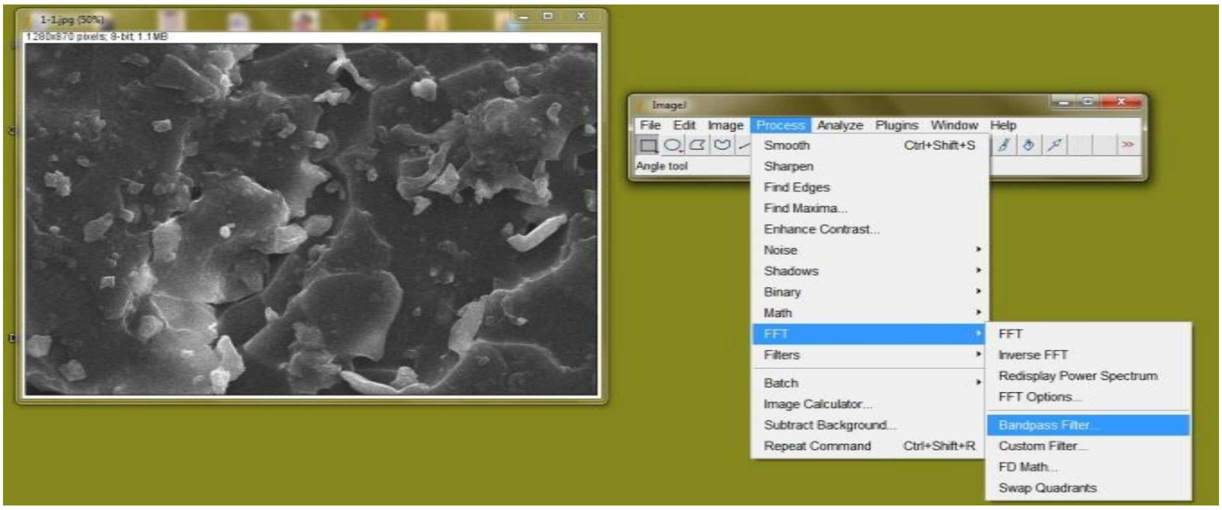
Rename...
Scale... Ctrl+E
Transform
Zoom
Overlay
Lookup Tables

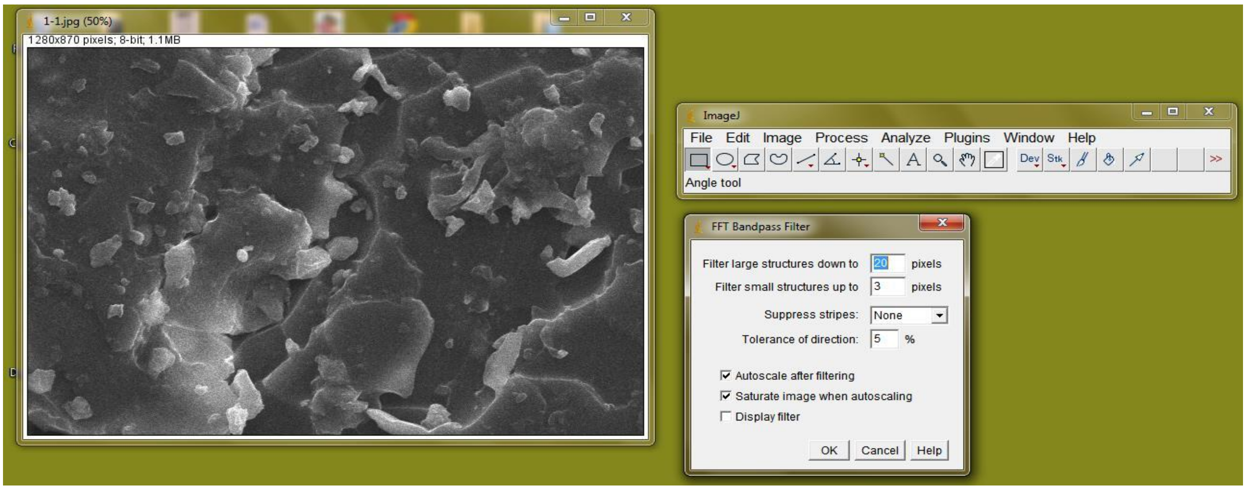
(d)



