

**CARBON NANOTUBES REINFORCED
COMPOSITES FOR WIND TURBINE BLADES**

by

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Dedication

To my beloved parents, Feng Yang and Zihua Chen. Thank you for supporting me and always being there for me the best you can.

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Carbon Nanotubes Reinforced Composites for Wind Turbine Blades

Abstract

by

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The effects of addition of eight different block copolymers on the dispersion stability of multi-walled carbon nanotubes (MWCNTs) have been systematically analyzed. The suspension of MWCNTs in vinyl ester (VE) have been evaluated by preparing suspensions using a tip sonicator and different amounts of block copolymers relative to the concentration of MWCNTs. The resistance to sedimentation of MWCNTs in the resin was investigated by using a centrifugation technique. The dispersing agent suitable for the acquisition of long-term stable suspensions of MWCNTs has been identified. Vinyl ester based composites reinforced with MWCNTs have been prepared with or without the use of the dispersing agent. Tensile tests have been performed in order to analyze the effect of different concentrations of MWCNTs and the use of the dispersing agent in the composites. Fracture surfaces of vinyl ester nanocomposites have been analyzed by using a scanning electron microscope (SEM).

Chapter 1 Introduction

1.1 Wind Energy and New Materials

In recent years, wind power has become an increasingly attractive source. Once the installation for production of wind energy is completed, the whole process does not generate any form of solid, liquid, or gaseous emissions or residues, nor does it consume any form of fuel. Nowadays, wind turbines from the leading manufacturers are usually guaranteed to operate over a lifetime of approximately 20 years. The most common design of wind turbine employs a rotor with three blades installed in a vertical plane, with a horizontal axis of rotation facing the wind.

In the beginning of the 1980s, only megawatt turbines existed but mainly for research purposes. Up until 2000 an ever-increasing growth in turbine size over time had taken place among manufacturers and was a general industry trend [1]. To fulfill the increasing needs for energy consumption and to obtain a longer lifetime, advanced wind blades which achieve adequate stiffness, strength, and extended fatigue resistance are desired. The blades must be stiff enough to prevent collision with the tower under extreme conditions. In addition, they need be strong enough to withstand the applied loads without failure, and the fatigue strength must be sufficient to withstand the time-varying loads throughout the life of the blade. To be cost-effective, the blade construction also requires being as light as possible; this has to be achieved

through optimization of the structural arrangement and dimensions in parallel with the materials selection [2, 3].

To meet all these demands, the blades are usually made of fiber-reinforced plastics, sometimes in combination with wood. The reinforcements are generally fabrics consisting of continuous glass fibers and/or carbon fibers. These are combined in several layers impregnated with and held together by an adhesive resin.

Glass fibers are amorphous with isotropic properties, e.g., stiffness and thermal expansion. They have diameters normally in the range of 10-20 μ m and are fabricated from molten glass by spinning into bundles of hundreds to thousands of individual fibers. Glass fibers desired for composites usually possess a combination of properties: moderate stiffness, high strength, and moderate density. Due to the requirement of ever-larger rotor blades and the decreasing price of manufacturing, carbon fibers recently become competitive reinforcement for wind blades. Carbon fibers are made of almost pure carbon, which is with a crystallographic lattice in a hexagonal shape. The crystallography indicates a high value of mechanical properties in the hexagonal planes, as well as a high degree of anisotropy. In order to achieve the potential properties, these hexagonal planes should be arranged parallel to the fiber axis, depending on the type of fiber and the production method. The advantages of carbon fibers are the combination of high stiffness, strength and low density [3]. While such glass fibers or carbon fibers strengthened composites may show exceptional mechanical properties in the direction aligned with the reinforcement, the properties in transverse directions may not always be acceptable.

The matrix materials for wind blades are typically thermosets or thermoplastics. They serve to bind the fibers and provide structural support for the composites. The thermosets mainly used are polyester, vinyl ester, and epoxy. They are two parts systems and go through a curing reaction. The thermoplastics have been studied for years. They have on average lower stiffness values and densities. However, they undergo a melting and solidification step during processing, which may cause thermal contraction leading to larger internal stresses by comparison with the thermosets.

For long-term considerations, there is opportunity for improving the materials used in wind turbine blades. As indicated previously, wind turbine blades need to be strong, stiff, and of low weight. The major weakness of fiber-reinforced composites is their anisotropic properties. Nanocomposites employing carbon nanotubes uniformly dispersed into the resin may offer advantages over the pristine resins in terms of increased stiffness and toughness [4].

1.2 Nanocomposites

Nanotechnology offers the promise of developing new polymer composite materials. Materials formed from a combination of nanomaterials and polymers could offer properties that are representative of both components.

Nanomaterials vary in size from 1nm to 100 to 200nm, which considering an average polymer gyration radius of 40nm explains the molecular-level interaction between the nanofillers and the resin, thereby greatly affecting the resulting properties

of the composite. In addition, nanostructured or nanophase materials are drawing attention because of their potential applications in areas such as electronics, catalysis, pharmaceuticals, materials science. The distinguished properties and enhanced performances are directly related to their sizes, surface structure and interfacial interactions [4].

Nanocomposites offer similar or improved properties at significantly lower filler loading levels than those with conventional fillers. The addition of nanomaterials to polymers for producing composites greatly impacts mechanical properties, flame retardancy and electrical conductivity. In specific applications, nanocomposites show improvement in tensile strength, thermal conductivity, stiffness and toughness.

1.3 Carbon Nanotubes

1.3.1 Introduction

In 1985, Kroto and his colleagues [5] discovered a new form of carbon, buckminsterfullerene C_{60} when they synthesized vapor-grown carbon fibers. However, it was until 1991, when Iijima [6] observed the tubular structure of carbon, which we know as carbon nanotubes (CNTs) nowadays. CNTs are tubular forms of carbon that can be visualized as a sheet of graphite rolled into cylindrical form [7]. There are two basic types of CNTs: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). SWCNTs consist of a single graphite sheet seamlessly wrapped into a cylindrical tube while MWCNTs comprise several concentric

graphene cylinders. These concentric nanotubes are held together by van der Waals forces. Their exceptional properties are depended on their symmetric structure, morphology, diameter, and the length of the tubes. Figure 1.1 shows an example of a SWCNT bundle [8].

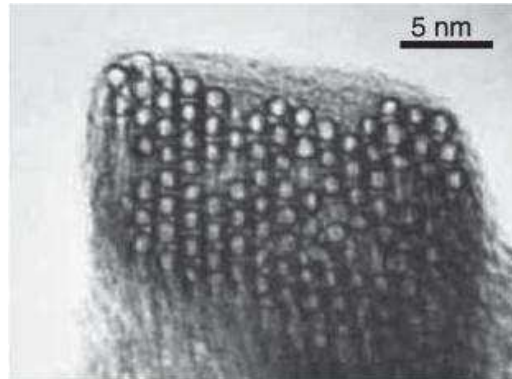


Figure 1.1 Transmission electron microscope image showing the lateral packing of SWNTs in a bundle [8].

The various ways of rolling graphene into tubes are described by the tube chirality as defined by the circumferential vector \vec{C}_h , $\vec{C}_h = n\vec{a}_1 + m\vec{a}_2$, where the integers (n,m) are the number of steps along the unit vectors (\vec{a}_1 and \vec{a}_2) of the hexagonal lattice [9]. Figure 1.2 illustrates how the graphite sheet is rolled to form a carbon nanotube [10].

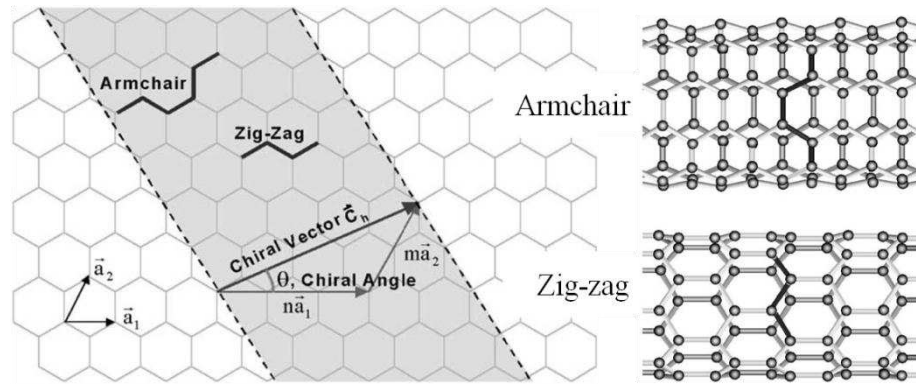


Figure 1.2 Schematic diagram showing how a hexagonal sheet of graphene is rolled in different directions to form nanotubes: armchair (n,m), zig-zag (n,0)[10].

1.3.2 Synthesis of CNTs

There have been a variety of techniques developed to produce carbon nanotubes. Primary synthesis methods for single and multi-walled carbon nanotubes include arc-discharge [11, 12], laser ablation [11, 13] and chemical vapor deposition (CVD) [14].

Arc discharge technique generally involves the use of two high-purity graphite rods as the anode and cathode. An arc discharge is generated between rods under an inert gas atmosphere. The material then deposits on the cathode to form a build-up consisting of an outside shell of fused material and a softer fibrous core containing nanotubes and other carbon particles [11, 12]. This method requires very high temperatures ($>5000^{\circ}\text{C}$) and results in a mixture of impurities.

Laser ablation is described as when a graphite target is vaporized by laser irradiation under flowing inert gas at high temperatures (near 1200°C) [11, 13]. The

graphite target can be doped with cobalt and nickel catalyst. The condensed material is then collected on a water-cooled target.

CVD involves the decomposition of carbon-containing gases on the substrate in the presence of metal catalyst particles (Ni, Co, Fe) [14]. One unique aspect of CVD is its ability to synthesize aligned arrays of carbon nanotubes with controlled diameter and length.

Both the arc discharge and laser ablation methods are limited in the volume of material they can produce because of the size of the carbon source. On the other hand, the CVD technique is able to continuously process and produce high purity nanotubes, as well as being more amendable for large-scale processing.

1.3.3 Properties of CNTs

Carbon nanotubes are among the strongest and stiffest materials, with Young's moduli as high as over 1TPa [15] and tensile strengths of up to 200 GPa [16], which is several hundred times more than that of steel. Besides, CNTs can suffer up to 15 % strain before fracture as the elastic response to deformation [17]. They also have excellent electrical properties as conductors with a high electrical conductivity (even $>10^3$ S/cm) [18]. In addition, CNTs are thermally stable up to 2800°C in vacuum; their thermal conductivity in the axial direction is about twice as high as of present commercial synthetic diamond [19]. All of these properties offer great opportunities for the use of CNTs as remarkable composite fillers.

