Thermo-Mechanical Properties of Stretchable Nanocomposites Based on Honeycomb Networks of Carbon Nanotubes

By

Patnarin Worajittiphon

Submitted for the degree of Doctor of Philosophy

Department of Physics
Faculty of Engineering and Physical Sciences
University of Surrey

March 2011

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Abstract

Waterborne polymer colloidal particles (i.e. latex) have been used as a template to fabricate carbon nanotube (CNT) composites. Plasticized colloidal crystals are able to assemble CNTs into ordered hexagonal, or honeycomb-like, networks with periodicity defined by the size and deformability of the polymer latex spheres used to form the nanocomposite. In this work, two-dimensional hexagonal networks have been formed by spin-coating the latex nanocomposite dispersion onto a substrate. The resulting monolayer composites have very interesting thermal expansion behaviour. Due to the significantly lower thermal expansion (CTE) of single-walled CNTs (SWNTs) compared to polymers, nanotube networks act as static belts surrounding latex particles in the thin film plane. The matrix with considerably higher CTE is, therefore, restricted to expand in the film plane. The polymer particles, consequently, expand in the out-of-plane direction, thus displaying a higher CTE in that direction. Ultimately the monolayer films may find application as nanoscale thermal actuators.

By using latex matrices with low and high glass transition temperature values, random and ordered honeycomb-like CNT networks can be formed in bulk composite samples, respectively. The ability to control CNT network formation results in a variation of thermal conductivity (K) of the nanocomposites. Compared to the composite with random CNT networks, a K enhancement has been found when ordered segregated nanotube networks are created, especially in the case of SWNT composites that offer higher K than the case of composites consisting of multi-walled CNTs. In addition, the thermal percolation threshold has been found to be markedly low due to large excluded volume of the polymer matrix in ordered networks of SWNTs.

After spin-coating particle monolayers of CNT-latex blends onto a polymer substrate, the mechanics of the unusual monolayer elasticity has been investigated. Polarized Raman spectroscopy reveals a uniform alignment of the nanotube networks in the strained monolayers. Systematic changes in the resulting Raman spectra of the monolayer under strain indicate that stress is transferred from the colloidal matrix to SWNT inclusions as observed from the Raman G'-band shift. These are explained by strain and slippage of individual SWNTs in the bundles. Additionally, elastic recovery of the monolayer has been found after being strained beyond failure, which may be related to the inter-tube van der Waals forces pulling individual tubes back to their bundles and, therefore, latex particles back to original morphology.
Acknowledgements

First of all, I would truly like to thank my supervisors: Dr. Alan Dalton and Prof. Joseph Keddie for their great contributions they have made for me. My research is on carbon nanotube-colloidal polymer composites. Having them together is a perfect match for advising me since Dr. Alan Dalton is an expert in carbon nanotubes, including their composites, and Prof. Joseph Keddie is a specialist in colloidal polymers and their film formation. They have advised me on academic work as well as general issues occurring throughout my study and strengthened my motivation in working on materials science. I also would like to thank them both for taking me out to national and international conferences. Lastly, I know it is a really hard work to go through my thesis draft but they are willing to provide me comments and suggestions from their points of view. Their great contributions they have given me will never fade away from my memory. Thank you very much again, my supervisors.

I would like to give true thank to academic staffs in Soft Condensed Matter Physics (SCMP) group: Dr. James Adams for our discussion on composite thermal expansion and mechanical properties, Dr. Jeff Hosea for our discussion related to Raman spectroscopy, and Dr. Richard Sear for his kind general suggestions and general assistance.

Several people in the SCMP Group have helped me in demonstrating in instrument operation, discussing with me scientific aspects, and being my friends in the laboratory. Especially, I would like to thank a very nice technician, Mrs. Violeta Doukova, for her kind general assistance in operating instruments. A special thanks for a colleague working in the laboratory goes to Dr. Izabela Jurewicz, who always helped me in the work related to sample preparation and data discussion. Another big thank is for Dr. Piyapong Asanithi. He is not only my colleague but also a very nice friend. He showed me how to work with the instruments at the beginning of my study. Actually, he is the one who helped me to settle down here at University of Surrey. I still remember the first day of mine in The United Kingdom with him to take me from Guildford Railway Station to the University. I also would like to thank my colleagues: Mrs. Che Azurahanim Che Abdullah, Ms. Azin Fahimi, Dr. Eric Brunner, and Mr. Argyrios Georgiadis for being with and helping me in the laboratory, including being with me out at conferences. Having them all fulfils my study life with joy while working there.
Thanks to Mr. Tom Gibbons and Mr. Bob Derham for their technical helps that enabled me to solve instrumental problems successfully. In addition, I would like to thank Mr. Chris Burt and Dr. Yanling Chen for their kind supervision while the operating scanning electron microscope at MicroStructural Studies Unit (MSSU). I wish to thank Mr. Jeff Dahlke and Mr. David Munro for their IT support throughout several years. I would also like to thank SCMP and Surrey Materials Institute that provide me proper facilities necessary for the research work in nanomaterials field.

