

MECHANICAL PROPERTIES OF BORON NITRIDE
NANOTUBE / EPOXY POLYMER COMPOSITES

by

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ABSTRACT

MECHANICAL PROPERTIES OF BORON NITRIDE NANOTUBE / EPOXY POLYMER COMPOSITES

Boron nitride nanotubes (BNNTs) have attracted significant interest of the scientific world due to their remarkable mechanical and thermal properties. They have high modulus and high strength similar to carbon nanotubes. In addition they are highly resistant to oxidation and structurally stable and inert to most chemicals. All these outstanding properties of BNNTs, as well as their low density and high aspect ratio make them an ideal candidate for the reinforcement of polymer composites.

In this study, BNNT/epoxy polymer composites with different nanotube concentrations were fabricated after a BNNT dispersion prepared by ultrasonication in dimethylformamide (DMF). Properties and structure of BNNT/epoxy composites were investigated by mechanical testing, thermal analysis and scanning electron microscopy. A good nanotube dispersion was achieved for composites with 0.1 wt. per cent of BNNTs, but presence of agglomerates in composites with 0.2 wt. per cent and 0.4 wt. per cent of BNNTs were determined by the examination of fracture surfaces. The tensile strength of the composites reinforced with 0.1 wt. per cent of BNNTs is 10.6% greater than that of the neat epoxy and onset of thermal degradation is delayed for 32 °C with 0.1 wt. per cent of BNNT loading. The improvements in mechanical and thermal properties of composites are attributed to good dispersion of BNNTs in epoxy matrix and high interfacial shear stress between BNNTs and the epoxy matrix.

ÖZET

BOR NİTRÜR NANOTÜP / EPOKSİ POLİMER KOMPOZİTLERİN MEKANİK ÖZELLİKLERİ

Bor nitrür nanotüpler (BNNT) sahip oldukları olağanüstü mekanik ve ısı özelliklerinden ötürü bilim dünyasında büyük ilgi toplamıştır. Karbon nanotüpler gibi yüksek elastik modülüne ve yüksek mukavemete sahiptirler. Bununla birlikte bor nitrür nanotüpler yüksek oksitlenme direncine ve kararlı bir yapıya sahiptir ve çoğu kimyasal maddeyle tepkimeye girmezler. Bor nitrür nanotüplerin bütün bu sıradışı özellikleri, düşük yoğunlukları ve yüksek en boy oranları onları polimer kompozitler için ideal bir takviye elemanı adayı yapmıştır.

Bu çalışmada, BNNT dağılımı dimetilformamid (DMF) içinde ses ötesi dalga uygulaması (ultrasonikasyon) ile hazırlandıktan sonra değişik oranlarda nanotüp içeren BNNT/epoksi polimer kompozitler üretilmiştir. BNNT/epoksi kompozitlerin yapısı, mekanik ve ısı özellikleri mekanik test, ısı analiz ve taramalı elektron mikroskopuyla incelenmiştir. İyi bir nanotüp dağılımı ağırlık oranı yüzde 0,1 BNNT destekli kompozitlerde elde edilmiş, fakat kırılma yüzeyi incelemelerinde ağırlık olarak yüzde 0,2 ve yüzde 0,4 BNNT destekli kompozitlerde topaklanmalar gözlenmiştir. Yüzde 0,1 BNNT destekli kompozitlerin çekme mukavemetinde yüzde 10,6'lık bir gelişme kaydedilmiş ve yüzde 0,1 BNNT desteğiyle ısı bozulma başlangıcı sıcaklığı 32°C geciktirilmiştir. Kompozitlerin mekanik ve ısı özelliklerindeki gelişimler nanotüplerin epoksi matriks içinde iyi dağılmasına ve BNNT ile epoksi matriks arasındaki yüksek arayüzey kayma gerilmesine bağlanmıştır.

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LIST OF SYMBOLS/ABBREVIATIONS

BN	Boron nitride
BNNT	Boron nitride nanotube
CNC	Computer numerical control
CNT	Carbon nanotube
CVD	Chemical vapor deposition
DLS	Dynamic Light Scattering
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
EDAX	Energy dispersive X-ray analysis
FTIR	Fourier transform infrared spectroscopy
NEMS	Nanoelectromechanical system
PCS	Photon Correlation Spectroscopy
SEM	Scanning electron microscope
STM	Scanning tunneling microscope
SWNT	Single wall nanotube
TEM	Transmission electron microscope
TGA	Thermal gravimetric analysis
XRD	X-ray diffraction analysis
DGEBA	Diglycidyl ether of bisphenol A
DMF	N,N-dimethylformamide
PmPV	poly(m-phenylenevinylene)-co-(2,5-dioctoxy-p-phenylene)
TETA	Triethylenetetramine
b	Thickness of the interfacial region
c_p	Specific heat
D	Fiber external diameter
D_i	Fiber internal diameter

ε	Strain
F	Force
H	Energy
$IFSS$	Interfacial shear strength
κ	Thermal conductivity
l	Length
l_c	Critical length
η_l	Length efficiency factor
η_o	Orientation efficiency factor
η_s	Strength efficiency factor
R	Nanotube radius
r	Distance from nanotube
σ	External stress
σ_f	Fiber strength
σ_m	Matrix strength
σ_C	Composite strength
σ_{Shear}	Shear strength of the interface
T	Temperature
t	Time
T_g	Glass transition temperature
τ	Interfacial stress transfer
V_f	Fiber volume fraction
Y	Elastic modulus
Y_C	Composite elastic modulus
Y_f	Fiber elastic modulus
Y_m	Matrix elastic modulus
wt.	Weight

1. INTRODUCTION

It is widely accepted that nanotechnology was first evoked by Dr. Feynman's talk entitled "There is plenty of room at the bottom" in 1959. He discussed the physical feasibility and potential benefits of manipulating materials at the atomic and molecular scales. This talk has motivated the great interests in exploring phenomena scaling down to nanometer scale and led to the emerging of what is known as nanotechnology [1].

Nanotechnology is defined as the design, characterization, production and application of structures, devices and systems by controlling shape and size at nanometer scale. The prefix 'nano' is derived from the Greek word for dwarf. One nanometer (nm) is equal to one-billionth of a meter, 10^{-9} m. A human hair is approximately 80,000 nm wide, and a red blood cell approximately 7000 nm wide. Atoms are below a nanometer in size. Many molecules such as some proteins have size greater than a nanometer. The size range that holds so much interest is typically from 100 nm down to the atomic level. In this range materials can have different properties compared with the same materials at a larger size [2].

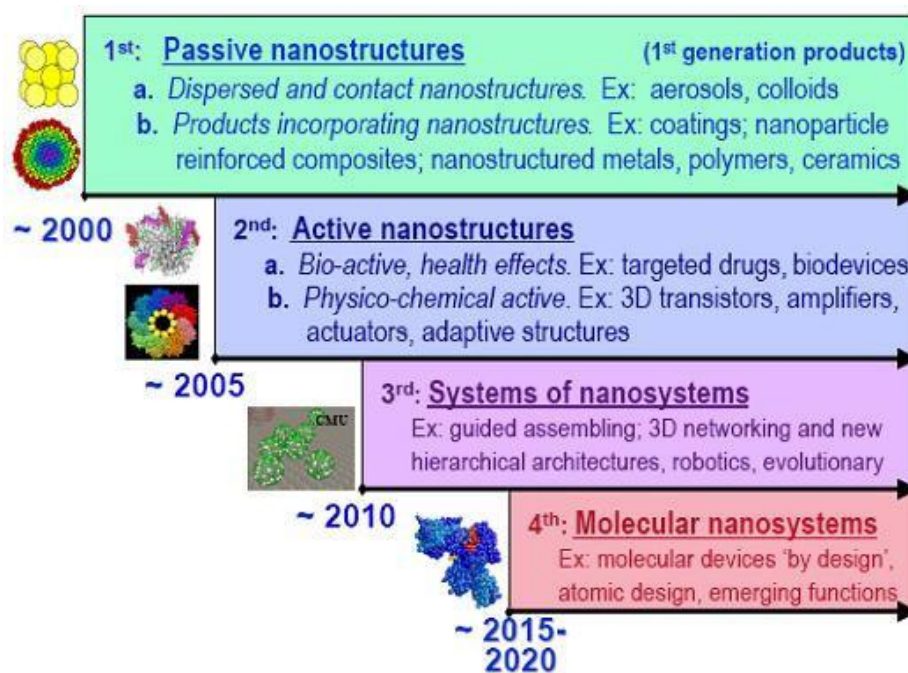


Figure 1.1. Four generations of nanotechnology development [3]

Nanotechnology development has been described in four generations as shown in Figure 1.1. The current period is that of passive nanostructures, materials designed to perform one task. The second phase, which we are just entering, introduces active nanostructures for multitasking such as actuators, drug delivery devices, and sensors. The third generation is expected to begin emerging around 2010 and will have nanosystems with thousands of interacting components. A few years after that, the first integrated nanosystems, functioning much like a mammalian cell with hierarchical systems within systems, are expected to be developed [3].

The ability to control structure of materials at smaller scales is important in the development of new materials that have excellent properties. As the understanding of materials at the nanoscale and the ability to control their structure improves, there will be great potential to materials with novel characteristics, functions and applications. Nanomaterials have been characterized as those which have structured components with at least one dimension less than 100 nm. Materials that have one dimension in the nanoscale are layers, such as thin films or surface coatings. Materials that are nanoscale in two dimensions include nanowires and nanotubes. Materials that are nanoscale in three dimensions are particles, for example precipitates and colloids [2].

The properties of nanomaterials change significantly from other materials due to two principal factors. These are increased surface area and quantum effects. As a particle decreases in size, a greater proportion of atoms are found at the surface compared to those inside. By increasing surface area quantum effects dominate the properties of matter as size is reduced to the nanoscale. These can affect the mechanical, electrical, optical and magnetic behavior of materials [2].

Many properties of nanotubes make them special compared with other reinforcing fibers. Nanotubes have molecular dimensions and consist of perfect sheets rolled into hollow cylinders. They resemble the polymer chains used as composite matrices both have covalently bonded structures, similar dimensions and mechanical flexibility. This makes nanotubes entirely different from traditional fibers such as carbon or glass, which are relatively large and brittle. The basic mechanical properties of nanotubes greatly exceed those of other fibers [4].

Nanotubes in polymer matrix would serve to increase stiffness, strength and toughness. At present, nanotubes can be manufactured only at lengths up to millimeter scale, so falling into short fiber category, for the future their dominant role in composites is to remain as matrix modifiers and providers of multifunctional properties. But once nanotubes can be efficiently assembled on a macroscopic scale, they could become serious competition for the continuous fibers that are woven and stacked to form load bearing elements in structural composites used in the building and engineering industries [4].

The biggest challenge is to fully disperse individual nanotubes in the matrices, because nanotubes tend to form clusters and bundles. These aggregates persist unless high shear forces are applied. However such mixing often damages nanotube structures, compromising their properties. Another issue is that the polymer nanotube mixtures are highly viscous because of the large surface area of nanotubes. This creates engineering problems, because the composites do not flow easily and are difficult to mould. Processing is also rendered difficult by the poor solubility of nanotubes in most solvents and polymers. Nevertheless, several approaches have been successfully adopted to obtain intimate mixing of nanotubes with polymer phases, including solution mixing, melt mixing and in-situ polymerization [4].

The purpose of this study is to fabricate boron nitride nanotube/epoxy polymer composites by adding different amounts of nanotubes and to investigate their mechanical and thermal properties. The effects of BNNTs to the epoxy matrix were evaluated. Dispersion characterizations of BNNTs in different dispersants (acetone, ethanol and DMF) were performed by nanoparticle size analyzer in order to use the most effective one for composite preparation.

2. BORON NITRIDE NANOTUBES

Since the first discovery of carbon nanotubes [5], the studies on the synthesis of boron nitride nanotubes (BNNTs) have been attracted attention to the development of their efficient and large scale production because of the structural similarity between carbon and hexagonal boron nitride. The idea of rolling up individual hexagonal sheets of boron nitride (BN) to form nanotubes similar to carbon nanotubes was first proposed by Rubio et al. [6] in 1994 and then they were successfully synthesized by Chopra et al. [7] in 1995. A typical BNNT produced by Chopra et al. is shown in Figure 2.1. In 1981, Ishii et al. [8] have studied on the formation of hexagonal boron nitride whiskers that are called bamboo-like BNNTs in today's terminology, but the authors did not use such a term at that time. An image of the simulation of single walled BNNT is shown in Figure 2.2.

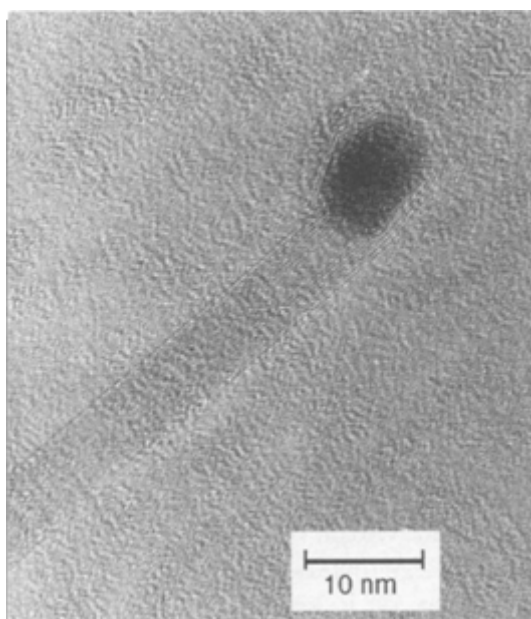


Figure 2.1. High resolution TEM micrograph of a BNNT, a dense particle is present at the tube end [7]

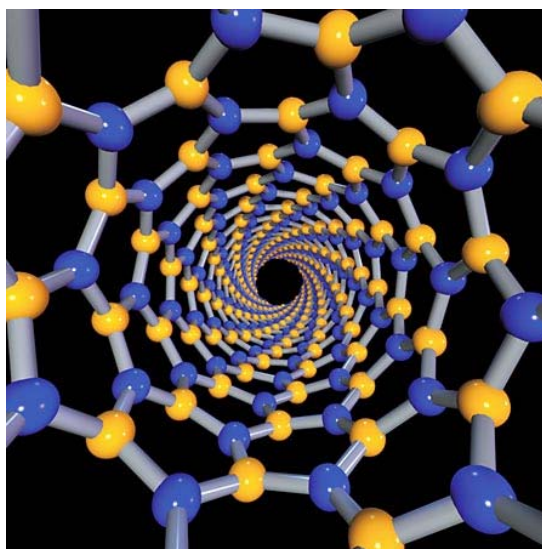


Figure 2.2 Molecular simulation of single walled BNNT [9]

Carbon nanotubes can be either metallic or semiconducting depending on their chirality [10], but purification and controlled synthesis of carbon nanotubes with selected chirality could not be achieved. This fact has made electronic device making with carbon nanotubes difficult [11]. Researchers have tried to find other nanoscale materials to fulfill the need for nanoscale circuit components. BNNT is an electrical insulator with a bandgap of 5.5 eV and this band gap is nearly independent of tube diameter, chirality and number of tube walls [6]. This predicted property of BNNT has attracted considerable research interest for the new synthesis techniques and investigation of these nanotubes. BNNTs can be used in production of new nanoscale electronic and photonic devices in which carbon nanotubes are not suitable to use.

The high thermal stability, high heat resistance and insulating properties, chemical resistance in various corrosive media and good workability have been well known features of BN. Structure of BN is much more thermally and chemically stable than graphitic carbon structure [12]. These advantageous properties may be inherited on the nanoscale level by the structure of BNNTs. Moreover, BNNTs have good mechanical properties and resistance to oxidation at high temperatures. All these factors may promote effective BNNT applications in different areas such as in nanotube reinforced composites.

2.1. Structures of Parent Materials (Graphite and Hexagonal Boron Nitride)

Boron nitride is a synthetically manufactured ceramic substance that consists of equal proportions of boron and nitrogen. They are neighbors of carbon in periodic table and they have the same number of outer shell electrons. The atomic radii of boron and nitrogen are similar to that of carbon. Therefore it is not surprising that boron nitride and carbon have similar crystal structure. Carbon exists as graphite and diamond, boron nitride can be synthesized in hexagonal and cubic forms [13].

Graphite and hexagonal boron nitride (h-BN) are parent materials for carbon nanotubes and BNNTs, respectively. Their crystal structures are compared in Figure 2.3. They are both layered materials composed of layers of hexagonal lattices. Graphite has carbon atoms at all lattice points, while h-BN is composed of alternating atoms of boron and nitrogen. In plane lattice constants are $2.456 \text{ \AA}$ for graphite and $2.504 \text{ \AA}$ for h-BN. One difference between these materials is in their layer stacking. In h-BN, layers are arranged so that boron atoms in one layer are located directly on top of nitrogen atoms in neighboring layers. As shown in Figure 2.3, the hexagons lie on top of each other. In graphite, the stacking is slightly different, hexagons are offset and do not lie on top of each other. Interlayer distances are similar: $3.35 \text{ \AA}$ for graphite and $3.33 \text{ \AA}$ for h-BN [14].

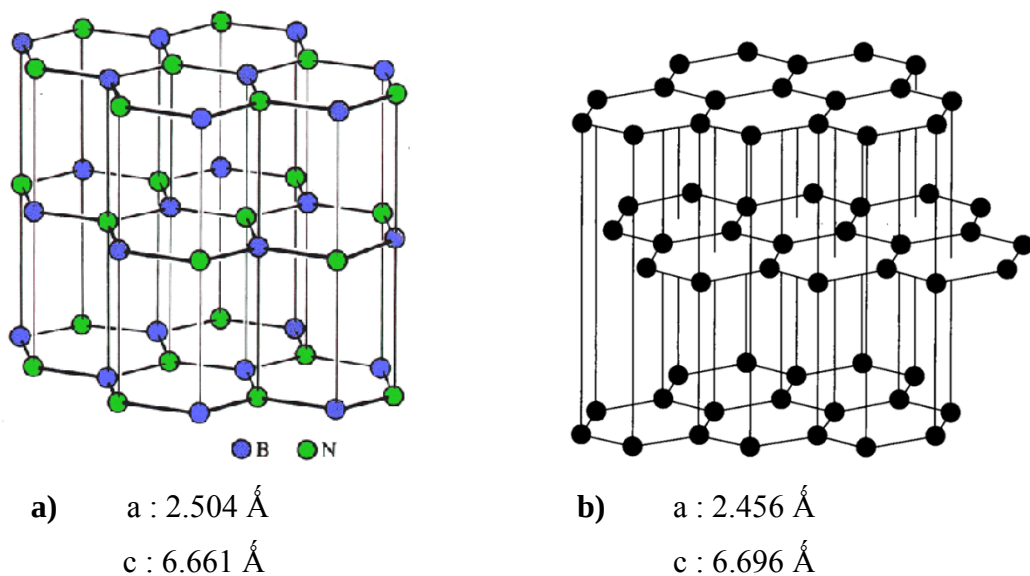


Figure 2.3. Crystal structure of a) boron nitride, b) graphite [14]

2.2. Properties of Boron Nitride Nanotubes

2.2.1. Mechanical Properties

The mechanical properties of BNNTs have been studied theoretically by Hernandez et al. [15]. Their results indicate that BNNTs have 30 per cent smaller Young's modulus than carbon nanotubes, but it is still the same order of magnitude. Young's modulus of BNNTs is predicted as about 900 GPa in their study. Chopra and Zettl [16] have experimentally determined the elastic properties of an individual multiwalled BNNT. They used the thermal vibration amplitude of a cantilevered BN nanotube observed in a transmission electron microscope and obtained the Young's modulus value of 1.22 ± 0.24 TPa. This value is consistent with theoretical ones and proves that Young's modulus of BNNTs 14 times greater than the measured in-plane modulus of bulk h-BN material. This difference is possibly due to the bulk h-BN containing defected layers while BNNTs are highly crystalline. These theoretical and experimental studies show that BNNTs are possibly the stiffest insulating tubes. They can be used in the production of highly resistant composite materials [16].

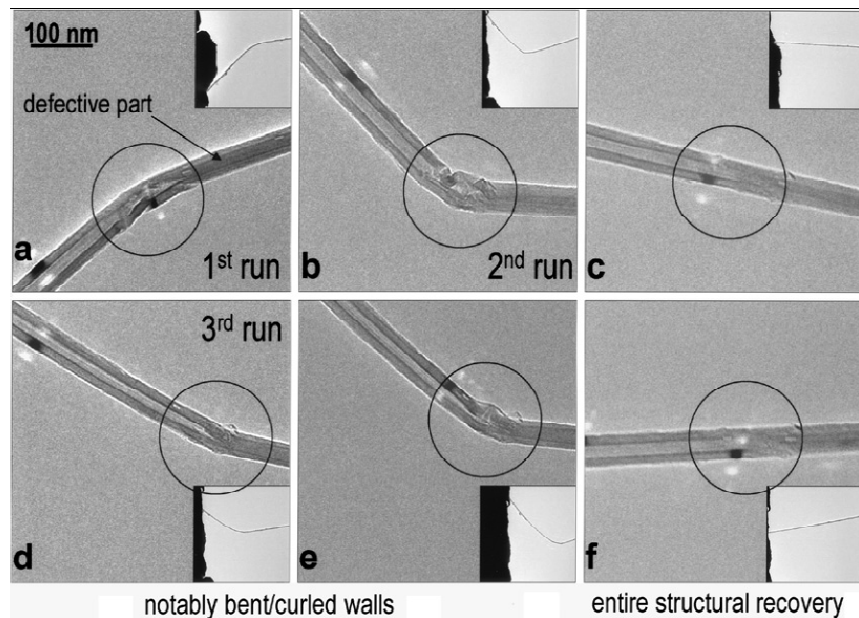


Figure 2.4. TEM images of an individual multiwalled BNNT indicating its unique elasticity and flexibility during in situ bending inside a TEM [17]

Experiments related to the individual BNNT elastic and plastic deformations were conducted by Golberg et al. [17] between the two gold leads inside a high resolution TEM using a piezo-driven STM-SEM holder, as shown in Figure 2.4. They found that BNNTs are very flexible. Reversible bending deformation of nanotubes was found to be very elastic and nanotubes can withstand with no traces of residual plastic deformation up to the reversible bending angles exceeding 70° . As shown in Figure 2.4, although there is severe distortion of tubular layers (a, b, d, e), they completely regain their original shape after reloading (c, f).

2.2.2. Thermal Stability

Thermal stability of BNNTs was studied by Golberg et al. [18] and Chen et al. [19]. They have demonstrated that BNNTs have higher thermal stability compared to carbon nanotubes. While carbon nanotubes oxidize in air at 400°C and burn completely at 700°C when sufficient oxygen is supplied, BNNTs are stable up to 700°C in air and thin nanotubes with perfect cylindrical structures can withstand up to 900°C . Because of their strong stability at high temperatures in air, BNNTs are good candidates for composite materials, such as ceramic, polymer nanotube composite that are designed for high temperature applications. Their thermal stability and chemical inertness have importance for the decent performance of nanotube based field emitters in flat panel displays and in field emission tips for scanning tunneling and atomic force microscopes.

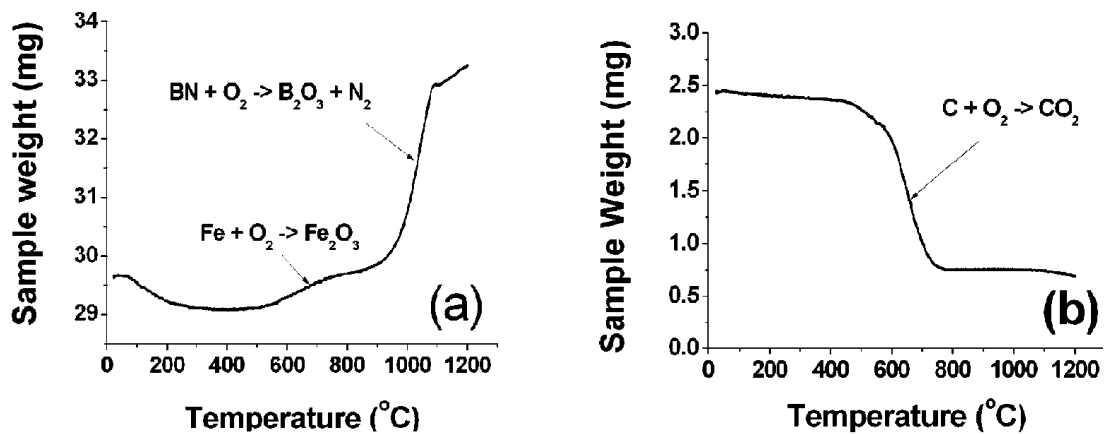


Figure 2.5. Weight changes (a) BNNT and b) carbon nanotube samples vs. temperature during heating in TGA [19]

The thermogravimetric analysis of nanotubes, as shown in Figure 2.5, revealed that BNNTs have stronger resistance to oxidation than carbon nanotubes. In Figure 2.5 (a), the weight loss (8 wt. per cent) observed at the beginning of the heating (<200 °C) is caused by vaporization of moisture and desorption of gases. The weight loss increase in temperatures between 500 °C and 800 °C is mainly due to the oxidation of iron particles. After 700 °C, sample weight increase is induced by oxidation of BNNTs or particles.

2.2.3. Thermal Conductivity

Chang et al. [20] have measured the temperature dependent thermal conductivity $\kappa(T)$ of individual multiwalled BNNTs. They have used microfabricated test fixture and characterized the nanotubes directly by transmission electron microscope. They have found values on the order of 350 WmK^{-1} at room temperature for the thermal conductivity of BNNTs having outer diameter of 30-40 nm. They have also demonstrated that $\kappa(T)$ is exceptionally sensitive to isotopic substitution, with a 50 per cent improvement in $\kappa(T)$ resulting for BNNTs with 99.5 per cent B^{11} isotope. This improvement value is the largest for any material known. They can be used as electrically insulating and highly thermally conductive wires that efficiently remove and pipe heat.

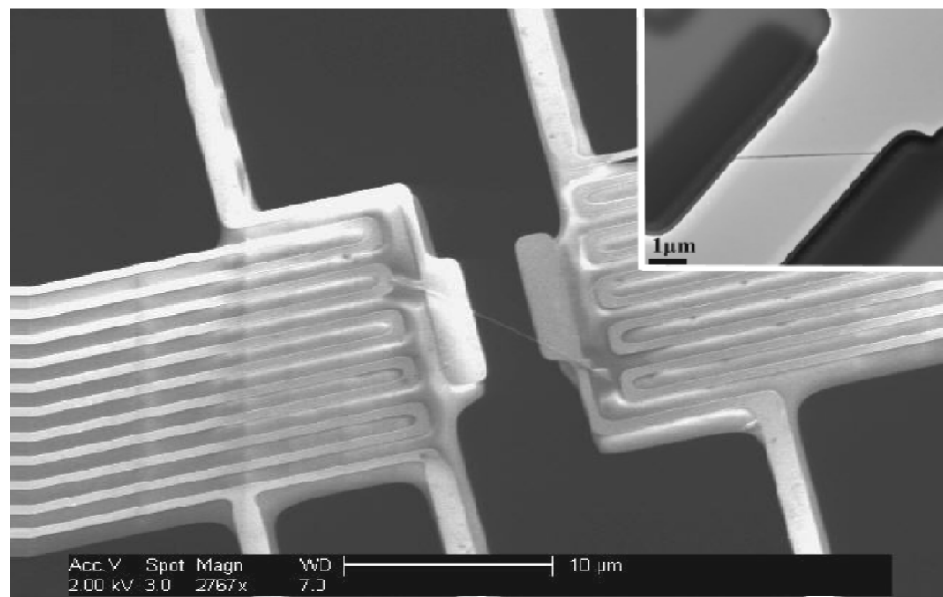


Figure 2.6. SEM image of the microfabricated fixture used by Chang et al. with a BNNT on it. The inset shows the TEM image of the same device [20]

2.2.4. Wetting Properties

The wetting properties of nanotubes are very important for understanding and performing nanotube filling with various substances. Contact angle of liquid on solid surface is a measure of the solid surface properties. In Wilhelmy method, the contact angle is determined by measuring the force when a sample is moving back and forth to the liquid. Yum and Yu [21] have measured wetting properties of BNNTs by applying this method. They have analyzed the interactions between multiwalled BNNTs and liquids, including polyethylene glycol, glycerol and water. The contact angles of BNNTs were found to be similar to those of carbon nanotubes, but they are slightly larger. For water, either partial wetting or nonwetting behaviors were observed. The total surface tension of BNNTs was estimated to be 27 mNm^{-1} .

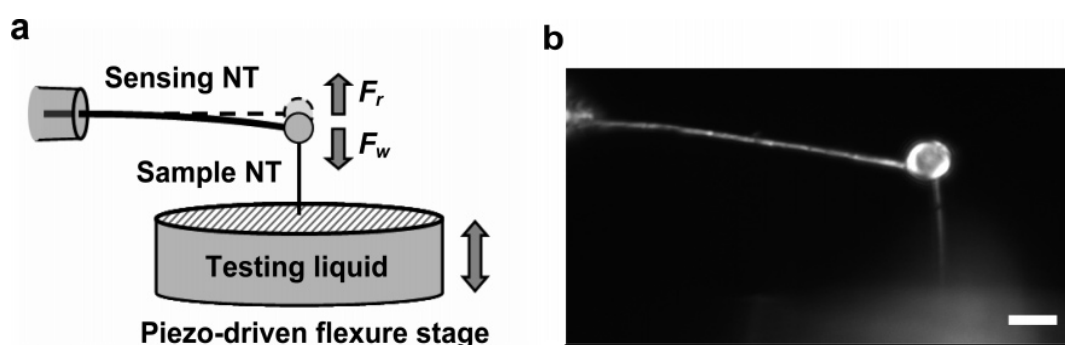


Figure 2.7. a) Schematic of the Wilhelmy method wetting experiment
b) Optical microscope image of the wetting experiment using a BNNT
with a diameter of 40 nm. Scale bar is $5 \mu\text{m}$ [21]

2.2.5. Electrical Properties

Although the structure of BNNTs is very similar to that of carbon nanotubes, they are entirely different electronically. A carbon nanotube could be metallic or semiconducting depending on its helicity and diameter. By contrast, a BNNT is expected to have stable insulating properties. Blase et al. [22] have predicted theoretically that BNNTs are wide bandgap semiconductors with a value of $\sim 5.5 \text{ eV}$, independently of their radius and helicity. This electronic property of BNNTs is very important for technological

applications, because samples that contain many different sizes and structures, single wall or multiwalled BNNTs can be synthesized with predictable electronic properties.

2.3. Synthesis of Boron Nitride Nanotubes

Historically, all useful and well established techniques of nanotube synthesis firstly developed for carbon nanotubes, have been tried to use for BNNT synthesis. Multiwalled BNNTs have been first synthesized in 1995 [7] and single wall BNNTs in 1996 [23]. Even though they have been known for more than 10 years, their synthesis is difficult and much effort is still needed to increase the purity and to improve the yield. In following section, synthesis techniques including arc discharge, chemical vapor deposition, laser ablation, substitution reactions, ball milling and a number alternative techniques are described.

2.3.1. Arc Discharge

For nanotube synthesis, arc discharge technique is performed by the passage of an electric current through two high purity electrodes in an inert atmosphere. This process produces a shell on the negative electrode (cathode). The positive electrode (anode) is continuously consumed. The inner part of the shell contains nanotubes and impurities. Figure 2.8 shows a diagram for arc discharge technique developed by Saito in 1995 [24].

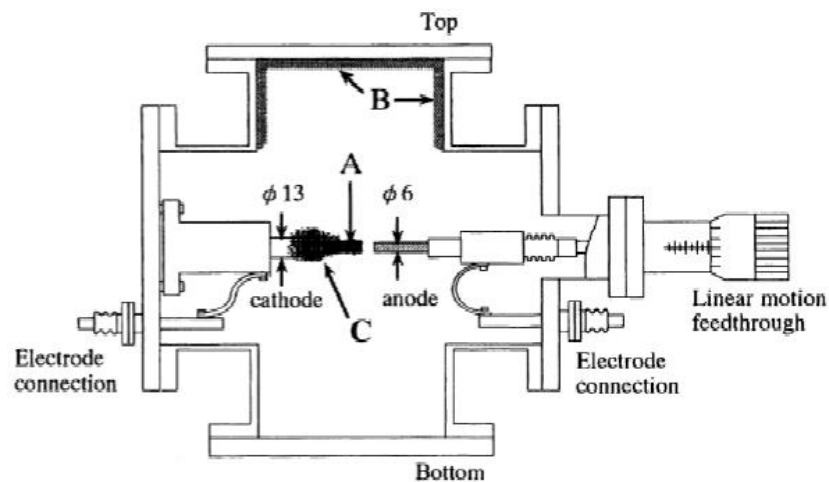


Figure 2.8. Schematic diagram for the arc discharge technique [24]

BNNTs were first discovered in an arc discharged material by Chopra et al. [7]. They used a tungsten electrode filled with h-BN powder as anode and a copper electrode as cathode in N₂ or He atmosphere. BNNTs were found on the cathode after arcing. These BNNTs always contain a metal particle at their tips and exhibit an interplanar distance of $\sim 3.3 \text{ \AA}$, which is consistent with the interplanar distance of bulk h-BN. Loiseau et al. [23] synthesized BNNTs by arcing HfB₂ electrodes in an inert atmosphere. This technique produces single and double walled BNNTs. Terrones et al. [25] reported the formation of BNNTs by arcing Ta-BN electrodes under N₂ atmosphere. In this synthesis, nanotube caps have metal particles and square morphologies. The disadvantage of the arc discharge technique is that the yield of BNNTs is not high and the products contain considerable amounts of encapsulated particles. Another one is overall cost, because in order to produce nanotubes with this technique, high purity electrodes, high purity metallic mixtures and high purity He and N₂ gases are required.