(e)



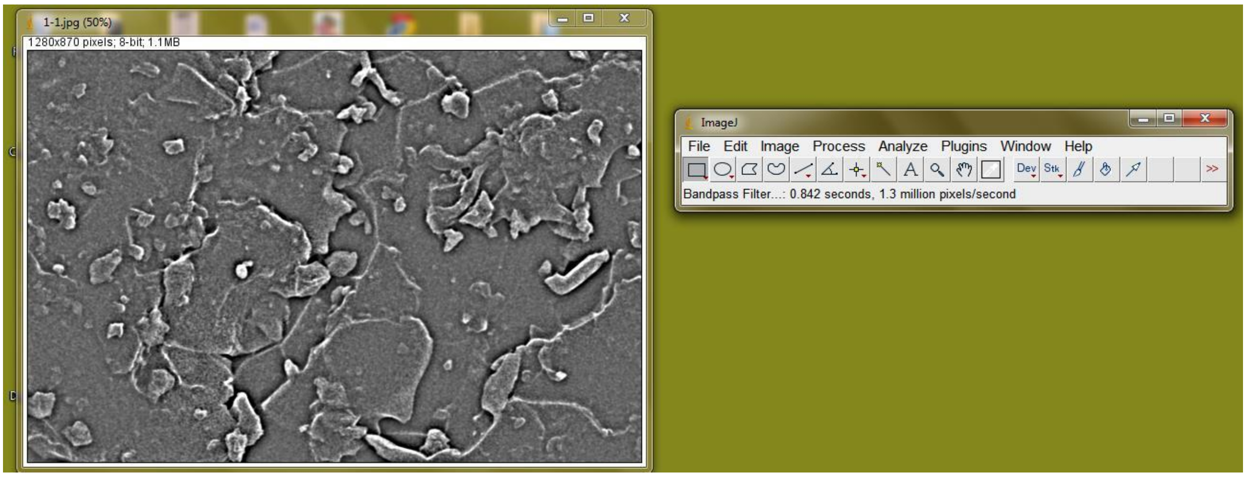
(f)



Filter large structures down to 20 pixels
Filter small structures up to 3 pixels
Suppress stripes: None
Tolerance of direction: 5 %

☑ Autoscale after filtering
☑ Saturate image when autoscaling
☐ Display filter

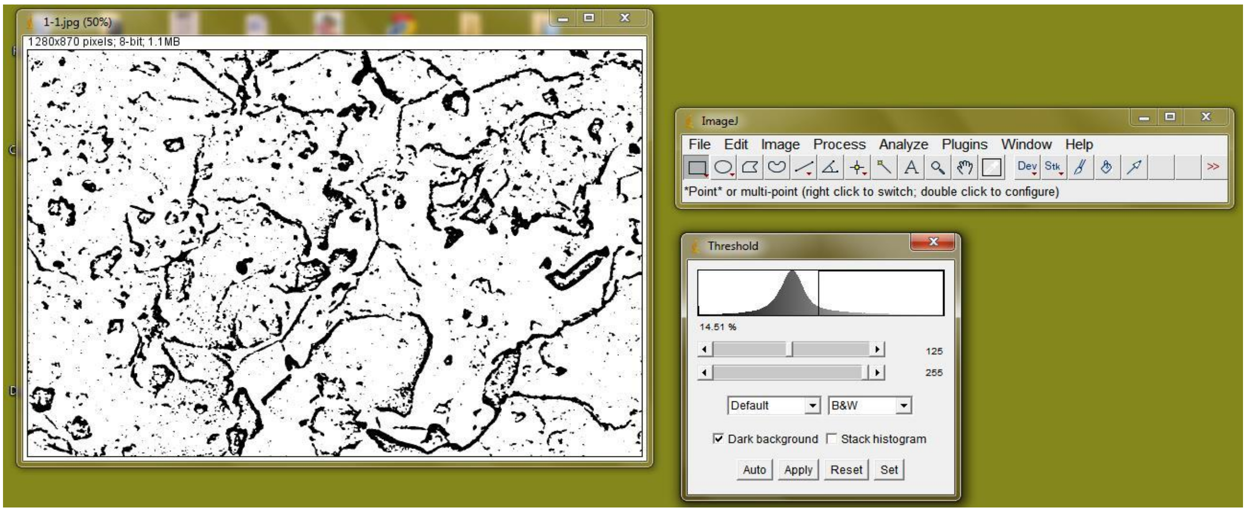
(g)