Thanks are also dedicated to my officemates: Dr. Tecla Weerakkody, Mr. Akarin Intaniwet, and Mr. Robert Gurney for our academic discussions and also for being my friends in the office chatting with me in all sorts of things, including all their helps over these several years. Additionally, I thank my previous housemates: Mrs. Jariyavadee Sirichantra, Ms. Doendara Malain, and Mr. Somporn Buapraphoorn. They were not only my kind housemates but they were also my older sisters and brother who always drew me out from stressful academic work and made me relaxed. I enjoyed living in the same house with them. My PhD life would never been this enjoyable otherwise!

Another great thank you I will not forget is The Royal Thai Government that has funded me for my PhD. Without this sponsorship, I would not be able to further my Doctoral Degree here at the University of Surrey. I also would like to acknowledge my previous mentor, Assoc. Prof. Sukon Phanichphant, who advised me about higher education and informed me about this “Nanoscience and Nanotechnology” scholarship for my PhD. She is the first one opening a new world of Nanoscience to me.

One of the proudest things in my PhD is being able to publish a paper in the prestigious journal “Advanced Materials”. This is a top journal in my dream to publish my work in. I would like to provide this space to thank all colleagues in the paper: Dr. Alan Dalton, Prof. Joseph Keddie, Dr. Izabela Jurewicz, and Alice King. Although it took our work a long time to get published, it is worth waiting for. I can say for my PhD study that, in my opinion, “mission accomplished!”

My family is always in my mind. Ultimately, I would like to thank my mother, father, and sister, who make me realize that I am not alone to be abroad. They always support, suggest, and encourage me to have stronger motivation in doing PhD. Thanks to my father
and mother’s words that I have listened to several times in the sentence “Finish your study soon and come back here as soon as possible”, this makes me able to finish my PhD within a proper time. Without their big support, I would not be furthering my study here in Surrey. I also thank all loved ones that are around me throughout my PhD.
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Chapter 1

Introduction

1.1 Overview

Nanoscience is the study of tiny objects and their behaviours on length scales ranging from 1 to 1000 nm.\(^1\) The utilization of nanoscience to manipulate objects at the nano-scale can be termed nanotechnology,\(^1\) which was first proposed by Richard P. Fyneman in 1959.\(^2\) Typically, nanotechnology can be categorized into two main groups: top-down and bottom-up approaches.\(^3\) The top-down method is the study of small objects produced by breaking macrometer scale bulk objects into very fine pieces. On the other hand, the bottom-up method assembles atoms and molecules into larger scale arrangements.

As material phases are smaller, their surface area per unit volume is significantly increased, resulting in an increment of material interaction at interfaces. Material properties at the nano-scale is, therefore, markedly different from that at the macro-scale. However, it was not until the discovery of fullerenes or Buckminster balls (C\(^{60}\)) by Richard E. Smalley and colleagues\(^4\) that nanomaterials, materials having structural components with sizes smaller than 1 \(\mu\)m in at least one dimension,\(^5\) were a popular topic published worldwide. Different materials have been studied, for example, silver nanoparticles, silicon nanowires, and carbon nanotubes. Nevertheless, the costs of nanomaterials are relatively high compared to production cost of more conventional materials. As a result, nanomaterials are less widely used compared to conventional materials.