2.3.2. Laser Ablation

The second synthesis technique reported for the production of BNNTs is the laser ablation. In this technique, a continuous CO₂ laser was focused on a target placed into a diamond anvil cell filled with liquid nitrogen. After squeezing of the diamond anvils, a super high nitrogen pressure of 10-20 GPa was generated inside the tiny chamber. A temperature of approximately 5000 °C was estimated on the laser irradiated BN target surfaces, where dozens of short pure BNNTs were found to protrude from an amorphous melted BN residue. The drawback of the synthesis was a relatively small number of BNNTs compared to dominant standard amorphous, cubic or hexagonal BN flakes [26].

Later on, catalyst assisted excimer laser ablation experiments at high temperature were performed and multiwalled BNNTs were produced. Catalyst free continuous CO₂ laser ablation of BN targets that led to the formation of the uncharacteristic single wall BNNTs was also reported by Lee et al. [27]. The tubes were organized in long bundles. Boron nanoparticles encapsulated into BNNT tip ends were considered to play a key role for the single wall BNNT growth [26].

2.3.3. Substitution Reactions

In 1998, Han et al. [28] reported a new synthesis technique that uses pyrolytically grown carbon nanotubes as templates to produce BNNTs. This technique is used to substitute C atoms with B and N. B_2O_3 powder is placed in an open crucible covered by carbon nanotubes and maintained the setup under flowing N_2 at 1500 °C for 30 min inside an induction furnace. After this reaction, BNNTs of similar diameters to the starting carbon nanotubes are obtained. Carbon nanotubes, which act as templates, are removed by the intense oxidation conditions caused by B_2O_3 , according to the reaction $3C + B_2O_3 \rightarrow 2B + 3CO$. Following this, B and N atoms may be simultaneously positioned in the vacancies generated within the hexagonal structure, resulting in the formation of BN.

In 1999, Golberg et al. [29] produced single walled BNNTs by using substitution technique. Pure carbon single wall nanotubes were placed with B_2O_3 inside a graphite crucible, which was then heated to 1250 °C, 1350 °C, and 1530 °C over 30 min in a N_2 atmosphere. The authors noted the crucial role of the temperature in the synthesis. It is only possible to obtain pure single wall BNNTs at 1350 °C as by-products in a sample preferentially composed of B_xC_{1-x} and $B_xC_{1-x-y}N_y$ SWNT bundles, whereas at 1530 °C the complete transformation of the single wall carbon nanotube bundles into bulk BN phases occurs.

It is important to note that the C substitution method is very sensitive to experimental conditions, and it is extremely difficult to remove all C atoms from the generated BNNTs. In relation to this, Golberg et al. [30] claim that the presence of MoO_3 reduces the amount of C remaining as an impurity by adding an extra oxidizing agent to remove the C atoms. In order to remove excess carbon atoms, the difference between the oxidation resistance of carbon nanotubes and BNNTs have also been used. While $B_xC_yN_z$ NTs are heated at oxygen environment, up to 700 °C all carbon atoms have been oxidized and pure BNNTs have been obtained.

2.3.4. Chemical Vapor Deposition

BNNTs were synthesized by using chemical vapor deposition (CVD) technique in 2000. Lourie et al. [31] produced BNNTs using a precursor (borazin, $B_3N_3H_6$) with NiB or Ni_2B powder as catalyst. The reaction is carried out 1000-1100°C for 30 min. Other results have been obtained by in situ synthesis of a different precursor, $B_4N_3O_2H$. In this case, the yield of highly pure BNNTs reached hundreds of milligrams in a single experimental run when B_2O_3 was used as a reactant. The CVD technique can be developed to produce high quantities of BNNTs [32].

2.3.5. Reactive Ball Milling

In 1999, Chen et al. [33] reported an alternative way of producing BNNTs involving the ball milling of elemental B in NH_3 gas followed by thermal annealing at 1000–1200°C under N_2 or Ar. The samples contain bamboo-like NTs composed of BN layers and have diameters of 50–75 nm. The authors used high-energy ball milling for 150 hours to produce significant structural changes and chemical reactions in the B powder. After the heat treatment, the BN phase can be identified. The presence of Fe separated from the milling balls appears to act as the catalyst. Soon after, Chen et al. [34] reported that it is also possible to obtain BNNTs after ball milling h-BN powder for 10 hours following a thermal annealing process. They proposed that the BNNTs are synthesized via a solid-state process that involves deposition from vapor, but in which chemical reactions do not occur. BNNTs have bamboo-like morphologies and diameters ranging from 11–280 nm. Chadderton and Chen [35] have proposed that the thermally activated process of surface self-diffusion in the milled powders is the main reason for growing BNNTs. They proposed a metal tip nanotube growth model. They believe that a Fe particle always located at the tip of the growing tube is responsible for the BN nucleation by a catalytic capillary process. A tip nucleated boron nitride nanotube synthesized by Chadderton and Chen et al. is shown in Figure 2.9.

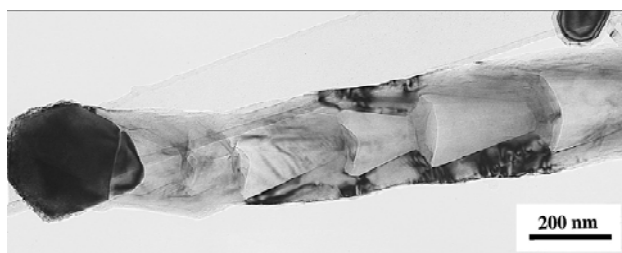


Figure 2.9. TEM image of a tip nucleated boron nitride nanotube [35]

Velázquez-Salazar et al. [36] have reported the synthesis of BNNTs by a ball milling, annealing method and proposed a new growth mechanism for the formation of BNNTs. This mechanism depends on agglomeration, crystallization and precipitation of BN material around Fe based nanoparticles that separated from ball milling container. Therefore, Fe particles become responsible for BNNT growth.

Figure 2.10 shows the BNNT growth during the annealing part of the ball-milling process performed by Velázquez-Salazar et al. [36] (a) small Fe-based alloy nanoparticles are spread in the BN amorphous material after ball milling; (b) as the temperature is increased, BN material starts to migrate and precipitate layers, which adopt the shape of small Fe-based alloy nanoparticles; (c) sliding of the first cone-shaped cup-like structure occurs as a result of the strains created inside the cup, leaving a gap below the tip; (d) repetition of the process resulting in agglomeration of additional Fe-based alloy nanoparticles, which start to attach to other metal particles; (e) following the coalescence of various metallic particles, the seeding particle increases in size, resulting in an enlargement of the precipitated BN cups; (f) the metal agglomeration process continues, as well as the sliding of the cups, resulting in nanotube growth; (g) Fe-based particles reach a critical size that inhibits the formation of additional BN layers and the growth process is interrupted. Scanning electron microscope (SEM) images showing BN NTs produced after annealing amorphous BN powders obtained from h-BN powders ball milled for 60 hours (h-i) and 72 hours (j-k). Note that these fibers are always attached to a larger particle (indicated by white arrows).

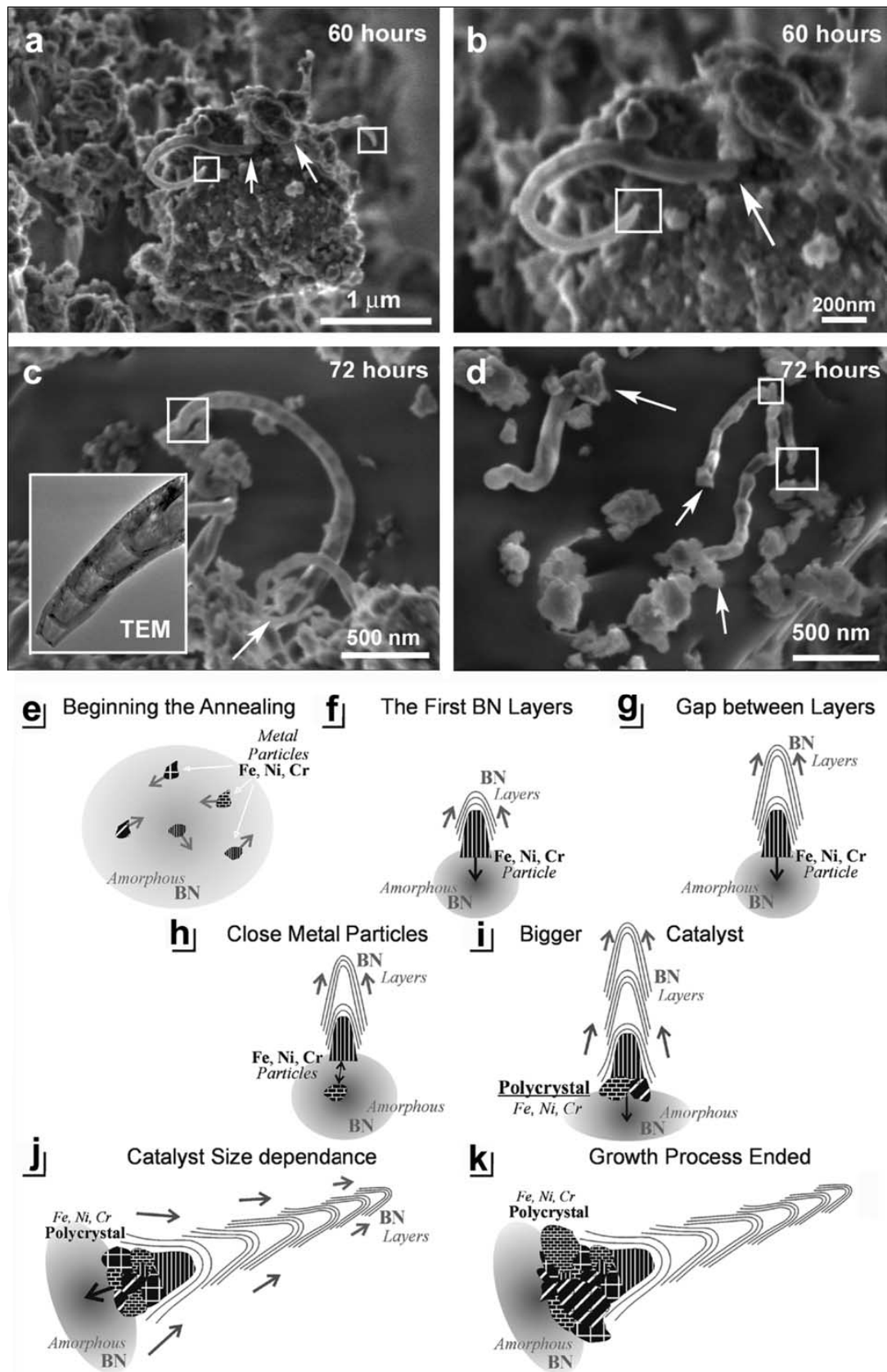


Figure 2.10. Schematic diagram of BNNT growth during ball milling process [36]

2.3.6. Plasma Jet Method

Shimizu et al. [37] synthesized BNNTs by a high temperature by a plasma jet method. Porous BC_4N sintered material was used as raw material. The plasma was operated by using Ar and a $\text{N}_2\text{-H}_2$ mixture as plasma gas and sheath gas, respectively. The porous BC_4N was evaporated by irradiation with a plasma flame. Nanotubes were formed in the high temperature zone of the chamber. BNNTs were found in the quantity of the surface of a BN sintered disk. Schematic of the apparatus and TEM image of a synthesized BNNT are shown in Figure 2.11.

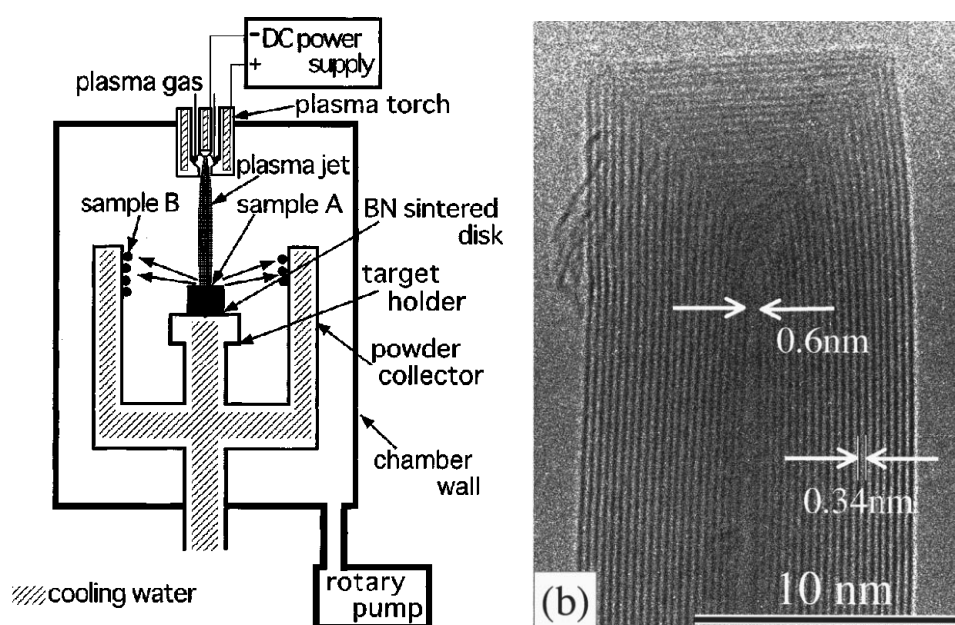


Figure 2.11. a) A schematic of apparatus for preparing BNNTs by plasma jet method b) TEM image of tip portion of a BNNT [37]

2.3.7. Alternative Methods

Bengu and Marks [38] described the synthesis of single wall BNNTs terminated by fullerene like structures using electron cyclotron resonance nitrogen and electron beam boron sources onto polycrystalline tungsten substrates. The nanostructures of 0.5 – 3.0 nm in diameter, that can be seen in Figure 2.12, were produced in an ultrahigh vacuum. The crystal structure of BN nanoparticles was not perfect, they contained buckled BN layers.

On the other hand, Bengu and Marks claimed that this technique could be useful for the production of different BN based thin coating with a well controlled structure.

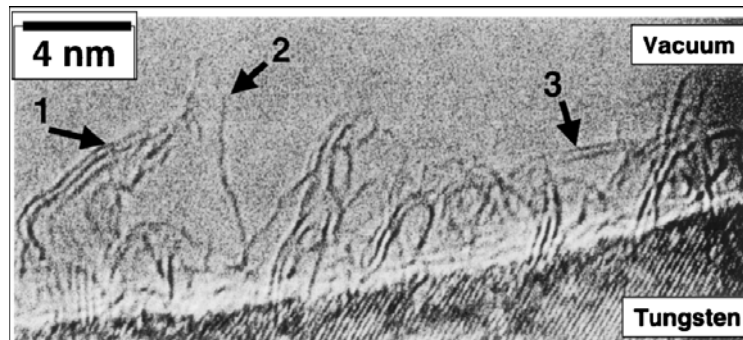


Figure 2.12. A TEM image of single wall BN nanostructures on tungsten substrate synthesized using ion beam assisted deposition. Arrows 1 and 3 show single wall BNNTs and arrow 2 shows a conical feature similar to a nanohorn [38]

A chemical technique was performed by Zhi et al. [26] through using a mixture of FeO, MgO and B powder heated within a wide temperature range of 1100-1700 °C in an induction furnace. The purity and diameter of BNNTs have not been affected by the temperature. A highly reactive B_2O_2 vapor formed as a result of the reaction between these precursors and reacted with NH_3 gas in the cold temperature of the furnace. This brought high yield production of pure multiwalled BNNTs. Several hundreds of milligrams of BNNT were produced in a single experimental run as shown in Figure 2.13.

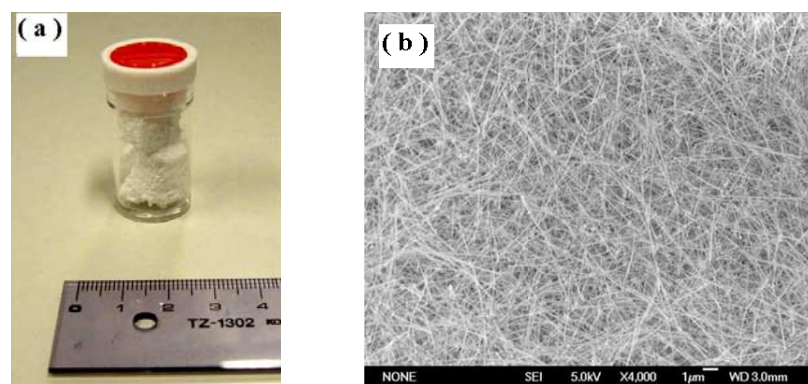


Figure 2.13. a) BNNTs obtained by Zhi et al. during one experimental run
b) SEM image of synthesized BNNTs [39]

Other synthesis techniques have also been developed in order to form BNNTs and other BN nanostructures, such as thermal annealing of powdered β -rhombohedral B and h-BN mixtures at 1200 °C in Li vapor, plasma assisted laser vapor deposition and pyrolysis of melamine diborate ($C_3H_6N_6 \cdot 2H_3BO_3$) in the absence of a metal catalyst [32].

2.4. Purification of Boron Nitride Nanotubes

After synthesis of BNNTs, samples contain significant amount of impurities such as B, amorphous BN, Fe, Cr and other metal catalysts. Therefore purification process is required to obtain pure BNNTs. A four step purification process was developed by Chen et al. [40]. In their reported process, firstly large aggregates of BNNTs are dispersed by ultrasonic treatment in ethanol solution. Then samples are leached in an HCl solution to remove metal particles such as Fe and Cr. The leached sample is collected by filtration and dried. After that BN particles are dissolved by selective oxidation at 800 °C in air. Finally, partially oxidized samples are washed with hot water and filtered with a membrane of 1 μm size until all oxides are dissolved into the solution.

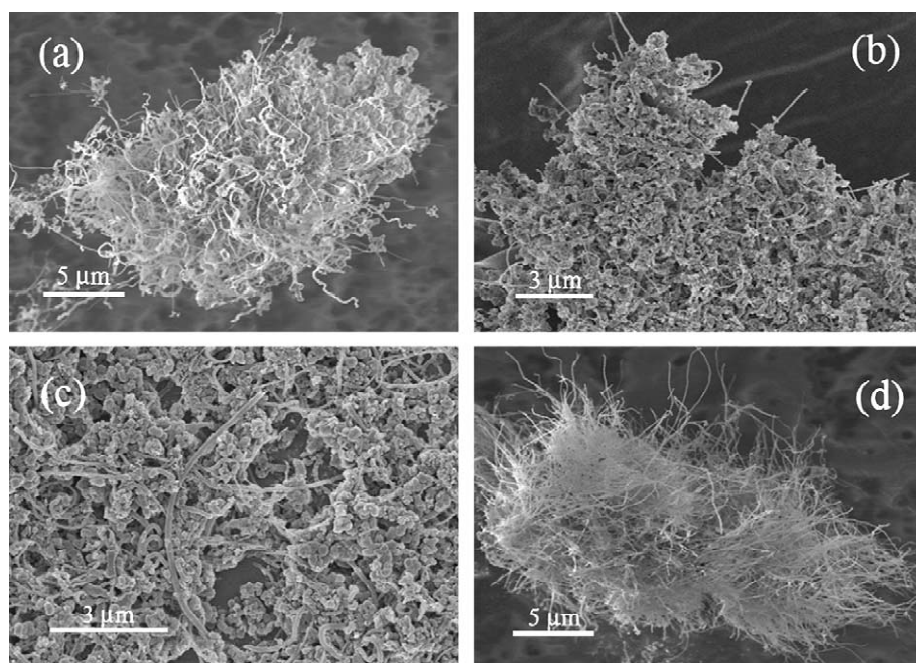


Figure 2.14. a) SEM image of the aggregate of BNNTs and nanoparticles before purification, b) BNNTs and nanoparticles after dispersion in ethanol, c) after oxidation at 800 °C in air, d) after dissolving oxide particles with hot water [40]

Another study for purification of BNNTs was reported by Zhi et al. [41]. They have focused on the removal of BN impurities such as nanoparticles, ribbons and amorphous material by using the strong interactions between BNNTs and a conjugated polymer. The conjugated polymer selectively covers BNNTs and then BNNTs can be separated from BN impurities. In this process, firstly a conjugated polymer, poly(m-phenylenevinylene)-co-(2,5-dioctoxy-p-phenylene) or PmPV, is used to wrap around BNNTs by mixing the PmPV and BNNTs in chloroform. Chloroform makes the wrapped BNNTs soluble, and then the mixture is centrifuged, so BN impurities are removed. Finally, by heat treatment of the mixture in air at 700 °C PmPV wrapping is removed and BNNTs are extracted.

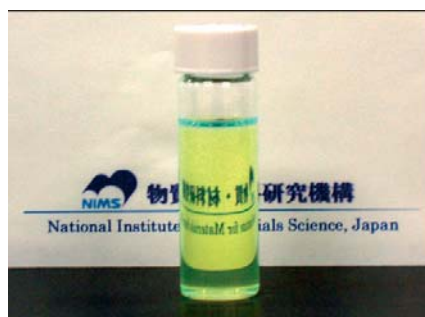


Figure 2.15. A fully transparent solution of multiwalled BNNTs in chloroform [42]

2.5. Applications of Boron Nitride Nanotubes

2.5.1. Boron Nitride Nanotube / Polymer Composites

BNNTs have several potentially unique and important properties for applications in polymer composites, such as very high Young's modulus, high oxidation resistance at high temperatures, thermal and chemical stability, good thermal conductivity and dissipation of visible light. These properties make them valuable for applications in hazardous and high temperature environment [26]. BNNTs may develop the polymer matrix's mechanical and thermal properties. There have been a few studies on the application of BNNTs for reinforcement in polymer matrix, because it is difficult to obtain highly pure BNNTs in large quantities. In order to achieve good composite properties, BNNTs also need to be dispersed in the matrix.

Zhi et al. [41] produced soluble BNNTs in chloroform solution through polymer wrapping as mentioned earlier in [40]. By using these solutions, they have fabricated BNNT reinforced polymer films based on polyaniline and polystyrene. Tensile tests on such films indicated that the elastic modulus of the films was improved by 21 per cent when just 1 wt. per cent soluble BNNTs was used. These BNNT composite films had better stability to oxidation and slightly lowered glass transition temperatures than the blank polymers [11].

2.5.2. Boron Nitride Nanotube Reinforced Glasses and Ceramics

There are a few studies on the application of BNNTs for reinforcement of glasses and ceramics. Bansal et al. [43] fabricated barium calcium aluminosilicate glass composites reinforced with 4 wt. per cent of BNNT by hot pressing. They have demonstrated that reinforcement with BNNTs improved both the flexure strength and fracture toughness of the glass. The strength of the composite was higher by 90 per cent and fracture toughness by 35 per cent than those of the glass. Through microscopic examination of fracture surfaces, pullouts showed that BNNTs were responsible for the strength and toughness improvements.

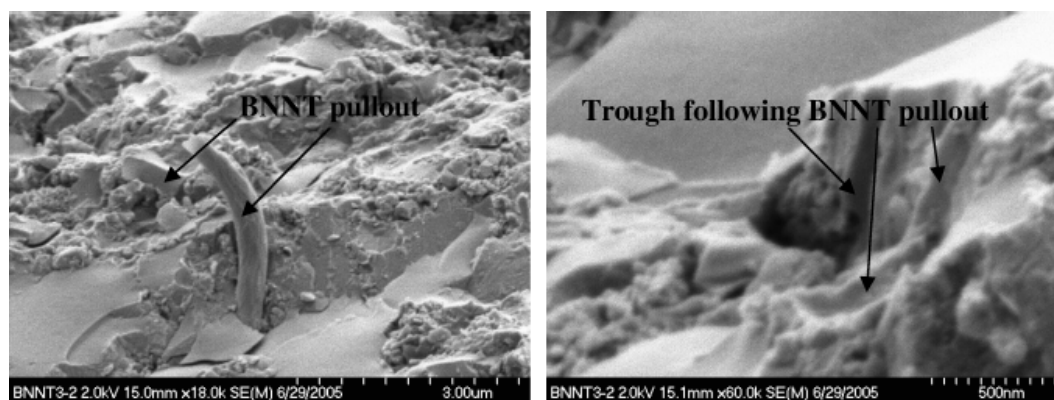


Figure 2.16. SEM images showing fracture surfaces of tested specimens of glass reinforced with 4 wt. per cent BNNTs, pull out of nanotubes is indicated by arrows [43]

Huang et al. [44] added PmPV wrapped BNNTs to the common engineering ceramics, Al_2O_3 and Si_3N_4 . They demonstrated that a small addition of BNNTs can improve the high temperature superplastic deformation of engineering ceramics. They

become much more moldable at a high temperature while other characteristic properties of ceramics do not change. In contrast, micro and nano sized BN powders were found not to be beneficial to the superplastic deformation.

2.5.3. Hydrogen Storage of Boron Nitride Nanotubes

Hydrogen is an important material for alternative energy source. It becomes popular as the cleanest energy source which can solve current environmental pollution problems with zero emission vehicles. High pressurized tanks, hydrides of some metals, and liquid hydrogen have been studying as possible hydrogen storage forms and materials. However, there are some disadvantages of them, such as low capacity, safety problems and impractical release temperatures. For developing new hydrogen storage techniques and materials, recent studies have focused on nanostructures materials. Nanoscale materials have advantages over bulk materials such as large surface area and high binding energy. BNNT properties have been studied for hydrogen storage after encouraging results were found for carbon nanotubes [26].

Ma et al. [45] experimentally demonstrated that multiwalled BNNTs can absorb 1.8 – 2.6 wt. per cent hydrogen under ~10 MPa at room temperature. Jhi et al. [46] computationally studied that an increase in specific area for BNNTs may be a solution for an increase in operating temperature and capacity for hydrogen storage. Through computational studies they proved that activated BNNTs can be good hydrogen storage media operating at room temperature. They considered the pore structure with oxygen edge is the most efficient activation. For pores of efficient size, it is found that hydrogen can diffuse inside the nanotube, which causes to an increase of available adsorption sites for hydrogen. Their study showed that making oxidized pores in BNNTs is an effective method of activating BNNTs and this makes BNNTs a strong candidate for hydrogen storage.

Tang et al. [47] experimentally studied that BNNTs with a collapsed structure could store up to 4.2 wt. per cent hydrogen at room temperature. By heating pure BNNTs in the presence of platinum provides the full collapse of nanotube walls. The open tube walls increase the specific area and number of channels for hydrogen uptake. Collapsed BNNTs

have higher hydrogen storage capacity than multiwalled BNNTs of conventional morphology.

Mpourmpakis and Froudakis [48] theoretically compared carbon nanotubes and BNNTs for hydrogen storage. They demonstrated that BNNTs are preferable to carbon nanotubes for hydrogen storage. The ionic character of the BNNTs bond increases the binding energy of hydrogen. They also showed that by increasing the nanotube diameter, decreasing its curvature, more efficient binding could be obtained.

2.5.4. Other Possible Applications of Boron Nitride Nanotubes

The insulating properties of BNNTs provide an application such as the electrically insulated nanocables with embedded metallic or semiconducting nanowires. These nanocables could be used in NEMS (Nanoelectromechanical Systems) due to the light weight and high strength to resist the mechanical deformation [26]. Zhang et al. [49] theoretically studied the nanocable consisting of a metallic carbon nanotube core and an insulating BNNT sheath. They demonstrated that BNNT could serve well as an insulating sheath while the carbon nanotube has excellent transport ability and nanocable is strong enough to mechanical deformation. Golberg et al. [50] proposed another nanocable application. BNNT filling with Fe is presented in Figure 2.17. Fe fills the nanotube via capillarity. Prepared nanocables are ferromagnetic. BNNT prevents Fe nanowire oxidation and degradation of ferromagnetism when the material is under use in air and at high temperatures.

Golberg et al. [50] proposed another application for BNNTs. Figure 2.18 shows a device made of a BNNT in which oxygen release compound, MgO_2 , was encapsulated under a high temperature synthesis followed by slow cooling to room temperature. MgO_2 is unstable on heating and it transforms to a stable MgO . Therefore this makes possible to locally release molecular oxygen from an open nanotube tip. Authors suggested that this is the first ever nanoscale oxygen burner or generator and this device may help to analyze living conditions of various viruses.

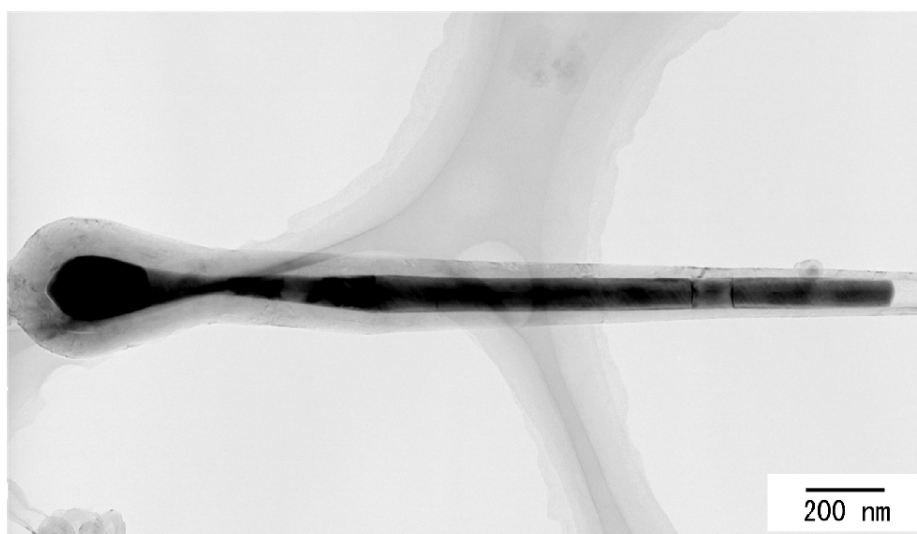


Figure 2.17. An iron filled BNNT [50]

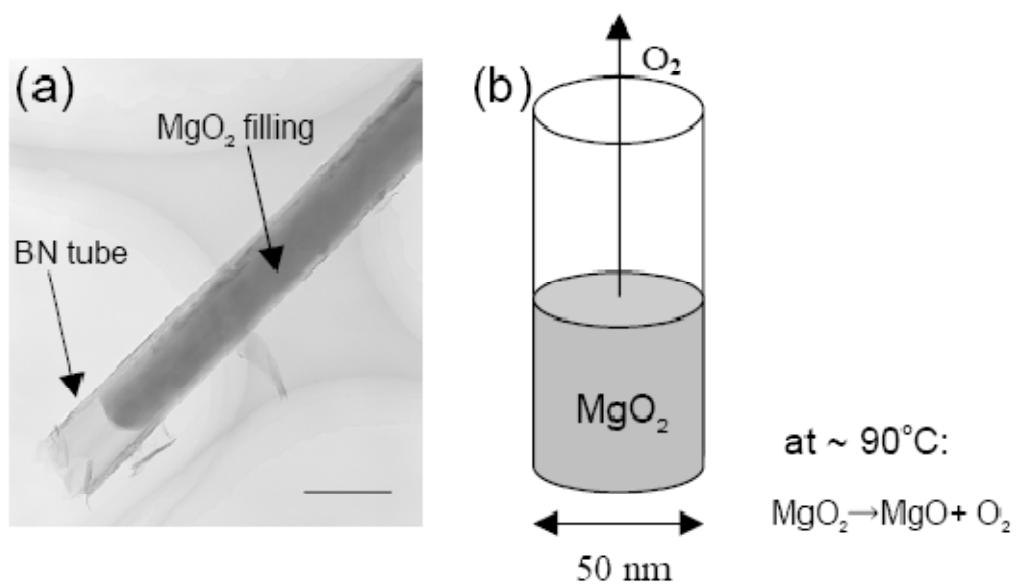


Figure 2.18. a) TEM image of a MgO_2 filled BNNT with an open tip end
b) Schematic of nanoscale oxygen generator [50]

Water filled nanoscale porous structures attracted great attention because of their important contributions to the performance and efficiency of many applications such as water purification systems, chemical systems and fuel cell devices. In 2007, BNNTs were theoretically studied by Won and Aluru [51] to simulate their water permeability properties. They found that BNNT with a smaller diameter than carbon nanotube can conduct water due to the Van der Waals interactions between water molecules and nitride atoms. They suggested that BNNT could be a promising candidate for water conduction applications such as water purification systems.

3. NANOTUBE REINFORCED POLYMER COMPOSITES

Nanotubes are new materials that are utilized by adding to polymers with potential to produce low weight composites that have extraordinary mechanical, electrical, thermal and optical properties. Since the discovery of carbon nanotubes in 1991, many researchers have been performed to understand and take the advantages of their unique properties in the form of composites for various applications. Transferring the properties of nanotubes to the composites successfully is the main problem encountered in these studies. The various nanotube/polymer composites fabrication techniques including solution mixing, melt mixing and in-situ polymerization are mentioned in this chapter. It is also introduced the mechanical and thermal properties of these composites and how these properties depend on the size, aspect ratio, loading, dispersion state and alignment of nanotubes within the polymer composites. Finally, the challenges for the future are summarized in terms of processing, characterization and nanotube availability [52].

While the subject of this thesis is about the properties of boron nitride nanotube/polymer composites, composites that are mentioned in this chapter are mostly carbon nanotube/polymer ones. Most of the work on polymer composites containing nanotubes involves carbon nanotubes. There are few studies about polymer composites with BNNTs, therefore in this thesis it is utilized for processing techniques from the studies that use carbon nanotubes as filler material in polymer matrix.