1280x870 pixels; 8-bit; 1.1MB

Bandpass Filter...: 0.842 seconds, 1.3 million pixels/second

(h)



1280x870 pixels; 8-bit; 1.1MB

Point or multi-point (right click to switch; double click to configure)

14.51 %

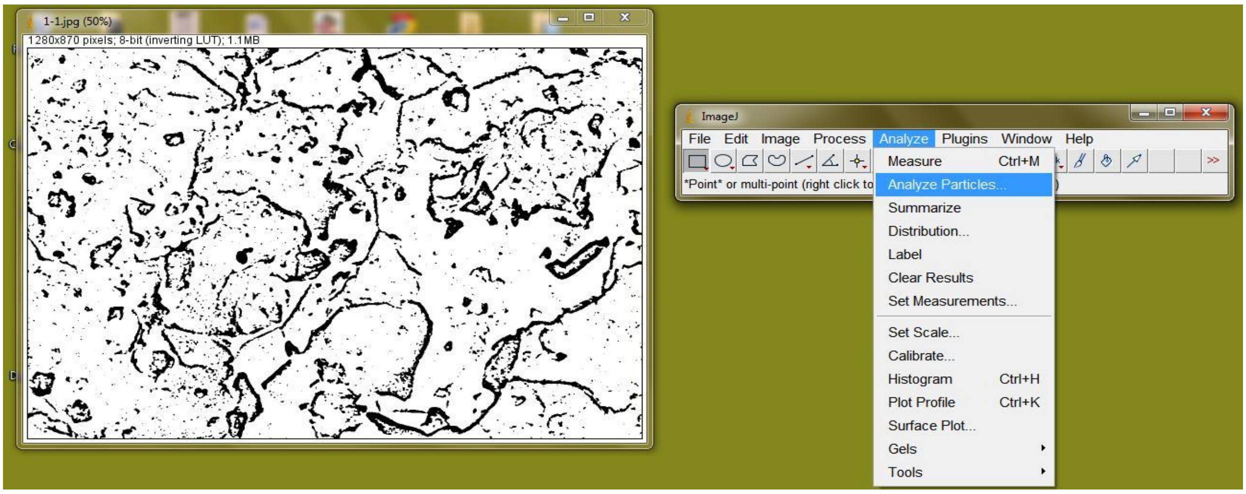
125

255

Default B&W

☑ Dark background ☐ Stack histogram

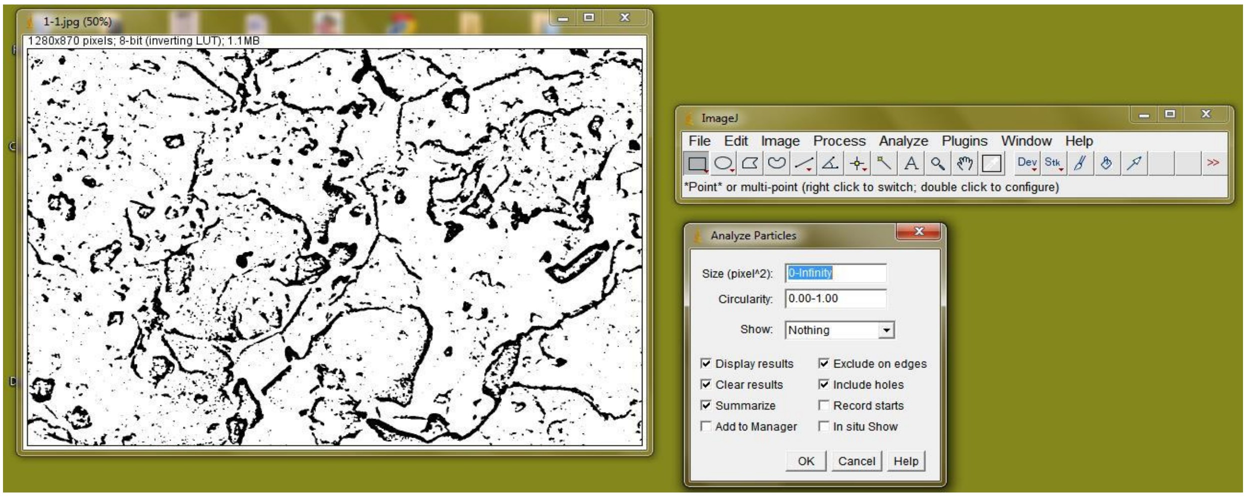
(i)



1280x870 pixels; 8-bit (inverting LUT); 1.1MB

Point or multi-point (right click to

(j)



1280x870 pixels; 8-bit (inverting LUT); 1.1MB

Point or multi-point (right click to switch; double click to configure)