A composite material is a blend of two or more different materials with separate phases remaining in the finished form.\(^6\) Such materials have been found practical in improving the properties of the whole composite system because all materials have their own distinct characteristics but none of them is perfect for all usages. When combined with others, each
constituent can exhibit its original prominent property. One well-known composite material system is fibre-reinforced polymer as shown in Figure 1.1.\textsuperscript{6-7}

![Diagram showing different orientations of fibers in a matrix: (a) random fiber orientation and (b) aligned fiber orientation](image)

**Figure 1.1.** Diagram showing different orientations of fibers in a matrix: (a) random fiber orientation and (b) aligned fiber orientation\textsuperscript{7}

In such a composite, polymer on its own cannot suffer high tensile stress but it is very flexible and economical. On the other hand, a mechanically robust fiber is able to undergo comparatively higher tensile load but accommodates with relatively higher production cost. By combining the two constituents, the resultant composite is then less expensive, promising for up-scaling manufacture and the original components' drawbacks can be lessened. At the macroscopic scale, numerous theories have been developed, especially for mechanical property investigations. A few examples are laminate theory,\textsuperscript{7} which involves strengthening materials using different filler orientations in each layer, woven composites,\textsuperscript{7} the study of failure and fatigue, and related simulations to predict composite behaviour at varied load applied.\textsuperscript{8} Fillers in the form of fibers is one of the most popular materials, since this particular material has a comparatively high ratio of the dimensions in the axial to radial directions. This characteristic allows the formation of fibre networks due to entanglement or bundling at low filler volume content. Continuous filler networks cannot be easily formed in the case of, for example, spherical or platelet fillers because of their lower aspect ratio.\textsuperscript{8-9} Knowledge of composites has been developed continuously; however, the advent of nanoscience and nanotechnology further opened researchers working on composite materials to a new world in this research field.

With their exceptionally promising properties, carbon nanotubes (CNTs) have come to the fore as a reinforcement or filler material for a wide range of mechanical, electrical, and thermal applications. The intrinsic properties of nanocomposite materials are different from the matrix component due to a large interfacial contact area of the matrix and filler. Among a variety of composite systems, polymer-CNT composites have attracted massive
research interest due to their diverse choices of materials and preparation feasibility. Typical conventional composites of this kind are made up of polymer melts or solvent-cast polymers and CNTs, which are able to improve native material’s characteristics. Homogeneity of filler distribution in a matrix is one important factor that can improve composite properties. Through the polymer melt approach, the filler distribution can not be controlled thoroughly. A typical outcome is random filler distribution, whose filler aggregation is not ordered throughout the composite; therefore, continuous filler networks or percolated paths can not be formed throughout the bulk. Having connected networks embedded in a matrix, reinforced materials can have enhanced toughness by absorbing energy from the matrix. In addition, the contribution of their extremely high surface to volume ratio allows for a high amount of external force to be distributed over the bulk. This greater interfacial region also provides an advantage of blending a polymer matrix with only small amount of CNTs because there are numerous numbers of interaction regions. In regard to electrical conductivity, these continuous percolated paths are crucial as they are the medium that electrons can travel on. Likewise, phonons, which are heat carriers in semiconducting materials, can move along high thermal conductivity continuous filler networks throughout the composite. Making connected filler percolated paths, therefore, leads to increasing thermal conductivity. One could imagine the possibility of having electrically and thermally conducting composites with high stiffness (high modulus) and high toughness that could be stretched cyclically for a number of times. One is also able to tune transparency of the composites based on polymeric materials.

Additionally, the mechanical strength can be varied by managing the orientation of CNTs in the matrix. Essentially, the composite with CNT orientation in one particular direction would have a higher stiffness in this arrangement compared to the composite with random CNT orientation. However, the composites mechanical properties also depend on interfacial bonding of matrix and filler. All of these properties will undoubtedly make such nanocomposites highly versatile for all sorts of applications in the future. In particular, CNT composites could be utilized in antistatic coating, electromagnetic wave shielding, or electrical conductors for electrical application. They are also potential candidates for thermal management such as heat conductors, or heat dissipaters.

As stated earlier, a homogeneous distribution of CNTs is of importance for fabricating high performance CNT composites. Consequently, extra care must be paid while dispersing
CNTs. Nevertheless, even when perfectly homogeneous CNT dispersion is obtained; it is extremely difficult to embed CNTs uniformly in melted polymers because of polymer's high viscosity. According to these concerns, it is mandatory to have a route to homogeneously disperse CNTs in the matrix.