1.3.4 Functionalized CNTs

Due to the smooth graphene like surface of nanotubes, there is usually a lack of interfacial bonding between the polymer matrix and carbon nanotubes [20]. Functionalization of carbon nanotubes is expected to improve the dispersion process and also the interfacial bonding between the nanotubes and the resin. There are mainly two types of functionalization: covalent and non-covalent.

Covalent functionalization can be realized by either modifying the surface-bound carboxylic acid groups on the nanotubes or directly attaching reagents to the sidewalls of nanotubes. Two main strategies for the covalent grafting of polymers to the nanotubes have been reported: “grafting from” and “grafting to” [21, 22]. A possible functionalisation process is schematically shown in Figure 1.3 [23]. At first, nanotube ends are oxidized in order to generate carboxylic groups (step1). The opening of the CNT cap would enable a direct bonding of the tube ends via the carboxylic groups to the matrix. In the second step, the carboxylic groups would react with other functional groups and form bonds with them (step 2). Thirdly, by adding the polymer resin, the free amino groups on the surface of CNTs will react with the polymer matrix forming equivalent bonds, leading to an improved nanotube matrix bonding (step 3).

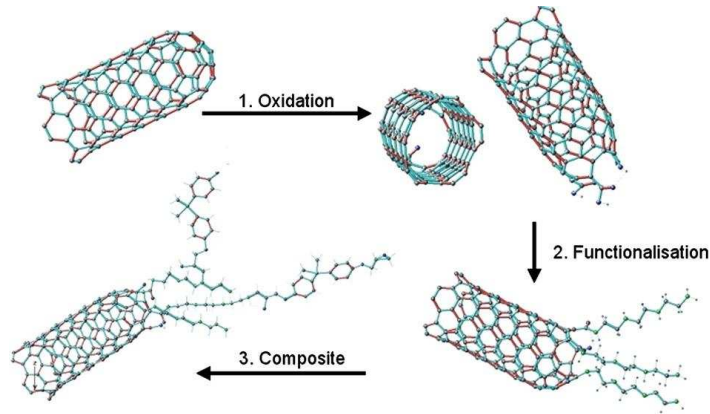


Figure 1.3 Scheme of the functionalization process of CNTs showing the whole cycle from the oxidation to the composite manufacturing [23].

Non-covalent binding between the polymer and nanotubes involves physical adsorption and wrapping of polymer molecules through van der Waals force and π - π interactions, which enables one to tailor their properties while still preserving nearly all of the nanotube's intrinsic properties [20, 24]. This method involves the use of surfactants, which coat the individual nanotubes and form a physical bridge to the matrix. The benefit of this procedure is that there is no disruption of the nanotube structure; however, the forces between CNTs and wrapped polymer are weak which may affect the efficiency of load transfer in the composites.

1.3.5 Fabrication of Nanotubes/Polymer Composites

Pristine carbon nanotubes have not yet been shown to be soluble in polymers illustrating the difficulty of overcoming the inherent thermodynamic drive of nanotubes to bundle [7, 9]. Because of the strong attractive interactions between the

individual nanotubes, they aggregate to form bundles which in turn create a highly entangled network. Two main issues have to be solved to improve the properties of the nanotube/polymer composites: homogenous dispersion of individual CNTs in the polymer matrix and the interfacial interactions between the nanotubes and the matrix [7].

The methods of solution blending, melt blending, and in situ polymerization are widely applied to produce nanotube/polymer composites and will be summarized here.

Solution blending is the most common method for fabricating polymer nanocomposites because of its effectiveness and small sample size. The general theme can be summarized as three major steps: disperse nanotubes in a suitable solvent for the polymer, mix with the polymer, and recover the composite by precipitating or casting a film. One of the benefits of this method is that agitation of the nanotube powders in a solvent facilitates nanotube de-aggregation and dispersion [20]. In general, agitation is provided by magnetic stirring, shear mixing, or sonication. Sonication can be used to prepare small batches of low viscosity matrix materials. In order to produce CNT nanocomposites, the sonication technique is best applied by first dispersing CNTs into an appropriate solvent. Note that sonication for a long time shortens the nanotube length, which is detrimental to the composite properties. The optimized sonication conditions that produce CNT dispersion are determined based on nanotube concentration and nanotube length distribution [9].

Melt blending is alternative for insoluble polymers. This technique involves the melting of polymer to form a viscous liquid and make use of high temperature and high shear forces to disperse nanotubes in a polymer matrix. The processing conditions are important and need to be optimized, because nanotubes can affect the viscosity of the nanotube/polymer suspensions, resulting in unexpected polymer degradation under conditions of high shear rates [25]. Advantages of this technique are its speed and simplicity, not to mention its compatibility with standard industrial techniques [26].

In situ polymerization strategies begin by dispersing nanotubes in monomer followed by polymerizing the monomers. It enables covalent bonding between functionalized nanotubes and the polymer matrix using condensation reactions. A simple case is to first disperse nanotubes in an epoxy resin followed by curing the resin with the hardener [9, 20].

1.4 Objective of the Thesis

The goal of the present study is to develop homogeneously dispersed and long-term stable suspensions of carbon nanotubes in vinyl ester (VE) systems for preparing master batches for composites used in wind turbine blades. A sonication method was used to disperse carbon nanotubes into a VE system with the help of eight different dispersing agents. Furthermore, a centrifugation approach was applied to screen suitable dispersing agents. The dispersion state of the CNTs within the

resulting polymer suspensions was analyzed via optical microscopy. The influences of CNTs and suitable dispersing agents on the mechanical properties of the system were studied through standard tensile testing and examination of fracture surfaces of the nanocomposites via SEM. We have looked at three thermoset resins, including epoxy, polyurethane and vinyl ester. Results for epoxy and polyurethane were presented in references [27, 28]. In this thesis, we will focus on vinyl ester resin.

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Chapter 2 Background

2.1 Vinyl Ester Resins

Vinyl ester (VE) resins are attractive alternatives for use in composite materials for wind-blade applications. VE resins possess superior properties including strong chemical resistivity, low viscosity during processing, relatively high mechanical properties after curing, as well as low cost and the ability to cure at room temperature.

VE resin is an epoxy-backbone based thermoset resin whose curing properties are similar to those of the unsaturated polyester resins [1]. Compared to polyester, VE resins differ primarily in the location of their unsaturated sites, which are reactive groups only at the ends of the molecular chains.

VE resins are the reaction products of epoxy resins with ethylenically unsaturated carboxylic acids [2]. The most common VE is made by esterifying a diepoxide resin with a monocarboxylic unsaturated acid such as methacrylic acid or acrylic acid. Such epoxy methacrylates or epoxy acrylates can be crosslinked in free radical polymerization alone or can be dissolved in unsaturated monomers such as styrene [1]. Figure 2.1 shows a typical reaction of VE polymerization.

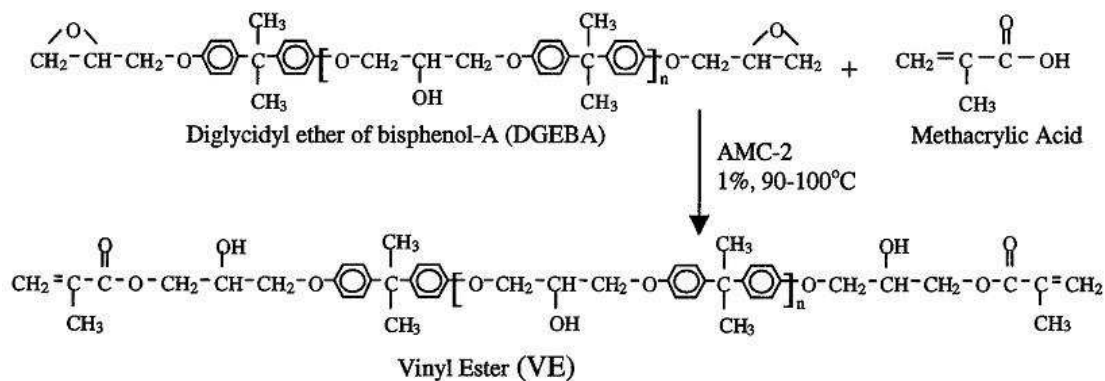


Figure 2.1 The polymerization of vinyl ester resin.

VE resins offer great toughness and chemical resistance properties which are generally superior to unsaturated polyesters [2]. The molecular weight of the VE resin can be varied by the choice of the epoxy backbone employed. In this manner, molecular weight and backbone structure dependent properties such as tensile strength and elongation, heat deflection point and reactivity can be varied for different applications. On the other hand, the superior chemical resistance of VE resins is in part due to the absence of ester linkages in the epoxy backbone in those sites where the polymer units are connected with phenyl ether linkages. These latter moieties are much more resistant than ester linkages to degradation in many chemical environments and especially in high pH alkaline conditions.

2.2 VE Nanocomposites

To improve the properties of VE resins, addition of various fillers, such as carbon nanotubes (CNTs) may be considered. CNTs based VE composite materials have the

potential to be used for a wide range of applications [3-18]. The presence of CNTs in the polymer matrix alone or along with other conventional reinforcements (e.g. glass and carbon fibers) gives rise to the development of two-phase or three phase carbon nanocomposites, respectively. In this section, we review the literature on two-phase and three phase VE/CNT composites.

2.2.1 Two-Phase VE/Carbon Nanotube Composites

As thermoset resins were commonly favored matrices for carbon nanotube incorporation, O. Gryshchuk et al [3] investigated the effect of adding MWCNTs in the matrixes of VE, VE-urethane and VE/epoxy (VE/EP) via sonication. The nanotube dispersion was studied by transmission electron microscopy (TEM). TEM images demonstrated that through sonication, disentangling aggregates of MWCNTs can only partially be achieved. To further study the dispersion state, electrical conductivity measurements were conducted and the results showed that VE/EP systems exhibited the highest electrical conductivity which may be related to the low cross-linking density of the matrix. As a result, this work concluded that MWCNTs may reinforce the ductile resin better, and for tightly cross-linked resins, i.e., VE-urethane matrix, lower aspect ratios of MWCNTs were suggested to achieve good dispersion.

Recent studies show that carbon nanotubes can be applied in polymer composites to make bipolar plates for polymer electrolyte membrane fuel cells because of their

extraordinary mechanical properties. S. Liao et al [4] used acid-treated MWCNTs together with poly(oxypropylene) (POP)-backboned diamines of molecular weights 400 and 2000 as the surfactant to fabricate VE nanocomposites. Results demonstrated that MWCNTs/POP2000 show better dispersion which led to greater electrical conductivity and higher flexural strength. It may imply the formation of an efficient network in the MWCNTs/POP2000 composites where many conductive paths are created to increase the conductivity.