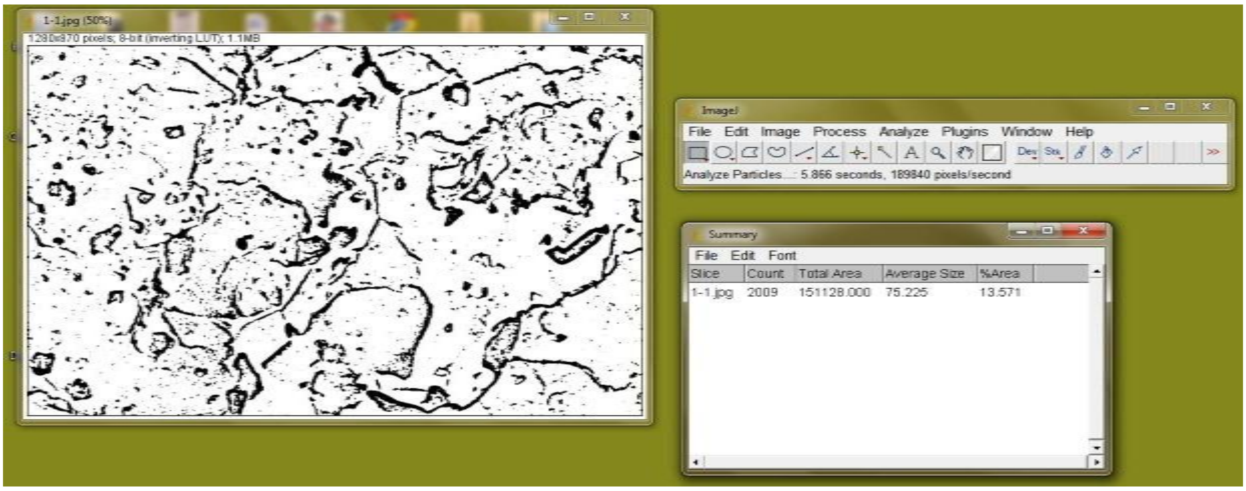
Size (pixel^2): 0-Infinity

Circularity: 0.00-1.00

Show: Nothing

☑ Display results ☑ Exclude on edges
☑ Clear results ☑ Include holes
☑ Summarize ☐ Record starts
☐ Add to Manager ☐ In situ Show

(k)



1280x870 pixels; 8-bit (inverting LUT); 1.1MB

Analyze Particles...: 5.866 seconds, 189840 pixels/second

Slice	Count	Total Area	Average Size	%Area
1-1.jpg	2009	151128.000	75.225	13.571

(l)

Figure 4.9: (a)-(l) shows procedure of calculating area of full SEM image i.e. “a” by the use of image J for evaluating sIndex.