In this study, latex is used as a template for CNT network formation. It is a colloidal dispersion of polymer particles in water. The technology is chemically simple and reproducible. It is a self-assembly technique in which CNTs are pushed to latex particle interstitial sites and highly ordered networks are subsequently formed. In making use of latex, water is the dispersant of polymer particles. To create stable dispersions of CNTs in water, it is often necessary to employ amphiphilic surfactant as an intermediate. Latex technology provides a uniform CNT distribution throughout the matrix yet requires a low CNT concentration to initiate continuous connected networks due to comparatively greater volume occupied by the latex host. This latex process has proved successful in the present work to enhance thermal properties with a low CNT content and also results in composites with excellent elastic behaviour. Generally, this technique could be applied to various types of both fillers and matrices to fabricate novel nanocomposite materials depending on the ultimate property one desires.

1.2 Objectives of the present work

Nanocomposites of CNTs and latex have been successfully prepared previously. This nanocomposite system was characterized to understand its electrical conductivity and mechanical properties, especially at high applied strain. However, with highly ordered CNT networks, not only could electrical properties be improved but thermal conductivity could be possibly enhanced as well. It is also interesting to investigate the reinforcement role of CNT networks in making the composite elastic. The similar preparation method to our previous work (Jurewicz et al.) has been adjusted to suit the current experimental parts with the aims as follows:

1. To understand the important principles of fabrication methods relevant to CNT and its composite dispersion, latex film formation, and CNT-latex film formation.
2. To be able to perform the associated fabrication methods in making CNT dispersions, preparing composite dispersion, fabricating thin films made up of particle monolayer and bulk samples from obtained dispersion via different approaches, and applying appropriate techniques to characterize the samples. The techniques used are ellipsometry, Raman spectroscopy, differential scanning calorimetry, scanning electron microscopy, and atomic force microscopy.

3. To investigate temperature-dependent thermal expansion behaviour of CNT-latex composite thin films.

4. To study thermal conductivity of the composites containing highly ordered CNT networks compared to the systems with random CNT arrangements.

5. To understand the mechanics of CNTs as reinforcement phase in the composites.

1.3 Outline of the thesis

This outline is to provide briefly a guide to what will be presented in each thesis chapter after this introduction.

Chapter 1: Introduction

Chapter 2: Carbon Nanotube-Colloidal Polymer Composites

The related details will be presented and explained concerning CNTs and latex on their own and additionally in their composite form. In addition, a literature review of the basic structure of CNTs, CNT dispersion and applications will be presented. Latex film formation, approaches for film preparation which can be applied to composite film fabrication, different methods in CNT-latex composite preparation, and applications of the composite will also be presented.
Chapter 3: Materials and Characterization Techniques
This chapter is relevant to the procedures to prepare composite samples. The details of the materials to be used will be provided, including the selected method to make composite samples in this work. Additionally, initial characterization of the materials will be shown. All characterization techniques will be stated with their operating principles. Sample preparation for particular techniques will be introduced as well.

Chapter 4: Thermal Expansion of Single Walled Carbon Nanotube (SWNT)-Colloidal Latex Composite Monolayer Thin Films
This chapter will be devoted to a thermal expansion study of thin composite films. It will contain a literature review, relevant theories, sample fabrication and experimental procedure details, results and discussion, and a brief conclusion. The results section will be divided into several parts, which contain different experimental varied parameters affecting composite film expansion, such as CNT content, heating temperature, and heating rate.

Chapter 5: Thermal Conductivity of Carbon Nanotube-Colloidal Latex Bulk Composites
This chapter has the similar structure as Chapter 4 but the study will be on thermal conductivity of different CNT-latex composite systems. The dependence of CNT type (multi-walled and single-walled CNTs), amount, and network morphology will be discussed. The results part will be discussed on glass transition temperature shift of the composites, physical sample characterization, and a few varied parameters will also be investigated for thermal conductivity behaviour of the composites.