Based on the previous work, S. Liao et al [5] further experimented on a different surfactant, maleic anhydride (MA) grafted on molecular weight 400 and 2000 poly(oxyalkylene) amines (POA400 and POA2000). The functionalized MWCNTs/MA-POA400 and MWCNTs/MA-POA2000 were also dispersed into a VE matrix. The results showed 2 wt% MWCNTs/MA-POA2000 reinforced VE composites exhibited 73% increase in flexural strength compared to neat resins. Furthermore, the in-plane and through-plane electrical conductivities and half-cell resistance of the nanocomposites all gave higher values than the ones with only 1 wt% MWCNTs/MA-POA2000. The better dispersion state for MWCNTs/MA-POA2000 could have resulted from the longer chains generating greater repulsion between MWCNTs, and preventing nanotube from bundling.

To continue studying the MWCNTs/MA-POA2000 composites, S. Liao et al [6] investigated the effect of surfactant POAMA with molecular weight 2000. The authors suggested that the terminal unsaturated double bonds of POAMA attached to MWCNTs can readily react with the VE and act as cross-links for polymer matrix. At

the same time VE continued to react with the styrene monomer curing agents. The SEM images showed that MWCNTs/POAMA exhibit higher dispersity in the VE matrix. Furthermore, the mechanical, electrical properties and contact resistances of MWCNTs/POAMA nanocomposites were enhanced significantly because of the better dispersion of MWCNTs. The overall performance was promising in terms of potential application of these materials for bipolar plates for fuel cells.

Direct mixing and sonication have been the most common techniques employed to disperse CNTs within thermoset polymer resins. Chen et al. [7] utilized the mechanical stirring to investigate the cure kinetics and dynamic mechanical behaviors of vinyl ester resins filled with MWCNTs. The degree of cure was decreased when CNTs were added into the system; however, the curing was enhanced after adding benzoyl peroxide as the second initiator in order to optimize the formulation. The resulting nanocomposites showed increased storage modulus and higher T_g compared to the neat resins using only one initiator.

Since dispersing CNTs into polymers is always a critical issue, other methods rather than sonication were employed to obtain a better dispersion state of CNTs. A.T. Seyhan et al [8] studied a three-roll milling method to disperse non-functionalized and amino-functionalized MWCNTs into VE resin. For polymer suspensions, the ones with non-functionalized and functionalized MWCNTs all behaved frequency independent in dynamic mechanical analysis, pseudo solid like at lower frequencies. The loss modulus values were observed to increase as the loading of CNTs increased. Besides, the suspensions demonstrated shear thinning behaviors regardless of

functional groups. Moreover, dynamic mechanical analysis revealed that amino-functionalized MWCNTs composites have better performances in loss and storage modulus and also exhibited a higher T_g . Those results were attributed to the improved chemical interactions between CNTs and polymer matrix when using amino functional groups. All these findings implied that three-roll milling is a powerful technique for the dispersion of CNTs into thermoset resins.

E. T. Thostenson et al [9] investigated the use of a calendaring approach to disperse CNTs in VE matrix. In this study, the high aspect ratios (length/diameter) of CNTs were preserved during processing and an electrical percolation network was formed with 0.1 wt% CNTs reinforcement. This finding offers great potential for future use of CNTs as in-situ sensors to detect deformation and damage in composites.

More research using three-roll milling was carried out to study the properties of CNTs composites. A.T. Seyhan et al [10] reported the mechanical and fracture behaviors of MWCNTs and double-wall carbon nanotubes (DWCNTs) dispersed in VE resins with and without amino functionalization. MWCNTs and MWCNTs-NH₂ reinforced composites demonstrated higher tensile modulus, fracture toughness and fracture energy values compared to the ones prepared with DWCNTs and DWCNTs-NH₂. Overall, regardless the type or loading level of CNTs, tensile properties did not show any significant improvement. The use of CNTs leads to increased tensile strength and fracture toughness in epoxy based composites. However, these behaviors are not likely to happen in resins polymerized via free radicals such as

VE and polyester, mainly due to the fact that free radicals generated by decomposition of initiator added to the resin system, could be easily trapped within the galleries of CNTs. Furthermore, post-curing at elevated temperatures causes built-in thermal residual stresses within the composites parts, which may induce voids and micro-cracks preferably located nearby or around the zone of agglomerated CNTs within the nanocomposites.

The basic kinetics of thermal curing of MWCNTs modified VE/polyester resins with and without amino functional groups was studied by A.T. Seyhan et al [11]. DSC measurements revealed that in the presence of CNTs, the polymer matrix exhibited higher heat of cure and lower activation energy compared with the neat resin. Both Infrared and Raman Spectroscopy demonstrated that amino functional groups at the surfaces of CNTs altered the chemical reactions by reacting with the double bonds of the VE resin, which were supposed to react with styrene.

H. Yurdakul et al [12] applied an alternating current electric field during cure of CNTs reinforced VE composites, aiming at inducing an aligned network of CNTs. Pristine DWNTs, MWCNTs and amino functionalized DWNTs, MWCNTs were dispersed into the matrix using a three-roll milling. It was found that composites with untreated CNTs exhibited higher electrical conductivity values than those with amino functionalized CNTs. In addition, catalyst particles (Fe and Co), which are the components of VE polymerization, were charged when the electric field was applied to induce alignment. Those particles moved around inside the matrix and contributed

to the orientation of CNTs and finally increased the electrical conductivity and thermal properties of the achieved composites.

2.2.2 Three-Phase VE/Carbon Nanotube Composites

Fan et al [13,14] investigated the effect of flow through glass fiber porous media on the dispersion of carbon nanotubes in VE. They found that the shear forces generated in flow through the glass fibers would break down the average aggregate size of MWCNTs and at the same time generate a filtering effect. To further study the orientation of CNTs in shear flow, they observed acid oxidized MWCNTs to go through a micro channel, nano channel and across a cylinder. The results showed that the degree of MWCNT alignment increased with increasing shear.

J. Zhu et al [15] introduced pre-dispersed single-walled carbon nanotubes into glass fiber reinforced VE composites through vacuum assisted resin transfer molding (VARTM). The use of functionalized nanotubes improved the interfacial interactions, which was evidenced by the 45% increase in interlaminar shear strength with only 0.015wt% content of nanotubes. The enhancement of shear strength was preliminarily explained as follows: nanotubes act as interfacial bonding agents to increase the adhesion between the VE matrix and the glass fiber at the interface especially in the presence of functional groups. This bridging effect would eventually toughen the system and lead to the increase of the delamination resistance of fibers. Meanwhile,

the nano-sized fillers would absorb more energy when the composite is deformed under stress due to their extensive surface areas.

In a related research, thermal conductivity of MWCNTs/glass fiber/VE resin was discussed. S. Wang and J. Qiu [16] dispersed MWCNTs into a low-viscosity polyester/VE resin by ultrasonication and shearing. Then the glass fiber polymer composites were fabricated via resin infusion molding. The measured local density showed a uniform distribution and SEM images indicated a homogeneous dispersion of CNTs. The thermal conductivity of corresponding composites increased 1.5-fold by incorporating 3wt% CNTs.

As CNTs offers opportunities to enhance interfacial interaction of polymer and glass fibers, a recent study focused on flame-synthesized carbon nanotubes (F-CNTs) in glass fiber reinforced plastic (GFRP) composites [17]. The F-CNTs were synthesized using ethanol as the carbon source and a pulse-plated Ni nanocrystalline layer upon a copper substrate as the catalyst. The intrinsic characteristics of F-CNTs include low crystallinity with a large number of defects and chemical functional groups on the surface. The SEM results revealed a better dispersion of the F-CNTs than SWCNTs and conventional CVD-prepared MWCNTs. Besides, no interfacial debonding was observed at the fracture surface between glass fibers and polymer matrix. The reason for the better reinforcing effect of F-CNTs was attributed to the unique surface reactivity resulting from the flame synthesis. The special preparation enabled F-CNTs reactivity for possible interactions with both glass fibers and polymer matrix.

Y.W. Kwon et al [18] explored the possibility of localized reinforcement of a weak point, the scarf joint, so as to prove that CNTs enhance the scarf joint bonding at the interface. First, a dispersing solution of CNTs in acetone was obtained. Secondly, different concentration levels of CNTs at certain surface area were compared when studying the strength of the composite joint. It was shown that concentration at 7.5g/cm^3 reflected a better reinforcement. Thirdly, the appropriate type of CNTs was determined. In general, conventional MWCNTs achieved the highest improvement in strength and elastic modulus.

In order to study the effect of CNTs at the fiber-matrix interface, M. A. Bily and Y. W. Kwon [19] investigated the interface fracture and crack growth of glass fiber or carbon fiber reinforced VE/nanotube composites. Carbon nanotubes were introduced to the interface using a two-step curing process and prepared for Mode II fracture testing. There was great improvement in interface fracture toughness because of CNTs for both glass fiber and carbon fiber reinforced composites. In addition the results indicated a linear relationship between crack length and electrical resistance for carbon fiber composites. This study revealed a potential use for CNTs in composites along the critical interface not only to improve fracture toughness, but also to detect and monitor interfacial damage.

In conclusion, many studies have been carried out on carbon nanotube/vinyl ester nanocomposites to explore the prospects of carbon nanotubes as reinforcement in polymer matrix. Carbon nanotubes were found helpful to enhance matrix properties such as strength, thermal conductivity, and electrical conductivity. The combination

of both carbon nanomaterials and other reinforcements leads to the development of advanced nanocomposites which can be used for various applications.

2.3 References

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Chapter 3 Experimental Procedures

3.1 Materials

The vinyl ester resin system used in this study was DION IMPACT 9102-75, kindly supplied by Reichhold. It is comprised of vinyl ester resin, styrene, and cobalt compounds. The catalyst (NOROX CHP) was made of cumene hydroperoxide. MWCNTs were obtained from Bayer Material Science, synthesized by chemical-vapor deposition. The MWCNTs (Baytubes C150P) exhibit an average diameter of 13 nm and a length larger than 1 μm . A number of block copolymers have been used as dispersing agents for the vinyl ester system: BYK-2150, BYK-2155 and BYK-9077 are block-copolymers with pigment affinic groups (BYK-Chemie); BYK-9076 is an alkylammonium salt of a high molecular weight copolymer; L-7500 and L-7602 are polyalkyleneoxide modified polydimethylsiloxanes (Momentive); L-7607 is a siloxane polyalkyleneoxide copolymer and B60H consists of a polyvinyl butyral (Kuraray). All chemicals were used as received.