The sIndex values for all the four nanocomposites having different operated homogenizing conditions are calculated as shown in Table 4.4. The nomenclature used is as explained in section 3.6.4.

Table 4.4: Calculations of sIndex for the nanocomposites at two different magnifications in SEM micrographs

Code Name	SEM of 1,000x					SEM of 500x				
	N	∑a (pixel^2)	max(a)	L	sIndex	N	∑a (pixel^2)	max(a)	L	sIndex
1PC	992	165502	21041	722	0.80	859	102382	14362	690	0.83
2PC	685	98029	5401	585	0.89	353	88224	5452	244	0.81
3PC	545	78623	8450	473	0.88	474	78809	9167	389	0.85
4PC	1460	108416	11829	998	0.90	776	125814	15769	652	0.85

It is seen that there is small difference in the values of sIndex of all the nanocomposites. High sIndex values show least size of agglomerates and maximum amount of tube breakage. 3PC and 4PC nanocomposites exhibit highest sIndex values, thus inducing maximum amount of tube breakage. As 3PC and 4PC nanocomposites are homogenized for longer duration (i.e. 10 min.), it implies that the amount of tube breakage is maximum when homogenizing takes place for longer duration.

The composite index compIndex is calculated as the arithmetic average of the dIndex and the sIndex but the two separate indexes should still be reported to better characterize the dispersion.

$$\text{compIndex} = \tfrac{1}{2}\,(\text{dIndex} + \text{sIndex}) \qquad (4.3)$$

The compIndex values for all the four nanocomposites having different operated homogenizing conditions are calculated as shown in Table 4.5.

Table 4.5: Calculations of compIndex for the nanocomposites at two different magnifications in SEM micrographs

Specimens Code	SEM of 1,000x			SEM of 500x		
	dIndex	sIndex	compIndex	dIndex	sIndex	CompIndex
1PC	0.77	0.80	0.78	0.74	0.83	0.78
2PC	0.45	0.89	0.67	0.34	0.81	0.57
3PC	0.61	0.88	0.74	0.53	0.85	0.69
4PC	0.80	0.90	0.85	0.83	0.85	0.84

As shown in fig. 4.8, MWCNT/epoxy nanocomposite prepared at homogenising speed of 15,000 rpm and 5 min duration (1PC) gives higher value of compIndex i.e. good dispersion. 1PC (15,000 rpm & 5 min) nanocomposite also shows improved tensile and flexural properties of all other nanocomposites.

On the other hand, 4PC nanocomposite, which is prepared at 7,500 rpm and 10 min shows highest dispersion (compIndex) due to possible nanotube damage and least agglomeration. Thus it can be concluded that the nanocomposites which are prepared at “high homogenising speed and less duration” (1PC) or “low homogenizing speed and long duration” produced good dispersion.