Chapter 6: Mechanical Behaviour of SWNT-Colloidal Latex Composite Monolayer
Besides thermal properties, mechanical properties of the composites will be studied to understand elastic recovery mechanisms of the composite monolayer which will be applicable for a wider range of applications when coupled with thermal properties of the composite. The structure of this chapter will be similar to those of Chapter 4 and 5, but the experimental part will be the characterization of the monolayer's polymer substrate first and then the composite monolayer itself. The investigation will be on strained and relaxed composite monolayers. Finally, an idea to describe the CNT role in monolayer elastic recovery will be proposed.
Chapter 7: Summary and Future Work
This chapter concludes significant results and related explanations from experiments in Chapter 4, 5, and 6. Potential future work for each chapter will also be suggested.
References


Chapter 2

Carbon Nanotube-Colloidal Polymer Composites

This chapter provides basic concepts about materials and sample preparation in order to understand materials' characteristics and to be able to apply the principles of sample fabrication in actual experiments. The details will be presented on carbon nanotubes (CNTs) and latex on their own along with their composites. In addition, the basic concepts of the structure of CNTs, CNT dispersion with their applications, a brief introduction about polymer film formation, approaches for film preparation which can be applied to composite film fabrication, different methods in CNT-latex composite preparation, and applications of the composite will be presented.

2.1 Carbon nanotubes

Since the discovery of CNTs in 1991 by Sumio Iijima,¹ there has been a great deal of work dealing with their basic understanding and their properties. They exhibit high electrical conductivity,²³ have high mechanical strength,⁴ and offer the ability to be functionalized.⁵

2.1.1 Structure of carbon nanotubes

Depending on the number of graphene sheets, carbon nanotubes can be categorized into two types: single-walled type (SWNT), a graphene sheet rolled into a cylindrical shape (Figure 2.1 (a)); and multi-walled type (MWNT), the rolling of more than one graphite sheets in concentric cylinders (Figure 2.1 (b)).⁵ Different sorts of CNTs have their own unique structures, resulting in different physical properties and, thus, various applications. For instance, SWNTs can be conducting wires due to their high electronic transport as demonstrated by Tans et al.⁶ On the other hand, MWNTs are of interest in mechanical properties because of high elasticity. Compared to MWNTs, SWNTs have higher thermal conductivity.⁷
CNTs can be either metallic or semiconducting depending on the way they are rolled up. A pair of integers \((n, m)\) is typically used to identify the direction which a CNT is rolled. Rolling a graphite sheet along different indices gives rise to varied tube diameter and chirality and, hence, different properties. Chirality is defined as the chiral angle between the tube axis and hexagons formed by carbon atoms. Chirality relates to a line linked between two crystallographically equivalent sites that can be represented by chiral vector \(C_h = na_1 + ma_2 = (n, m)\), where \(a_1\) and \(a_2\) are basis vectors of the hexagonal lattice. Figure 2.2 represents an example of the way a CNT can be rolled. The angle \(\theta\) in Figure 2.2 is a chiral angle, which is the angle between zigzag direction of the graphite plane and the direction of chiral vector \(C_h\). Chiral angle \(\theta\) can be defined in equation (2.1). Zigzag-typed tubes have \(\theta = 0^\circ\) while armchair tubes have \(\theta = \pm 30^\circ\).

\[
\theta = \tan^{-1} \left[ -\frac{\sqrt{3}m}{2n+m} \right]
\]

In Figure 2.2, a cartoon is shown to represent how a CNT can be formed through rolling a grapheme sheet into a cylinder. The directionality (and resultant orientation of carbon - carbon bonds) is defined by the seamless connection of the outer edges of the graphene segment (i.e. point A is connected to another point A in the cartoon resulting in the connection of the edges along the dashed lines). Figure 2.3 shows different ways to create a CNT from grapheme sheet rolling.
The nanotube diameter, $d$, can be defined in equation (2.2) with $a$, the lattice constant (1.42 x $\sqrt{3}$ angstroms).\(^9\)

$$d = \frac{|C_h|}{\pi} \frac{\sqrt{n^2 + nm + m^2}}{\pi}$$  \(2.2\)

It was reported theoretically by Hamada \textit{et al.},\(^{10}\) Mintmire \textit{et al.},\(^{11}\) and Saito \textit{et al.}\(^9\) that geometric structure of CNTs affect strongly the electronic properties of CNTs. It was shown that the factors contributing to a CNT to be metallic or semiconducting with variation in energy gaps are the tube diameter and helicity. In particular, CNT electronic properties depend greatly on the pair of intergers (n, m). Armchair CNTs are metallic and
can be created when \( n = m \). When \( n = 0 \) or \( m = 0 \), zigzag tubes are formed. Besides these two conditions, CNTs are chiral for all other \( n \) and \( m \). Semiconducting tubes with a tiny small band gap are created when \( n - m = 3k \), where \( k \) is an integer and is not zero. For other conditions, CNTs are semiconducting and have large band gaps inversely proportional to tube diameter.\(^\text{12}\) Specifically, the gap sizes of large gaps and tiny gaps are decreasing proportional to \( 1/R \) and \( 1/R^2 \), respectively, when tube radius \( R \) decreases. For the tubes with large band gaps, the relationship between energy band gap, \( E_g \), and tube diameter, \( d \), can be defined as follows:

\[
E_g = \frac{2\gamma_0 a}{d}
\]