3.2 Screening of Dispersing Agents for Vinyl Ester via Centrifugation

MWCNTs were added to vinyl ester and dispersed by using simultaneous sonication (Sonics CP750, 165W) and magnetic stirring for 10 min. Suspensions of MWCNTs in the vinyl ester system have been prepared with or without the addition of dispersing agents. The concentration of CNTs has been fixed at 0.1 wt% in relation

to the vinyl ester resin. The amount of dispersing agent has been fixed at 1x (one times) or 10x the amount of CNTs. After finishing the dispersion process, the suspensions have been subjected to centrifugation at 150 *g* for 2 hr.

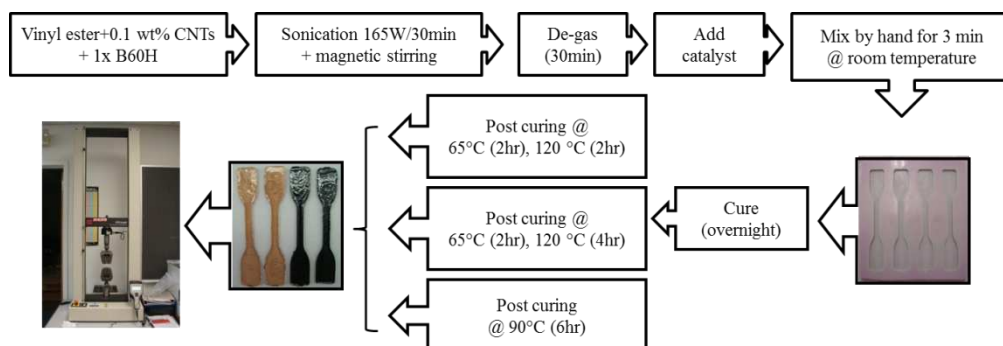
3.3 Curing Conditions of VE for Tensile Tests

Neat vinyl ester resins have been prepared using three curing conditions. Vinyl ester resin and the catalyst (1.5 wt% in relation to VE) were mixed for 3 min by stirring and the mixture was allowed to cure at room temperature overnight. Three routes of post-curing conditions have been applied to optimize the resin performance.

3.4 Fabrication of Vinyl Ester Composites

Based on the dispersion and curing condition results, vinyl ester composites have been prepared for mechanical testing. In a typical experiment, MWCNTs and block copolymers were dispersed in vinyl ester using simultaneous magnetic stirring (400 rpm) and sonication during 30 min. The suspension of MWCNTs was then degassed by applying vacuum for 30 min to remove trapped bubbles. Further, the suspension was mixed with the catalyst (1.5 wt% in relation to vinyl ester) for 3 min by stirring and the mixture was allowed to cure at room temperature overnight and finally post-cured at 90 °C for 6 hours. Reference samples of neat resin were also prepared following the same route. Three different concentrations of MWCNTs were used, namely 0.1, 0.2, 0.3 wt% correlated to the vinyl ester. Scheme 3.1 summarizes the

experimental procedure applied to samples preparation and the three different curing cycles used.



Scheme 3.1 Experimental procedure for preparation of vinyl ester composites reinforced with 0.1wt% MWCNTs.

3.5 Characterization Techniques

Optical microscopy was carried out by using an Olympus BX51 in the transmitted light configuration. Samples had nominal dimensions of 20 mm by 15 mm with a thickness of $100 \pm 50 \mu\text{m}$. The tensile properties of the composites were investigated according to ASTM 638-03 using an Instron 1011 universal tensile tester at a crosshead speed of 1 mm/min. Fracture surfaces of the composite samples were observed using a scanning electron microscope (JEOL JSM-6510LV) with an operating voltage of 30 kV.

Chapter 4 Results and Discussion

4.1 Screening of Dispersing Agents

4.1.1 Epoxy System

Figure 4.1 shows the resistance to sedimentation of 0.1 wt% CNTs dispersed in epoxy and hardener after sonication. The suspensions containing nanotubes were stable for at least 168 hr for the both the neat epoxy and for the systems using 1x amount of CNTs of any of the eight block copolymers. The high viscosity of the suspensions after the addition of CNTs makes the neat epoxy could sustain CNTs without sedimentation. The findings that all block copolymers were efficient for the stabilization of the CNTs in epoxy may also due to the elevated viscosity of the system which kept the fillers in the suspension. However, even with the aid of block copolymers, sedimentation of large aggregates of CNTs can be expected due to density differences.

On the other hand, considering the dispersions in the hardener, only BYK-9076 was not effective for the stabilization of the suspensions. As shown in Figure 4.1, the CNTs were already stably dispersed in the neat epoxy and hardener, thus the result obtained by the addition of various block copolymers using sonication was not sufficient to confirm a real positive effect of the aid of dispersing agents on the stability of the suspensions. Therefore, to further check the stability of the suspensions of nanotubes, a more extreme approach has been applied by having the dispersions

centrifuged at 150 *g* for 2 hr. Again suspensions of 0.1 wt% CNTs in different components of epoxy have been prepared with the aid of eight different dispersing agents. The resistance to sedimentation of the CNTs in different media obtained is summarized in Table 4.1.

The neat epoxy results in unstable CNT dispersions; however, all of the eight different dispersing agents investigated are suitable for the stabilization of CNTs suspensions. Note that the concentration of dispersing agents is relatively low: 1x the amount of CNTs. On the other hand, only four among the eight dispersing agents, namely BYK-2155, L-7500, L-7602 and B60H, were found to be effective for stabilizing CNTs into the hardener. Therefore the centrifugation method has proved to be a reliable and efficient method for studying the resistance to sedimentation of the different systems, compared to leaving the samples undisturbed for several days [1].

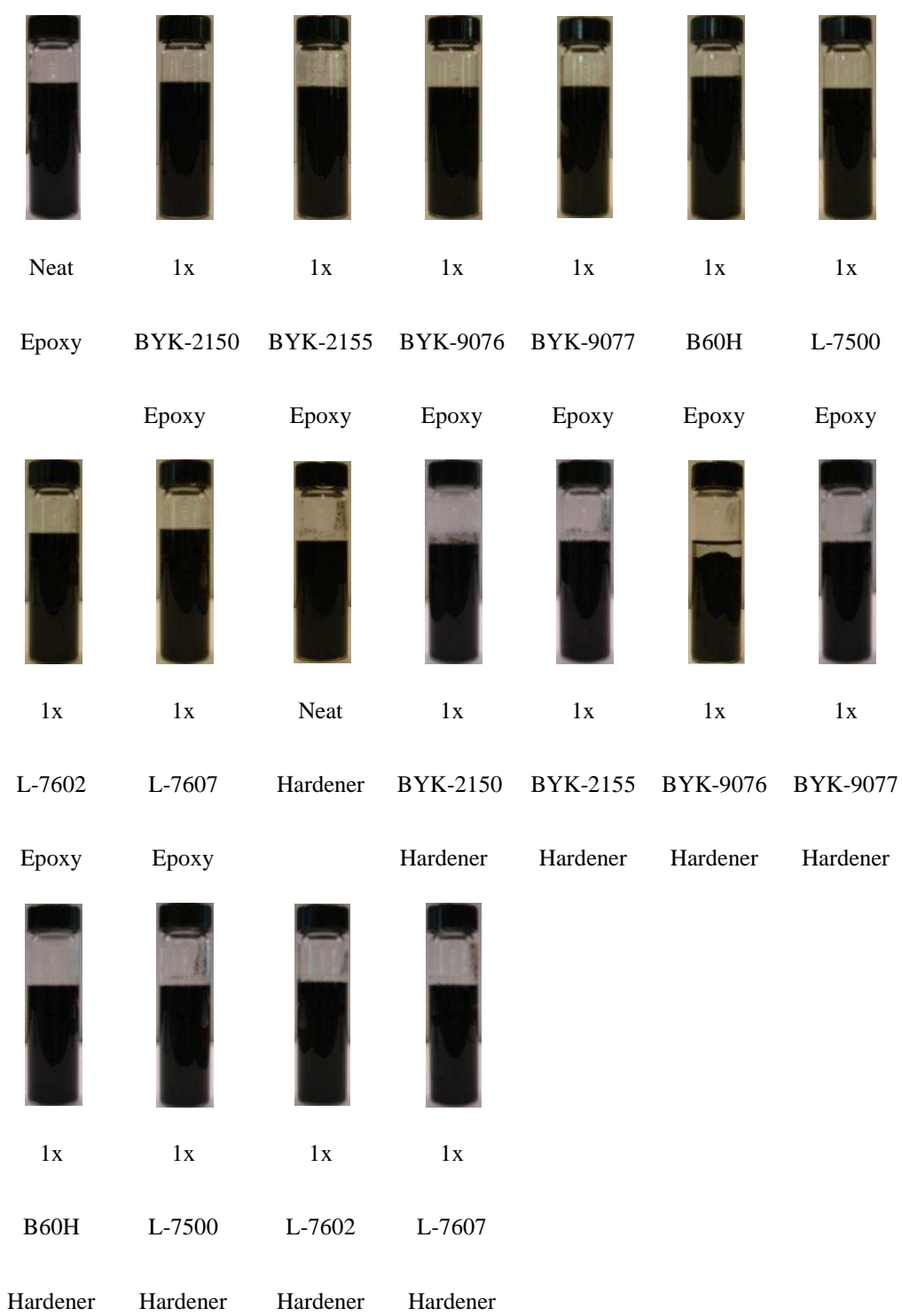


Figure 4.1 Dispersion stability of CNTs in epoxy and hardener after 168 hr. The amount of dispersing agent used is the same as the CNTs (1x). Differences in the color of some images are due to lighting variations only.

Table 4.1 Stability state observed using centrifugation for dispersions of CNTs in epoxy system using various dispersing agents at 1x the CNT concentration. Key: (✓) = stable; (x) = unstable.

Dispersing Agent	Epoxy	Hardener
None	x	x
BYK-2150	✓	x
BYK-2155	✓	✓
BYK-9076	✓	x
BYK-9077	✓	x
B60H	✓	✓
L-7500	✓	✓
L-7602	✓	✓
L-7607	✓	x

4.1.2 Polyurethane System

Figure 4.2 summarizes the resistance to sedimentation of 0.1 wt% CNTs dispersed in polyol and isocyanate using the sonication method. The results show that CNTs cannot be stably dispersed in both neat polyol and isocyanate. In addition, the viscosity of the polyol and isocyanate are lower than that of the neat epoxy which may enhance the effect of block copolymers in suspension stability. Dispersions in polyol stable for 192 hr were obtained by using 1x B60H. On the other hand,

dispersions of CNTs in isocyanate, stable for more than 192 hr have been obtained by adding 10x L-7602.