3.1. Theory of Fiber Reinforced Composite Materials

A great deal of theoretical work has been carried out since the 1950s with the aim of modelling the mechanical properties of fiber reinforced composites. While some of these models are quite complicated, two of the simplest and most common is considered in this chapter. These are the rule of mixtures and the Halpin–Tsai equations.

In the simplest possible case a composite can be modelled as an isotropic, elastic matrix filled with aligned elastic fibers that span the full length of the specimen [53]. It is assumed that the matrix and fibers are very well bonded. Then, on application of a stress in

the fiber alignment direction, the matrix and fibers will be equally strained. Under these circumstances, the composite tensile modulus in the alignment direction, Y_C , is given by

$$Y_C = (Y_f - Y_m)V_f + Y_m \quad (3.1)$$

where Y_f is the fiber modulus, Y_m is the matrix modulus and V_f is the fiber volume fraction. This is the well-known rule of mixtures [54].

However, this provides an idealized situation, fibers are generally much shorter than the specimen length. For short fibers the matrix–fiber stress transfer must be considered. When the matrix is under stress, the maximum stress transferred to the fiber is described by the interfacial stress transfer, τ . The stress transferred scales with fiber length, l , so that at some critical length, l_c , the stress transferred is large enough to break the fiber. For a hollow cylinder, this critical length is given by

$$l_c = \frac{\sigma_f D}{2\tau} \left[1 - \frac{D_i^2}{D^2} \right] \quad (3.2)$$

where σ_f is the fiber strength, D and D_i are the fiber external and internal diameters, respectively [53].

In effect, the stress transferred to the fiber builds up to its maximum value (σ_f , that which causes break) over a distance l_c from the end of the fiber. This suggests that short fibers carry load less efficiently than long fibers meaning that they can be thought of as having a lower effective modulus for reinforcement purposes. This situation was first considered by Cox who showed that for aligned fibers the composite modulus is given by [53].

$$Y_C = (\eta_l Y_f - Y_m)V_f + Y_m \quad (3.3)$$

where η_l is the length efficiency factor, which is described by [55].

$$\eta_l = 1 - \frac{\tanh(al/D)}{al/D} \quad (3.4)$$

with

$$a = \sqrt{\frac{-3Y_m}{2Y_f \ln V_f}} \quad (3.5)$$

The length efficiency factor approaches 1 for $l/D > 10$, underlining the fact that high aspect ratio fillers are preferred.

In many situations the fibers may not be aligned. For non-aligned, short fibers, the composite modulus is given by

$$Y_C = (\eta_o \eta_l Y_f - Y_m) V_f + Y_m \quad (3.6)$$

where η_o is the orientation efficiency factor. This has values of $\eta_o = 1$ for aligned fibers, $\eta_o = 3/8$ for fibers aligned in plane and $\eta_o = 1/5$ for randomly oriented fibers [53].

A similar calculation can be used to derive an equation for composite strength. For very long aligned fibers ($l > \sim 10l_c$), the composite strength is described by

$$\sigma_C = (\sigma_f - \sigma_m) V_f + \sigma_m \quad (3.7)$$

where σ_C , σ_f and σ_m are the composite, fiber and matrix¹ strengths, respectively. However, as with composite moduli, reinforcement is reduced as fiber length is decreased. For mid length fibers ($l > l_c$) the composite strength can be described by

$$\sigma_C = (\eta_s \sigma_f - \sigma_m) V_f + \sigma_m \quad (3.8)$$

where η_s is the strength efficiency factor, given by $\eta_s = (1 - l_c/2l)$. It should be stressed that when $l > l_c$, the fibers break under large applied stress. However, when $l < l_c$, enough stress cannot be transferred to the fibers to break them and the matrix fails with the fiber pulling out of the matrix.

In this situation, the strength can be described by [53]

$$\sigma_c = (\tau l/D - \sigma_m)V_f + \sigma_m \quad (3.9)$$

This model describes failure by nanotube pullout, thus the strength is controlled by strength of the matrix–fiber interface, τ , and not the fiber strength. In certain cases the polymer–nanotube interaction may result in the formation of an interfacial polymer region with mechanical properties different to the bulk polymer [56]. Under these circumstances failure may occur at the bulk polymer–interfacial polymer interface. The composite strength is then given by

$$\sigma_c = \left(1 + \frac{2b}{D}\right) \left[\frac{\sigma_s l}{D} - \frac{1 + 2b}{D} \sigma_m \right] V_f + \sigma_m \quad (3.10)$$

where b is the thickness of the interfacial region and σ_{Shear} is the shear strength of the interface [57].

Another common model is that developed by Halpin and Tsai. For aligned fiber composites, the Halpin–Tsai model gives the composite modulus to be [53].

$$Y_c = Y_m \frac{(1 + \zeta \eta V_f)}{(1 - \eta V_f)} \quad (3.11)$$

where

$$\zeta = \left(\frac{2l}{D}\right) \quad (3.12)$$

$$\eta = \frac{\frac{Y_f}{Y_m} - 1}{\frac{Y_f}{Y_m} + 1} \quad (3.13)$$

For randomly orientated composites the expression gets slightly more complicated:

$$\frac{Y_c}{Y_m} = \frac{3}{8} \left[\frac{1 + \zeta \eta_L V_f}{1 - \eta_L V_f} \right] + \frac{5}{8} \left[\frac{1 + 2\eta_T V_f}{1 - \eta_T V_f} \right] \quad (3.14)$$

where

$$\eta_L = \frac{\frac{Y_f}{Y_m} - 1}{\frac{Y_f}{Y_m} + \zeta} \quad (3.15)$$

and

$$\eta_T = \frac{\frac{Y_f}{Y_m} - 1}{\frac{Y_f}{Y_m} + 2} \quad (3.16)$$

The Halpin–Tsai equation is known to fit some data very well at low volume fractions but to underestimate stiffness at high volume fraction.

Both models have two factors in common, the stiffness is predicted to scale with both volume fraction and aspect ratio. In both cases a more or less linear increase of modulus with volume fraction is predicted. This suggests that a good measure of the reinforcement is given by dY_C/dV_f at low V_f . This takes into account both the magnitude of the stiffness increase and the amount of fiber required to achieve it and has the advantage that it can easily be extracted from experimental data. For the rest of this paper, dY_C/dV_f will be used to represent the magnitude of the reinforcement effect. For brevity we will write this quantity as dY/dV_f and refer to it as the reinforcement. This will be used to allow the comparison of results quoted in the literature [53].

In terms of the rule of mixtures, the reinforcement is then

$$\frac{dY_C}{dV_f} \approx \eta_o \eta_l Y_f - Y_m \quad (3.17)$$

while for the Halpin–Tsai model (random orientation) the reinforcement is approximated by

$$\frac{dY_C}{dV_f} \approx \frac{3}{8} Y_m \eta_L (\zeta + 1) + \frac{15}{8} Y_m \quad (3.18)$$

This approximation is valid as $V_f \rightarrow 0$ and for stiff fibers where $Y_f \gg Y_m$.

3.2. Requirements for Mechanical Reinforcement

The properties of polymer composites containing nanotubes depend on several factors in addition to the polymer material. These are production method and purification process of nanotubes, amount and type of impurities in the nanotubes, diameter, length and aspect ratio of the nanotubes in composites and nanotube orientation in the polymer matrix [53].

There are mainly four system requirements for effective reinforcement. These are large aspect ratio, good dispersion, alignment and interfacial stress transfer [53].

Dispersion is the most fundamental issue. Nanotubes must be uniformly dispersed to the level of isolated nanotubes individually coated with polymer. Isolated nanotubes provide the highest interfacial area for stress transfer to the polymer matrix [58]. This also results in a more uniform stress distribution and minimizes the presence of stress concentration centers. The effects of poor dispersion can be seen in a number of systems when the nanotube loading level is increased beyond the point where aggregation begins. This is generally accompanied by a decrease in strength and modulus [53].

Alignment is another factor that affects the mechanical reinforcement. As discussed in theory section, the difference between random orientation and perfect alignment is a factor of five in composite modulus. While alignment is necessary to maximize strength and stiffness, it is not always helpful. Aligned composites have very anisotropic mechanical properties, which may need to be avoided in bulk samples. In fibers however alignment has no downside and is a good way to maximize reinforcement [53].

The most important requirement for a nanotubes reinforced composite is that external stresses applied to the composite as a whole are efficiently transferred to the nanotubes, allowing them to take a disproportionate share of the load. Using the simplistic isostrain approximation where we assume both matrix and nanotubes are equally strained, then the ratio of the loads carried by nanotubes to matrix, F_{NT}/F_m is

$$\frac{F_{NT}}{F_m} = \frac{Y_{NT}}{Y_m} \frac{V_f}{(1 - V_f)} \quad (3.19)$$

demonstrating that the fillers take a significantly larger share of the load ($Y_{NT} \gg Y_m$) [53].

In reality, on application of an external stress, σ , the matrix undergoes greater strain, ε , than the nanotube, simply because $Y_{NT} \gg Y_m$ and $\sigma = Y\varepsilon$. This results in a shear stress field, with the shear stress, $\tau_s(r)$, increasing with decreasing distance from the nanotube, r . Adjacent to the nanotube, the shear stress in the matrix, $\tau_s(R)$ can be very large (R is the nanotube radius). It is this matrix shear stress at the interface, $\tau_s(R)$, that controls stress transfer to the nanotube. The force applied to the nanotube, dF , over a length dl is given by [53].

$$dF = 2\pi R \tau_s(R) dl \quad (3.20)$$

In addition it can be shown that $\tau_s(R)$ increases linearly with applied external stress (for small stresses). This means that the force and hence the stress felt by the nanotube increases linearly with external stress. However at some critical value of the interfacial shear stress, $\tau(R)$, either the matrix in the vicinity of the interface or the matrix/nanotube bond will rupture, resulting in debonding. This value for the shear stress is known as the interfacial shear strength (IFSS) and governs the maximum stress transfer to the nanotube. Debonding occurs when either the nanotube-matrix interface fails or the matrix fails under the large shear stresses near the interface [53].

3.3. Processing Techniques of Nanotube/Polymer Composites

There are many processing techniques that are available for producing nanotube-polymer composites. Although the techniques are different, all of them have focused on improving the composite properties such as dispersion, alignment and interfacial stress transfer [52]. The techniques of solution mixing, melt mixing and in-situ polymerization are widely applied to produce nanotube/polymer composites and are briefly described. There are also other techniques for processing of nanotube/polymer composites that use different approaches from traditional ones.

The physical properties of nanotube/polymer composites result from the properties of nanotube and polymer as well as from the microstructures produced while fabricating and processing these composites. In order to prepare nanotubes for processing on a macroscopic scale, sometimes preprocessing is required and enhances the final composite characteristics. For typical preprocessing, the following steps [52] are usually taken:

Purification to remove non-nanotube material: Most synthesis techniques of nanotube generate some impurities. Therefore a purification process is needed to obtain pure nanotubes. The most common method to remove impurities includes thermal annealing and acid treatment. For example after synthesis of BNNTs, a four step purification process, that includes thermal annealing and acid treatment, are applied in order to purify the sample. Details of this technique were mentioned in Section 3.4.

Deagglomeration for dispersing individual nanotubes: the most common method for deagglomeration is ultrasonication of a nanotube solution. It should be noted that ultrasonication for a long period of time may introduce defects into the nanotubes. Polymer wrapping have also been proposed to overcome entangling of nanotubes.

Chemical functionalization for improving nanotube/polymer interactions: Nanotubes typically form bundles that cause poor nanotube dispersion in polymer matrices and because of the smooth surface of nanotubes, there is a lack of interfacial stress transfer between nanotubes and polymer matrix. Chemical functionalization of the nanotube surface is expected to resolve these problems [53]. Several approaches to functionalization have been developed, including defect functionalization, covalent functionalization of the side walls and noncovalent functionalization with polymers or surfactants as supramolecular adducts [52].

1.3.1. Solution Mixing

The most common technique for preparing polymer nanotube composites has been to mix the nanotubes and polymer in a suitable solvent before evaporating the solvent to form a composite film. One of the benefits of this technique is that agitation of the nanotubes

powder in a solvent facilitates nanotube deaggregation and dispersion. Solution mixing technique can be summarized as [53]

1. Dispersion of nanotubes in either a solvent or polymer solution by energetic agitation.
2. Mixing of nanotubes and polymer in solution by energetic agitation.
3. Controlled evaporation of solvent leaving a composite film.

Agitation is provided by magnetic stirring, shear mixing, reflux or most commonly ultrasonication. Sonication can be provided in two forms, mild sonication in a bath or high power sonication using a tip or horn [53]. It should be noted that ultrasonication for a long period of time shortens the nanotube length and therefore reduces the aspect ratio, which is detrimental for the composite properties. The minimum sonication time and power that produce nanotube degradation are yet to be determined and they depend on nanotube concentration and initial nanotube length distribution [58].

When using solution mixing, nanotubes tend to agglomerate during slow solvent evaporation, leading to inhomogeneous distribution of the nanotubes in the polymer matrix [58]. The evaporation time can be reduced by putting the nanotube/polymer mixture on a rotating substrate (spin-casting) or dropping the nanotube/polymer mixture on a hot substrate (drop-casting). To avoid agglomeration during solvent evaporation, Du et al. developed the versatile coagulation method that involves pouring a nanotube/polymer mixture into an excess of nonsolvent. The precipitating polymer chains entrap the single wall nanotubes, thereby preventing the nanotubes from debundling [58].

3.3.2. Melt Mixing

While solution processing is a valuable technique for both nanotube dispersion and composite, it is completely unsuitable for the many polymer types that are insoluble. Melt mixing is an alternative technique which is especially useful for thermoplastic polymers. It uses high temperature and high shear forces to disperse nanotubes in a polymer matrix [58]. This range of techniques use of the fact that thermoplastic polymers soften when heated. Amorphous polymers can be processed above their glass transition temperature

while semi-crystalline polymers need to be heated above their melt temperature to induce sufficient softening. Advantages of this technique are its speed, simplicity and compatibility with current industrial practices. This technique is also useful because it is free of solvents and contaminants. An additional advantage is recycling thermoplastic composites to improve cost effectiveness and to create environmentally friendly materials [52]. However, relative to solution mixing, melt mixing is generally less effective at dispersing nanotubes in polymers and is limited to the high viscosities of the composites at higher nanotube loadings [53].

In general, melt processing involves the melting of polymer pellets to form a viscous liquid. Any additives, such as nanotubes can be mixed into the melt by shear mixing. Bulk samples can then be fabricated by techniques such as compression molding, injection molding, internal mixing or extrusion. However it is important that processing conditions are optimized, not just for different nanotube types, but for the whole range of polymer nanotube combinations. This is because nanotubes can affect melt properties such as viscosity, resulting in unexpected polymer degradation under conditions of high shear rates [53].

3.3.3. In-situ Polymerization

This processing technique starts by dispersing nanotubes in monomer followed by polymerizing the monomers. Like solution mixing, functionalized nanotubes can improve the initial dispersion of the nanotubes in the liquid (monomer, solvent) and consequently in the composites [58]. The main advantage of this technique is that it allows grafting of polymer macromolecules onto the walls of nanotubes. It is easier to get intimate interactions between polymer and nanotube during the growth stage. Depending on how the reaction is carried out some polymer strands can be covalently attached to the nanotubes. In addition, it is very convenient processing technique which allows the preparation of composites with high nanotube loading and very good miscibility with almost any polymer type. This technique is particularly important for the preparation of insoluble and thermally unstable polymers, which cannot be processed by solution or melt mixing. Depending on required molecular weight and molecular weight distribution of

polymers, chain transfer, radical, anionic and ring opening metathesis polymerizations can be used for in-situ polymerization processing [53].

Nanotube/epoxy polymer composites include the majority of reports using in-situ polymerization techniques, where the nanotubes are first dispersed in the resin followed by curing the resin with the hardener.

3.3.4. Other Techniques

In traditional composite fabrication techniques, it is generally needed to avoid the high viscosities of nanotube/polymer composites. However, some researchers have decreased the temperature to increase the viscosity to the point of processing in the solid state. Solid state mechanochemical pulverization processes have mixed nanotubes with polymer matrices. Pulverization methods can be used alone or followed by melt mixing. Composites prepared by this technique have the advantage of grafting the polymer on the nanotubes, which results for good dispersion, improved interfacial adhesion and improved tensile modulus [58].

An innovative latex fabrication method for making nanotube/polymer composites disperses nanotubes in water and then adds a suspension of latex nanoparticles. Freeze-drying and subsequent processing of this colloidal mixture produces composites with uniform dispersion of nanotubes even in a highly viscous matrix like high molecular weight polystyrene. This promising method can be applied to polymers that can be synthesized by emulsion polymerization or formed into artificial latexes, e.g., by applying high-shear conditions [58].

In order to obtain nanotube/polymer composites with very high nanotube loadings, Vigolo et al. developed a "coagulation spinning" method to produce composite fibers comprising predominately nanotubes. This method disperses SWNT using a surfactant solution, coagulates the nanotubes into a mesh by wet spinning it into an aqueous poly(vinyl alcohol) solution, and converts the mesh into a solid fiber by a slow draw process [58].

3.4. General Information about Epoxy Systems

Epoxy resins are high-performance thermosetting resins that have a unique combination of properties. Epoxy resins have been commercially available for about 60 years. Epoxy resins are one of the most multi-purpose polymers with uses across a wide variety of industries. The outstanding physical properties of epoxy resins include [59]:

- Low cure shrinkage
- No volatiles given off during cure
- Compatibility with a great number of materials
- Strength and durability
- Adhesion
- Corrosion and chemical resistance
- Electrical insulation.

Furthermore, epoxy resin systems are capable of curing at either ambient or elevated temperatures and they require only minimal pressure during the cure. Thus, epoxies can be applied and cured under many conditions. These properties provide great added value in many industries engaged in product assembly. Many new applications are being developed that will ensure the significance of epoxy resins in the future. For example, epoxies are the material of choice for the reinforcement of aging or damaged concrete structure including walls, ceiling beams, bridge columns, and anchoring mechanisms. They are the main binders for graphite-reinforced composites such as those used in manufacturing tennis rackets, fishing rods, skis, snowboards and golf club shafts. They have also been used for manufacturing high-strength, lightweight carbon fiber pultrusion as replacements for steel rebar in special concrete expansion projects [59].

Industries using epoxy adhesives include aerospace, civil engineering, automotive, chemical, electrical, marine, leisure, and many others. The common reason for the broad acceptance of epoxy resins in these important and diverse markets is their capacity to provide a good balance of handling characteristics and ultimate physical properties. They adhere well to a very large variety of substrates, and they generate tough, environmentally resistant films or matrices [59].

One of the major advantages of epoxy chemistry is that it provides the engineer freedom for solving technical problems. Epoxies can be designed to be flexible or rigid; high or low modulus; homogeneous, filled, or foamed; conductive or insulative; fire-retardant; and resistant to heat and chemicals. The number of raw materials that the formulator has to work with is enormous. These include epoxy resins and modified epoxy resins of all types and forms, fillers and additives, modifiers, reinforcements, diluents, and solvents. The possible curing agents that can be used also provide great latitude in formulation. Often the curing agent becomes an integral part of the resulting compound. Its choice is a controlling influence on the curing properties of the mixture and on the performance properties of the cured adhesive. One of the main advantages of epoxy resins is that they generally allow easy incorporation of additives, and the resulting formulation is one that can be easily adapted to many manufacturing processes, such as [59]

- Pultrusion
- Lamination
- Filament winding
- Molding
- Casting and potting
- Coating
- Adhesive bonding

Epoxy resins are not the lowest-cost resins potentially available for most applications. Thus, epoxy resins must provide added value to justify their additional cost. This added value is usually realized by the incorporation of a special property or combination of properties into the final product. Epoxy resins are composed of polymeric molecules that are converted to a solid by a chemical reaction. Epoxy systems physically comprise two essential components: a resin and a hardener. The hardener causes the chemical reaction, which turns the epoxy resin into a solid, crosslinked network of molecules. This polymer is called a *thermoset* polymer because, when cured, it is irreversibly rigid and relatively unaffected by heat. Cure of the epoxy resins is initiated once the resin is mixed with a hardener. The cure of all epoxy resins is an exothermic process where heat is generated as a natural result of the chemical reaction [59].

3.4.1. Diglycidyl Ether of Bisphenol A (DGEBA)

Epoxy resins were first introduced by Ciba-Geigy, Ltd., in 1946 although their development began decades earlier. The most common commercial epoxy resin is formed from the reaction of bisphenol A and epichlorohydrin. This resin is known as the diglycidyl ether of bisphenol A or DGEBA. The primary reasons for their popularity have been the relatively low cost of raw materials used to synthesize these resins, their ability to be cured by a large number of different crosslinking agents at both room and elevated temperatures, their relatively good mechanical and chemical properties that are exhibited by the cured resins. The DGEBA family of epoxy resins provides superior overall performance in a variety of end use applications. With proper additives or modifiers, these base polymers enable formulators to achieve practically any desired performance level, while optimizing processability and durability in many environments [59].

A majority of the world's epoxy resin market consists of the DGEBA type. The liquid DGEBA resins are typically used where low viscosity, high reactivity, and high crosslinking density are required. The low viscosity allows them to be easily compounded with fillers and other additives. The relatively high functionality allows them to be cured at low temperatures and with conventional curing agents. This reactivity produces reasonably high crosslink density necessary in applications requiring high heat and chemical resistance [59].

DGEBA epoxy resins are formed by reacting bisphenol A with epichlorohydrin. The reaction proceeds via chlorination intermediate to produce bisphenol A diglycidyl ether. Variation of the bisphenol A and epichlorohydrin ratios enables resins to be produced with different molecular weights and viscosities [59].

Liquid DGEBA epoxy resins can be cured by a great variety of curing mechanisms. The liquid form enables convenient formulation with additives and fillers. Formulated systems can be easily mixed prior to application and applied as uniform films to the substrates to be joined. Because the resulting adhesives are high-viscosity liquids or pastes, they will wet the substrate well. Yet they do not readily flow out of the joint area to cause adhesive starvation. Pressure is not a requisite to cure these adhesives as only contact

pressure is generally applied. These liquid DGEBA resins provide all the general properties of the epoxies with the following additional advantages [59]:

- Better wetting of fillers and reinforcements and better penetration of porous substrates due to low viscosity
- Increased crosslink density (increased T_g and heat distortion temperature)
- Greater chemical uniformity (often preferred in electronic applications because of purity)

3.5. Mechanical Properties of Nanotube/Epoxy Polymer Composites

Due to their wide range of industrial uses, thermosetting polymers in general and epoxy resins in particular have been widely studied as a matrix material for nanotube reinforced composites. In terms of mechanical properties, nanotube epoxy composites have found to be either weaker or slightly higher strength than the pure epoxy. In most of the studies, more than 1 wt. per cent of nanotubes were added to get any improvement in the elastic modulus of the epoxy matrix.

The first record of the formation of epoxy-nanotube composites comes from a paper by Ajayan et al. in 1994 [60]. In this work nanotubes were aligned within the epoxy matrix by the shear forces induced by cutting with a diamond knife. However no quantitative mechanical measurements were made.

The first mechanical study was made by Schadler et al. in 1998 [61]. They measured the stress–strain properties of a MWNT–epoxy composite in both tension and compression. In tension the modulus increased from 3.1 GPa to 3.71 GPa on addition of 5 wt.per cent nanotubes. However better results were seen in compression with an increase in modulus from 3.63 to 4.5 GPa. Better stress transfer between the nanotubes and epoxy matrix is shown in compression than in tension. It is proposed that during load transfer to multiwalled nanotubes, only the outer layers are stressed in tension whereas all the layers respond in compression.

A number of other studies have observed increases in modulus but either increase or a slight decrease in strength and toughness [62-64]. Xu et al. observed a 20 per cent increase in elastic modulus from 4.2 to 5 GPa when 0.1 wt. per cent of MWNT were added [65]. This corresponds to a massive reinforcement value of dY/dV_f 1200 GPa. According to the rule of mixtures this value is close to the maximum possible reinforcement for a material filled with perfectly aligned, well-dispersed nanotubes displaying perfect stress transfer. As these measurements were made by flexural testing using the Shaft loaded blister method, it would be interesting to see them confirmed using tensile testing [53].

Allaoui et al. obtained improved properties for MWNT/epoxy composites in 2002 [66]. They investigated the mechanical properties of the composites with different weight percentages of nanotubes. They measured an increase in modulus from 0.12 GPa to 0.47 GPa on addition of 4 wt. per cent nanotubes, a reinforcement of 13 GPa. This was accompanied by a doubling in strength from 5 to 10 MPa and a reduction in ductility from 20 per cent to 10 per cent compared to pure epoxy resins.

Further work was carried out on CVD-MWNT epoxy composites. Significant increases in modulus from 2.75 GPa to 4.13 GPa were observed on addition of 6 wt. per cent nanotubes corresponding to dY/dV_f 45 GPa. They attributed the large reinforcement values to residual oxygen containing groups that had covalently bonded to the nanotubes during purification. The presence of these groups may have improved interfacial bonding [53].

Bai et al. [67] observed a doubling of Young's modulus from 1.2 to 2.4 GPa on addition of 1 wt. per cent CVD-MWNT. This corresponds to a reinforcement value of dY/dV_f 330 GPa which is the largest observed for an epoxy-based composite as measured by tensile testing. In addition, significant increases in strength from 30 to 41 MPa were recorded. Good nanotube/matrix adhesion was investigated by the observation of nanotube breakage during fracture surface studies.

Finally Li et al. [68] studied SWNT-epoxy composites by nanohardness testing. They observed an increase in modulus from 4 to 7 GPa with 5 wt. per cent SWNT (dY/dV_f 94 GPa). Increases in hardness from 0.35 to 0.45 GPa were also observed.

3.6. Thermal Properties of Nanotube/Epoxy Polymer Composites

The thermal conductivity of nanotube reinforced composites is affected by the overall size of the interface, the aspect ratio of the nanotubes and interfacial adhesion between the nanotubes and the matrix. Carbon nanotube/epoxy composites show increases in thermal conductivity [69].

Bryning et al. [70] reported the thermal conductivity measurements of purified single wall carbon nanotube epoxy composites. Thermal conductivity of two types of composites prepared using suspensions of nanotubes in DMF and surfactant stabilized aqueous SWNT suspensions was investigated and it was found that DMF-processed samples, where higher nanotube loadings are difficult to obtain, exhibit a modest enhancement in the range of nanotube loadings 0.1 wt. per cent to 0.5 wt. per cent. At 0.5 wt. per cent nanotube loading, the improvement is about 27.5 per cent as compared to pure epoxy, whereas surfactant processed samples, which permit greater nanotube loading, shows no measurable enhancement of thermal conductivity below 1 wt. per cent and larger enhancement of 64.9 per cent at 10 wt. per cent nanotube loading. The difference in the enhancement of thermal conductivity with nanotube loadings of the two types of suspensions is due to a ten-fold larger nanotube/matrix composite interfacial thermal resistance in the surfactant-processed composites compared to DMF-processed composites [69].

Nanotubes influence the glass transition temperature of the epoxy composites. In a study by Gojny and Schulte they investigated the thermo-mechanical behavior of the epoxy composites reinforced with different loadings of functionalized and non-functionalized carbon nanotubes. A dependence of the nanotube content on the glass transition temperature (T_g) was observed by DMA. An increase in the amount of nanotubes causes an increase of T_g , and also composite samples containing amino functionalized nanotubes showed a stronger influence on T_g in comparison to composites containing non-functionalized nanotubes. This is because functionalization of carbon nanotubes has a strong influence on the interfacial interaction between the epoxy matrix and CNT [69].

3.7. Advantages and Applications of Nanotube/Polymer Composites

The mechanical properties of CNTs encourage that they may be used as reinforcing fibers in polymer composites, where stiffness, strength and low weight are important considerations. There are various possible applications of nanotube/polymer composites. Some examples are aerospace structural panels, sporting goods, ultra-lightweight thin-walled space structures for use in space, and high stiffness-to-weight space mirror substrates. Short lifetime is an important problem in the optical-limiting and light-emitting devices consisting of polymers. Nanotube reinforcement may increase the lifespan, and thus the commercial value, of these devices [52].

The nanoscale of the reinforcement enables thinner, flatter structures to be produced, such as a composite mirror. Conventional carbon fibers with a diameter of approximately 8 μm protrude from the surface of the composite mirror (referred to as “print-through”), and reduce its optical quality. This is not the case for CNTs, whose print-through is smaller than the wavelength of visible light [52].

Nanotubes have advantages over metals, such as greater flexibility, space and weight savings, mechanical strength and better durability. Typical values are less than 5 wt. per cent nanotube loading as compared to 8-20 wt. per cent for most carbon black containing compounds. Low particle contents are also important for electronic cleanroom applications, where particle contamination is a major problem [52].

CNT/thermoplastic composites offer a number of additional advantages over other materials. The nanotubes can be added in the compounding stage without compromising the mechanical and processing properties of the matrix. The finished product is lighter in weight, appealing in surface finish, corrosion-resistant, easier to handle, and less expensive to ship [52].

A new application for nanotube reinforced composites is automobile bumpers. The bumper will have good mechanical properties and lower weight than the standard fiberglass bumpers, since only 1-5 wt. per cent of carbon nanotube will be needed compared to 30 wt. per cent or more of fiberglass. The motivation for using CNT

nanocomposites for automobile bumpers is their multifunctionality, enabling good mechanical properties, low weight and electrical conductivity. The conductivity of the bumper will allow for direct application of electrostatic spray of base and clear coats, eliminating the need for an additional primer coat prior to painting. Additional advantages are savings in paint consumption and reductions in volatile emissions from paint lines. Electrostatic painting may be extended even further to mirror shells, door handles and grills by using carbon nanotubes. This has been recently demonstrated by Hyperion Catalysis International Inc., who manufactured plastic side view mirror housings for Ford Taurus™ in order to increase conductivity for electrostatic painting [52].

The high thermal conductivity of nanotubes has a number of applications, especially in heat sinks for electronics, motors and tires. This property is important in thermal applications and in precision structures where thermally induced distortions reduce the ability to hold tolerances. Multifunctional applications include housing for electronics in a satellite that needs to be mechanically supported, to have excess heat transported away, and to be protected by electromagnetic irradiation. Other examples include batteries, and structures used to store hydrogen for fuel cells [52].

Additional applications are membranes for molecular separations, which utilize the very small pores existing in the nanotubes, abrasive resistance layers for surface engineering of composites, biomaterial applications, such as drug delivery, which use the inertness of SWNTs, nanosensors inside a polymer for monitoring and quantifying deformation or for detecting polymer transitions, light bulletproof vests, earthquake resistant buildings exploiting the unique flexibility of the carbon nanotubes, smart polymer coatings to protect components under extreme physical conditions such as microsatellites and plastics requiring strict tolerances [52].

4. EXPERIMENTAL PROCEDURE

4.1. Starting Materials

4.1.1. Boron Nitride Nanotubes

Multiwalled BNNTs synthesized by ball milling and annealing method (Figure 4.1) [71] were purchased from Research School of Physical Sciences and Engineering at Australian National University [72]. According to the manufacturer, the chemical composition of nanotubes is > 97 wt. per cent of BN, ~1.5 wt. per cent of metal catalysts, such as Fe and Cr derived from the milling process and ~1.5 wt. per cent of absorbed O₂. They have diameter up to 100 nm and length ranging from 5 μ m to several tens of microns. BNNTs having a gray color were used as received from the manufacturer without further purification.



Figure 4.1. 250 mg as-received BNNT (The diameter of the bottle is 15 mm)

Morphological structure and compositional structure of BNNTs were confirmed by scanning electron microscope (SEM), energy dispersive X-ray analysis (EDAX) and X-ray diffraction analysis (XRD). EDAX and SEM analyses were performed in a Philips XL30 ESEM-FEG/EDAX system by operating at the secondary imaging mode at an accelerating voltage of 5-10 kV. BNNT samples were sputter coated with a thin gold layer prior to their observation. XRD was performed by a Rigaku D/MAX-Ultima+/PC X-ray diffraction equipment with Cu/K-alpha radiation source.

4.1.2. Epoxy Matrix System

Epoxy resin and curing agent were commercial grade and used as received from the supplier, Izomas A.S., Kartal, İstanbul. The epoxy resin used for making the composite was diglycidyl ether of bisphenol A (Epikote 828, Hexion) (DGEBA). DGEBA has a Brookfield viscosity of 110-150 poise and a density of 1.16 g/cm³ at 25 °C [73]. Viscosity is an important parameter for good dispersion and interfacial stress transfer of BNNT/epoxy composite. The curing agent was triethylenetetramine (Epicure 925, Hexion) (TETA). Fourier transform infrared spectrometer (FTIR) was used to confirm the structure of epoxy resin and curing agent. FTIR spectra of epoxy resin and curing agent are shown in Appendix A.

Technical grade purity solvents N,N-dimethylformamide (Sigma-Aldrich, 99.8 per cent) (DMF), ethanol (Riedel-de Haen, 99.8 per cent) and acetone (Riedel-de Haen, 99.5 per cent) were used for dispersion characterizations of BNNT.

4.2. Visual Stability Comparison and Agglomerate Size Analysis

Preparation of nanotube dispersion is the most critical step for developing high performance nanotube reinforced polymer composites [69]. High power bath ultrasonication in solvents is one of the effective methods for preparation of homogenous and relatively aggregate free dispersions. Acetone, ethanol and DMF are mostly used solvents to prepare successful nanotube dispersions [74]. In this study, in order to find the most effective solvent for BNNT dispersion to achieve good composite properties, stability and agglomerate size analysis of BNNTs in acetone, ethanol and DMF were performed.