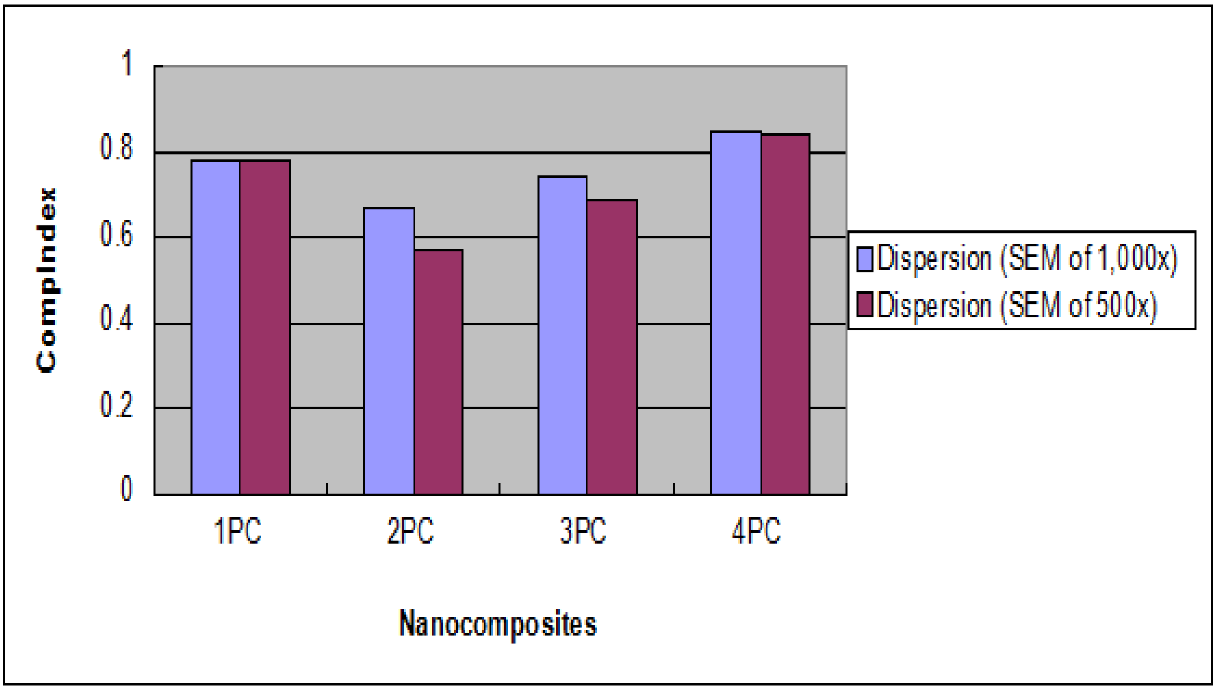


Figure 4.10: Degree of dispersion of nanocomposites as a function of homogenizing speed and duration.

Chapter 5

Conclusion and Future Scope

5.1 Conclusion

The effect of homogenizing speed and their respective time period on the mechanical properties and dispersion of MWCNT/epoxy nanocomposite has been investigated.

- Nanocomposite samples fabricated at 15,000 rpm for 5 min. exhibit higher Young's modulus and tensile strength. This significant improvement in tensile properties at high homogenizing speed has been attributed to good dispersion.
- The mechanical properties decrease with an increase in homogenizing time period of 10 min. This was related to possible nanotube breakage caused by long-time homogenizing.
- The flexural modulus and bending strength has no significant effect with the varying homogenizing conditions.
- SEM studies and dispersion quantification using image J software indicated that homogenization of (15,000 rpm, 5 min) and (7,500 rpm, 10 min) shows high compIndex values i.e. good dispersion. Hence, better dispersion is achieved at "high homogenizing speed, short duration" and "low homogenizing speed, long duration".

5.2 Future scope of work

- Effects of functionalized MWCNT on the dispersion of CNT/epoxy nanocomposite can be evaluated. Silane functionalized, amino functionalized and acid functionalized MWCNT can be prepared and respective nanocomposites can be analyzed by quantifying dispersion through compIndex method and by evaluating mechanical properties.
- Dispersion of surfactant assisted processing of MWCNT/ epoxy nanocomposite can

be quantified and correlated with their respective mechanical properties.

- Effects of MWCNT concentration in addition to processing parameters on the mechanical properties of MWCNT/epoxy nanocomposite can be evaluated with the quantification of dispersion by compIndex method.
- CompIndex method for Dispersion quantification can also be done with MATLAB dispersion characterization tool and compared with values obtained by compIndex method.

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