(2.3)

where \( \gamma_0 \) is the nearest-neighbour overlap integral (2.45 eV). Generally, large band gaps of SWNTs are about 0.5 eV for the tubes with diameter of 1.5 nm and their small band gaps are about 10 meV with almost similar tube diameter.\(^\text{13}\) Semiconducting CNTs have their band gaps ranging from 0.1 to 2 eV while zero band gap for metallic tubes.\(^\text{14-15}\)

\[\text{2.1.2 Physical properties of carbon nanotubes}\]

CNTs have excellent physical properties. Here the thermal and mechanical properties are presented in detail because these two characteristics are the main features being investigated in the present study.

\[\text{Thermal properties of CNTs}\]

Fascinating thermal properties of CNTs relating the present work can be divided into two major groups: thermal expansion and thermal conductivity.

\[\text{Thermal expansion:}\] Thermal expansion of SWNT bundles has been investigated by Maniwa et al.\(^\text{16}\) In their measurement, X-ray diffraction was applied and a small expansion was found. Particularly, thermal expansion of the tube diameter is \(-0.15 \pm 0.20 \times 10^{-5} \text{ K}^{-1}\), indicating strong in-plane bonds between carbon atoms, and that of lattice constant, at 300-
950 K, is $0.75 \pm 0.25 \times 10^5 \text{ K}^{-1}$. The very small thermal expansion of CNTs corresponds well with the expansion of graphite sheet, which has an extremely low thermal expansion in the in-plane direction and high thermal expansion between sheets. Based on this tiny value of thermal expansion, there is a mismatch occurring when CNTs are blended with other materials in composites. Intrinsic strain is, therefore, introduced in most CNT-based composite materials. In a given composite, CNTs act as a static phase with comparatively no expansion while other materials act as an expanding phase.\textsuperscript{17}

**Thermal conductivity:**

The theoretical work from Berber et al. indicated that thermal conductivity of SWNTs is 6600 W/m-K at room temperature, which is on the same magnitude of a diamond crystal and graphite sheet.\textsuperscript{12-13} High thermal conductivity is a result of the feasibility in the propagation of phonons, which are thermal energy carriers, along nanotubes.\textsuperscript{12} Crystallite size, on the other hand, is the parameter limiting thermal conductivity. Long-range highly ordered arrangement of carbon atoms and a long mean free path of phonons lead to higher thermal conductivity of CNTs compared to that of graphite. Low-frequency phonons are thermal energy carriers governing thermal conductivity along the axial direction. This thermal energy can be written as kinetic energy $K$ shown in equation (2.4).\textsuperscript{8} $K$ is dependent on the specific heat $C$, group velocity $v$, and relaxation time of a phonon state $\tau$.

\[
K = \Sigma C v^2 \tau
\]  

(2.4)

The total thermal energy is the summation of energy of all phonon states. As seen from this equation, thermal conductivity can be enhanced when the band velocity and phonon mean free path, or time for phonons to scatter, increase. Thermal conductivity along the axial direction is at least two orders of magnitude higher compared to that in radial direction. In materials containing nanotube bundles, inter-tube heat conduction plays an important role and dominates heat transfer along individual tubes.\textsuperscript{18} In addition, it was found that aligned SWNT bundles provide higher thermal conductivity (> 200 W/m-K)\textsuperscript{15-16} at room temperature compared to that (~ 35 W/m-K)\textsuperscript{18} of nanotube sheets with tubes randomly arranged.
Mechanical properties of CNTs