To compare the visual stability of BNNTs in organic solvents, 200 mg l⁻¹ concentration of BNNTs in acetone, ethanol and DMF was high power bath ultrasonicated for 1 h. Then they were hand-shaken for 1 min to remove any gradients produced by non-uniform ultrasonication [74]. The dispersions were then placed on a shelf to observe their aggregation behaviors for different time intervals.

Zetasizer nano-particle size analyzer (series Malvern-nano ZS) was used to investigate the aggregation of BNNTs in various solvents. The results were analyzed by using standard “Dispersion technology software, version 5.10”. The instrument performs size measurements using a process called “Dynamic Light Scattering (DLS)”. It is also known as Photon Correlation Spectroscopy (PCS) and measures brownian motion and relates this to the size of the particles. In liquid, particles move randomly and their speed of movement is used to determine the size of the particles. It illuminates the particles with a laser source and analyzes the intensity fluctuations in the scattered light. DLS is sensitive to the intensity of light that scattered by particles, and large particles scatter more light than small particles, therefore it determines the presence of aggregates [75]. This technique is very useful for agglomerate size analysis and the stability of nano particle dispersions.

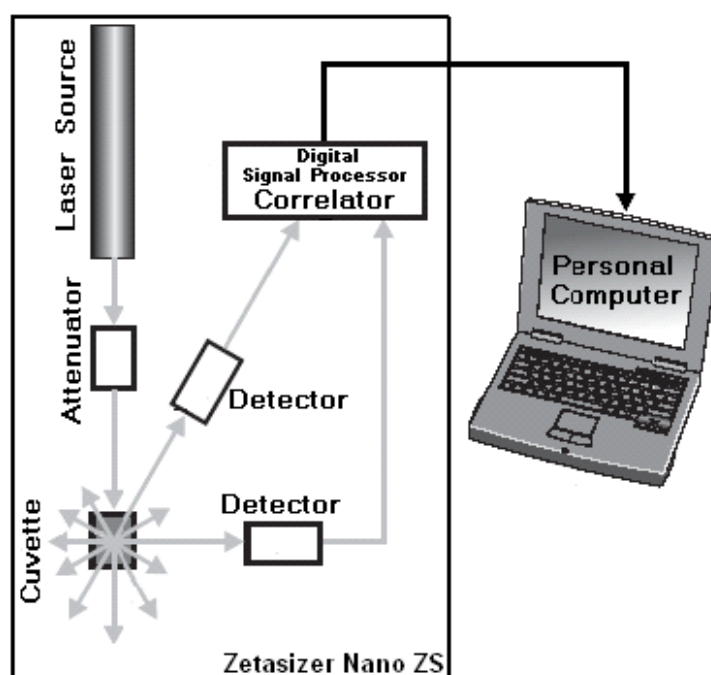


Figure 4.2. Working principle of Zetasizer nano-particle analyzer [73]

For agglomerate size analysis, BNNTs were hand-mixed for 1 min in acetone solution (200 mg l^{-1}) and high power ultrasonicated for 15, 30, 45 and 60 mins. They were then hand shaken for another 1 min to remove any gradients produced by non-uniform ultrasonication. The solutions were transferred to standard glass cuvettes (10 mm x 10 mm x 45 mm) and placed in a Malvern Zetasizer Analyzer (Nano ZS). The software was

programmed to record the average of at least 40 readings for quantification of the agglomerates' size and distribution. All of these procedures were then repeated with ethanol and DMF to allow a comparison between the effects of acetone, ethanol and DMF in nanotube dispersion.

4.3. Preparation of Composite and Neat Resin Specimens

As received BNNTs material consists of aggregates of different sizes. The bigger ones are millimetric. This would be an obstacle to the uniform dispersion of BNNTs into the epoxy matrix. In order to reduce the size of the BNNT aggregates, they were first dispersed in DMF for 60 min at room temperature by using a high power ultrasonic bath. The DMF/nanotube solution stayed in ultrasonic bath for another 60 min at 75 °C after epoxy resin was added. The DMF was fully evaporated by heating the BNNT / resin suspension at 100 °C in a vacuum oven for 24 h.

After a homogenous BNNT/epoxy resin mixture was prepared, the curing agent, TETA, was added to the nanotube/epoxy resin mixture. The weight ratio of epoxy resin and curing agent is 100:13, respectively [73]. After manual homogenization, the samples were put into the dog bone shaped silicone molds. Because of the high viscosity of the mixture, air is introduced to it during hand mixing. Therefore samples were put into a vacuum oven at 60 °C and evacuated at 20 mmHg for 6 minutes to get the entrapped air out of the mixture. Degassing time is critical for specimen preparation. If samples are left in vacuum oven for a longer time, polymerization occurs at high temperature while air bubbles are moving to the surface therefore entrapped air stays in the composite. All these preparation processes of composites are summarized in Figure 4.3.

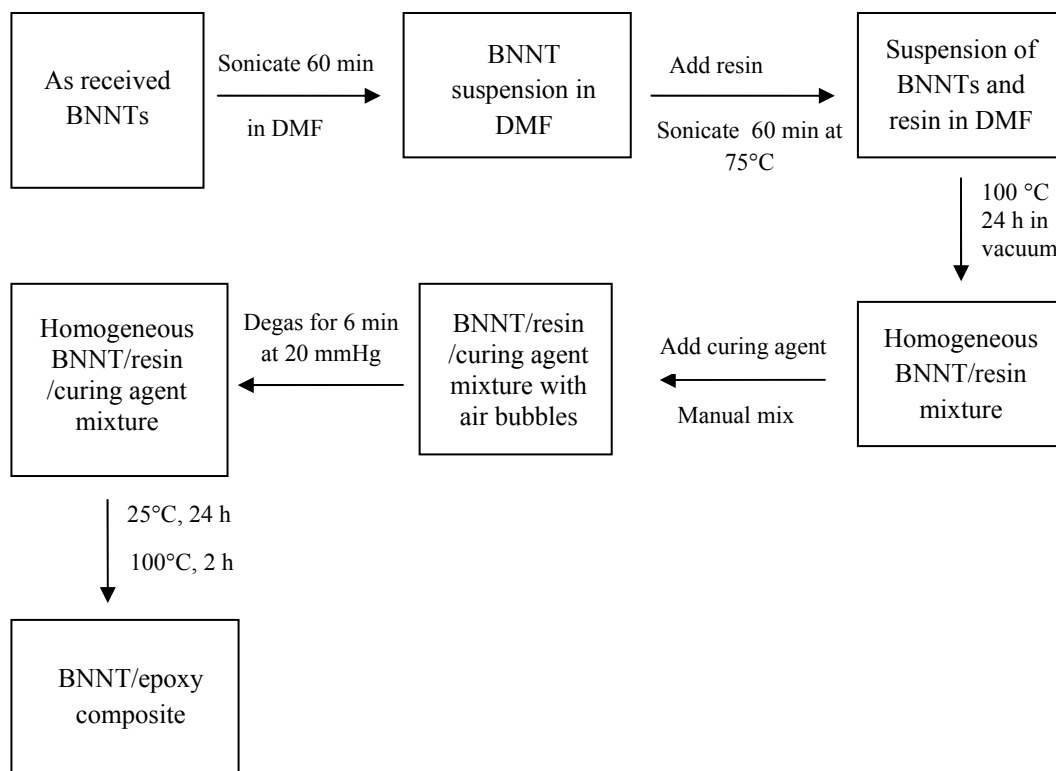


Figure 4.3. Scheme of the preparation of BNNT/epoxy composites

The composites were cured at 25 °C for 24 h followed by 2 h curing at 100 °C to complete the crosslinking reaction. In order to investigate effect of nanotube concentrations to the properties of composites, they are loaded with 0.1 wt. per cent, 0.2 wt. per cent and 0.4 wt. per cent of BNNTs. Neat epoxy specimens (without nanotube loading) were fabricated simply mixing the curing agent with the epoxy resin, casting and degassing the specimens following an identical curing cycle as for the nanotube/epoxy composites.

Before mechanical measurements, the surfaces of the specimens were milled at Manufacturing Laboratory of Mechanical Engineering Department and mechanically polished with silicon carbide paper to minimize the influence of surface flaws and porosity. For specimen preparation, open molding method is selected to spend minimum amount of material. Firstly, master mold made of aluminum AA 5083 was designed by using Autocad and manufactured by using a CNC milling machine that has 0.001 mm dimensional tolerance. For the preparation of silicon mold, RTV 2 Alpina K18 and B161 were mixed

by the weight ratio of 100:2, respectively. The mixture was poured onto the master mold then it was cured at room temperature for 24 h. Manufactured master mold and silicone mold are shown in Figure 4.4 and Figure 4.5, respectively.



Figure 4.4. Master mold used for silicone mold preparation

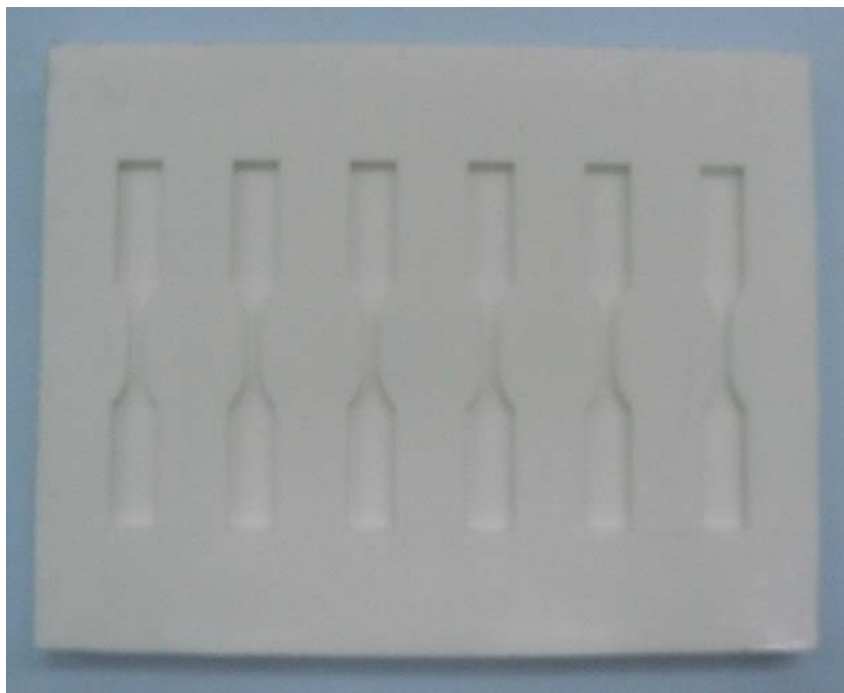


Figure 4.5. Silicone mold for casting tensile test specimens

4.4. Mechanical Characterization of BNNT / Epoxy Composites

4.4.1. Tensile Properties

Tensile tests of the neat epoxy and BNNT/epoxy composites were conducted according to the ASTM D638-03 standard test method for tensile properties of plastics by using Zwick Z100 universal testing machine with a 10 kN load cell and a cross-head speed of 1 mm/min. The reason of this quite low loading rate is the brittle behavior of the thermosets. Longitudinal strain was measured by using a clip type extensometer with gage length of 9.6 mm. ASTM D-638 Type 5 dog bone shaped specimens that have 80 mm length and 9.74 mm width were used [76]. The thickness of specimens after polishing is between 2.8 mm and 3.2 mm. The average dimensions of the test specimens used are shown in Figure 4.6. At least five specimens were tested for each sample. The modulus was calculated from the initial straight line region of the stress-strain plot. This initial straight line region was specified by zooming onto the stress strain plot and locating the exact points until which the stress strain curve was linear. Average and standard deviation values of tensile strength, tensile modulus and break strain were calculated after testing.

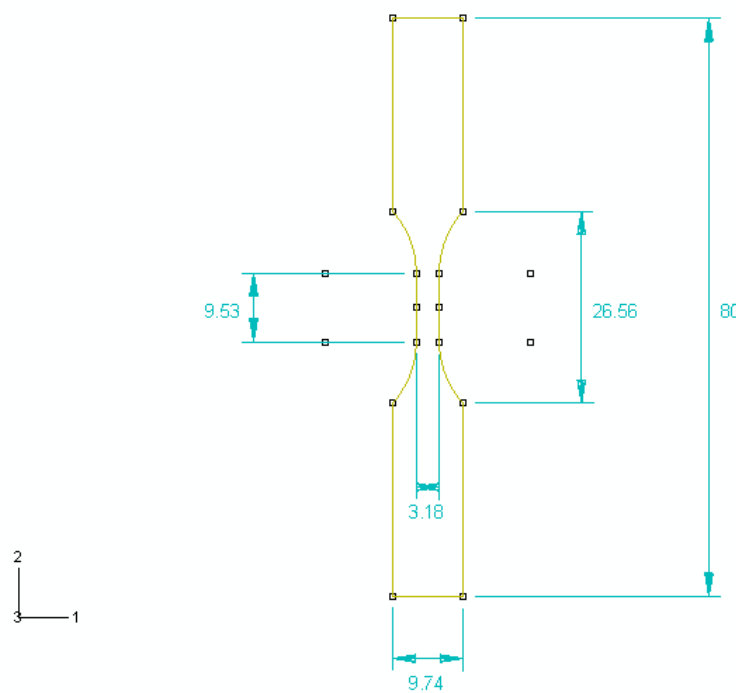


Figure 4.6. Dimensions (mm) of specimens for tensile test measurements

4.4.2. Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) is widely used for characterization of the viscoelastic behavior of polymer based composite materials. In order to describe the properties of viscoelastic materials, the modulus is commonly expressed as complex modulus, which is comprised by two terms, first is the storage modulus that expresses the materials' ability to restore energy when deformed and second is the loss modulus that describes the dissipation of energy into heat when a material is deformed. The storage modulus E' is closely related to its elastic modulus. The loss modulus E'' reflects damping effects in the viscoelastic material and is evaluated by energy loss due to the intermolecular friction. In order to express the dynamic mechanical property of the viscoelastic material loss tangent is introduced by $\tan\delta = E''/E'$. In general, when the loss tangent increases, the energy loss that is generated and dissipated in the material increases [1].

In order to characterize the thermomechanical properties, the composites with different nanotube concentrations were tested with a dynamic mechanical thermal analyzer. A TA Instruments Q800 was used in dual cantilever beam test mode (Figure 4.7). Samples that have dimensions 80 mm span length, 8 mm width, and 2.5 mm thickness, were tested in a temperature range of 30 °C-200 °C. This temperature range covers the transitions of the neat epoxy and composites. The tests were run at a heating rate of 3 °C/min with oscillating frequency of 1Hz. Storage modulus E' , loss modulus E'' and $\tan\delta$ curves were recorded by DMA.

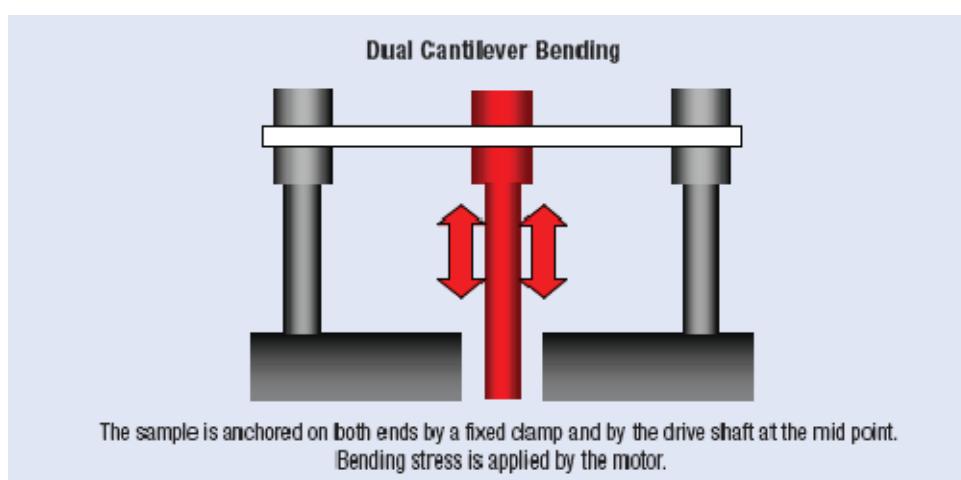


Figure 4.7. Dual cantilever beam mode in DMA [77]

4.4.3. Microhardness Test

Microhardness measurements were carried out at room temperature by using Shimadzu Microhardness Tester equipped with a diamond square pyramid having an included angle at the tip of 136°. A load of 100 g was applied for 15 seconds from time of contact of the diamond until the load was removed. The lengths of the diagonals of the indentation formed by the diamond were measured immediately after the removal of the load using a micrometer eyepiece mounted on the microscope. In order to facilitate the process of sample preparation for Vicker's indentation measurements, short bars (3 mm x 9 mm x 10 mm) of neat epoxy and composites reinforced with 0.1 wt. per cent, 0.2 wt. per cent and 0.4 wt. per cent of BNNT were cut and mounted in acrylic resin, followed by polishing to 3 µm surface finish by using Struers DiaPro. Microhardness was calculated from the equation:

$$H_v = \frac{2 F \sin\left(\frac{\theta}{2}\right)}{\left(\frac{d_1 + d_2}{2}\right)^2} \quad (4.1)$$

where θ , d_1 , d_2 and F denote the face angle of a pyramidal indenter, two diagonal lengths (mm) and test load (kg-f), respectively. A total of 10 points on each of the neat epoxy and BNNT/epoxy polymer composites were measured in order to get average readings.

4.5. Examination of Fracture Surfaces

The fracture surfaces of the failed tensile test specimens were analyzed by Philips XL30 ESEM-FEG/EDAX system by operating at the secondary imaging mode at an accelerating voltage of 5-10 kV. They were sputter coated with a thin gold layer prior to observation to get a good conductive path. Nanotube dispersion and effect of BNNTs to the epoxy matrix were investigated.

4.6. Thermal Characterization of Composites

4.6.1. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is an analytical technique used to determine the material's thermal stability and its fraction of rapidly evaporating components by recording the weight change that occurs as a specimen is heated in air or controlled atmosphere [78]. In order to obtain information on the effect of the BNNTs on the thermal stability of epoxy composites, TGA was performed for neat epoxy and BNNT/epoxy polymer composites. TGA was carried out on a TA Instruments TGA-Q50 at a temperature range 25-575 °C with a heat rate of 10 °C under nitrogen atmosphere which prevents the mass loss due to BNNT oxidation. Mass loss was obtained as a function of temperature. The initial weight loss in the TGA plots can determine whether DMF was completely evaporated during the preparation of composite or not. The temperature that decomposition starts, T_{onset} , the temperature of maximum rate of weight loss, T_{max} and char yield at 550 °C were obtained from TGA curves.

4.6.2. Differential Scanning Calorimetry Analysis

The glass transition temperature, T_g , of a polymer separates regions of dramatically different polymer properties. A polymer behaves like a hard, brittle, elastic solid below T_g . In this glassy region, the motion of polymer chains is frozen and strain occurs by stretching of bonds. The elastic modulus decreases with increasing temperature in this region. On heating above T_g , an entangled, amorphous polymer shows a rubbery region in which it is soft and pliable due to the ability of polymer chain segments and entire polymer chains to move past each other in a reversible manner [79].

One of the methods of measuring T_g is through the use of a differential scanning calorimeter (DSC). A DSC contains two sample holders, each provided with its own heater. The actual sample is placed in one of the sample holders in an aluminum pan and other sample holder contains an empty pan as a reference. The temperature of both the sample holders is increased at a constant rate, such as 10 °C/min and the difference in the

energy H supplied to the two pans is measured to keep them at the same temperature at all times. From an energy balance, the rate of differential heat flow is:

$$\frac{dH}{dt} = mc_p \frac{dT}{dt} \quad (4.2)$$

where m is the mass of the sample, c_p is the specific heat and dT/dt is the programmed rate of temperature increase. If the specific heat increases on heating the polymer sample through the glass transition temperature, dH/dt must go from one constant value to a higher constant value at T_g . Thus T_g can be determined by plotting dH/dt as a function of the instantaneous sample temperature [79].

Characteristics of polymer which raise T_g will have tendency to raise its maximum use temperature. In general, thermosets have higher thermal stability temperatures than thermoplastics because the crosslinks in thermosets raise T_g [80].

In order to determine the effect of BNNTs to the glass transition temperature of epoxy matrix, DSC analyses of neat epoxy and BNNT/epoxy polymer composites were performed with differential scanning calorimeter (DSC Q200, TA Instruments, New Castle, DE, USA) under nitrogen atmosphere at a heating rate of 10 °C/min between -10 °C and 160 °C.

5. RESULTS AND DISCUSSION

5.1. Characterization of BNNTs

Morphology and content of as-received BNNTs were investigated by using scanning electron microscope (SEM), energy dispersive X-ray analysis (EDAX) and X-ray diffraction analysis (XRD).

Figure 5.1 shows the SEM image of the as-received BNNTs. Nanotubes are highly entangled and randomly organized. They have formed small bundles and aggregates. Lengths of the nanotubes can be followed up to 10 μm . An interesting morphology can be obviously seen in the sample. In Figure 5.1 a large nanotube bundle that forms helical shape is observed. In this bundle, nanotubes have lengths more than 50 μm . There are also non tubular structures beside the nanotubes that can be observed in SEM images.

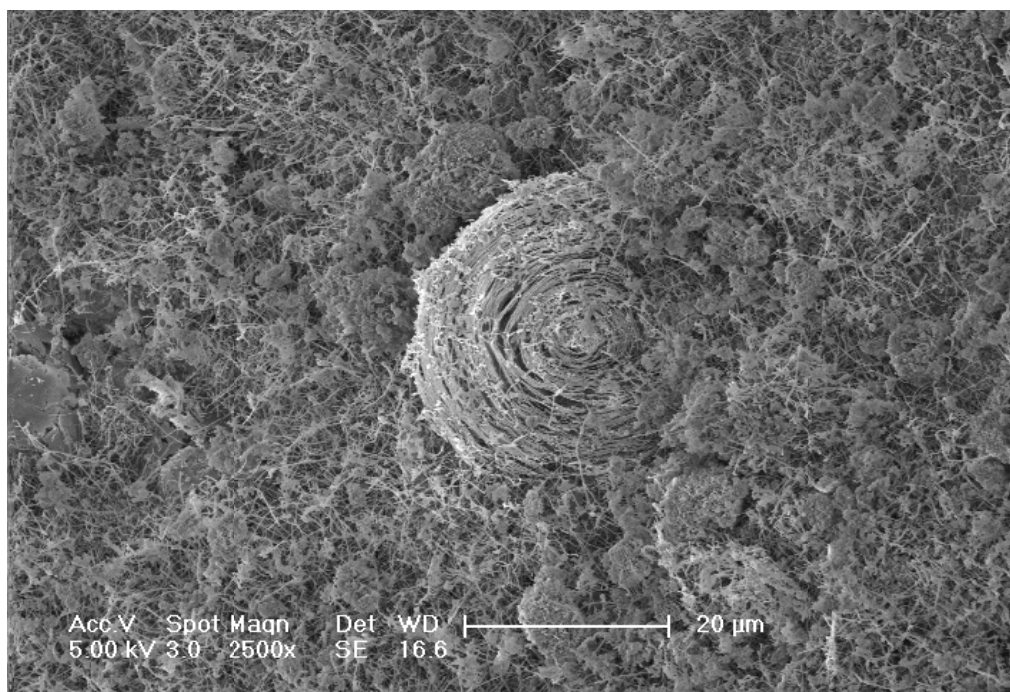


Figure 5.1. SEM image of the entangled BNNTs

Figure 5.2 shows individual nanotubes that have outer diameter varying from 60 nm to 120 nm. Most of them have good cylindrical structures. A broken twisting BNNT that has diameter of 70 nm can be seen in Figure 5.3.

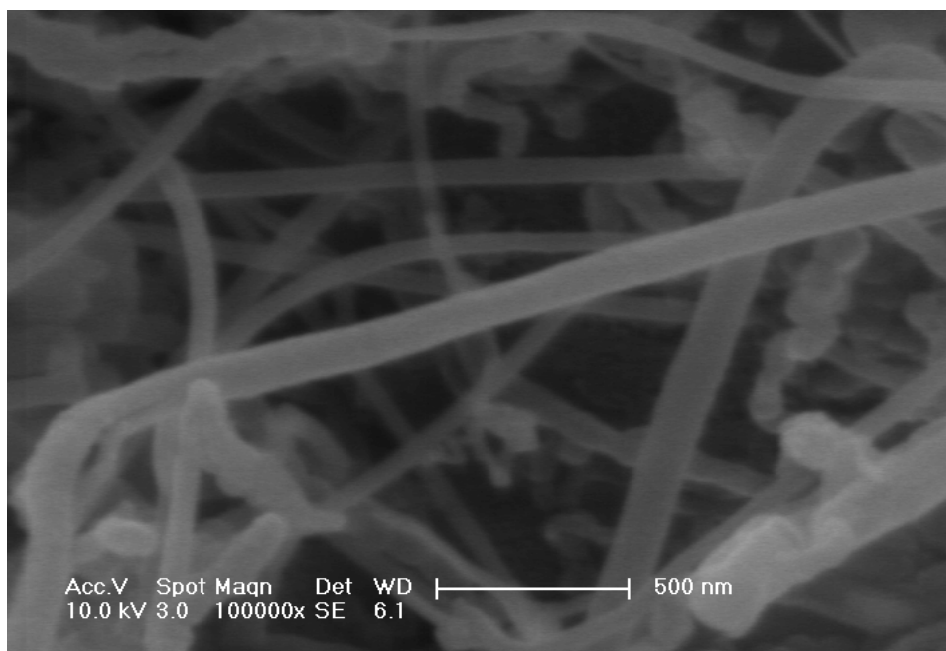


Figure 5.2. SEM image of the individual nanotubes

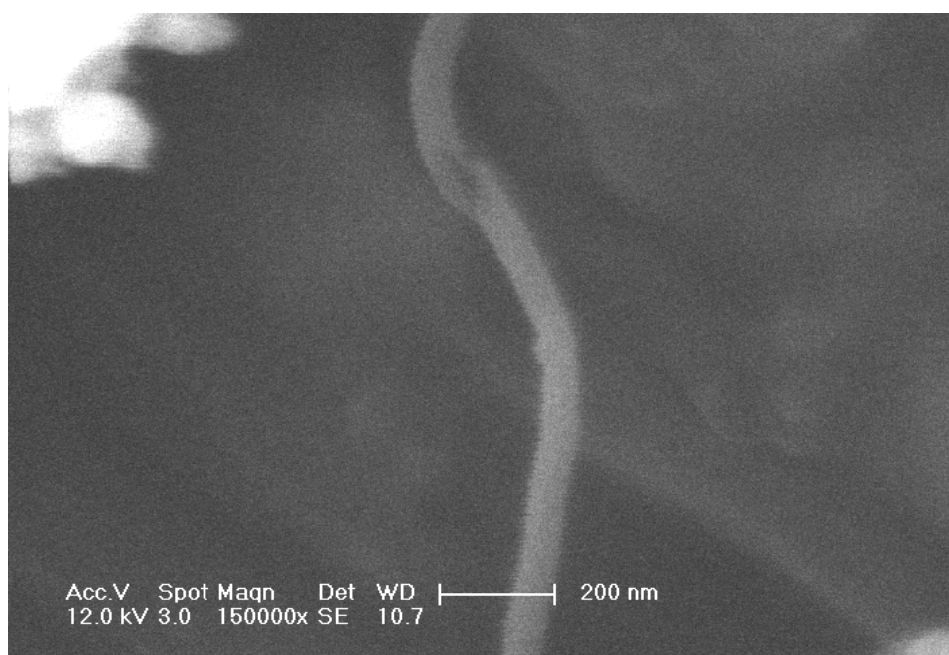


Figure 5.3. High magnification SEM image of a broken BNNT

In Figure 5.4, SEM image shows the bumpy surface and the closed tip of BNNTs. Bright particles are observed at the end of the tubes. As can be seen in the literature [74], the brightness is probably due to the metal particles. Bamboo-like tubes are most often capped with a Fe particle which appears to have catalyzed the nanotube growth. The as-received nanotubes synthesized by ball milling and annealing method [74] contains Fe contamination that comes from abrasion of steel balls and the milling container.

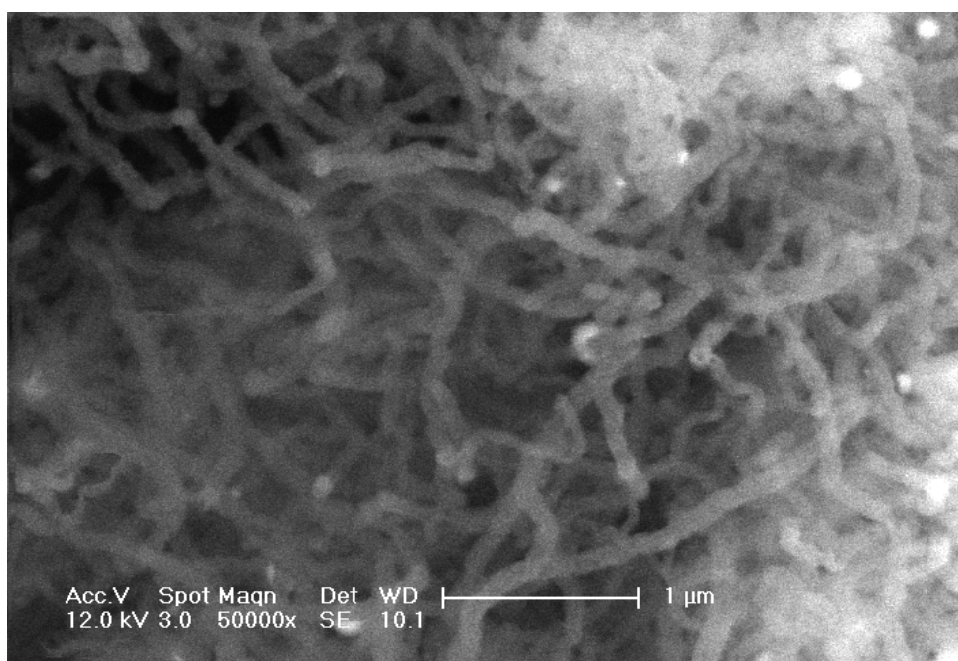


Figure 5.4. SEM image of BNNTs that have encapsulated catalyst particles at their tip

EDAX spectrum of BNNTs and atomic ratio of present elements are shown in Table 5.1 and Figure 5.5. The atomic ratio of B:N was determined as 50.88:40.87 indicating that beside BN there is an excess amount of boron. There are also O, Mg, Si, Cr and Fe impurities whose atomic ratios are 3.67, 0.32, 0.63, 0.21 and 3.42, respectively.

Table 5.1. EDAX ZAF quantification of as-received BNNTs

Element	wt. %
B	50.88
N	40.87
O	3.67
Mg	0.32
Si	0.63
Cr	0.21
Fe	3.42

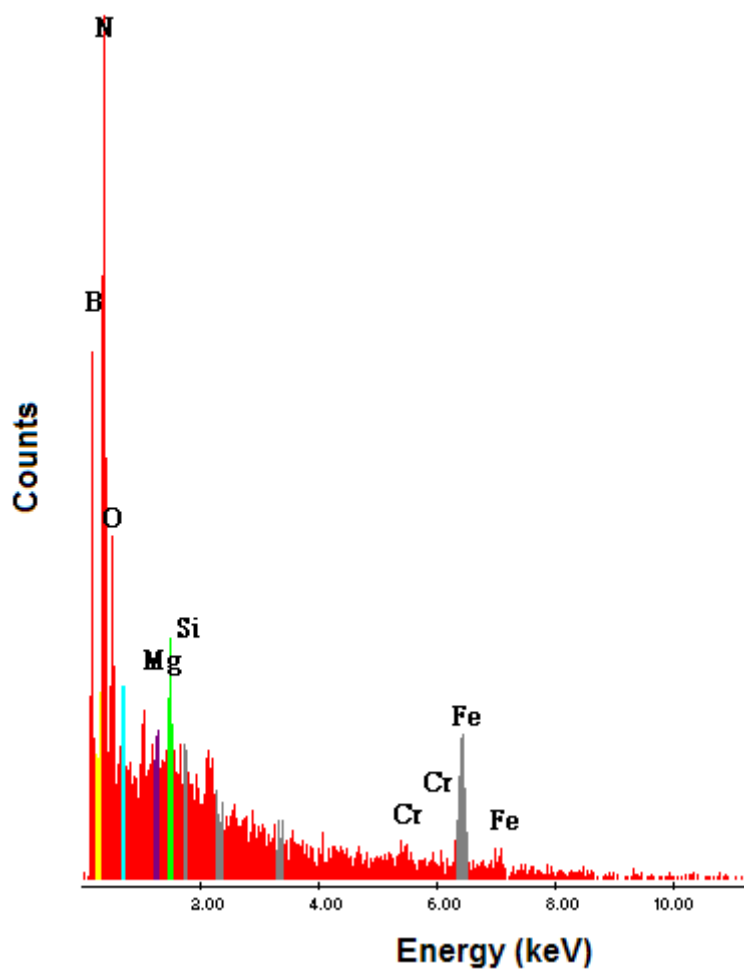


Figure 5.5. EDAX spectrum of the as-received BNNTs

Figure 5.6 shows the XRD pattern of the as-received BNNTs. Three peaks at d-spacings of 3.3306, 2.1685 and 1.6653 Å can be indexed as hexagonal BN with lattices (002), (100) and (004), respectively. The lattice constants are calculated as $a = 2.504$ Å and $c = 6.661$ Å, which are very close to the reported values of hexagonal BN, $a = 2.503$ Å and $c = 6.661$ Å (JCPDS card no. 73-2095). Beside BN, a martensite $C_{0.09}Fe_{1.91}$ phase (JCPDS card no. 76-0545) and $MgFeSi_2O_6$ phase (JCPDS card no. 44-1292) are detected in the XRD pattern. Martensite phase comes from steel balls and steel container that are used for ball milling and it is responsible for the catalysis of the nanotube growth. $MgFeSi_2O_6$ is not an expected phase for the as-received material, it may be caused by use of ceramic container during anneal of the nanotube at 1000-1200°C. Low intensity of $MgFeSi_2O_6$ phase confirms the data taken from the EDAX analysis. In XRD analysis Cr phase cannot be determined while a low percentage of Cr has been detected in EDAX analysis. This may be due to the local existence of Cr in the sample.