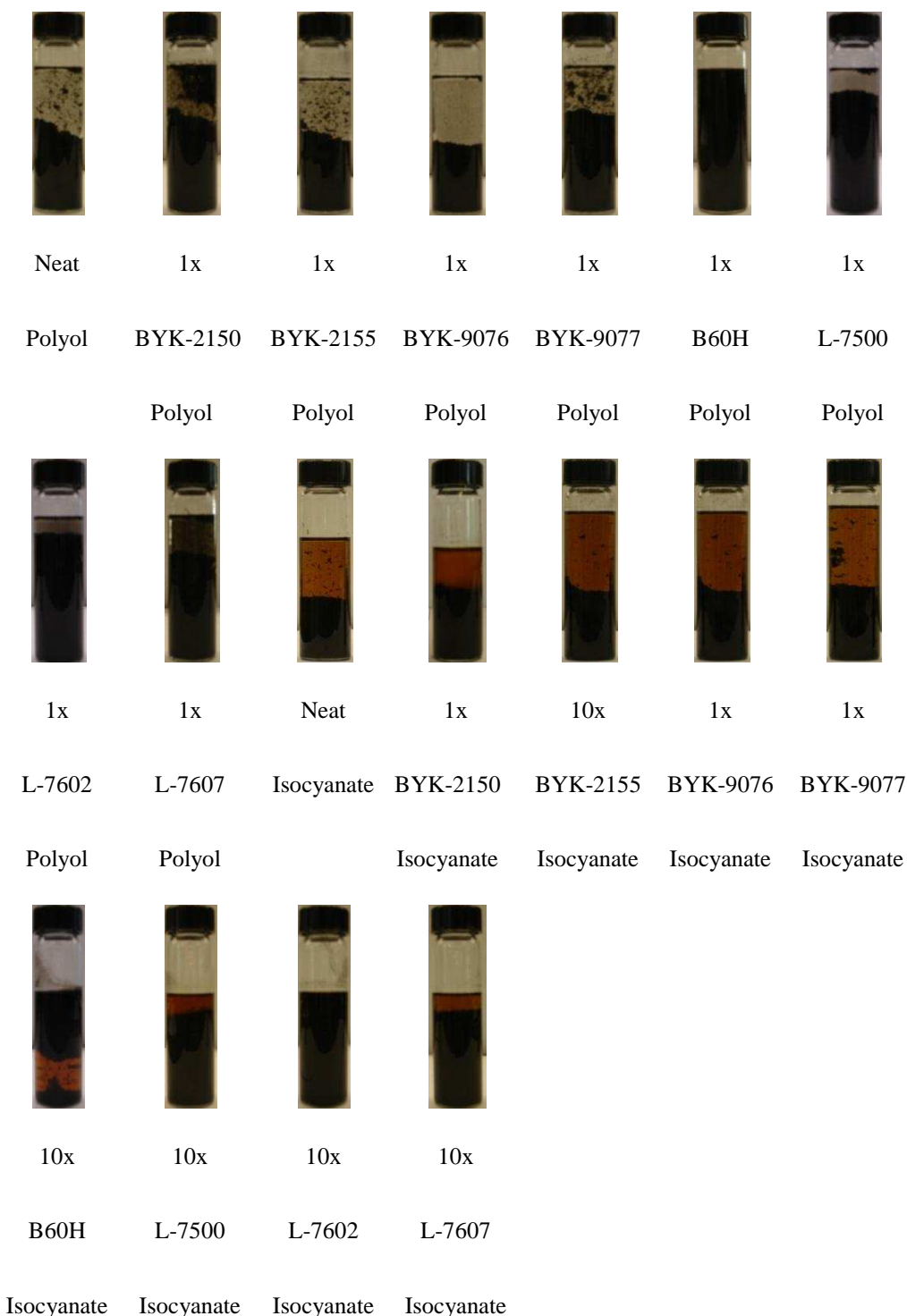


Figure 4.2 Dispersion stability of CNTs in polyol and isocyanate after 192 hr. The amount of dispersing agent used is either the same as the CNTs (1x) or 10x. Differences in the color of some images are due to lighting variations only.

To further check the stability of the suspensions, the centrifugation method has been applied. The results confirmed that suspensions prepared using 1x B60H in polyol were stable to sedimentation and there was no dispersing agent suitable for stabilizing CNTs in isocyanate [2].

4.1.3 Vinyl Ester System

Based on our dispersion studies of CNTs in epoxy and polyurethane systems [1, 2], the centrifugation method proved to be reliable and effective to identify suitable dispersing agents to obtain long-term stably dispersed CNTs in polymer resins. According to this qualitative methodology, we assume that if a suspension doesn't show visible phase separation after the centrifugation, the block copolymer is a suitable candidate for the stabilization of CNTs. Figure 4.3 summarizes the resistance to sedimentation of 0.1 wt% CNTs dispersed in the vinyl ester resin after centrifugation. The use of the neat resin does not render stable dispersions of CNTs. The only suitable dispersing agent is B60H at 1x of the amount of CNTs. None of the other tested dispersing agents at either 1x or 10x of the amount of CNTs proved to be effective against sedimentation.

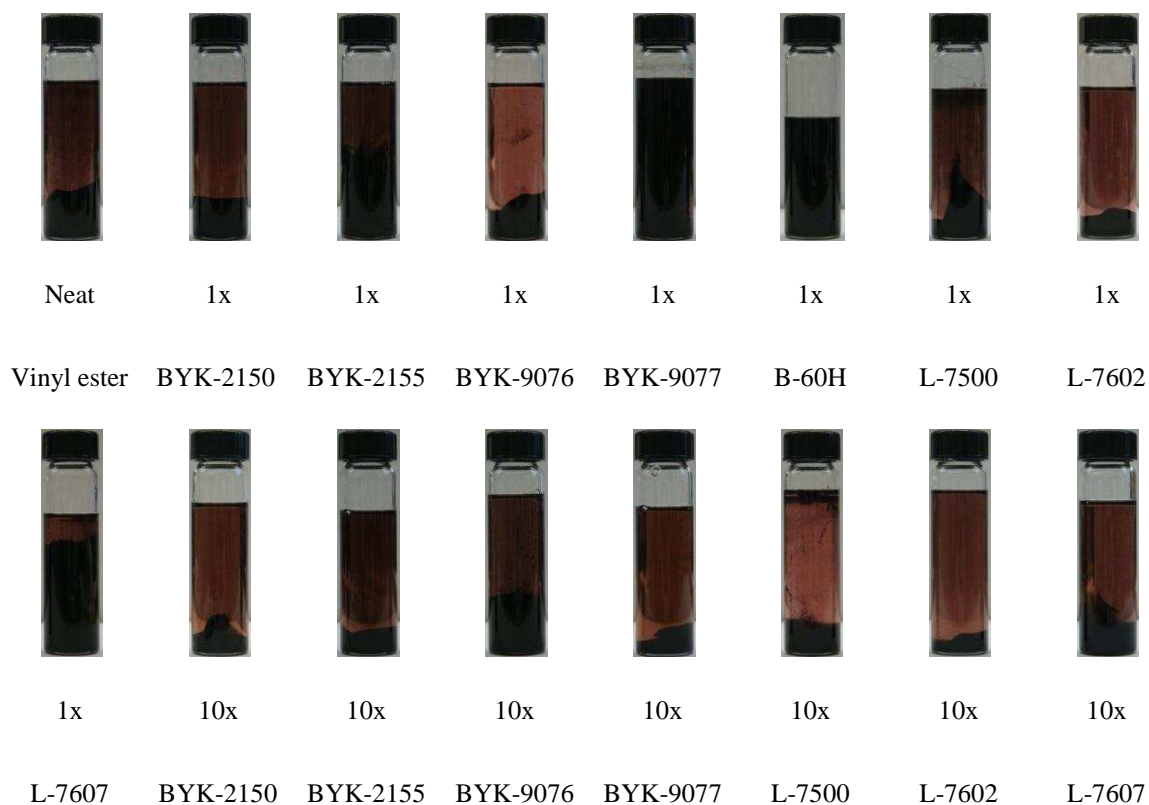


Figure 4.3 Dispersion stability of CNTs in the vinyl ester after 2 hr centrifugation. The amount of dispersing agent used is indicated in the figure. Differences in the color of some images are due to lighting variations only.

4.2 The Effect of Dispersing Agents

The results observed in dispersion stability obtained by using the block copolymers can be explained in terms of specific interactions as outlined below. B60H is a polyvinyl butyral (PVB) based block polymer which could react with epoxy groups via the remaining hydroxyl groups of the non-acetylated polyvinyl molecular part [3]. For vinyl ester resins, it is possible that the electronegative oxygen atom near the unsaturated sites attracts the hydrogen atom in the PVB molecules,

building hydrogen bonds between the vinyl ester and PVB polymer chains (Figure 4.4). This non-covalent interaction has only 5% or so of the strength of a covalent bond. However, when many hydrogen bonds form between those two molecules, the final network can be sufficiently strong. As a result this B60H acts as a plasticizer, by building gaps between polymer chains for greater mobility and reduced inter-chain interactions. At the same time, it may induce chemical bonding with the CNTs and create an effective filler-matrix interface, further improving stress transfer between the CNTs and the polymer matrix.

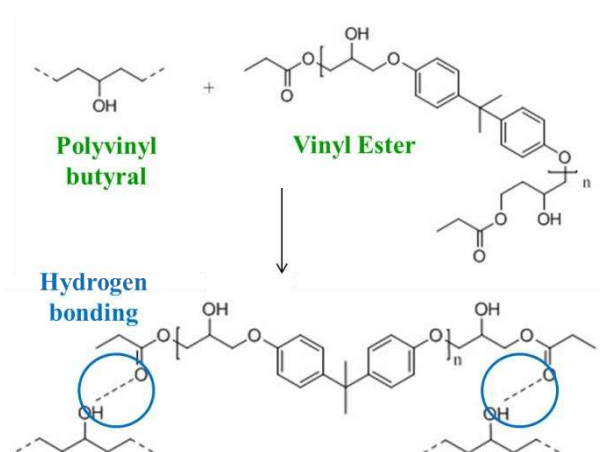


Figure 4.4 The proposed formation of hydrogen bonds between polyvinyl butyral and vinyl ester.

BYK-9077 is a high molecular weight copolymer with pigment affinic groups, consisting of a lyophobic and a lyophilic block. The lyophobic part adsorbs onto the surface of MWCNTs, while the lyophilic part is swollen by the solution, preventing agglomeration (Figure 4.5). In addition, block copolymers may also act as interfacial binding agents improving stress transfer between the filler and the polymer matrix [4].