Preparation of good nanotube dispersion is the most critical step for developing high performance nanotube reinforced polymer composites [69]. High power bath ultrasonication in solvents is one of the effective methods for preparation of homogenous and relatively aggregate free dispersions. In this study for the production of BNNT/epoxy polymer composites, DMF is used to prepare good dispersion of nanotubes. Morphology of BNNTs after high power bath ultrasonicated for 1 h in DMF was investigated by using SEM. Figure 5.7 shows the BNNTs after a dispersion treatment in DMF. It seems that roughness of BNNT surface increases by DMF treatment as compared to as-received BNNTs shown in Figure 5.4.

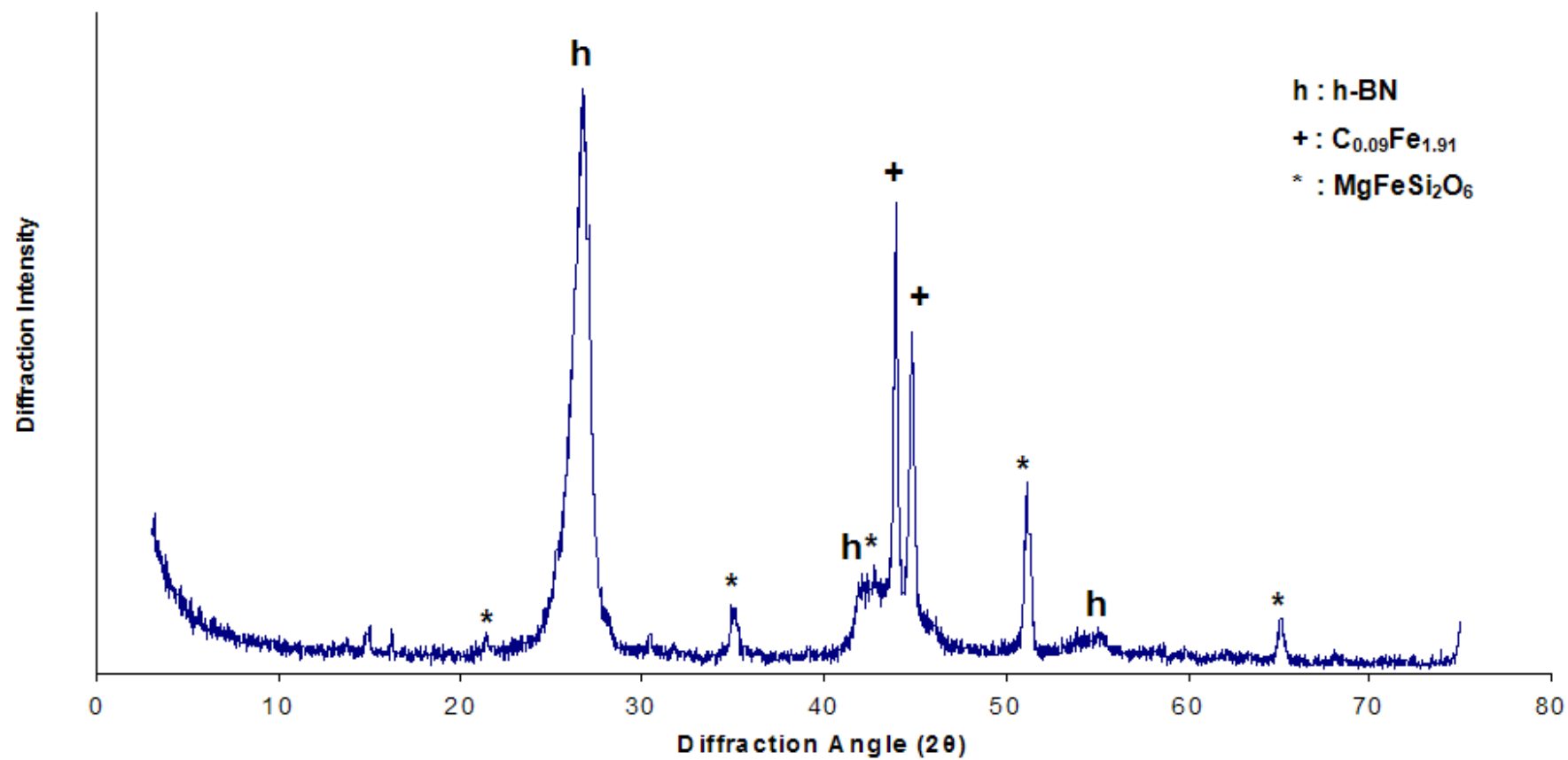


Figure 5.6. X-ray diffraction spectra of as-received BNNTs

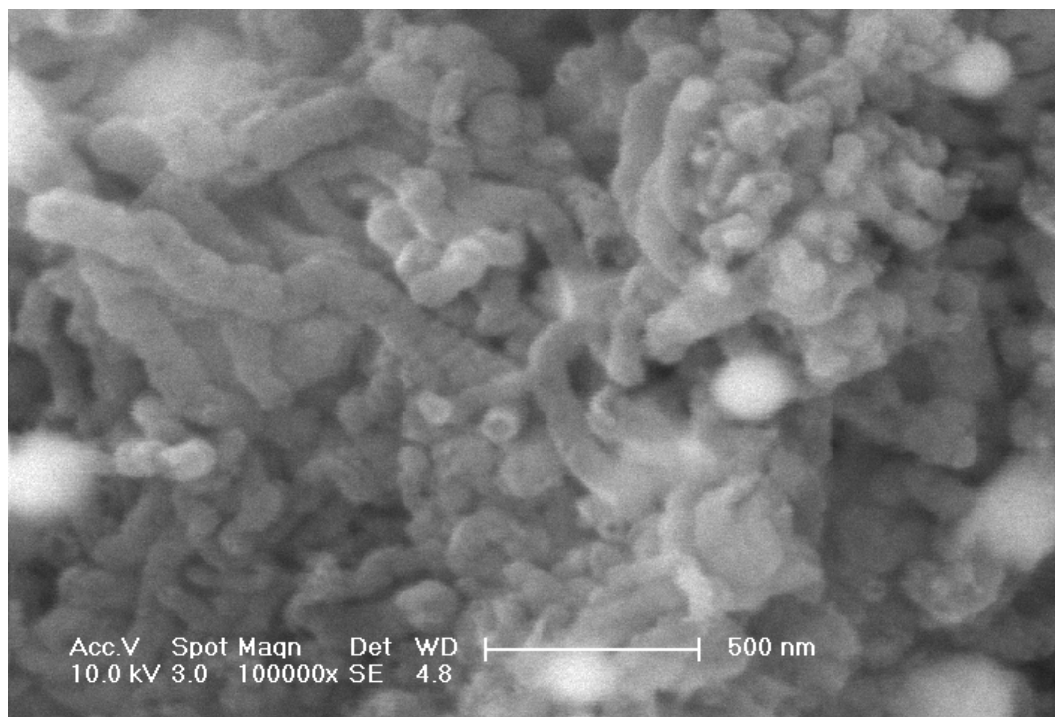


Figure 5.7. SEM image of BNNTs after a dispersion treatment in DMF

5.2. Characterization of BNNT Dispersion in Different Solvents

Substantial entanglement of nanotubes occurs during nanotube synthesis [74]. Successful production of nanotube/polymer composites depends on especially aggregate free mixtures of the nanotubes and matrix phase before polymer curing [81]. Agglomerates tend to weaken many characteristics of composites like reducing the mechanical properties, increasing the free volume and decreasing the glass transition temperature [82]. In the literature, it has not been found so much information about dispersion of BNNTs in organic solvents, but there are many studies about dispersion of carbon nanotubes and they give important information about nanotube dispersion.

To compare the stability of BNNTs in organic solvents, 200mg l⁻¹ concentration of BNNTs in acetone, ethanol and DMF was high power bath ultrasonicated for 1 h. Then they were hand shaken for 1 min to remove any gradients produced by non-uniform ultrasonication [74]. The dispersions were then placed on a shelf to observe their

aggregation behaviors. Figure 5.8, Figure 5.9 and Figure 5.10 show the dispersion of BNNTs in acetone, ethanol and DMF, respectively, after various ultrasonication durations. There are agglomerations of nanotubes precipitated in acetone for every time interval. In ethanol and DMF, it cannot be seen any precipitation at the bottom of bottle. DMF is the darkest solution as compared to ethanol and acetone.

Figure 5.11 shows the visual stability comparisons for BNNTs in acetone, ethanol and DMF after 1 h high power bath ultrasonication and at different time intervals. After 1h BNNT- acetone dispersion agglomerated rapidly, BNNT- ethanol dispersion agglomerated significantly and BNNT- DMF dispersion shows no signs of agglomeration. In acetone and ethanol dispersions BNNTs precipitate completely within one day, however BNNTs in DMF do not completely agglomerated after one week. This qualitative analysis shows that BNNTs are more stable in DMF as compared to acetone and ethanol.



Figure 5.8. Dispersion of BNNTs in acetone solution after 0, 15, 30, 45 and 60 minutes of high power ultrasonication, respectively



Figure 5.9. Dispersion of BNNTs in ethanol solution after 0, 15, 30, 45 and 60 minutes of high power ultrasonication, respectively



Figure 5.10. Dispersion of BNNTs in DMF solution after 0, 15, 30, 45 and 60 minutes of high power ultrasonication, respectively

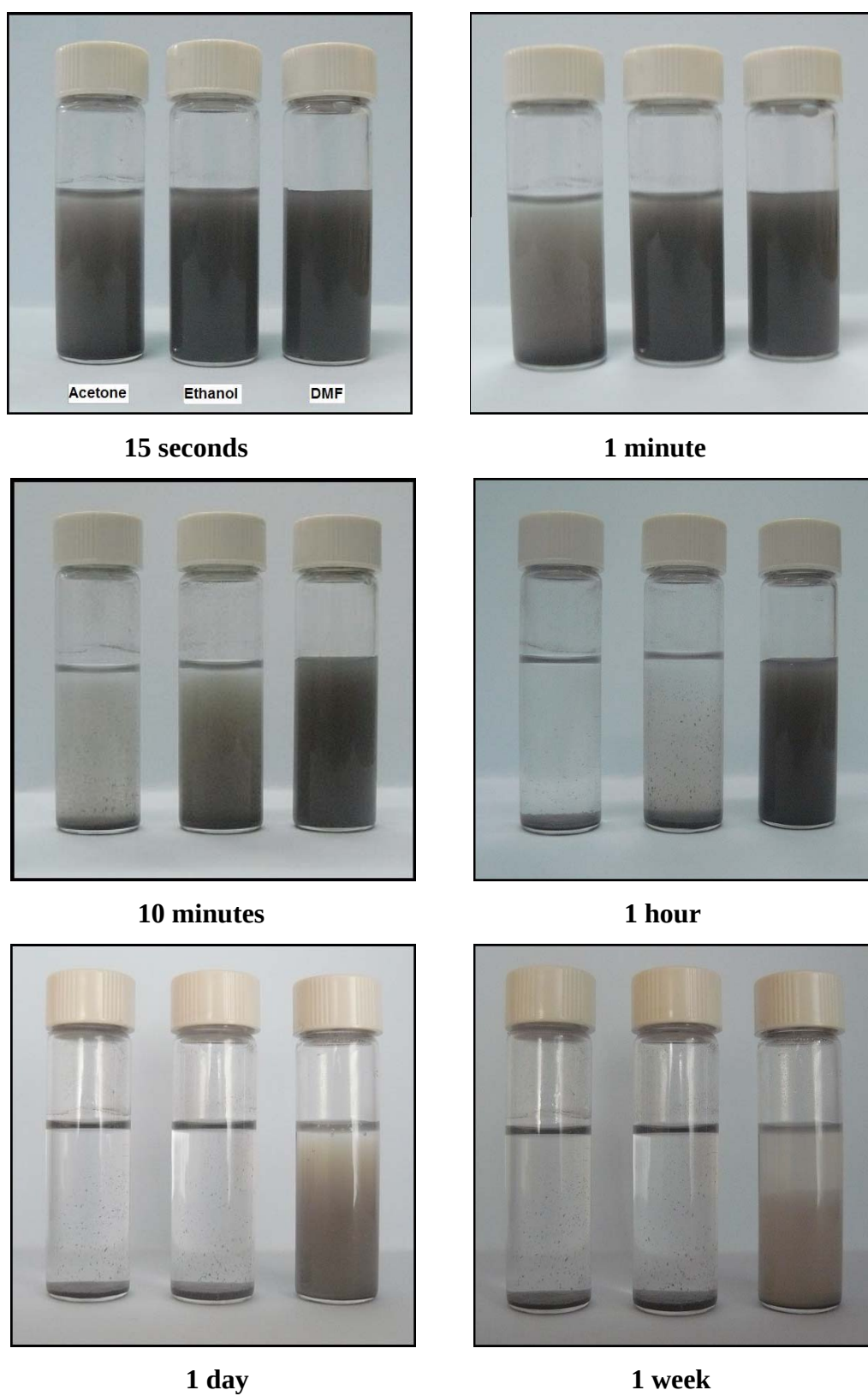


Figure 5.11. Dispersion stability comparison after various time intervals

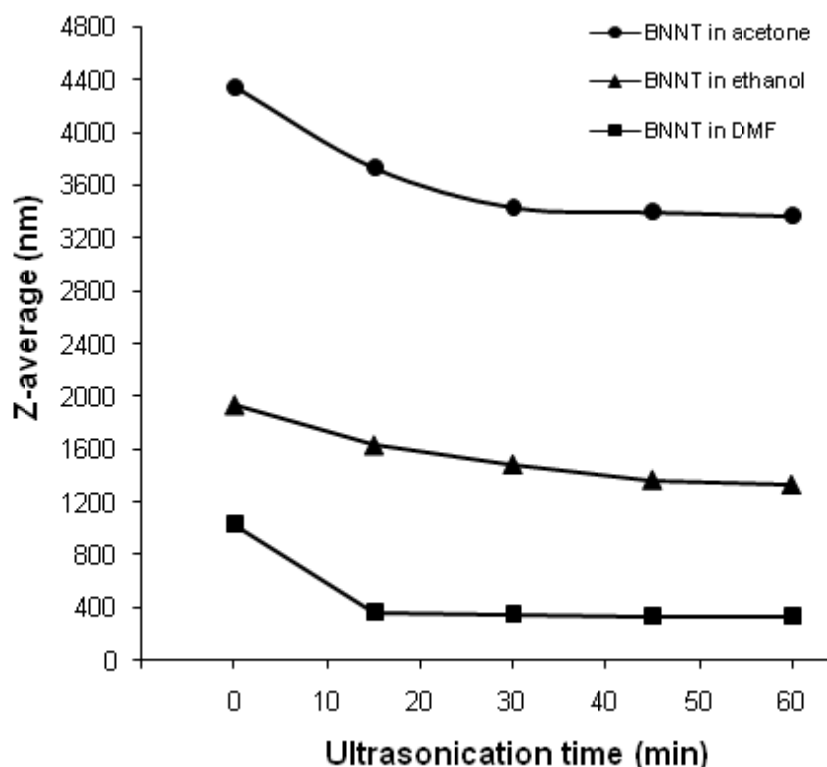


Figure 5.12. Agglomerate size analysis of BNNTs with respect to ultrasonication time in acetone, ethanol and DMF

BNNTs were ultrasonicated in acetone, ethanol and DMF solutions (200mg l^{-1}) for various durations and their agglomerate sizes were then measured immediately by using nanoparticle size analyzer as shown in Figure 5.12. In a solution, particles move randomly and their speed of movement is used to determine the size of the particles. The z-average diameter is the mean diameter of the agglomerates based on the intensity of scattered light. All samples were ultrasonicated for maximum one hour, because prolonged ultrasonication can separate nanotubes by breaking them into short pieces. Short nanotubes are not required because they cannot maximize the stress transfer ability which is an important factor for producing a high performance composite [83].

For all of the ultrasonication durations, efficiency of DMF for making stable BNNT dispersion is much better as compared to ethanol and acetone. These results are all in agreement with the results that were observed for carbon nanotube dispersion in literature [74]. DMF has been used by many researchers to reduce the agglomerate size of nanotubes in long procedures before curing of polymers [63, 74, 84]. However, thermal and

mechanical properties of composites decrease significantly, if entire DMF cannot be removed from the polymer matrix because of its high boiling point (151°C) [85].

5.3. Mechanical Characterization of BNNT / Epoxy Composites

5.3.1. Tensile Properties

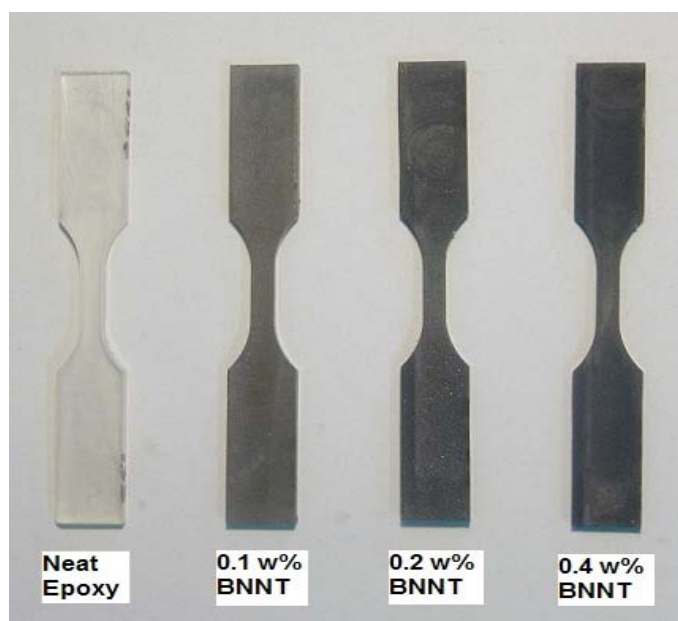


Figure 5.13. Tensile test specimens for neat epoxy and composites reinforced with 0.1, 0.2 and 0.4 wt. per cent BNNT

Tensile tests were started immediately after placing the specimen in the grips according to test method ASTM D638 with a cross-head speed of 1mm/min. A correction was used in order to determine the zero strain point by applying a tangent to the point of the maximum slope, because specimens were not pre-stressed at the beginning of tensile tests. The point that tangent line crosses the strain axis corresponds to the corrected zero point. Prepared tensile test specimens for neat epoxy resin and composites reinforced with different weight percentages of BNNT are shown in Figure 5.13. It can be clearly seen that the specimens become dark in color with the increase in nanotube concentration. There are different numbers of successful specimens for different percentages of nanotube loading, because some of them, especially specimens with 0.2 wt. per cent and 0.4 wt. per cent of

nanotube, were broken out of the gage length. Figure 5.14 shows a broken tensile test specimen of BNNT/epoxy composite with 0.1 wt. per cent of nanotube. It does not show necking and suddenly ruptures. This confirms the brittle behavior of thermosets.



Figure 5.14. Typical broken tensile test specimen

Thermosetting resins have been considered to be brittle materials, because it is assumed that the crosslinking in thermosets prevents extensive viscous flow [86]. Figure 5.15 shows the representative stress strain curves of neat epoxy resin and epoxy composites reinforced with 0.1 wt. per cent, 0.2 wt. per cent and 0.4 wt. per cent BNNT, respectively. The brittle behavior of examined materials can be seen by their stress strain relation. The stress strain curves show non linearity before reaching maximum stress, but no obvious yield point can be found in the curves. The data provided in Table 5.2 is the average and standard deviation values of the modulus, ultimate strength and break strain of neat epoxy and composites with different wt. per cent of BNNT. The tensile modulus, ultimate strength and break strain of all successful specimens are provided in Appendix B.

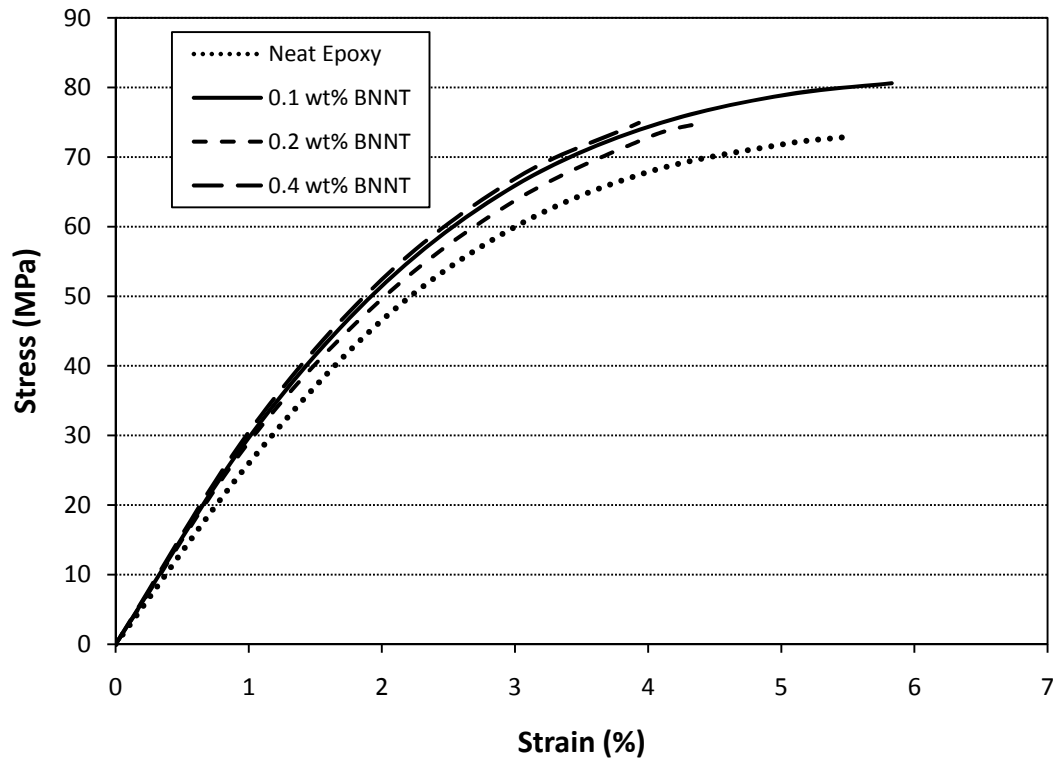


Figure 5.15. Representative tensile behaviors of neat epoxy and BNNT/epoxy polymer composites with 0.1 wt. per cent, 0.2 wt. per cent and 0.4 wt. per cent of nanotubes

Table 5.2 shows evidently enhancement in modulus and ultimate strength for all nanotube reinforced composites. The maximum tensile modulus increase of 13.6 per cent is observed for 0.4 wt. per cent BNNT loaded composites as compared to neat epoxy. 10.6 per cent and 10.3 per cent increases are observed in tensile modulus for 0.1 wt. per cent and 0.2 wt. per cent BNNT loaded composites, respectively. The ultimate strength of neat epoxy is 72.9 ± 3.9 MPa. It increases to 74.9 ± 7.0 MPa and 74.9 ± 1.6 MPa for 0.2 wt. per cent and 0.4 wt. per cent nanotube loadings, respectively. The ultimate strength reaches the maximum value of 80.6 ± 2.1 MPa at 0.1 wt. per cent BNNT loading, which is 10.6 per cent greater than that of the neat epoxy. The tensile strength is higher for composites with 0.1 wt. per cent of nanotube probably because of the better BNNT dispersion compared to those of composites with 0.2 and 0.4 wt. per cent of nanotubes.

Table 5.2. Tensile modulus, ultimate tensile strength and break strain of materials

Material	Tensile Modulus (MPa)	Ultimate Tensile Strength (MPa)	Break Strain (%)
Neat Epoxy	2683 ± 83	72.9 ± 3.9	5.50 ± 1.64
0.1 wt. % BNNT Loaded Epoxy Composite	2967 ± 166	80.6 ± 2.1	5.83 ± 1.17
0.2 wt. % BNNT Loaded Epoxy Composite	2960 ± 200	74.9 ± 7.0	4.40 ± 1.02
0.4 wt. % BNNT Loaded Epoxy Composite	3048 ± 270	74.9 ± 1.6	3.93 ± 0.17

The break strain of BNNT / epoxy polymer composites slightly increases from 5.50 ± 1.64 per cent to 5.83 ± 1.17 per cent with 0.1 wt. per cent nanotubes loading. The break strain of composites with a further increase in nanotube concentration is seen to be comparatively less than that of neat epoxy resin indicating an increase in brittleness. The break strain declines to 4.40 ± 1.02 per cent for 0.2 wt. per cent nanotube loading and 3.93 ± 0.17 per cent for 0.4 wt. per cent nanotube loading. This is possibly due to the presence of nanotube aggregates in BNNT- epoxy mixture.

This study indicates that tensile modulus, ultimate strength and break strain enhancement are achievable in BNNT/epoxy polymer composites if proper processing parameters and good dispersion are provided. Fully dispersed BNNTs in epoxy contribute to tensile modulus enhancement and good interfacial bonding between nanotube and epoxy matrix which plays a major role in strength increase.

The tensile modulus of BNNT/epoxy composites, that are experimentally obtained in this study, are compared with theoretical values that are determined according to the modified rule of mixtures (Eq. 3.6) for short and non-aligned fibers and Halpin-Tsai model for randomly oriented composites (Eq. 3.11).

In theoretical calculations, aspect ratio and elastic modulus of BNNTs are taken as 500 and 1000 GPa, respectively. Experimental value for the elastic modulus of the neat epoxy is as matrix modulus. In order to calculate nanotube volume fraction, the density of matrix is taken as 1.16 g/cm^3 [73], but no data can be found for BNNT density. While graphite has a density of 2.25 g/cm^3 , the density of carbon nanotubes have been found as about 1.3 g/cm^3 [53]. That of boron nitride is also known as, 1.9 g/cm^3 . If the relation between the densities of graphite and carbon nanotubes is assumed to be similar to the relation between the densities of BN and BNNTs, for the density of BNNTs it can be reached to the approximate value of 1.1 g/cm^3 .

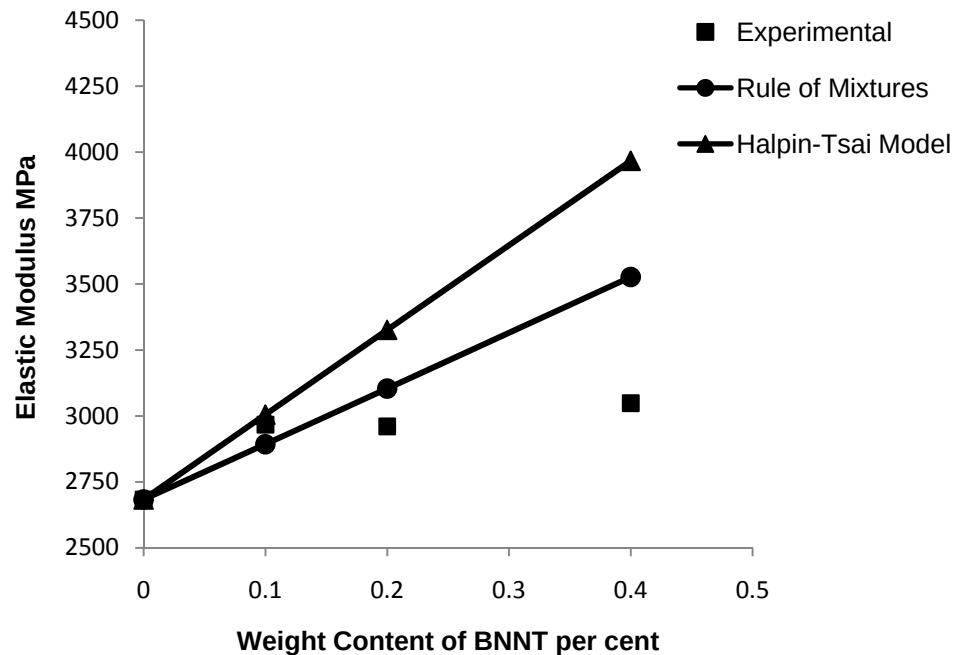


Figure 5.16. Comparison between experimental and theoretical values of elastic modulus for BNNT/epoxy composites

For 0.1 wt. per cent BNNT/epoxy composites experimental elastic modulus is greater than the theoretical one which is predicted according to the rule of mixtures, as can

be seen in Figure 5.16, and it is slightly less than the value that is calculated by Halpin-Tsai model. However, while further increase in nanotube content significantly increases the theoretical values, experimental ones do not change so much. This is possibly due to the presence of agglomerates and the decrease in the effective content of BNNTs in 0.2 and 0.4 wt. per cent BNNT reinforced composites. This behavior shows that BNNT content reaches a critical value for good dispersion and therefore, for tensile property enhancement in 0.1 wt. per cent BNNT reinforced composites.

The reinforcement of elastic modulus takes into account both the stiffness and amount of nanotube and it has the advantage that it allows the comparison of results in the literature. The experimental elastic modulus reinforcement, dY_C/dV_f , of composites reinforced with 0.1 wt. per cent BNNTs is determined as 270 GPa by using the equation,

$$(Y_C - Y_m) / V_f \quad (5.1)$$

In terms of the rule of mixtures (Eq. 3.16), the reinforcement is predicted as 180 GPa. For Halpin-Tsai model (Eq. 3.17), the reinforcement is 278 GPa.

Due to their wide range of industrial uses, epoxy resins have been widely used as a potential matrix for nanotube based composites. There are number of studies about carbon nanotube / epoxy composites, but no study about BNNT / epoxy polymer can be found in the literature. Therefore, the reinforcement that has been obtained in this experimental study is compared with the reinforcement of carbon nanotube based epoxy composites.

The reinforcement that has been observed in BNNT/epoxy composites is moderate when it is compared to other reinforcement values as shown in Table 5.3. According to rule of mixtures this experimental value is close to the maximum reinforcement for a material filled with non-aligned and well dispersed nanotubes.

Table 5.3. Reinforcement of nanotube/epoxy polymer composites in the literature

Resin / Hardener	Y_m (GPa)	Y_C (GPa)	Nanotube content %	dY_C/dV_f (GPa)	Reference
EPON 828/TETA	3.1	3.71	5	~18	[61]
EPON SU-8	4.2	5.0	0.1	~1200	[65]
DGEBA/TETA	0.118	0.465	4	~13	[66]
DGEBA/TETA	1.2	2.4	1	~330	[67]

5.3.2. Dynamic Mechanical Behavior

The storage modulus and $\tan \delta$ versus temperature plots of the neat epoxy and BNNT/epoxy composites are shown in Figures 5.17 and 5.18, respectively. During glass transition, the storage moduli of the composites are significantly decreased. The glass transition temperatures are determined as the onset temperature of decrease in the storage modulus E' of the composites [87]. Determined glass transition temperatures are 116.3, 117.4, 115.6 and 115.8 °C for the neat epoxy and composites with 0.1 wt. per cent, 0.2 wt. per cent and 0.4 wt. per cent of BNNTs, respectively.

The slight increase in the glass transition temperature of the composite reinforced with 0.1 wt. per cent of BNNTs may be explained in terms of free volume. If nanotubes are dispersed uniformly, more epoxy-nanotube interactions may occur and create a constrained region at the nanotube surface. Polymer chains packed onto the nanotube surface reduces the free volume. Mobility of the polymer segments near the interface is restricted and this leads to an increase in glass transition temperature [88]. Glass transition temperature of the composites with 0.2 wt. per cent and 0.4 wt. per cent of BNNTs decrease, because the amount of restricted polymer chains among the nanotubes decreases with some aggregated BNNTs [89].

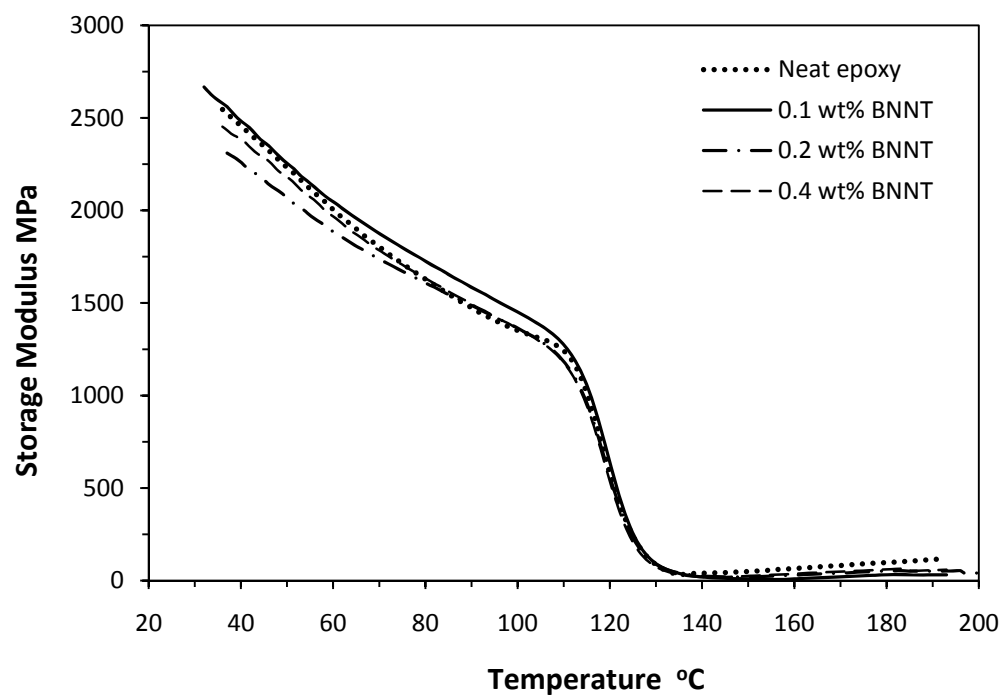


Figure 5.17. Storage modulus vs. temperature plots of the neat epoxy and BNNT/epoxy composites

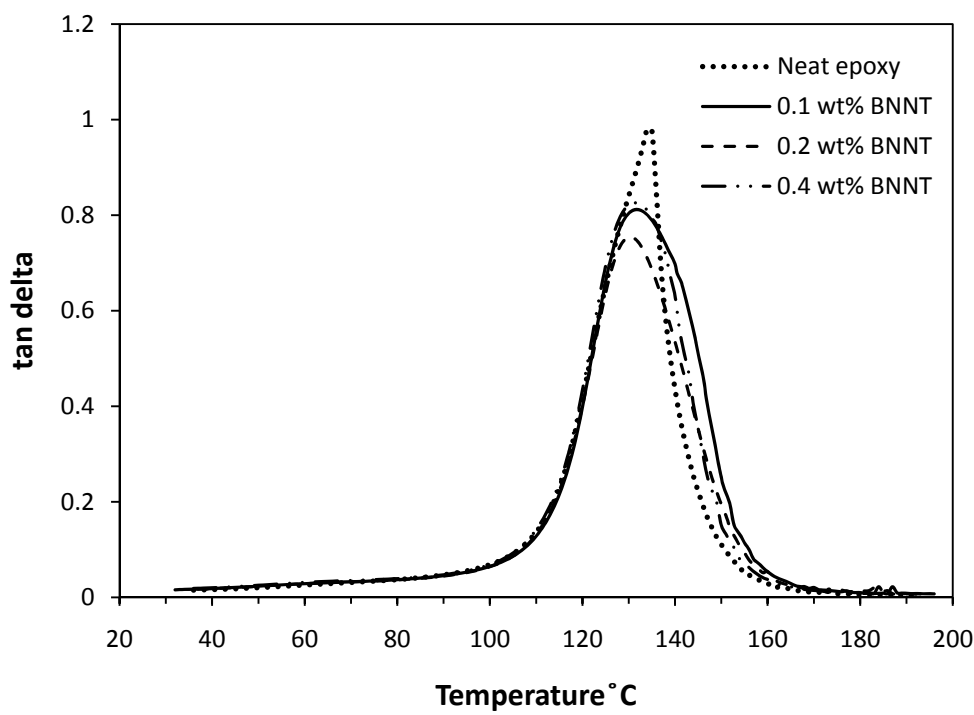


Figure 5.18. Tan δ vs. temperature plots of the neat epoxy and BNNT/epoxy composites

It is observed that maximum $\tan \delta$ values of the composites decrease by the incorporation of BNNTs. The decreased $\tan \delta$ is possibly due to the restricted mobility of the polymer chains by the uniformly dispersed nanotubes [90]. However, the height of the $\tan \delta$ peak for 0.4 wt. per cent BNNT reinforced composite increases, which may be attributed to the aggregation of nanotubes at relatively higher content in the epoxy resin.

5.3.3. Microhardness Measurements

Vicker's microhardness measurements were carried out at room temperature by using Shimadzu Microhardness Tester with a load of 100 g applied for 15 seconds. Star-shaped Vicker's impressions shown in Figure 5.19 were observed for neat epoxy and BNNT/epoxy polymer composites. Star shape exhibits the much greater extents of elastic recovery along the faces of the impression. However, the elastic recovery in the direction of the diagonals is generally negligible or very small. Therefore, the measurement of diagonal lengths gives valid hardness values for polymers. [91]

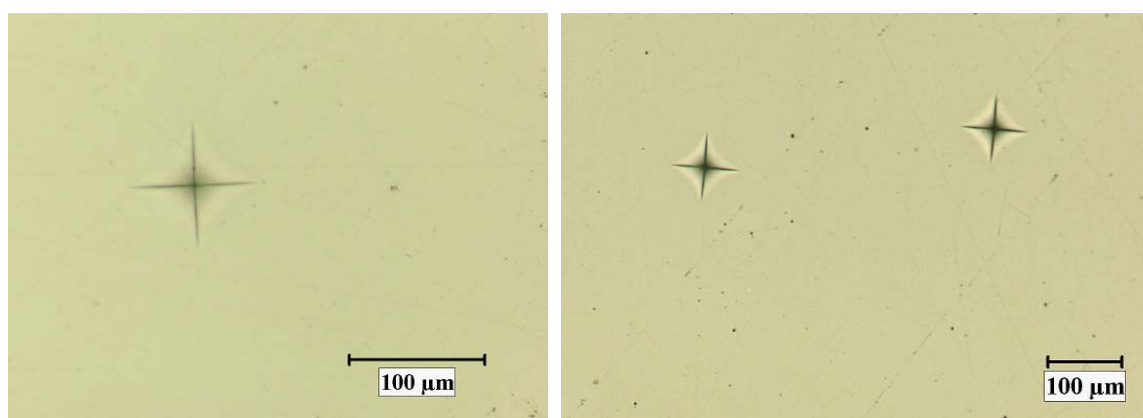


Figure 5.19. Morphology of Vicker's indent for neat epoxy and BNNT/epoxy composite

Vicker's hardness measurements for neat epoxy and composites reinforced with 0.1 wt. per cent, 0.2 wt. per cent and 0.4 wt. per cent of BNNT are shown in Figure 5.20. Hardness tends to increase with the increase in nanotube content. Average of ten measurements for neat epoxy and composites with 0.1 wt. per cent, 0.2 wt. per cent and

0.4 wt. per cent of BNNTs are 19.03, 20.74, 21.23 and 21.35, respectively. Vicker's hardness value reaches the maximum value at 0.4 wt. per cent BNNT loading that is 12.2 per cent greater than that of the neat epoxy.

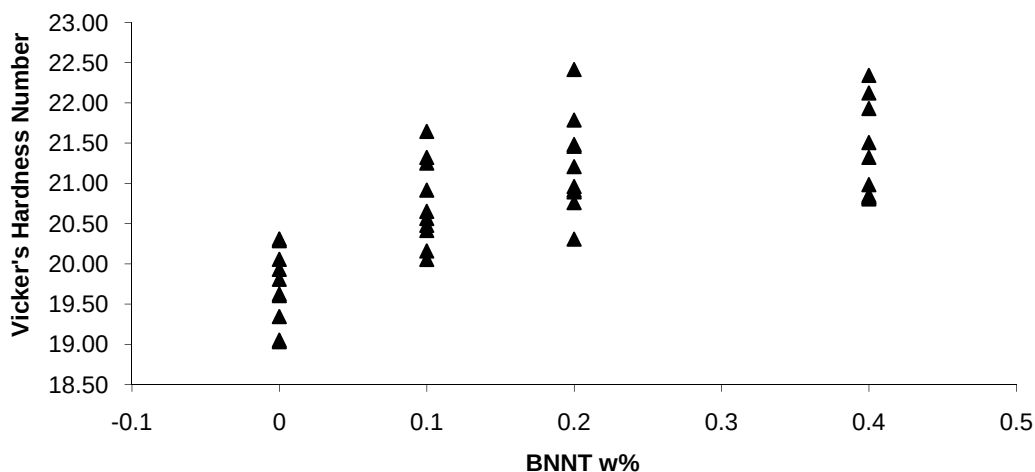


Figure 5.20. Vicker's hardness of neat epoxy and composites reinforced with 0.1 wt. per cent, 0.2 wt. per cent and 0.4 wt. per cent of BNNT.

5.4. Examination of Fracture Surfaces

Fracture surfaces of broken tensile test specimens of neat epoxy and BNNT/epoxy polymer composites with different nanotube contents were studied by SEM to see the state of nanotube dispersion in epoxy matrix and to characterize the process of failure. The features on the surface identify how the product failed. They show how a crack is initiated and grew with time.

Examination of tensile fracture surfaces of BNNT/epoxy polymer composites by using SEM reveals the presence of four zones which are shown schematically in Figure 5.21. These are defect, mirror zone, smooth zone and rough zone. Examined surfaces are differed from that of the filled epoxy resins mentioned in Ref [92] by lacking of debonded zone beyond the initiation region. In this zone filled particles are separated from matrix and act as a stress concentrator. On the fracture surface of BNNT/epoxy composites, it is not observed the presence of nanotubes departed from epoxy matrix beyond the initiation region.

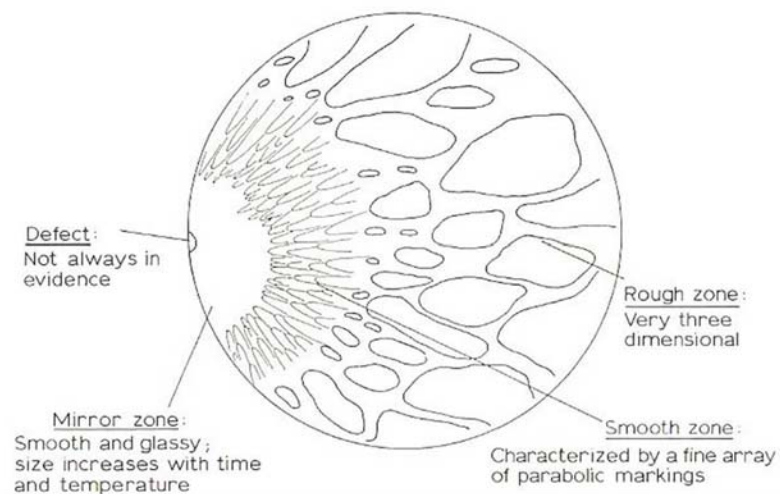


Figure 5.21. Schematic diagram of the regions on the fracture surfaces of neat epoxy and BNNT/epoxy polymer composites [92]

Initiation of the fracture is attributed to the presence of a defect [92]. It can arise from the specimen preparation that includes air bubbles, resin rich areas, mould scratches and foreign matter joined during molding by mistake. As can be seen in Figures 5.22, 5.23 and 5.24, fracture may begin due to a surface defect. Agglomerates and poorly bonded particles that link up and create larger units may also initiate fracture. For example as can be seen in Figure 5.25, fracture initiates due to nanotube agglomeration larger than 100 μm .

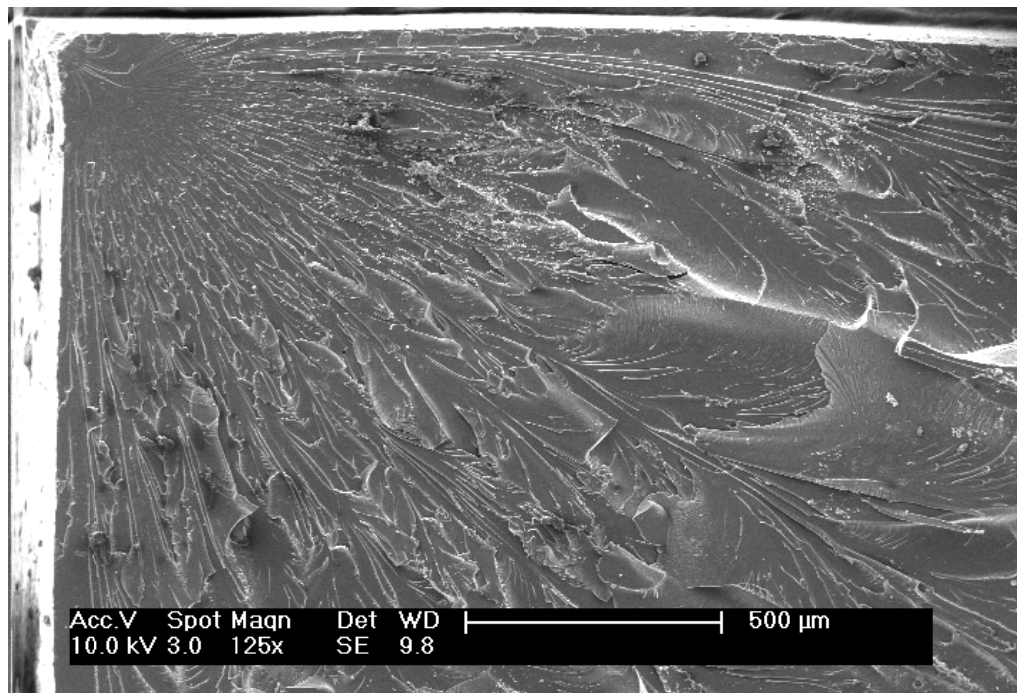


Figure 5.22. Fracture surface of neat epoxy

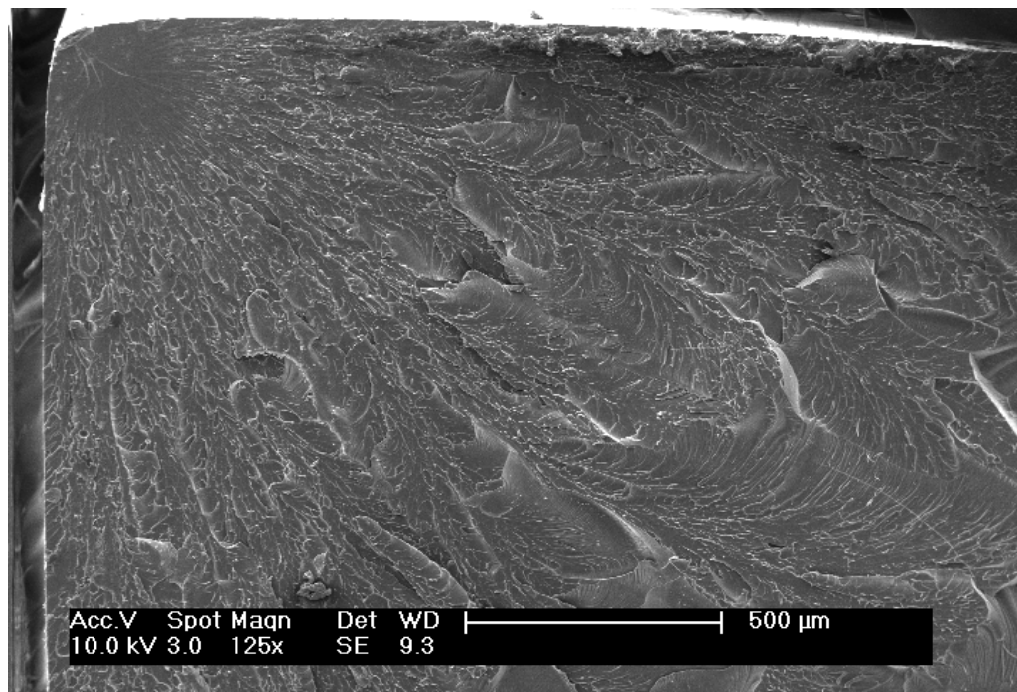


Figure 5.23. Fracture surface of the composite with 0.1 wt. per cent of BNNT

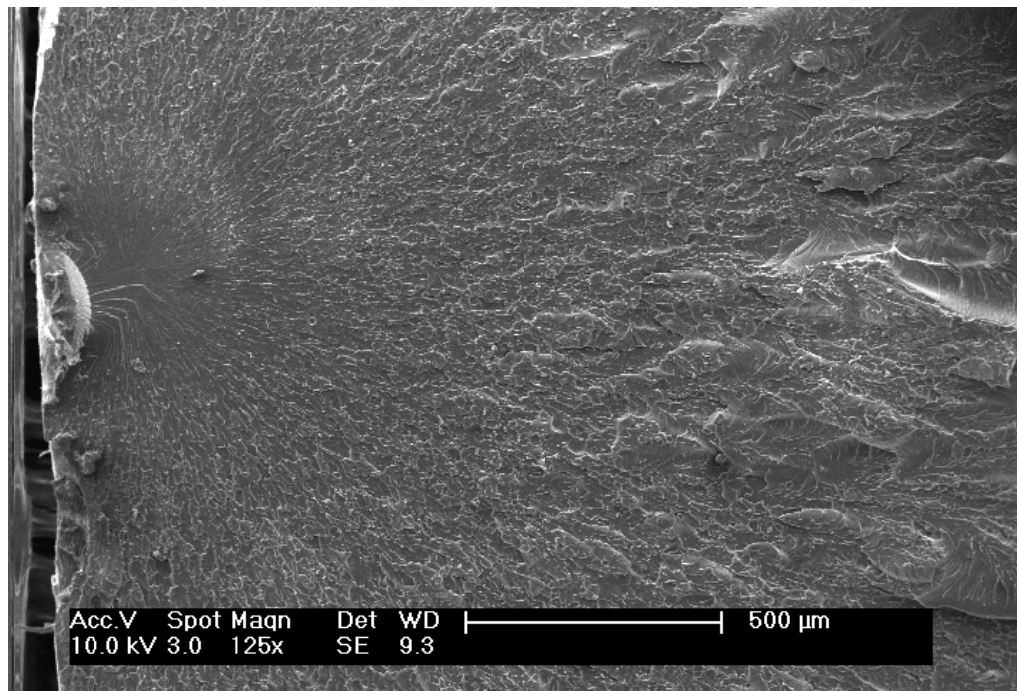


Figure 5.24. Fracture surface of the composite with 0.2 wt. per cent of BNNT

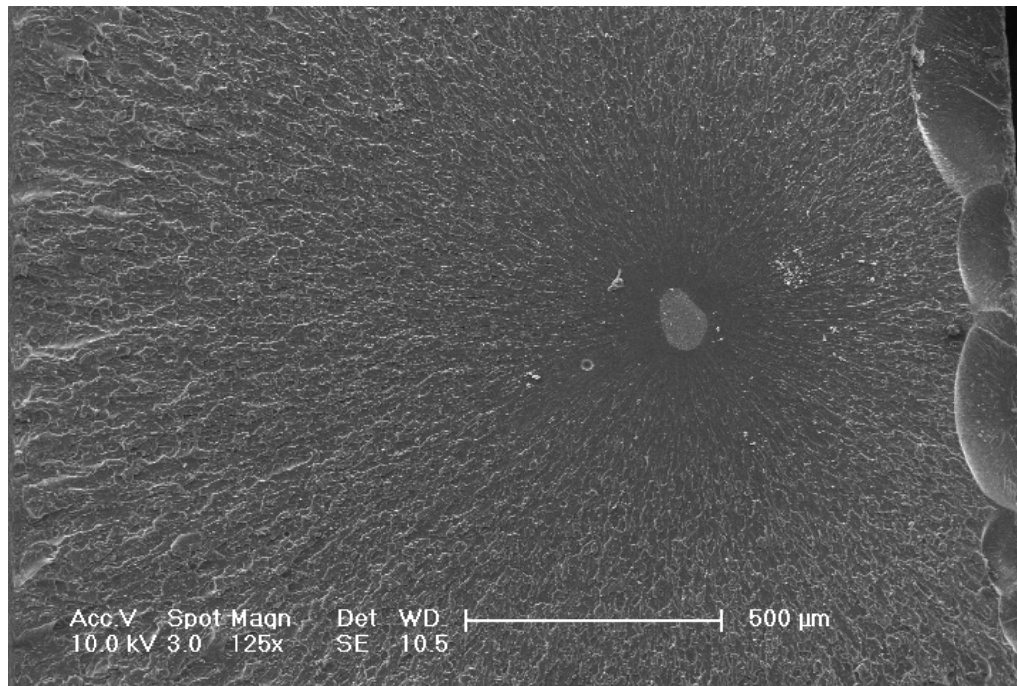


Figure 5.25. Fracture surface of the composite with 0.4 wt. per cent of BNNT

The area which surrounds the initiation region is generally smooth and featureless, therefore it is called mirror zone. It is associated with slow crack growth phase of the fracture [93]. The size of this area depends on the test temperature, the moisture content, the strain rate at failure and the resin flexibility [92]. It is not observed any significant size change for this zone due to nanotube loading. It is shown in Figures 5.26 and 5.27, the typical mirror zones of neat epoxy and composite with 0.4 wt. per cent BNNT loading, respectively. While there is no cavity on the surface of the neat epoxy, some cavities are seen on that of the composite.

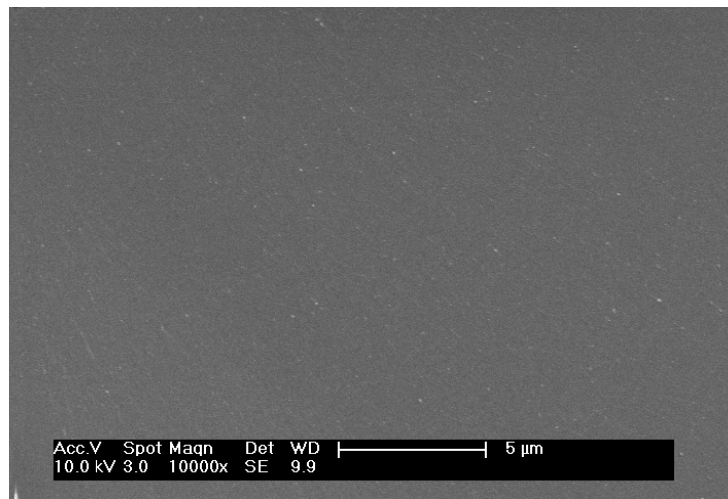


Figure 5.26. Mirror zone on the fracture surface of neat epoxy

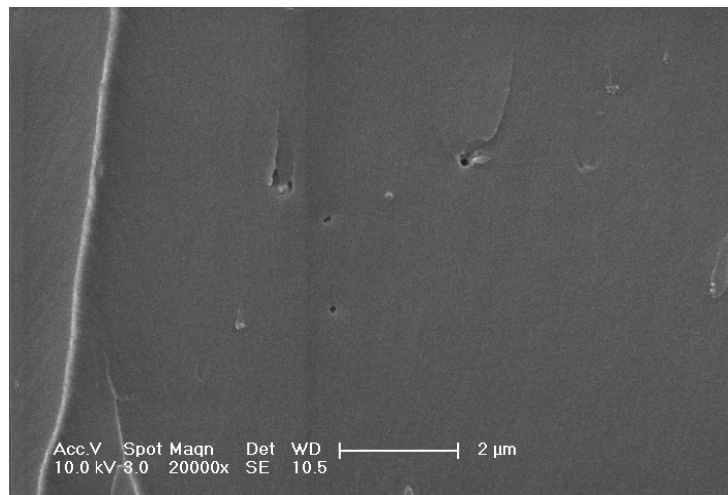


Figure 5.27. Mirror zone on the fracture surface the composite with 0.4 wt. per cent BNNT

Beyond mirror zone, surface is characterized by fine array of parabolic markings and termed as smooth zone [92]. It is sometimes called as mist region [93]. It corresponds to the region where the crack is accelerating. It can be seen from Figures 5.22, 5.23, 5.24 and 5.25 that the dimensions of this zone increase with increasing nanotube content of the composites.

The rest of the tensile fracture surface is very rough and three-dimensional. It indicates the fast crack propagation and considerable crack branching. This region is called as rough zone [92]. Further away from the origin of the fracture the parabolic features interact and overlap and produce more complex geometrical shapes. This region often covers most of the fracture surface. As can be seen in Figures 5.22, 5.23, 5.24 and 5.25, rough zone size of the tensile fracture surfaces and the depth of roughness tend to decrease with increasing nanotube content, however the number of features tends to increase with increasing nanotube content. The fracture surfaces of BNNT/epoxy polymer composites are relatively rough as compared to neat epoxy and shows great deal of short and highly curved patterns of crack propagation. In all of the examined fracture surfaces, lines radiating outward from the fracture origins are observed clearly.

Figure 5.28 shows the SEM image of the fracture surface of neat epoxy. It has areas of smooth fracture and it shows the uplifting of thin flakes of the material.

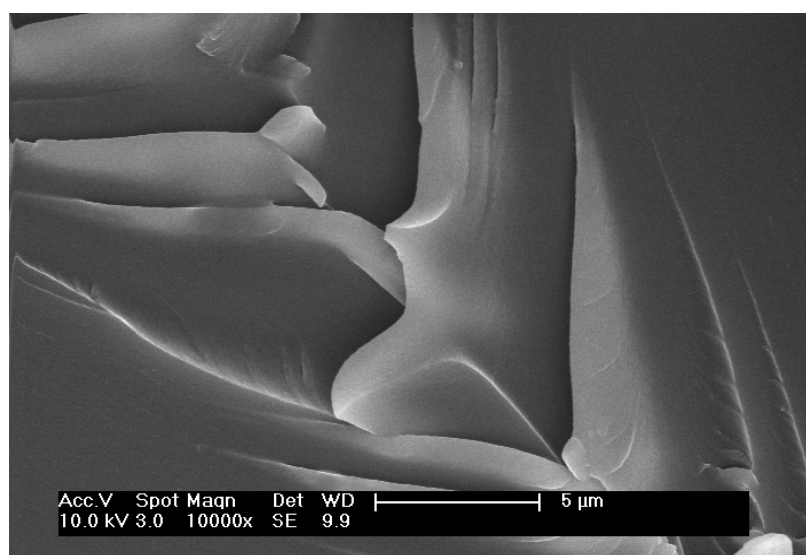


Figure 5.28. Fracture surface of neat epoxy

Figure 5.29 shows the river pattern of crack lines in the smooth zone of the fracture surface of composite with 0.1 wt. per cent nanotube loading. Some round cavities are observed. It can be seen in Figure 5.30 that the diameter of these holes is greater than 500 nm.

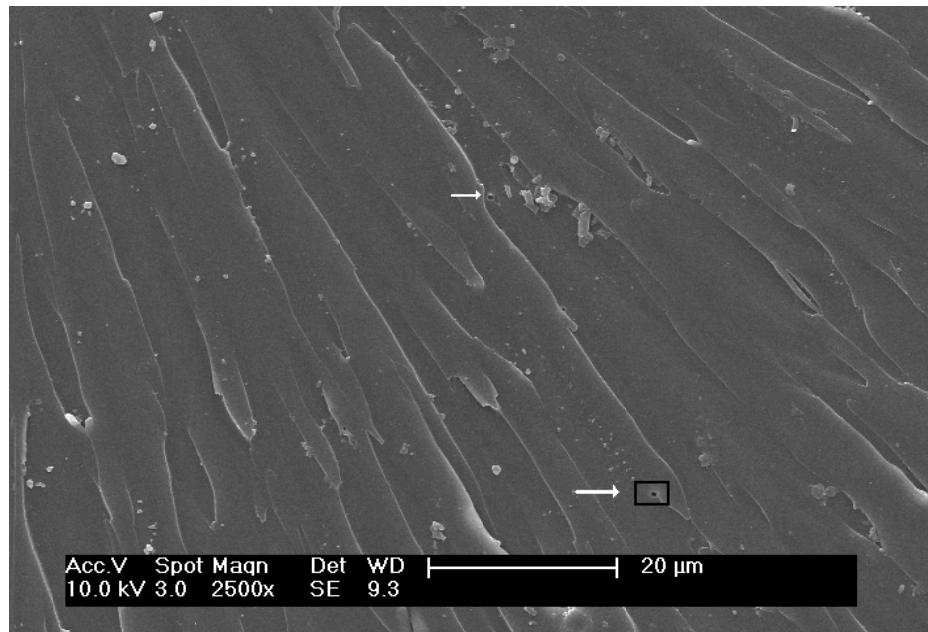


Figure 5.29. River pattern of the smooth zone on the fracture surface of the composite with 0.1 wt. per cent BNNT (Holes are shown with arrows)

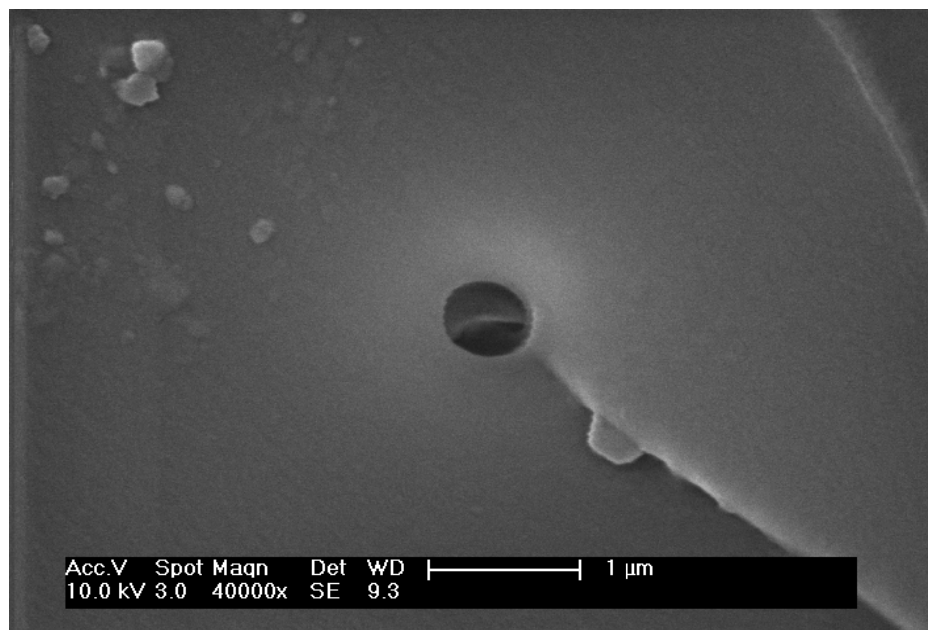


Figure 5.30. A typical hole on the fracture surface of the composite with 0.1 wt. per cent BNNT (High magnification of Figure 5.25)

Figures 5.31, 5.32 and 5.33 show the nanotube bundles on the fracture surface of BNNT/epoxy composite with 0.1 wt. per cent, 0.2 wt. per cent and 0.4 wt. per cent of nanotubes, respectively. The diameter of these bundles ranges from 300 nm to 600 nm, which is larger than that of the as-received nanotubes, as shown in Figure 5.2. This indicates that nanotubes are embedded and held to the epoxy matrix. It shows that the interfacial bonding between BNNT and epoxy matrix is strong in the composites. This leads the transferring the stress load and preventing the sliding of nanotubes during tension. Therefore, it brings the mechanical reinforcement of the composites. It is expected that during pull out the stresses around the nanotube cause the epoxy matrix to yield and fail before the interface. Thus, the pull out nanotube bundle is surrounded by polymer that is yielded during the pull out process. The properties of polymer surrounding the nanotube bundles are different from those of the bulk, with the strength in that area being higher than the bulk strength [94, 68].