The dispersing agent L-7602 is a polyalkyleneoxide modified polydimethylsiloxane (PDMS). It has been shown in the literature that silicone surfactants demonstrate advantages in dispersing carbon nanotubes [5, 6]. They possess better properties than traditional alkyl chain surfactants in terms of wettability and extremely low surface tension. The siloxane based copolymers contain a flexible -Si-O-Si- hydrophobic main chain and hydrophilic pendant parts of PDMS. The -Si-O-Si- chain can easily coat the surface of CNTs through hydrophobic and other intermolecular interactions, while the hydrophilic parts provide the solubilization of CNTs and prevent CNTs from aggregating via steric stabilization.

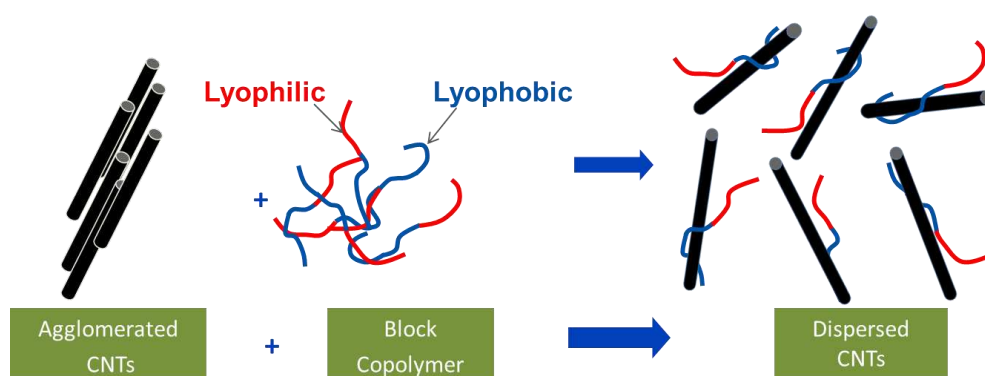


Figure 4.5 Schematics for CNTs interactions with block copolymers [4].

4.3 Optical Microscopy Characterization

Figure 4.6 shows optical micrographs for the suspensions obtained after sonication. We notice the presence of large agglomerates (10-100 μm in diameter) in the images taken right after sonication. Moreover, we also see some bridging effects between nanotubes after 50 hr (Figure 4.6b). When left undisturbed, the dispersed

CNTs reaggregate because of the van der Waas forces. The only system which did not exhibit bridging effects was the one employing B60H as a dispersing agent (Figure 4.6c). It is interesting to note that, whereas some large agglomerates were still present in the system employing B60H right after sonication, re-agglomeration did not occur after 50 hr at rest, indicating once the nanoparticles were separated by sonication, steric equilibrium was achieved (Figure 4.6d). This result is consistent with the centrifugation test screening of the various dispersing agents discussed previously. Another interesting result is the apparent effectiveness of the dispersing agent L-7602 at 10x in preventing further carbon nanotube agglomeration in the suspensions kept at rest for 50 hr after sonication (Figure 4.6f). However, the centrifugation test results did not corroborate the finding and L-7602 was not used in further studies.

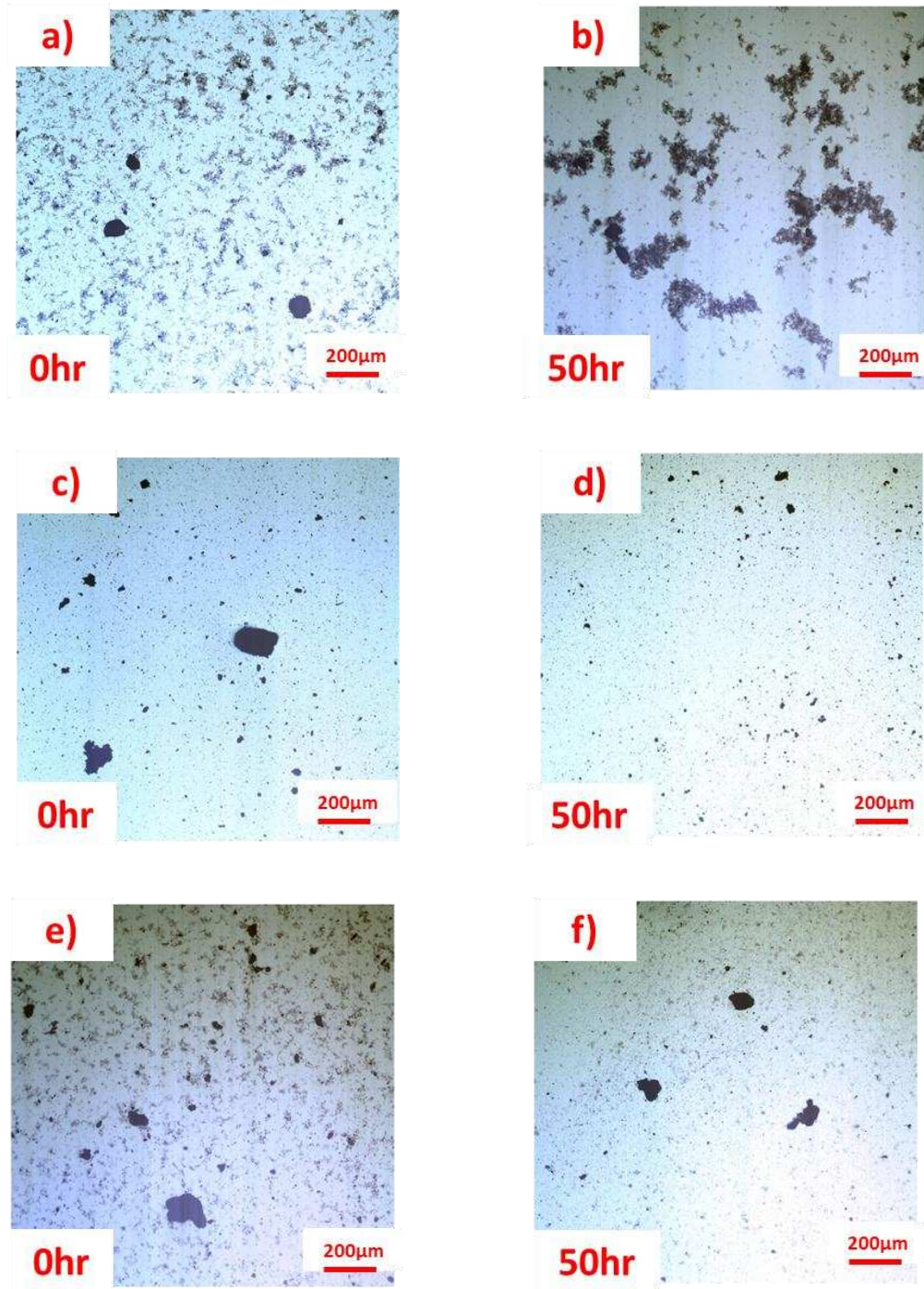


Figure 4.6 Optical microscope images of 0.1 wt% CNTs in the vinyl ester resin: a, b) neat vinyl ester; c, d) VE+CNTs+1x B60H; e, f) VE+CNTs+10x L-7602. The images were taken immediately after the dispersion step (0 hr) and 50 hr after finishing the sonication.

4.3 Curing Conditions of VE for Tensile Tests

The crosslinking reaction of vinyl ester proceeds by free-radical polymerization with organic peroxides as initiators. The rate of the polymerization reaction depends on the temperature and concentration of the monomer and initiator [7]. In our case, the ratio of the monomer and initiator has been fixed, while curing temperatures need to be determined for optimum resin performances and desired material properties.

Table 4.2 shows the tensile test results for three different post-curing conditions of the neat vinyl ester. The best results in terms of tensile strength and elongation at break are obtained when post-curing the samples for 6 hours at 90°C. The representative stress-strain curve is shown in Figure 4.7.

Table 4.2 Tensile properties of VE resins prepared under different post-curing conditions. E_t : Young's modulus. σ_M : Tensile strength. ϵ_B : Elongation at break.

Sample code	E_t (GPa)	σ_M (MPa)	ϵ_B (%)	Post-curing conditions
1	1.70±0.10	28.14±5.74	1.63±0.31	65°C (2hr), 120° C (2hr)
2	2.03±0.22	21.20±5.24	1.11±0.19	65°C (2hr), 120° C (4hr)
3	1.89±0.19	36.14±6.45	2.09±0.37	90°C (6hr)

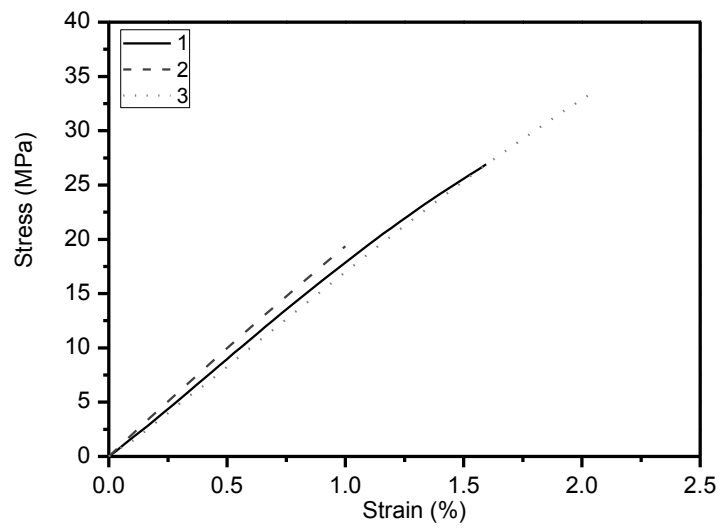


Figure 4.7 Representative stress-strain curves for neat vinyl ester resins at different curing conditions.

4.4 Tensile Properties of VE Composites

Table 4.3 summarizes the tensile test results for vinyl ester composites with different concentrations of CNTs prepared with (1x the amount of CNTs) and without the dispersing agent.

Table 4.3 Tensile properties of vinyl ester composites reinforced with CNTs.

E_t : Young's modulus. σ_M : Tensile strength. ϵ_B : Elongation at break.

Sample Code	CNTs (wt%)	B60H (wt%)	E_t (GPa)	σ_M (MPa)	ϵ_B (%)
1	--	--	1.89±0.19	36.14±6.45	2.09±0.37
2*	--	--	1.89±0.12	58.07±0.68	3.51±0.29
3	--	0.1	2.05±0.25	51.86±4.08	2.84±0.44
4	0.1	--	1.84±0.17	41.39±3.18	2.43±0.35
5	0.1	0.1	1.84±0.23	45.45±5.11	2.66±0.16
6	--	0.2	1.82±0.07	47.13±1.85	2.87±0.17
7	0.2	--	2.01±0.10	44.89±0.73	2.28±0.04
8	0.2	0.2	1.89±0.31	41.40±6.58	2.29±0.40
9	--	0.3	1.95±0.15	49.35±4.61	2.84±0.45
10	0.3	--	1.76±0.12	40.69±4.72	2.30±0.18
11	0.3	0.3	1.77±0.21	39.43±3.35	2.30±0.20

*No.2 neat resin was prepared with sonication for 30min.

Figure 4.8 shows the effect of B60H on the Young's modulus, tensile strength and elongation at break for the vinyl ester composites at different concentrations of CNTs. For the reference samples, tensile properties of two sets of neat vinyl ester resins were compared, one was cured right after mixing with the catalyst; the other was sonicated for 30 min before adding the catalyst. It was interesting to see that the sample subjected to sonication exhibited a more ductile behavior with higher tensile strength and higher elongation at break compared to the one without sonication (Figure 4.9). The differences may be a result of the use of sonication, which

potentially could allow chemical bonds of polymers to break and thus enhance polymerization. It has been demonstrated that the sonication involves the formation and collapse of cavitation bubbles, that produces locally elevated temperature (around 5000K) and high pressures (roughly 1000 atm) [8-10]. Double bonds in monomers like vinyl monomers, in or beside the cavitation bubbles (which are caused by the ultrasound waves) may rupture to radicals, initiating the polymerization [11].

Figure 4.8b-c also shows that vinyl ester resins with only the B60H exhibit good mechanical properties in terms of relatively high tensile strength and elongation at break. The reason could be due to the strong hydrogen bonds formed between vinyl ester and PVB polymer chains, which finally leads to a reinforcing effect of PVB for vinyl ester resins.

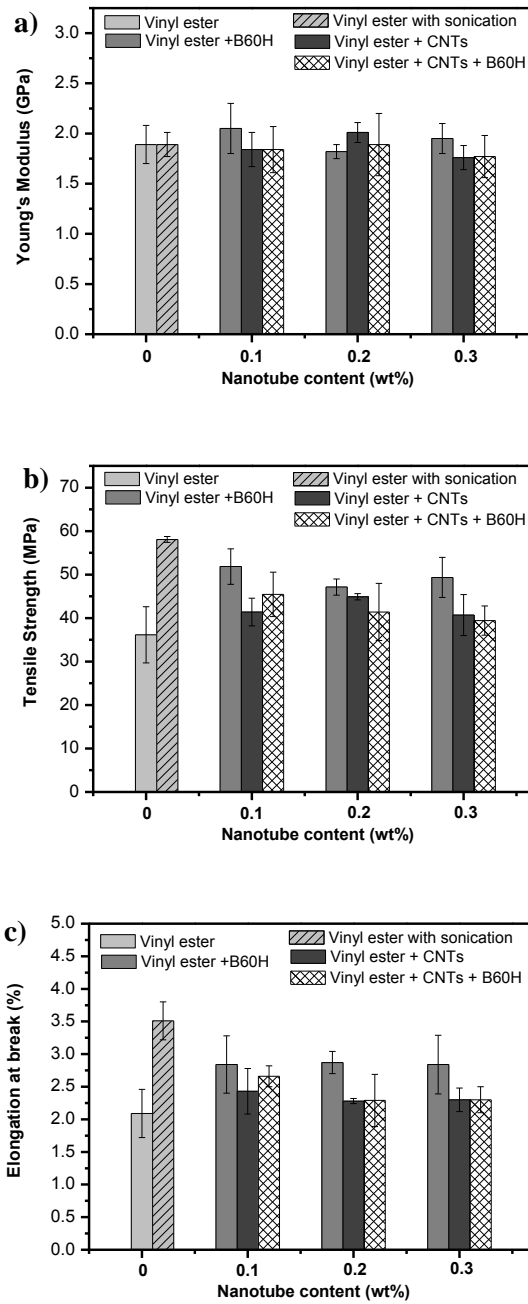


Figure 4.8 Effect of the dispersing agent and concentrations of CNTs on: a) Young's modulus; b) tensile strength; c) elongation at break of vinyl ester composites. Note that the dispersing agent is always used at 1x of CNTs.

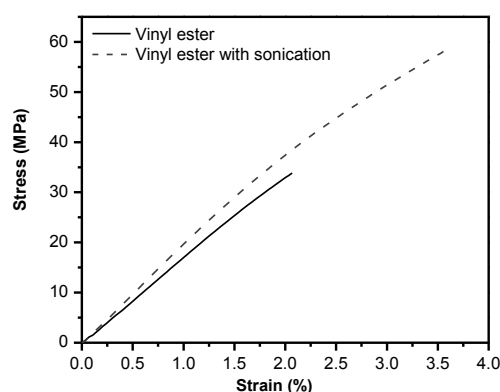


Figure 4.9 Representative stress-strain curves for vinyl ester with and without sonication.

For the tensile properties of vinyl ester composites, most composites show similar Young's modulus in comparison with the neat resin. The samples prepared with 0.1 and 0.2 wt% CNTs show slightly improved modulus and tensile strength. The Young's modulus for the sample with 0.2 wt% CNTs is the highest among all the nanocomposites, while it is still within the range of the neat resin considering standard deviations. For composites with 0.3 wt% CNTs, both with and without the dispersing agent, the modulus and tensile strength were found to be reduced, whereas the elongation at break was not affected. This decline can be attributed to the less uniform dispersion of CNTs at high concentrations and the presence of CNT agglomerates which act as defects in the composite and result in a brittle and fast failure.

Interesting to note is the decline in the tensile properties of the composites by comparison with the effect of using only the dispersing agent with the resin. In related studies we reported that the addition of CNTs using block copolymers leads to improved elastic modulus and tensile strength for epoxy based composites [1, 2].

However, this effect is not so pronounced in the case of vinyl ester resins which are polymerized via free radicals. This is believed to result from the retardation of the vinyl ester polymerization at the CNT interface [12, 13]. Since CNTs can effectively react with peroxides and trap free radicals, this can affect the polymerization at room temperature and greatly reduce the crosslinking density within the vinyl ester resin.

Another possible reason for the decreased modulus of the systems containing CNTs may reside in the post-curing. It has been reported that post-curing at elevated temperatures may cause built-in thermal residual stresses within the composite, which further can induce voids and micro-cracks concentrated at the CNT agglomerate sites which manifests as a reduced mechanical strength of the final composites [14]. However, in comparison with neat vinyl ester, higher tensile strength and greater elongation at break could be achieved for some of the composites reinforced with CNTs.

Figure 4.10 shows the stress-strain curves of the nanocomposites with CNTs and the dispersing agent. As the concentrations of CNTs and B60H increase, the reinforcement role seems to be diminished. However, composites with 0.1 wt% CNTs and 1x dispersing agent indicate improved ductility and increased toughness. In brief, the use of the dispersing agent is beneficial in achieving a balanced performance of tensile properties for low loading levels of CNTs in vinyl ester composites.

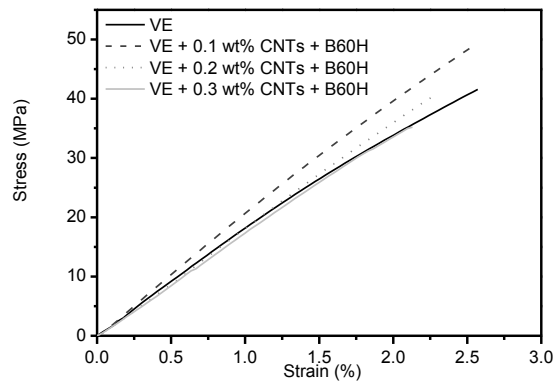


Figure 4.10 Representative stress-strain curves for vinyl ester based composites with CNTs and B60H. B60H was fixed at 1x of CNTs.

4.5 Fracture Surface of the Nanocomposites

The fracture surface for neat vinyl ester is shown in Figure 4.11. The neat resin revealed a relatively smooth fracture surface and the higher magnification image indicates typical fracture features for brittle polymers with river patterns, thus accounting for the low strength and strain of the unfilled vinyl ester.

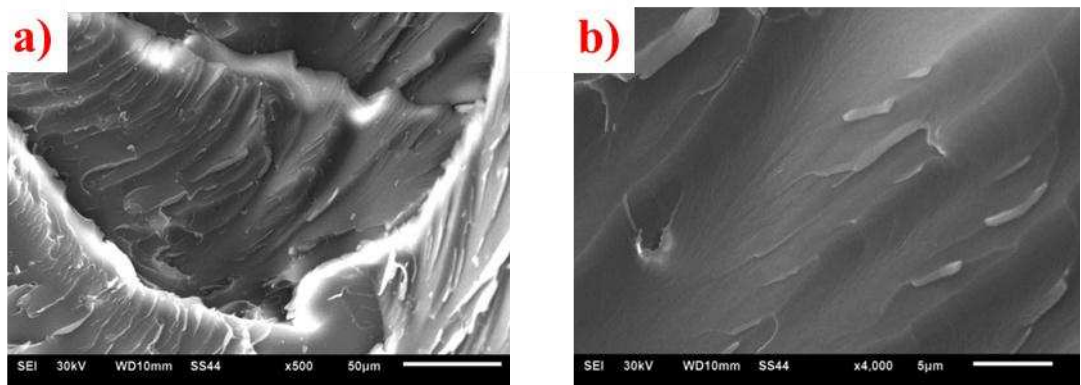


Figure 4.11 Fracture surfaces of neat vinyl ester (a, b) at different magnifications after tensile testing.

The fracture surfaces of the nanocomposites show considerably different fractographic features (Figure 4.12a-f). As individual nanotubes are seen as white short threads after sputtering, the distribution of the carbon nanotubes can be detected at high magnifications (Figure 4.12b, 4.12d). In the composites, the increased surface roughness implies that the path of the crack tip may be distorted because of the carbon nanotubes, making crack propagation more difficult.

The granular regions in the fracture surface become smaller and smaller with increasing CNT loading in nanocomposites both with and without dispersing agent. As the content of CNTs increases, composites without dispersing agents show uniformly dispersed nanotubes and even large aggregates of CNTs at the surface, which indicates the poor interactions of CNTs and vinyl ester matrix. When the CNT content reached 0.3 wt%, more agglomerates of carbon nanotubes were observed at the fracture surface (Figure 4.12e). These agglomerates could act as defects and cause detrimental effects in mechanical properties of composites. The heterogeneity may explain the variation in tensile results obtained in the study. On the other hand, the composites prepared with the dispersing agent exhibit better CNT distribution within the matrix compared to those without the dispersing agent. The SEM images for composites with dispersing agent illustrate that the CNTs are more homogeneously dispersed, with only a few agglomerates at each concentration. At 0.1 wt% CNT content with the dispersing agent, both modulus and strength were increased in spite of the fact that CNTs could alter the resin chemistry by trapping free radicals. Additional work is needed to test and validate the above inference.