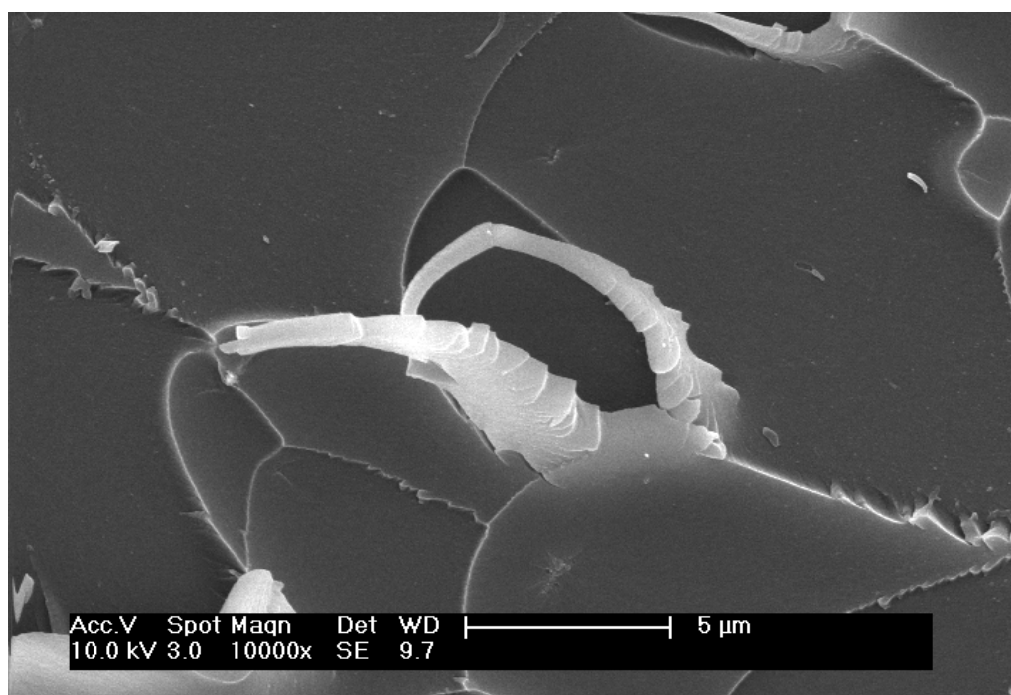


Figure 5.31. Fracture surface of the composite with 0.1 wt. per cent BNNT

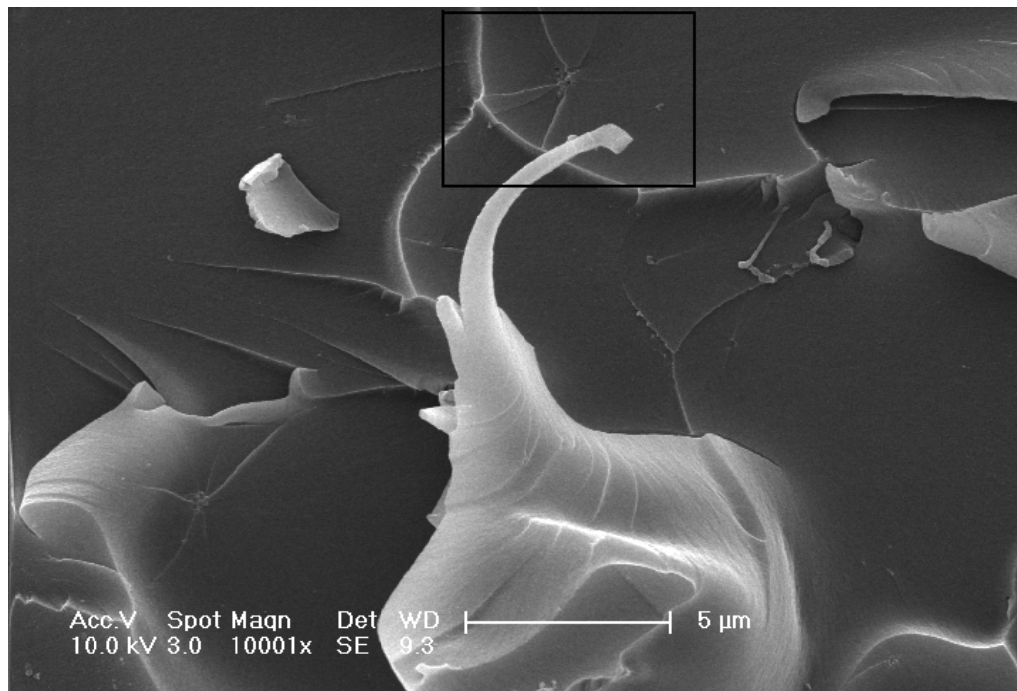


Figure 5.32. Fracture surface of the composite with 0.2 wt. per cent BNNT

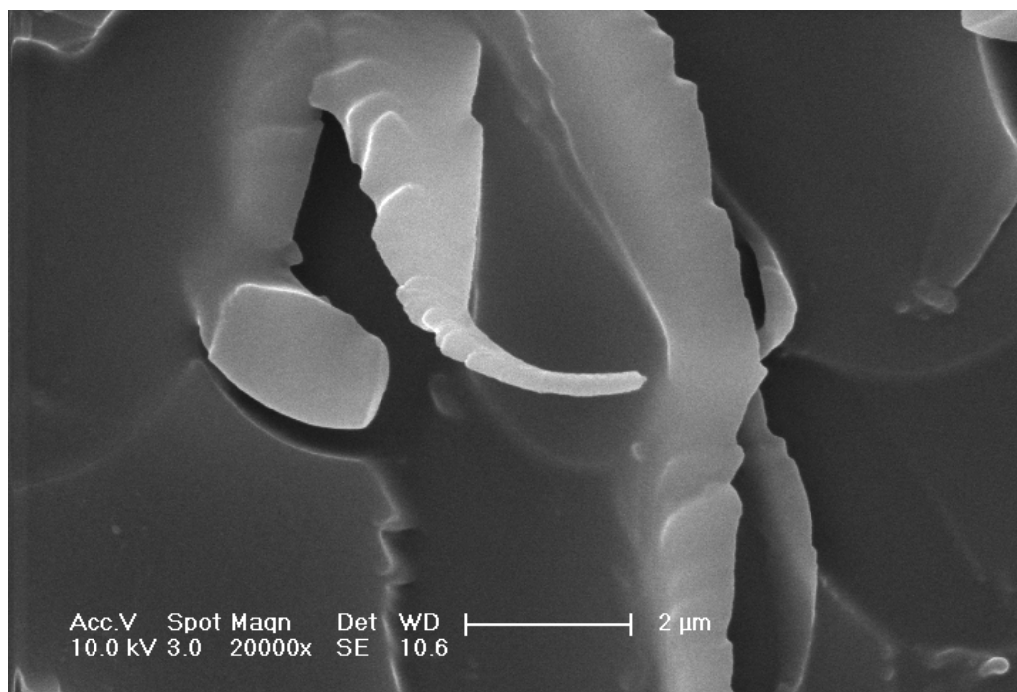


Figure 5.33. Fracture surface of the composite with 0.4 wt. per cent BNNT

Holes that are possibly caused by pull out of the nanotube bundles are observed on the fracture surface of BNNT/epoxy polymer composites as shown in Figures 5.26, 5.34 and 5.35. In Figure 5.26, a typical hole on the fracture surface of 0.1 wt. per cent BNNT reinforced composite is seen that has diameter about 600 nm. A good correlation was found between the diameter of the hole and diameter of the nanotube bundle coated by epoxy resin in Figure 5.31. When the nanotube content is increased in the epoxy matrix, the diameter of these holes decreases but the number of them increases. As shown in Figure 5.34, there are small agglomerations of nanotubes that are embedded in epoxy matrix on the surface of composite with 0.2 wt. per cent of BNNT. Some of the nanotubes are pulled out and form these holes and some of them are still embedded in matrix as indicated by arrows. On the fracture surface of BNNT/epoxy composites with 0.4 wt. per cent nanotubes, many distinct small holes and nanotube agglomerates can be seen in Figure 5.35. These nanotube agglomerates are larger than those of the composites with 0.2 wt. per cent BNNT.

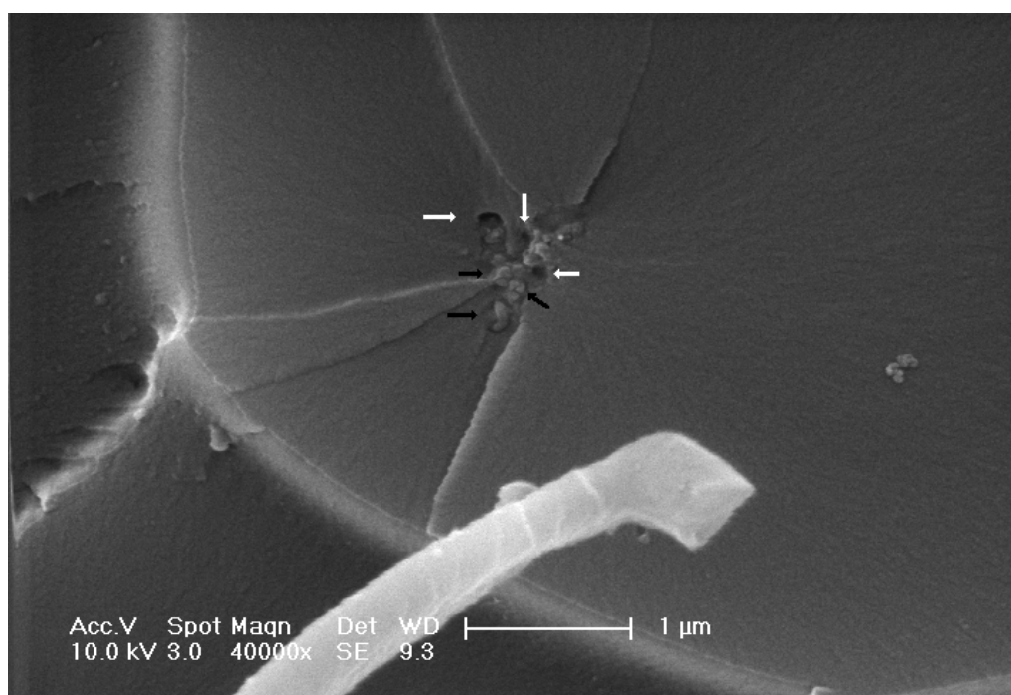


Figure 5.34. Exit hole left by pull out of the nanotube on fracture surface of the composite with 0.2 wt. per cent BNNT (High magnification of rectangle region in Figure 5.32)
(Nanotubes are shown by black arrows, holes are shown by white arrows)

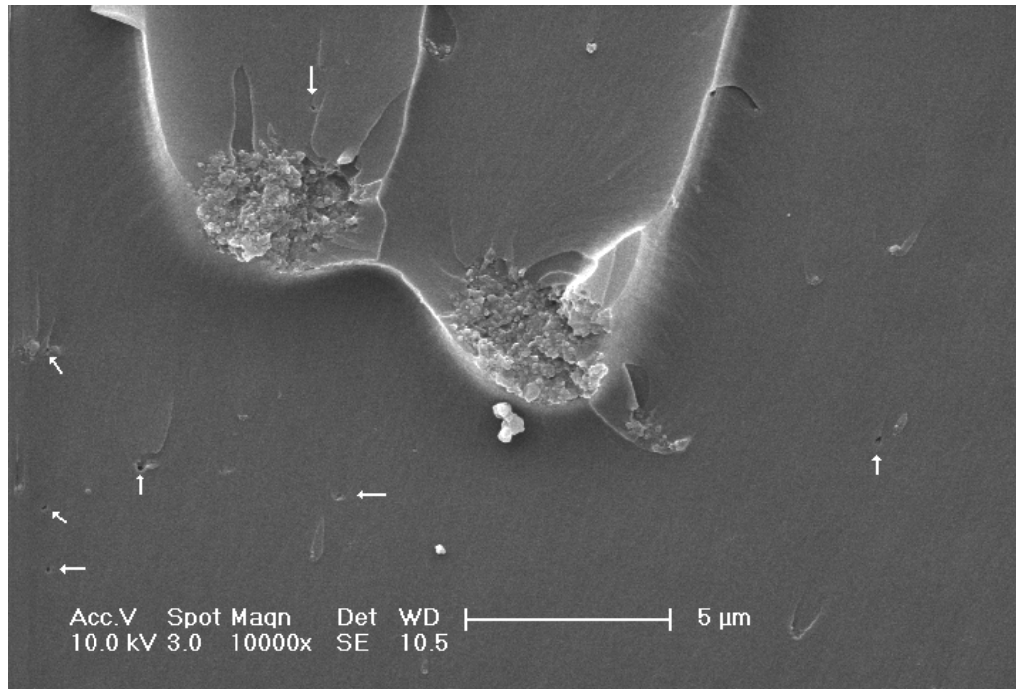


Figure 5.35. Agglomerates of nanotubes on 0.4 wt. per cent BNNT composite fracture surface (Holes are shown by arrows)

Presence of agglomerates in composites with 0.2 wt. per cent and 0.4 wt. per cent BNNT indicates the poor dispersion of nanotubes in epoxy matrix. The aggregation of nanotubes decreases the effective content of them in the epoxy matrix and may behave as a defect in the composite [68]. Existence of aggregates is responsible for the relatively low tensile strength and modulus values of the composites with 0.2 wt. per cent and 0.4 wt. per cent BNNTs, as compared with the values of the composites reinforced by 0.1 wt. per cent BNNTs.

5.4. Thermal Characterization of BNNT/Epoxy Polymer Composites

5.4.1. Thermogravimetric Analysis

In order to obtain information on the effect of the BNNTs on the thermal stability of epoxy composites, thermogravimetric analysis (TGA) was carried out for neat epoxy and BNNT/epoxy polymer composites. TGA was performed by TA Instruments TGA-Q50 at a temperature range 30-600 °C with a heat rate of 10 °C under nitrogen atmosphere.

Table 5.4. Results of TGA for neat epoxy and composites reinforced with 0.1 wt. per cent, 0.2 wt. per cent and 0.4 wt. per cent of BNNT

Material	T _{onset} (°C)	T _{peak} (°C)	Weight Loss % (0-200 °C)	Char wt.% at 575 °C
Neat Epoxy	310	342.8	1.08	25.7
0.1 wt. % BNNT Loaded Epoxy Composite	342	368.2	0.54	9.5
0.2 wt. % BNNT Loaded Epoxy Composite	338	366.6	0.90	13.8
0.4 wt. % BNNT Loaded Epoxy Composite	340	365.7	0.75	10.5

As can be seen in Table 5.4 and Figure 5.36, TGA data shows < 1 wt. per cent weight loss of BNNT/epoxy polymer composites up to 200 °C, which is less than that of neat epoxy, due to the release of absorbed water indicating complete removal of the DMF [63]. The onset temperature of mass loss (T_{onset}) increases by the incorporation of nanotubes to the epoxy matrix. T_{onset} reaches maximum value of 342 °C at 0.1 wt. per cent of BNNT loading, which is 32 °C greater than that of the neat epoxy. The effect of higher thermal conductivity of BNNTs facilitates the heat dissipation within the composite.

Dispersed nanotubes slow down the flux of degradation product and therefore delay the onset of degradation [95].

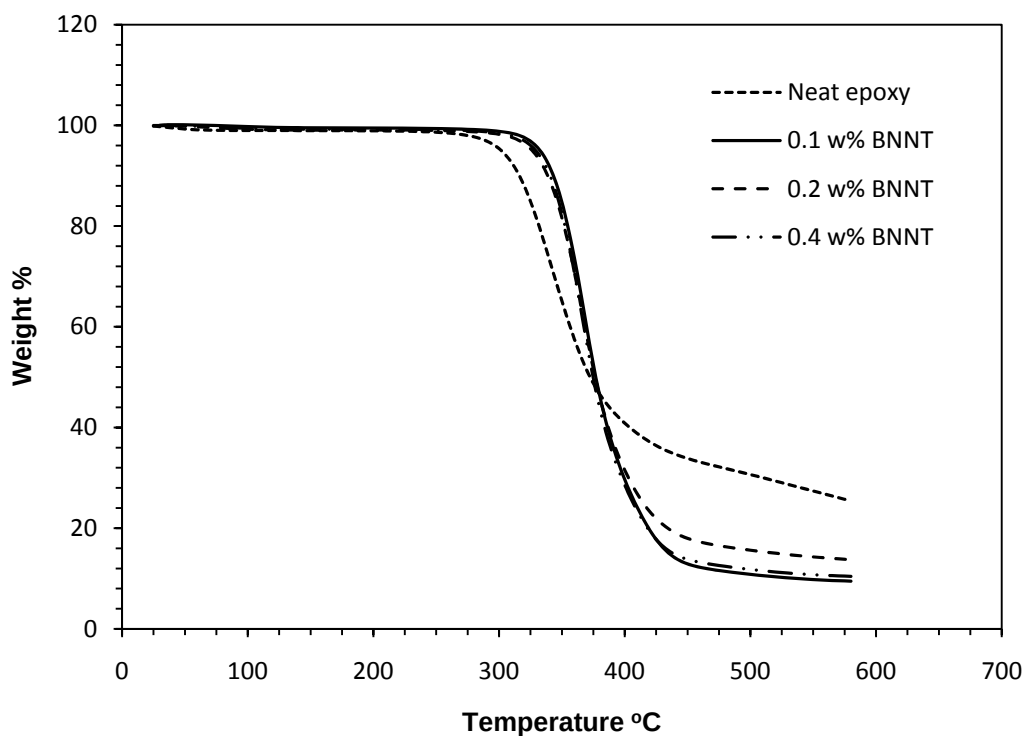


Figure 5.36. TGA curves of the neat epoxy and BNNT/epoxy polymer composites

The temperatures of maximum weight loss rate, T_{peak} , are higher in BNNT/epoxy polymer composites than T_{peak} in neat epoxy, as shown in Table 5.4 and Figure 5.37. 0.1 wt. per cent of BNNT reinforced composite shows a 25 °C shift in T_{peak} as compared to that of the neat epoxy. Polymers near the nanotubes may degrade more slowly, that would shift T_{peak} to higher temperatures [58].

The values of T_{onset} and T_{peak} in composites with 0.2 wt. per cent and 0.4 wt. per cent of BNNT are less than that of the composite with 0.1 wt. per cent of BNNT. This may be due to the poor dispersion of BNNTs in composites with 0.2 wt. per cent and 0.4 wt. per cent as can be seen by the examination of the fracture surfaces (Figure 5.34 and Figure 5.35). The effective content of the BNNTs decreases with the agglomeration of nanotubes.

The study about carbon nanotube reinforcement of the epoxy resin carried out by Puglia et al. [96] shows that nanotube incorporation influences the cure reaction of the DGEBA based epoxy resins. They found that nanotubes act as a strong catalyst and improve the rate of cure reaction and thermal degradation because of the higher thermal conductivity of the nanotubes which can be dispersed well in the matrix at low concentration. At higher nanotube concentration this catalyzing effect is not seen because of the saturation of nanotube in matrix. In the present study, one reason for the delay of thermal degradation of BNNT/epoxy polymer composites may be that BNNTs act as a catalyst because of their high thermal conductivity and improve the rate of cure reaction.

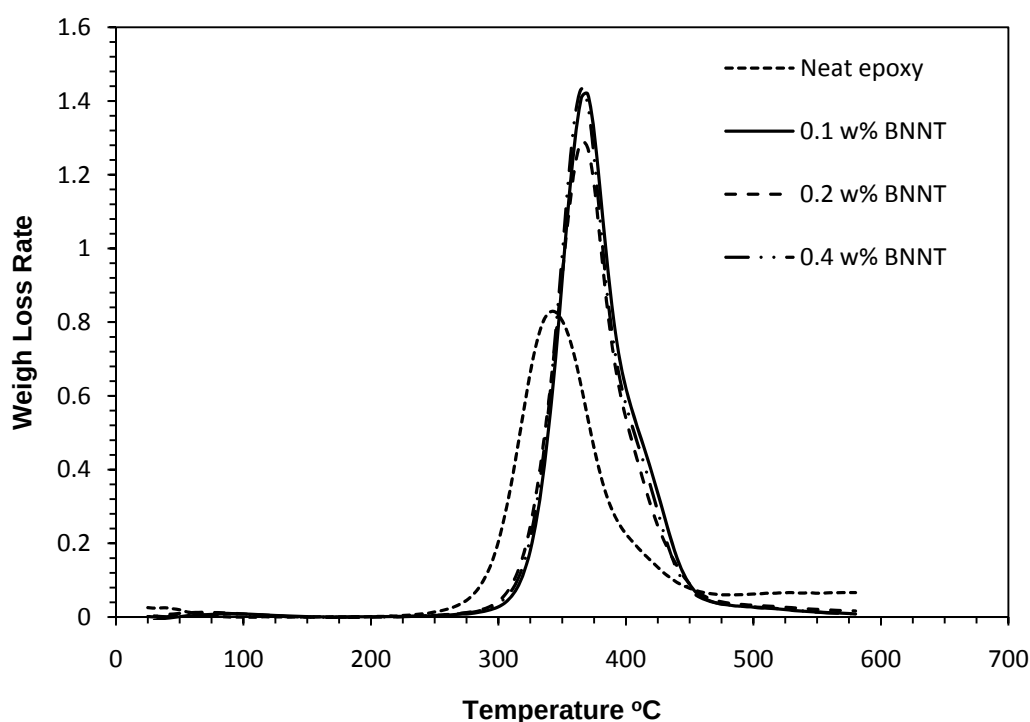


Figure 5.37. Weight loss rate of the neat epoxy and BNNT/epoxy polymer composites

As shown in Table 5.4 and Figure 5.36, the weight losses of the BNNT/epoxy polymer composites are increased compared with that of the neat epoxy. While char yield of neat epoxy is 25.7 per cent at 575 °C, the char yields of the composites with 0.1 wt. per cent, 0.2 wt. per cent and 0.4 wt. per cent are 9.5 wt. per cent, 13.8 wt. per cent and 10.5 wt. per cent, respectively. The increased weight loss may be due to the higher dm/dT values of composites as compared to that of the neat epoxy, as shown in Figure 5.37, because of the high thermal conductivity of BNNTs.

6.5.2. Differential Scanning Calorimeter Analysis

The glass transition temperatures of the neat epoxy and BNNT/epoxy composites are also measured by Differential Scanning Calorimeter (DSC) to compare with the results taken by DMA and it should be noted that DMA is more sensitive as compared to DSC. DSC analyses were performed under nitrogen atmosphere at a heating rate of 10 °C/min between -10 °C and 160 °C.

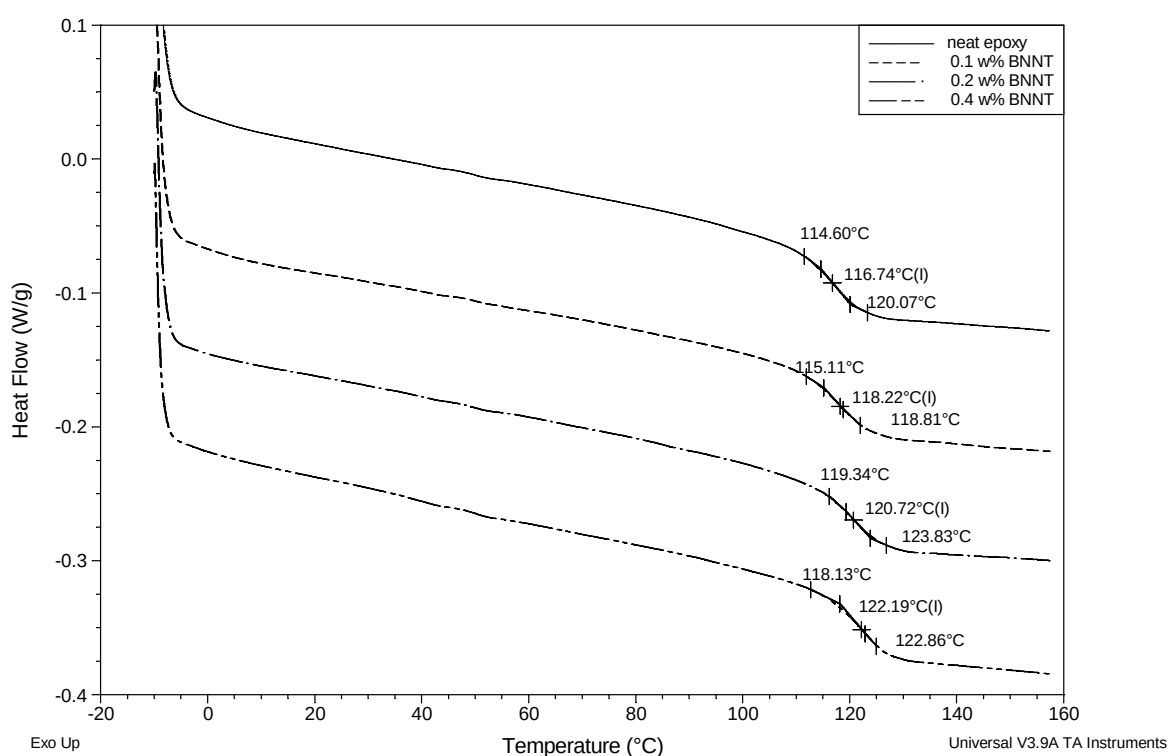


Figure 5.38. DSC thermograms of the neat epoxy and BNNT/epoxy polymer composites

As shown in Figure 5.38, T_g values of BNNT/epoxy polymer composites are higher as compared to T_g value of the neat epoxy. T_g value of the neat epoxy is 116.7 °C and those of the composites with 0.1, 0.2 and 0.4 wt. per cent of BNNT are determined as 118.2 °C, 120.7 °C and 122.2 °C, respectively. It is needed to remember that T_g values of the neat epoxy and the composites with 0.1, 0.2 and 0.4 wt. per cent of BNNT measured by DMA was 116.3, 117.4, 115.6 and 115.8 °C. While T_g value of the neat epoxy measured by DSC and DMA are so close, values of these two different techniques diverge from each other by the incorporation of BNNTs and do not show any consistency.

6. CONCLUSIONS

BNNTs were ultrasonicated in acetone, ethanol and DMF solutions and their agglomerate sizes were then measured by using nanoparticle size analyzer. It is seen that DMF is much better for making stable BNNT dispersion as compared to ethanol and acetone.

Neat epoxy and BNNT/epoxy composites with 0.1 wt. per cent, 0.2 wt. per cent and 0.4 wt. per cent of BNNTs were prepared after nanotubes were ultrasonicated in DMF. SEM examinations of the composites indicate that good dispersion has obtained for composites reinforced with 0.1 wt. per cent of BNNTs. However, the agglomeration of nanotubes decreases the effective content of nanotubes and behaves as a defect in composites reinforced with 0.2 wt. per cent and 0.4 wt. per cent of BNNTs.

Tensile strength reaches the maximum value of 80.6 MPa for composites reinforced with 0.1 wt. per cent BNNT, which is 10.6 per cent greater than that of the neat epoxy. The break strain slightly increases from 5.50 per cent to 5.83 per cent with 0.1 wt. per cent nanotubes loading. However, it declines to 4.40 per cent and 3.93 per cent with 0.2 wt. per cent and 0.4 wt. per cent of BNNTs, respectively. Dynamic mechanic analysis of the composites shows that while the glass transition temperatures of the composites reinforced with 0.1 wt. per cent of BNNTs slightly increases from 116.3 °C to 117.4 °C, those of composites with 0.2 wt. per cent and 0.4 wt. per cent of BNNTs decreases to 115.6 °C and 115.8 °C, respectively. Onset of thermal degradation is delayed for 32 °C with 0.1 wt. per cent of BNNT loading. Vicker's hardness measurements of neat epoxy and composites show that hardness tends to increase with the increase in nanotube content.

In this study, it is concluded that if good dispersion is provided with successful processing techniques, enhancement of mechanical and thermal properties is achievable in BNNT/epoxy composites. It is required to have knowledge of the elastic and fracture behavior of BNNTs and interactions at the nanotube/matrix interface to understand fully the mechanical and thermal behavior of these composites. There is also need for development of new BNNT production techniques for producing cost effective composites.

APPENDIX A. FTIR SPECTRA

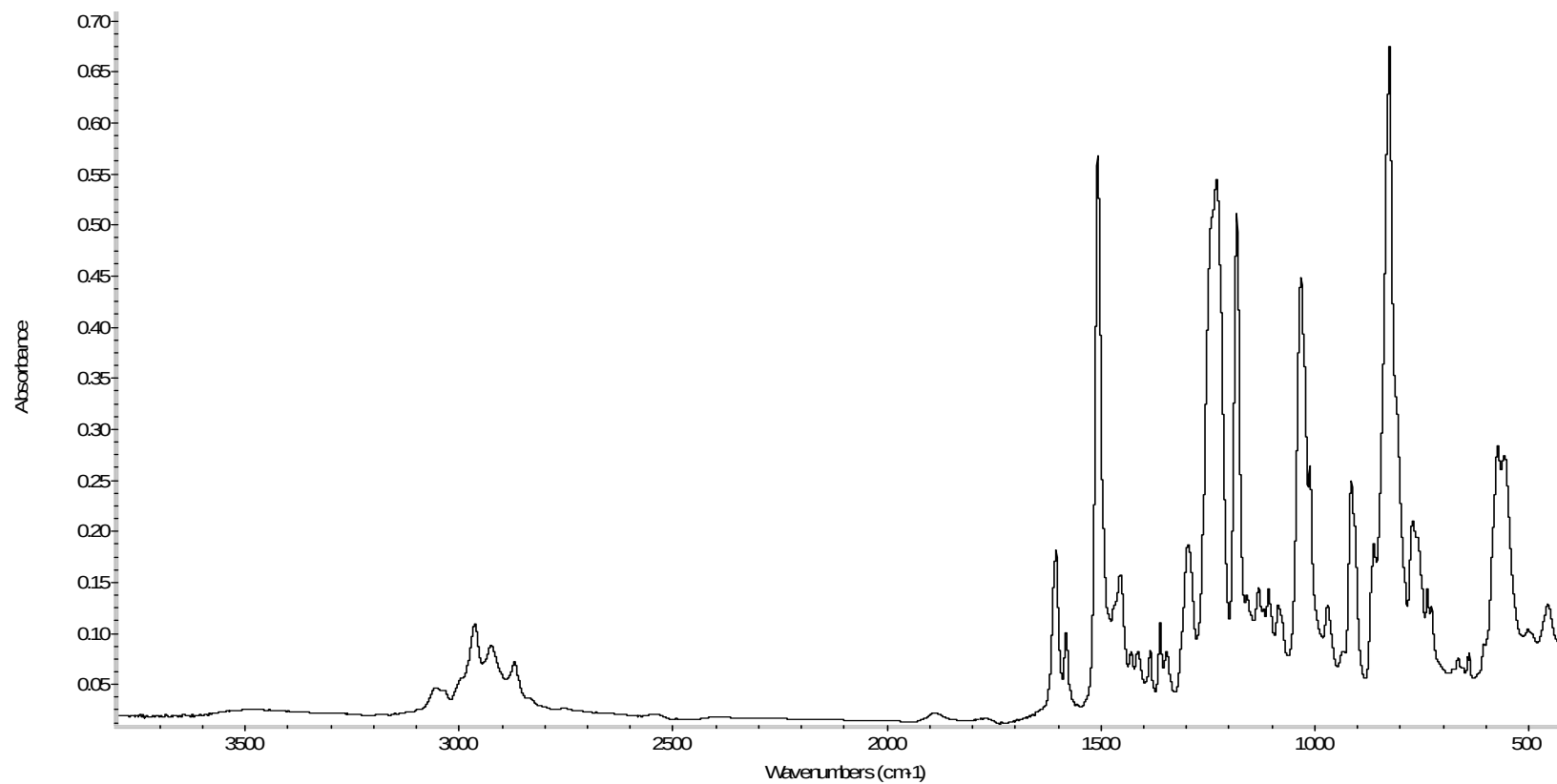


Figure A.1. FTIR Spectrum of diglycidyl ether of bisphenol A (DGEBA)

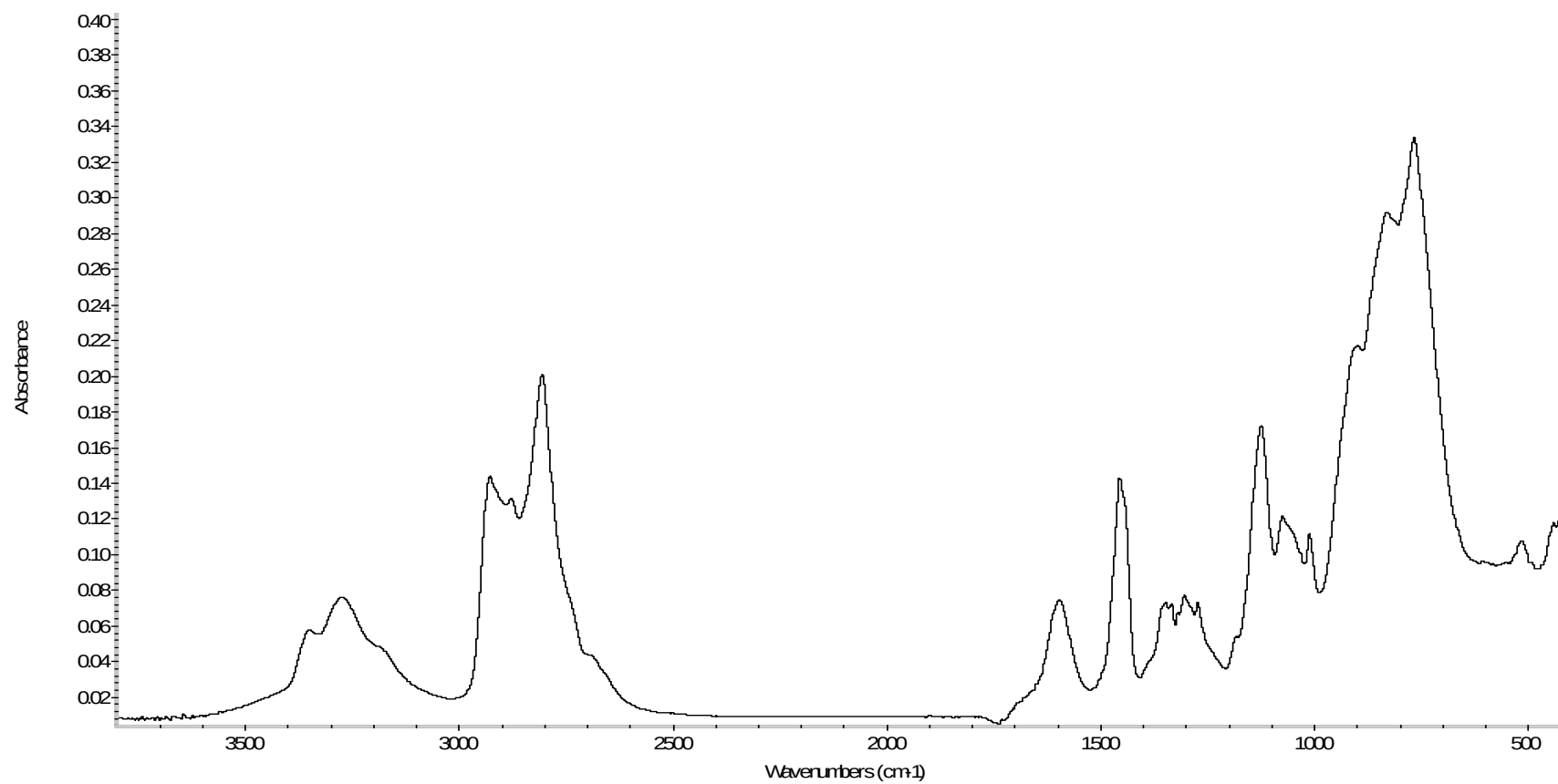


Figure A.2. FTIR Spectrum of triethylene tetramine (TETA)