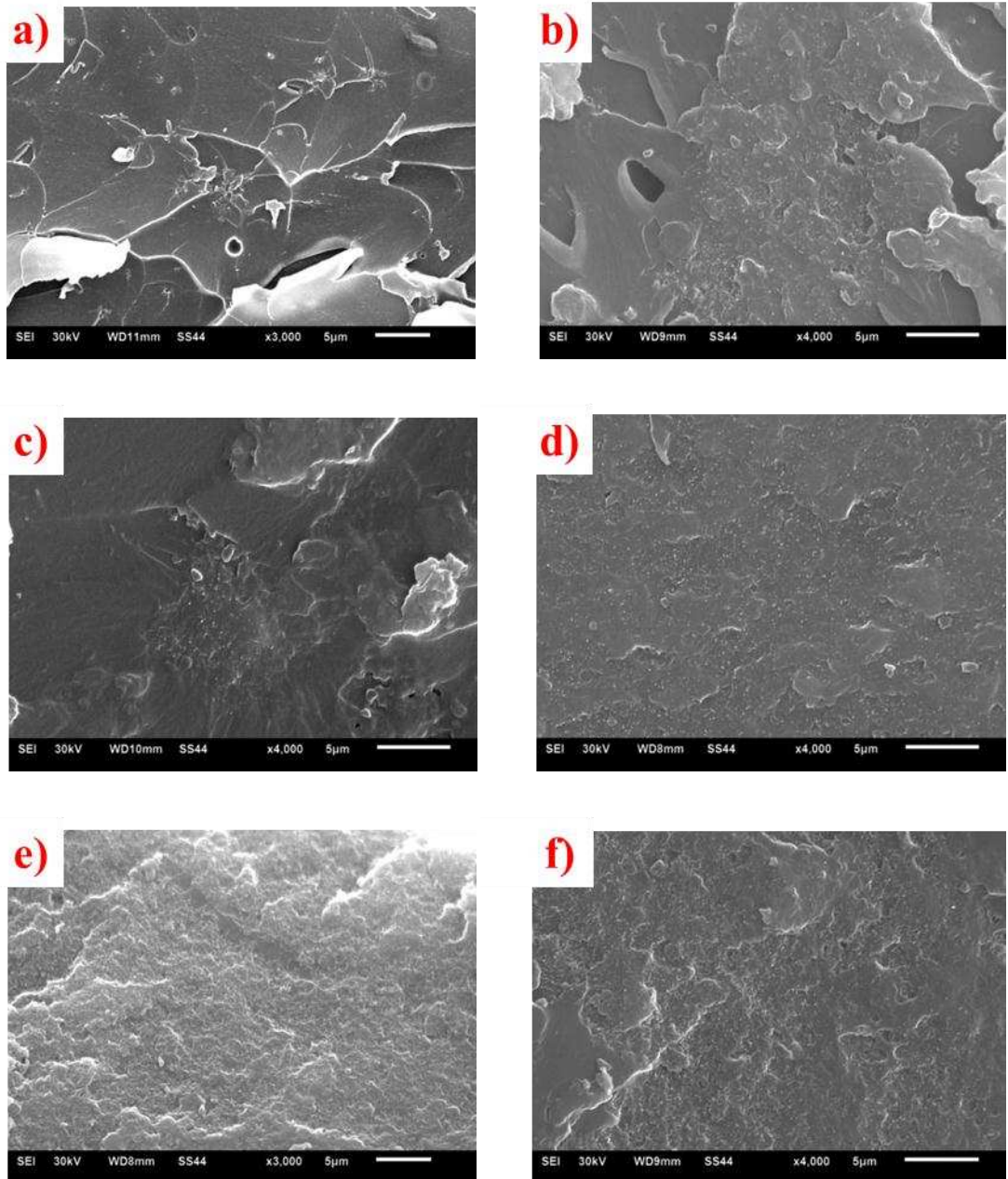


Figure 4.12 Fracture surfaces of vinyl ester nanocomposites with a) 0.1wt% CNTs; b) 0.1 wt% CNTs and B60H; c) 0.2wt% CNTs; d) 0.2 wt% CNTs and B60H; e) 0.3wt% CNTs; f) 0.3 wt% CNTs and B60H. B60H was fixed at 1x related to CNTs.

Figure 4.13 presents the lower magnification images of the fracture surfaces. At 0.2 wt% and 0.3 wt% CNT loading (Figure 4.13c, 4.13d), the initial crack started at the tension edge of the nanocomposite sample where the agglomerate sites were

located, and then it grew through the whole matrix like emitting radial waves. Stress concentration caused by the agglomerated particles initiated a crack, which leads to failure under load. The sample with 0.1 wt % CNT and dispersing agent exhibits a different fracture surface (Figure 4.13b). These findings are consistent with the results obtained in this study that composites with 0.1 wt% CNTs and the dispersing agent show good dispersion and improved tensile properties.

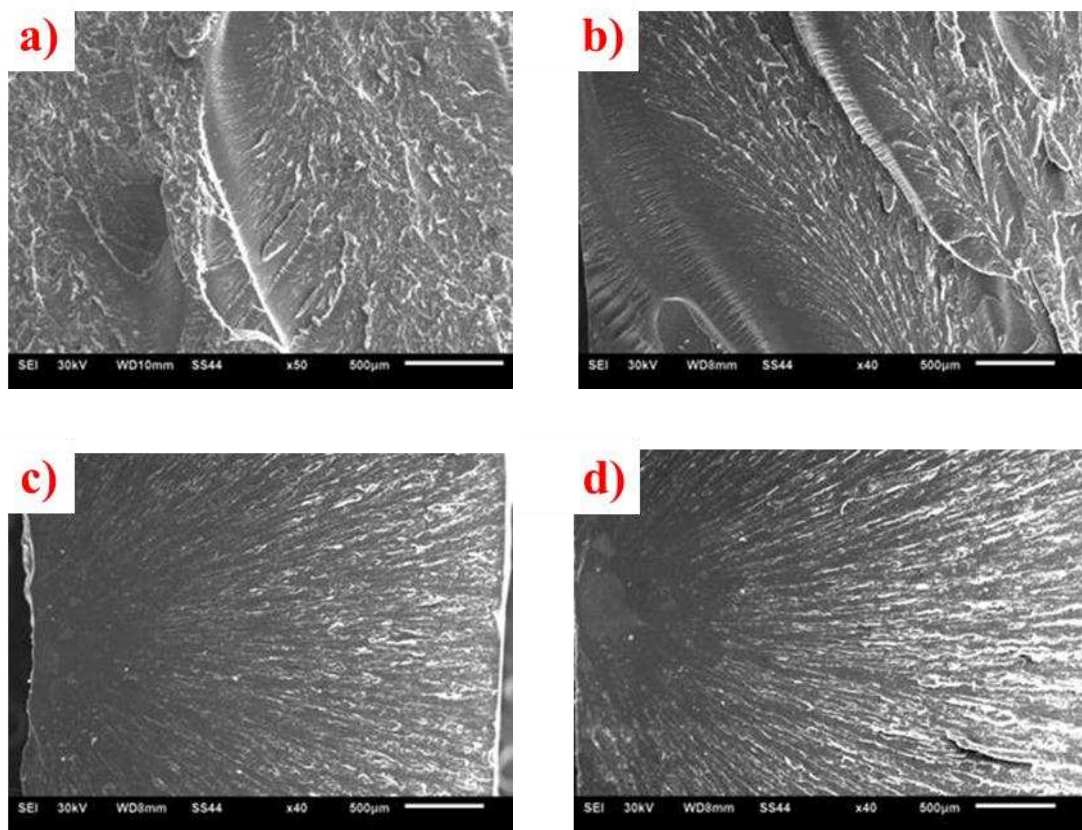


Figure 4.13 Fracture surfaces at low magnification, showing a) neat vinyl ester; b) 0.1 wt% CNTs and B60H; c) 0.2 wt% CNTs and B60H; d) 0.3 wt% CNTs and B60H. B60H was fixed at 1x related to CNTs.

4.6 References

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Chapter 5 Conclusions and Future Work

5.1 Conclusions

1. Different strategies for the development of homogeneously dispersed and long-term stable suspensions of CNTs in different thermoset polymers have been systematically analyzed. The dispersions of MWCNTs with the help of eight different dispersing agents into vinyl ester resins have been prepared. A suitable dispersing agent for the preparation of stable dispersions of MWCNTs has been identified via a centrifugation technique. Optical micrographs confirmed the efficiency of the dispersing agent in preventing CNTs agglomeration at rest for 50 hr after sonication.
2. Tensile properties of neat resin samples obtained using three different post-curing cycles have been analyzed and have indicated an optimum performance for post-curing for 6 hr at 90°C.
3. Vinyl ester composites containing CNTs have been successfully prepared. Nanocomposites with 0.1 wt% MWCNTs and 1x B60H showed improved ductility and toughness by comparison with the neat resin and composites with higher concentrations of MWCNTs and B60H. The improved reinforcement effect of CNTs obtained using B60H in vinyl ester composites could be observed analyzing SEM images of the composite fracture surfaces. After the infusion of CNTs with the help of the dispersing agent, the composites exhibited a rougher

surface and uniformly distributed MWCNTs could be observed at the fracture surface, indicating good adhesions between the CNTs and the polymer matrix.

4. As the content of MWCNTs increases, the composites show poor tensile properties because of the increasing number of CNT aggregates present in the system. Those large agglomerates act as defects or stress concentrators at the nanotube-matrix interface, resulting in quick and brittle failure during the tensile test.
5. Screening various dispersing agents via centrifugation may lead to the development of a strategy for preparing CNT masterbatches for thermoset systems.
6. In some related work published elsewhere [1, 2, 3], enhancements of the tensile properties for epoxy based composites have been achieved by using two different block copolymers (L-7602 and BYK-9077), which also provided dispersions resistant to sedimentation for more than 168 hr. The addition of small amounts of MWCNTs has been shown to significantly improve the fatigue performance of epoxy and polyurethane systems. This work demonstrates the huge potential of CNTs to improve the tensile fatigue performance of thermosetting systems widely used in structural applications, such as in the wind energy industries.

5.2 Future work

In order to better assess the potential use of vinyl ester composites containing CNTs for wind blades application, it will be important to perform fatigue tests on such samples. Further insight into the mechanisms of CNT reinforcement can be obtained by studying the fracture surfaces of samples tested under cycling loading. Another interesting direction for future research is the use of functionalized CNTs for vinyl ester reinforcement.

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