APPENDIX B: TENSILE PROPERTIES OF BNNT/EPOXY POLYMER COMPOSITES

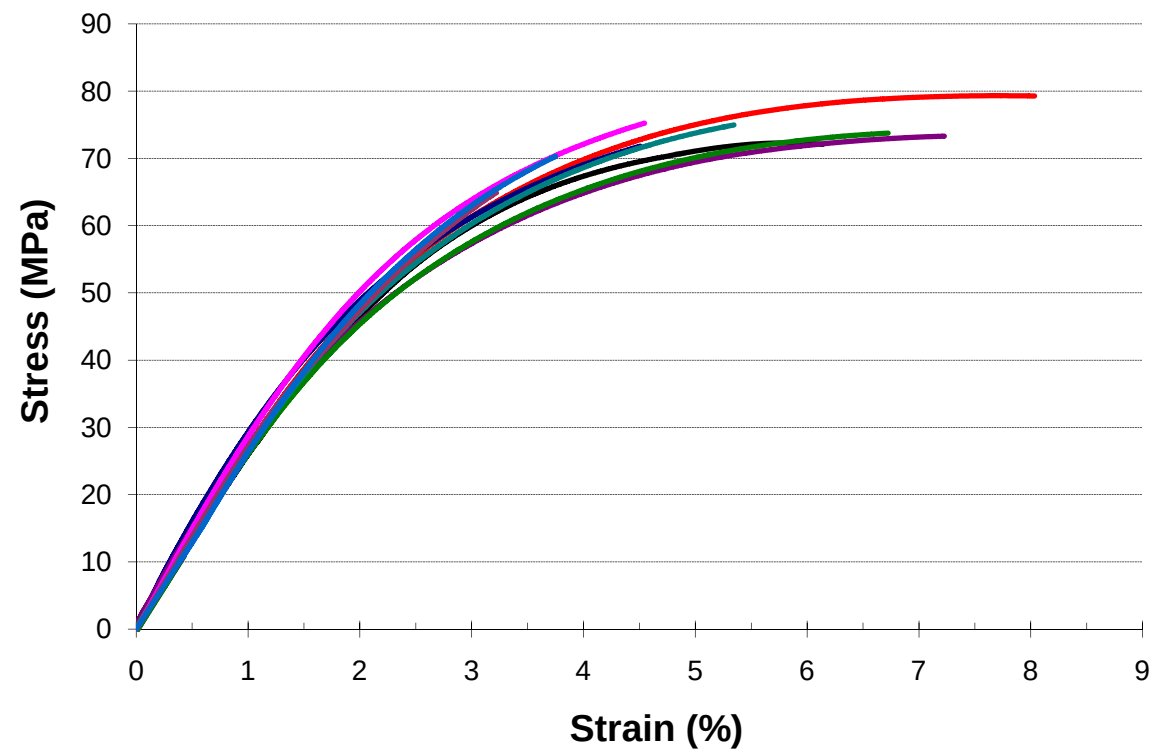


Figure B.1. Stress versus strain curves of neat DGEBA/TETA epoxy system

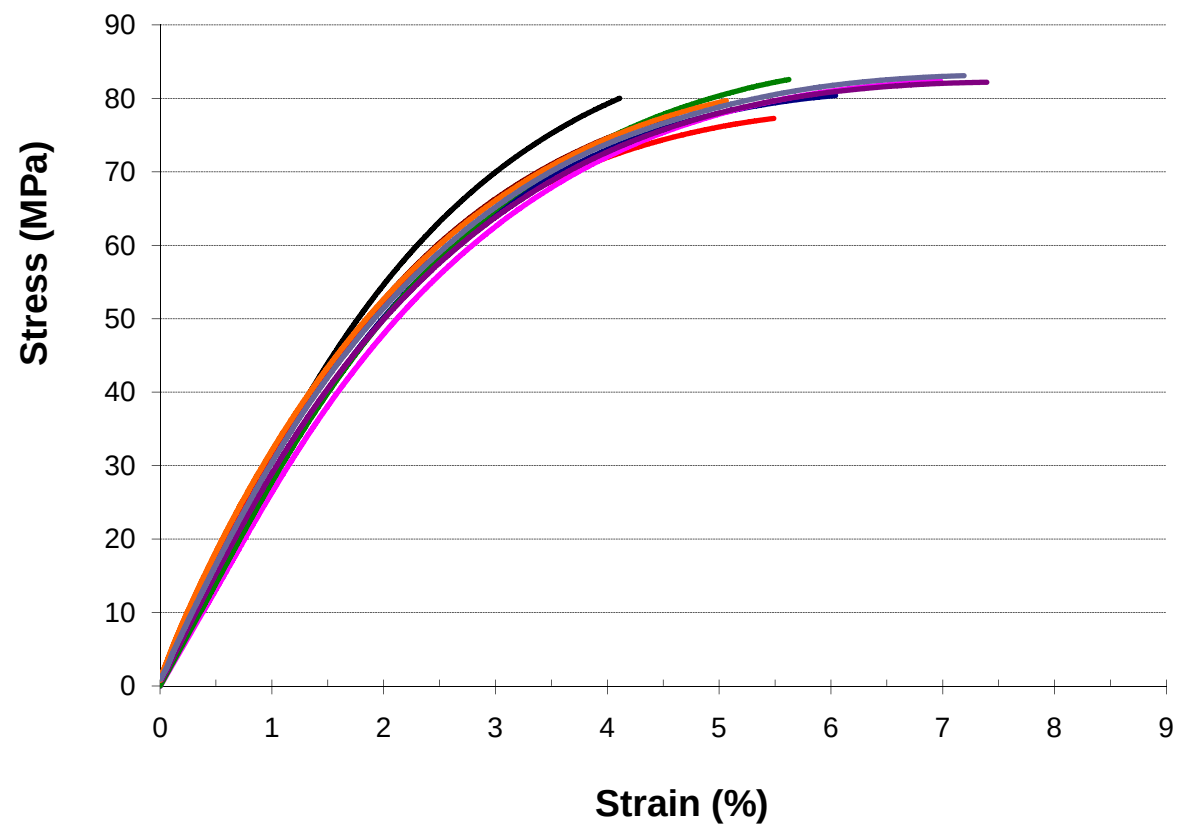


Figure B.2. Stress versus strain curves of 0.1 wt. per cent BNNT loaded DGEBA/TETA epoxy polymer composite

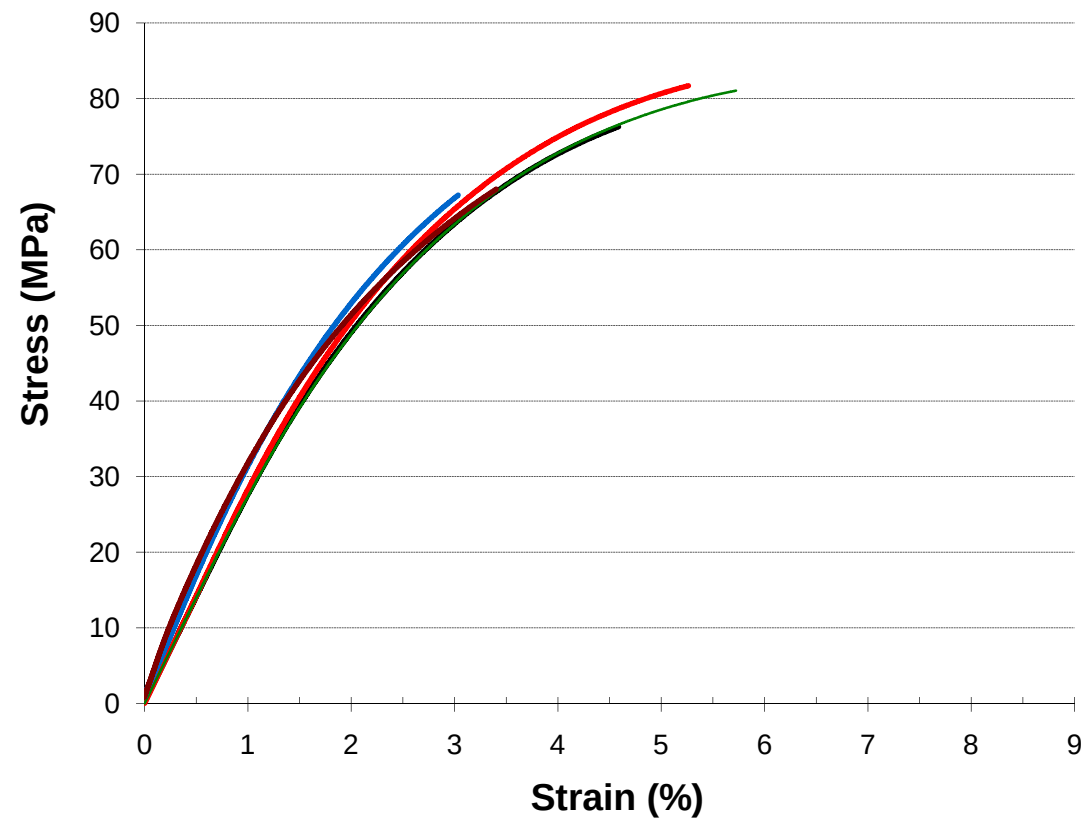


Figure B.3 Stress versus strain curves 0.2 wt. per cent BNNT loaded DGEBA/TETA epoxy polymer composite

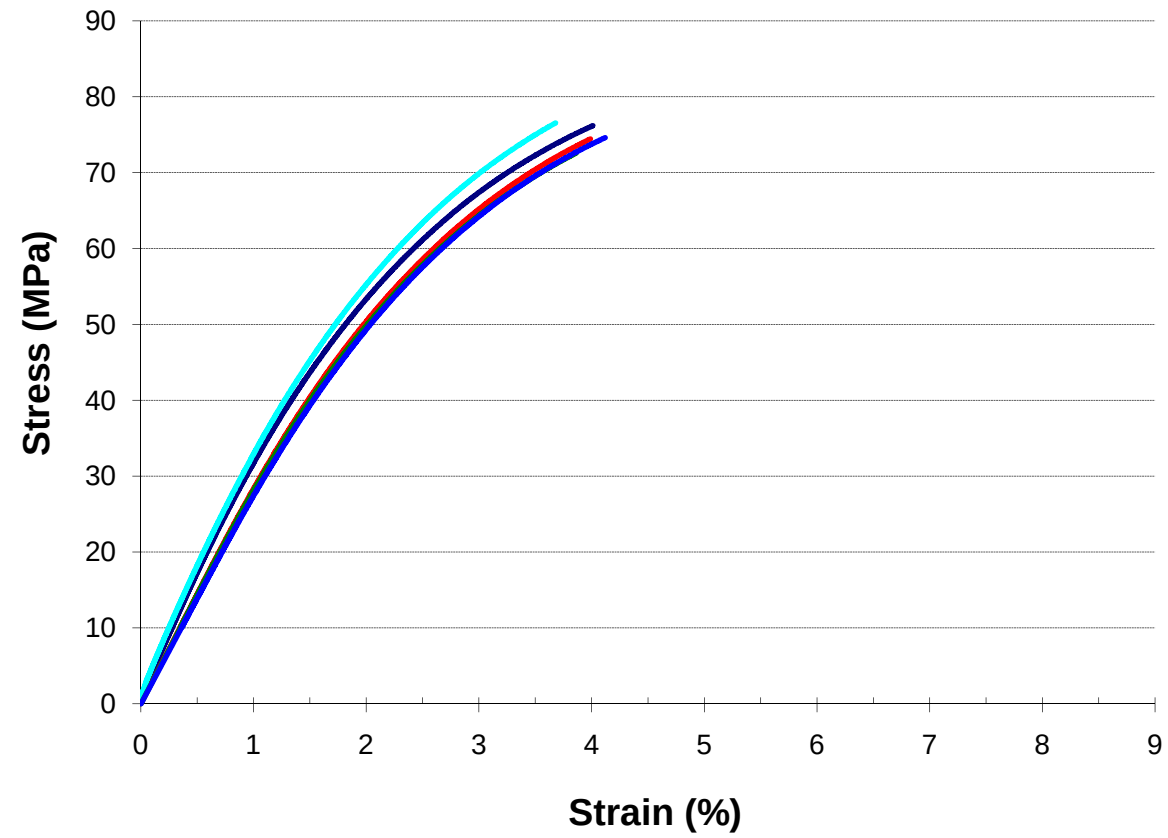


Figure B.4. Stress versus strain curves of 0.4 wt. per cent BNNT loaded DGEBA/TETA epoxy polymer composite

Table B.1. Tensile properties of successful neat epoxy and BNNT reinforced epoxy composite specimens

Material	Tensile Modulus (MPa)	Ultimate Tensile Strength (MPa)	Break Strain (%)
Neat Epoxy	2580	72.3	6.14
	2720	79.3	8.03
	2700	71.8	4.51
	2590	73.3	7.23
	2670	73.7	6.72
	2660	75.0	5.35
	2860	75.2	4.54
	2720	64.9	3.22
	2650	70.3	3.75
0.1 wt. % BNNT Loaded Epoxy Composite	3010	77.8	4.61
	2800	80.4	6.04
	3140	80.0	4.11
	3050	77.3	5.49
	2980	82.2	7.40
	2820	82.6	5.62
	3110	79.7	5.07
	3120	83.1	7.19
	2670	82.3	6.98
0.2 wt. % BNNT Loaded Epoxy Composite	2780	76.3	4.59
	2880	81.7	5.26
	2790	81.1	5.72
	3160	67.2	3.04
	3190	68.0	3.40
0.4 wt. % BNNT Loaded Epoxy Composite	3320	76.2	4.01
	2900	74.4	3.99
	3360	76.5	3.68
	2870	72.6	3.87
	2790	74.6	4.12

REFERENCES

1. Gao, H., “Mechanical Characterization of Low Dimensional Nanomaterials and Polymer Composites”, PhD Thesis, University of South Carolina, USA, 2006.
2. The Royal Society and Royal Academy of Engineering report entitled “Nanotechnology and Nanoscience”, <http://www.nanotec.org.uk/finalReport.htm>, 2008.
3. Center for Responsible Nanotechnology, <http://www.crnano.org/whatis.htm>, 2008.
4. Ajayan, P.M., J.M. Tour, “Nanotube Composites”, *Nature*, Vol. 447, pp.1066-1068, 2007.
5. Iijima, S., “Helical Microtubules of Graphitic Carbon”, *Nature*, Vol. 354, pp. 56-58, 1991.
6. Rubio, A., J. L. Corkill and M. L. Cohen, “Theory of Graphitic Boron Nitride Nanotubes”, *Physical Review B*, Vol. 49, pp. 5081-5084, 1991.
7. Chopra, N.G., R. J. Luyken, K. Cherrey, V. H. Crespi, M. L. Cohen, S. G. Louie and A. Zettl, “Boron Nitride Nanotubes”, *Science*, Vol. 269, pp. 966, 1995.
8. Ishii, T., T. Sato, Y. Sekikawa and M. Iwata, “Growth of Whiskers of Hexagonal Boron Nitride”, *Journal of Crystal Growth*, Vol. 52, pp. 285-289, 1981.
9. Cohen, M.L., “Looking Back and Ahead at Condensed Matter Physics”, *Physics Today*, Vol. 59, No. 6, pp. 48-53, 2006.
10. Wildoer, J.W.G., L. C. Venema, A. G. Rinzler, R. E. Smalley and C. Dekker, “Electronic Structure of Automatically Resolved Carbon Nanotubes”, *Nature*, Vol.391, Issue 6662, pp. 59-62, 1998.

11. Golberg, D., Y. Bando, C. Tang and C. Zhi, "Boron Nitride Nanotubes", *Advanced Materials*, Vol. 19, pp. 2413-2432, 2007.
12. Pouch, J.J and A. Alterovitz, "Synthesis and Properties of Boron Nitride", Trans Tech, Switzerland, 1990.
13. Nanowerk Nanomaterial Database, <http://www.nanowerk.com/>, 2008
14. Ishigami, M., S. Aloni and A. Zettl, "Properties of Boron Nitride Nanotubes", Physics Department, University of California Berkeley, 2003.
15. Hernandez, E., C. Goze, P. Bernier, A. Rubio, "Elastic Properties of C and BxCyNz Composite Nanotubes", *Physical Review Letters*, Vol. 80, pp. 4502-4505, 1998.
16. Chopra, N.G. and A. Zettl, "Measurement of the Elastic Modulus of a Multi-wall Boron Nitride Nanotube", *Solid State Communications*, Vol. 105, pp. 297-300, 1998.
17. Golberg, D., X. D. Bai, M. Mitome, C. Tang, C. Y. Zhi and Y. Bando, "Structural Peculiarities of In Situ Deformation of a Multi-walled BN Nanotube Inside a High-resolution Analytical Transmission Electron Microscope", *Acta Materialia*, Vol. 55, pp. 1293-1298, 2007.
18. Golberg, D., Y. Bando, K. Kurashima and T. Sato, "Synthesis and Characterization of Ropes Made of BN Multiwalled Nanotubes", *Scripta Materialia*, Vol. 44, pp. 1561-1565, 2001.
19. Chen, Y., J. Zou, S. J. Campbell and G. Caer, "Boron Nitride Nanotubes: Pronounced Resistance to Oxidation", *Applied Physics Letters*, Vol. 84, pp. 2430-2432, 2004.
20. Chang, C. W., A.M. Fennimore, A. Afanasiev, D. Okawa, T. Ikuno, H. Garcia, D. Li, A. Majumdar, A. Zettl, "Isotope Effect on the Thermal Conductivity of Boron Nitride Nanotubes", *Physical Review Letters*, Vol. 97, 085901, 2006.

21. Yum, K. and M. F. Yu, "Measurement of Wetting Properties of Individual Boron Nitride Nanotubes with the Wilhelmy Method Using a Nanotube-Based Force Sensor", *Nano Letters*, Vol. 6, No. 2, pp. 329-333, 2006.
22. Blasé, X., A. Rubio, S. G. Louie and M. L. Cohen, "Stability and Bandgap Constancy of Boron Nitride Nanotubes", *Europhysics Letters*, Vol. 28, pp. 335-340, 1994.
23. Loiseau, A., F. Willaime, N. Demoncy, G. Hug, and H. Pascard, "Boron Nitride Nanotubes with Reduced Numbers of Layers Synthesized by Arc Discharge", *Physical Review Letters*, Vol. 76, pp. 4737-4740, 1996.
24. Saito, Y., "Nanoparticles and Filled Nanocapsules", *Carbon*, Vol. 33, pp. 979-988, 1995.
25. Terrones, M., N. Grobert and H. Terrones, "Synthetic Routes to Nanoscale BxCyNz Architectures", *Carbon*, Vol. 40, pp. 1665-1684, 2002.
26. Golberg, D., Y. Bando, C. Tang and C. Zhi, "Boron Nitride Nanotubes", *Advanced Materials*, Vol. 19, pp. 2413-2432, 2007.
27. Lee, R.S., J. Gavillet, M. L. de la Chapelle, A. Loiseau, J. L. Cochon, D. Pigache, J. Thibault, F. Willaime, "Catalyst-free synthesis of boron nitride single-wall nanotubes with a preferred zig-zag configuration", *Physical Review B*, Vol. 64, pp.121405, 2001.
28. Han, W., Y. Bando, K. Kurashima and T. Sato, "Synthesis of Boron Nitride Nanotubes from Carbon Nanotubes by a Substitution Reaction", *Applied Physics Letters*, pp. 3085, 1998.
29. Golberg, D., Y. Bando, W. Han, K. Kurashima and T. Sato, "Single-walled B-doped Carbon, and BN Nanotubes Synthesized from Single-walled Carbon Nanotubes through a Substitution Reaction", *Chemical Physics Letters*, Vol. 308, pp. 337-342, 1999.

30. Golberg, D., Y. Bando, W. Han and T. Sato, "MoO₃-promoted Synthesis of Multi-walled BN Nanotubes from C Nanotube Templates", *Chemical Physics Letters*, Vol. 323, pp. 185-191, 2000.
31. Lourie, O.R., C.R. Jones, B.M. Bartlett, P.C. Gibbons, R.S. Ruoff, W.E. Buhro, "CVD Growth of Boron Nitride Nanotubes", *Chemistry of Materials*, Vol. 12, pp. 1808-1810, 2000.
32. Terrones, M., J.M. Romo-Herrera, E. Cruz-Silva, F. Lopez-Urias, E. Munoz-Sandoval, J.J. Velazquez-Salazar, H. Terrones, Y. Bando, D. Golberg, "Pure and Doped Boron Nitride Nanotubes", *Materials Today*, Vol. 10, pp. 30-38, 2007.
33. Chen, Y., J. F. Gerald, J. S. Williams and S. Bulcock, "Synthesis of Boron Nitride Nanotubes at Low Temperatures Using Reactive Ball Milling", *Chemical Physics Letters*, Vol. 299, pp. 260-264, 1999.
34. Chen, Y., L. T. Chadderton and J. F. Gerald, "A Solid-state Process for Formation of Boron Nitride Nanotubes", *Applied Physics Letters*, Vol. 74, pp. 2960, 1999.
35. Chadderton, L.T. and Y. Chen, "Nanotube Growth by Surface Diffusion", *Physics Letters A*, Vol. 263, pp. 401-405, 1999.
36. Velazquez-Salazar, J.J., E. Munoz-Sandoval, J.M. Romo-Herrera, F. Lupo, M. Ruhle, H. Terrones, M. Terrones, "Synthesis and State of Art Characterization of BN Bamboo-like Nanotubes: Evidence of Growth Mechanism Catalyzed by Fe", *Chemical Physics Letters*, Vol. 416, pp. 342-348, 2005.
37. Shimizu, Y., Y. Moriyoshi and H. Tanaka, "Boron Nitride Nanotubes, Webs, and Coexisting Amorphous Phase Formed by the Plasma Jet Method", *Applied Physics Letters*, Vol. 75, pp. 929-931, 1999.
38. Bengu, E. and L. D. Marks, "Single-walled BN Nanostructures", *Physical Review Letters*, Vol. 86, pp. 2385-2387, 2001.

39. Zhi, C., Y. Bando, C. Tan and D. Golberg, "Effective Precursor for High Yield Synthesis of Pure BN Nanotubes", *Solid State Communications*, Vol. 135, pp. 67-70, 2005.
40. Chen, H., Y. Chen, J. Yu and J. S. Williams, "Purification of Boron Nitride Nanotubes", *Chemical Physics Letters*, Vol. 425, pp. 315-319, 2006.
41. Zhi, C., Y. Bando, C.C. Tang, S. Honda, K. Sato, H. Kuwahara, D. Golberg, "Purification of Boron Nitride Nanotubes through Polymer Wrapping", *Journal of Physical Chemistry*, Vol. 110, pp. 1525-1528, 2006.
42. Zhi, C., Y. Bando, C.C. Tang, R.G. Xie, T. Sekiguchi, D. Golberg, "Perfectly Dissolved Boron Nitride Nanotubes Due to Polymer Wrapping", *Journal of American Chemical Society*, Vol. 125, pp. 15996-15997, 2005.
43. Bansal, N.P., J. B. Hust and S. R. Choi, "Boron Nitride nanotubes-Reinforced Glass Composites", *Journal of American Ceramic Society*, Vol. 89, pp. 388-390, 2006.
44. Huang, Q., Y.S., Bando, X. Xu, T. Nishimura, C.Y. Zhi, C.C. Tang, F.F. Xu, L. Gao, D. Golberg, "Enhancing Superplasticity of Engineering Ceramics by Introducing BN Nanotubes", *Nanotechnology*, Vol. 18, 485706, 2007.
45. Ma, R., Y. Bando, H.W. Zhu, T. Sato, C.L. Xu, D.H. Wu, "Hydrogen Uptake in Boron Nitride Nanotubes at Room Temperature", *Journal of American Chemical Society*, Vol. 124, pp. 7672-7673, 2002.
46. Jhi, S-H., "Activated Boron Nitride Nanotubes: A Potential Material for Room-Temperature Hydrogen Storage", *Physical Review B*, Vol. 74, 155424, 2006.
47. Tang, C., Y. Bando, X. Ding, S. Qi and D. Golberg, "Catalyzed Collapse and Enhanced Hydrogen Storage of BN Nanotubes", *Journal of American Chemical Society*, Vol. 124, 14550, 2002.

48. Mpourmpakis, G. and G. E. Froudakis, "Why Boron Nitride Nanotubes are Preferable to Carbon Nanotubes for Hydrogen Storage? An ab Initio Theoretical Study", *Catalysis Today*, Vol.120, pp. 341-345, 2007.
49. Zhang, Z., W. Guo and G. Tai, "Coaxial Nanocable: Carbon Nanotube Core Sheathed with Boron Nitride Nanotube", *Applied Physics Letters*, Vol. 90, pp. 103-133, 2007.
50. Golberg, D., Y. Bando, Y.B. Li, J.Q. Hu, Y.C. Zhu, Y.H. Gao, C.C. Tang, "Metal-filled Nanotubes: Synthesis, Analysis, Properties and Applications", *Electronic Properties of Synthetic Nanostructures*, pp. 229-233, 2004.
51. Won, C.Y. and N. R. Aluru, "Water Permeation through a Subnanometer Boron Nitride Nanotube", *Journal of American Chemical Society*, Vol. 129, pp. 2748-2749, 2007.
52. Breuer, O., U. Sundararaj, "Big Returns from Small Fibers: A Review of Polymer/Carbon Nanotube Composites", *Polymer Composites*, Vol.25, pp.630-645, 2004.
53. Coleman, J.N., U. Khan, W.J. Blau, Y.K. Gun'ko, "Small but Strong: A Review of The Mechanical Properties of Carbon Nanotube-polymer Composites", *Carbon*, Vol. 44, pp. 1624-1652, 2006.
54. Callister, W.D., "*Materials Science and Engineering, An Introduction*", New York, Wiley, 2003.
55. Karman, G.P., K.L. Reifsnider, "Micromechanics of short fiber composites", *Composites Science and Technology*, Vol. 42, pp. 137-146, 1992.
56. Cooper, C.A., S.R. Cohen, A.H. Barber, H.D. Wagner, "Detachment of nanotubes from a polymer matrix", *Applied Physics Letters*, Vol. 81, pp. 3873-3875, 2002.

57. Coleman, J.N., M. Cadek, R. Blake, V. Nicolosi, K.P. Ryan et al., "High performance nanotube-reinforced plastics: understanding the mechanism of strength increase", *Advanced Functional Materials*, Vol. 14, pp. 791-798, 2004.
58. Moniruzzaman, M., K.I. Winey, "Polymer Nanocomposites Containing Carbon Nanotubes", *Macromolecules*, Vol. 39, pp.5194-5205, 2006.
59. E.M. Petrie, "*Epoxy Adhesive Formulations*", New York, Mc-Graw Hill, 2006.
60. P.M. Ajayan, Stephan, O., Colliex, C., Trauth, D., "Aligned carbon nanotube arrays formed by cutting a polymer resin–nanotube composite", *Science*, Vol. 265, pp. 1212–1214, 1994.
61. L.S. Schadler, Giannaris, S.C., Ajayan, P.M., "Load transfer in carbon nanotube epoxy composites", *Applied Physics Letters*, Vol. 73, pp. 3842–3844, 1998.
62. Schartel, B., U. Braun, U. Knoll, M. Bartholmai, H. Goering, D. Neubert, P. Pötschke, "Mechanical, Thermal and Fire Behavior of Bisphenol A Polycarbonate/Multiwall Carbon Nanotube Nanocomposites", *Polymer Engineering and Science*, Vol.48, pp.149-158, 2008.
63. Moniruzzaman, M., F. Du, N. Romero, K.I. Winey, "Increased Flexural Modulus and Strength in SWNT/epoxy Composites by a New Fabrication Method", *Polymer*, Vol. 47, pp. 293-298, 2006.
64. Liu, L., H.D. Wagner, "Rubbery and glassy epoxy resins reinforced with carbon nanotubes", *Composites Science and Technology*, Vol. 65, pp. 1861-1868, 2005.
65. Xu, X., M.M. Thwe, C. Shearwood and K. Liao, "Mechanical properties and interfacial characteristics of carbon-nanotube–reinforced epoxy thin films", *Applied Physics Letters*, Vol.81, pp. 2833–2835, 2002.

66. Allaoui, A., S. Bai, H.M. Cheng and J.B. Bai, "Mechanical and electrical properties of a MWNT/epoxy composite", *Composite Science and Technology*, Vol. 62, pp.1993–1998, 2002.
67. Bai, J., "Evidence of the reinforcement role of chemical vapour deposition multi-walled carbon nanotubes in a polymer matrix", *Carbon*, Vol.41, pp.1325-1328, 2003.
68. Li, X.D., H.S. Gao, W.A. Scrivens, D.L. Fei, X.Y. Xu and M.A. Sutton et al., "Nanomechanical characterization of single-walled carbon nanotube reinforced epoxy composites", *Nanotechnology*, Vol. 15, pp. 1416–1423, 2004.
69. Rana, S., R. Alagirusamy, M. Joshi, "A review on carbon epoxy nanocomposites", *Journal of Reinforced Plastics and Composites*, July 18, 2008.
70. Bryning, M. B., D.E. Milkie, M.F. Islam, J.M. Kikkawa, A.G. Yodh, "Thermal Conductivity and Interfacial Resistance in Single-Wall Carbon Nanotube Epoxy Composites", *Applied Physics Letters*, Vol. 87, pp.161909–161913, 2005.
71. Y. Chen, J.S. Williams and M.J. Schultz, "Synthesis of boron nitride nanotubes using ball milling and annealing method", *Nanoengineering of Structural, Functional and Smart Materials*, pp. 169-195, 2005.
72. *Research School of Physical Sciences and Engineering, Australian National University, Canberra, Australia*, <http://www.rspysse.anu.edu.au>, 2008.
73. *Product Bulletin of Hexion Epoxy Resins*, <http://www.hexion.com/Products/TechnicalDataSheets.aspx>, 2008.
74. Inam, F., H. Yan, M. J Reece and T. Peijs, "Dimethylformamide: An effective dispersant for making ceramic-carbon nanotube composites", *Nanotechnology*, Vol.19, pp. 195710-195715, 2008.
75. Zetasizer Nano Series User Manual, Malvern Instruments Ltd. UK, 2006.

76. ASTM 638-03 Standard test Method for Tensile Properties of Plastics, 2008.
77. *DMA 800 Perkin Elmer Dynamic Mechanical Analyzer brochure*, www.PerkinElmer.com, 2008.
78. *Natinal Institute of Standards and Technology*, http://www.msrl.nist.gov/Nanotube2/Practice%20Guide_Section%202_TGA.pdf, 2008.
79. Kumar, A., R. K. Gupta, “*Fundamentals of Polymer Engineering*”, Marcel Dekker, New York, USA, 2003.
80. Strong, A.B., “*Plastics Materials and Processing*”, Prentice Hall, New Jersey, USA, 1996.
81. Bae, J., J. Jang, S-H. Yoon, “Cure Behavior of the Liquid-Crystalline Epoxy/Carbon Nanotube System and the Effect of Surface Treatment of Carbon Fillers of Cure Reaction”, *Macromolecular Chemistry and Physics*, Vol. 203, pp.2196-2204, 2002.
82. Peijs, T and F. Inam, “Re-aggregation of Carbon Nanotubes in Two-Component Epoxy System”, *Journal of Nanostructured Polymers and Nanocomposites*, pp. 87-95, 2006.
83. Badaire, S., P. Poulin, M. Maugey, and C. Zakri, “In Situ Measurements of Nanotube Dimensions in Suspensions by Depolarized Dynamic Light Scattering”, *Langmuir*, Vol. 20, pp. 10367 – 10370, 2004.
84. Thomson, K, E., D. Jiang, R.O. Ritchie and A.K. Mukherjee, “A preservation study of carbon nanotubes in alumina based nanocomposites via Raman spectroscopy and nuclear magnetic resonance”, *Applied Physics A: Materials Science and Processing*, Vol. 89, pp. 651-654, 2007.

85. Lau, K., M. Lu, C. Lam, H. Cheung, F. Sheng. and H. Li, "Thermal and mechanical properties of single-walled carbon nanotube bundle-reinforced epoxy nanocomposites: the role of solvent for nanotube dispersion", *Composites Science and Technology*, Vol. 65, pp. 719-725, 2005
86. Kausch, H.-H., "*Polymer Fracture*", Springer-Verlag, Ecole Polytechnique Federal de Lausanne, Suisse, 1987.
87. ASTM D 7028 Standard Test Method for Glass Transition Temperature of Polymer Matrix Composites by Dynamic Mechanical Analysis (DMA), 2008.
88. Brown, J., I. Rhoney, R.A. Pethrick, "Epoxy resin based nanocomposites: 1. Diglycidylether of bisphenol A (DGEBA) with triethylenetetramine (TETA)", *Polymer International*, Vol.53, pp. 2130-2137, 2004.
89. Liu, M., B. Guo, M. Du, Y. Lei, D. Jia, "Natural Inorganic Nanotubes Reinforced Epoxy Resin Nanocomposites", *J Polym Res*, Vol.15, pp. 205-212, 2008.
90. d'Almeida, J.R.M., S.N. Monteiro, G.W. Menezes, R.J.S. Rodriguez, "Diamond-Epoxy Composites", *Journal of Reinforced Plastics and Composites*, Vol. 26, pp. 321-330, 2007.
91. Low, I.M. and C. Shi, "Vickers Indentation Responses of Epoxy Polymers", *Journal of Materials Science Letters*, Vol. 17, pp. 1181-1183, 1998.
92. Roulin-Moloney, A.C., "*Fractography and Failure Mechanisms of Polymers and Composites*", Elsevier Applied Science, England, 1989.
93. Parrington, R.J., "*Fractography of Metals and Plastics*", IMR Test Labs, New York, 2002.

94. Li, S.Q., F. Wang, Y. Wang, J.W. Wang, J. Ma and J. Xiao, "Effect of Acid and TETA Modification on Mechanical Properties of MWCNTs/epoxy Composites", *Journal of Materials Science*, Vol. 43, pp. 2653-2658, 2008.
95. Huxtable, S.T., D.G. Cahill, S. Shenogin, L. Xue, R. Ozisik, P. Barone, M. Usrey, M.S. Strano, G. Siddons, M. Shim and P. Keblinski, "Inrefacial Heat Flow in Carbon Nanotube Suspensions", *Nature Materials*, Vol. 2, pp. 731-734, 2003.
96. Puglia, D., L. Valentini, I. Armentano and J. M. Kenny, "Effects of single-walled carbon nanotube incorporation on the cure reaction of epoxy resin and its detection by Raman spectroscopy", *Diamond and Related Materials*, Vol. 12, pp. 827-832, 2003.