Because of the strong covalent bonds between carbon atoms in nanotubes and the nanotube’s small diameter, CNTs exhibit exceptional mechanical properties. Specifically, the Young’s modulus of CNTs has been found to be very high, in the order of a terapascal, which is much higher than that of metals. In addition, their stiffness and strength are also extremely high, leading to many promising applications such as light weight reinforced materials. There are some available theories and explanations about mechanical properties of materials at the macroscopic scale; for example, theories about Young’s modulus, Poisson ratio, and elastic constants. In the case of CNTs, these theories can still be adopted but some parameters need to be modified. Theory modification comes from the dimensional reduction of such nano-scale materials. Essentially, the cross section area of CNTs is significantly small, thus leading nanotube volume to be relatively small. As a result, rather than dealing with CNT volume, one would consider their surface area instead. Such concern does not occur for macro-scale materials since their size in all three dimensions is measurable. At the macroscopic scale, the Young’s modulus along a given direction is a function of the total energy $E$, system equilibrium volume $V_{eq}$, and strain $\varepsilon$ as written in equation (2.5).

\[ Y = \frac{1}{V_{eq}} \left( \frac{\partial^2 E}{\partial \varepsilon^2} \right)_{\varepsilon=0} \quad (2.5) \]

At the nanoscale, the equilibrium volume $V_{eq}$ is better replaced by the CNT surface area $S_{eq}$ with no strain applied in order to compare this to Young’s modulus of graphite. Therefore, equation (2.5) can be rewritten as equation (2.6).

\[ \bar{Y} = \frac{1}{S_{eq}} \left( \frac{\partial^2 E}{\partial \varepsilon^2} \right)_{\varepsilon=0} \quad (2.6) \]

However, if it is mandatory to calculate $Y$ from nanotube volume, $V_{eq}$ in the equation (2.5) can be substituted by $V_{eq} = S_{eq} h$, where $h$ represents the graphite inter-layer spacing whose dimension is 0.34 nm.
A theoretical report on mechanical properties of CNTs by Landau and Lifshitz mentioned nanotube strain energy, which is the energy difference per atom between a nanotube and an infinite flat graphite sheet. It was stated that strain energy is associated with nanotube stiffness and is inversely proportional to $d^2$, where $d$ is the diameter of nanotube. Lu applied an empirical force field to investigate the Young's modulus of MWNTs and SWNTs. It was reported that, for individual SWNTs, the Young's modulus is approximately constant at $\sim 1$ TPa and is independent of tube diameter. In bundle form, SWNTs have decreasing Young's modulus as a nanotube diameter is increasing. The value of $\sim 1.11$ TPa was reported for MWNTs. By comparing among several types of nanotubes (carbon-based, nitrogen-based, and boron-based compound nanotubes): C, BN, BC$_3$, and BC$_2$N nanotubes, carbon nanotubes offer highest Young's modulus ($\sim 1.26$ TPa) through a nonorthogonal tight-binding formalism with the use of $\hbar=0.34$ nm. A comparatively high value of Young's modulus ($\sim 1$ TPa) of isolated SWNTs was also stated by Sanchez-Portal et al. In their work, first-principles electronic structure approaches were applied. The simulation was adapted from density functional theory and $\hbar=0.34$ nm was applied to their work. Interestingly, SWNT bundles, whose chirality is $(10, 10)$, show a different Young's modulus of $0.5$ TPa.

Experimental studies on Young's modulus determination of CNTs are rather difficult since they are all at the nano-scale, giving rise to uncertainty in measurement, as found by Treacy et al. Through the use of transmission electron microscopy and the fact that the mean-squared vibrational amplitude of the free nanotube end is proportional to temperature but inversely proportional to Young's modulus, the mean value obtained was 1.8 TPa while the value for individual MWNTs was in the range of 0.4-4.15 TPa. SWNTs were also investigated by Krishnan et al. using similar experimental procedures. An average Young's modulus of 1.25 TPa was reported. Another approach was performed by Wong et al. with the use of an AFM tip to monitor Young's modulus of individual MWNTs. In their work, AFM tip was dragged to bend a free end of CNT, which was attached on a cantilever. By analyzing the relationship between bending force and the displacement that the AFM tip moved, an elastic buckling behavior of MWNTs was found. In addition, Salvetat and co-workers demonstrated a different method to study mechanical properties of SWNTs. They deposited nanotubes on a porous filtration membrane. The resultant nanotubes that were suspended across the pores were pressed by AFM tip. However, SWNTs were in both individual and bundle forms, they thus showed a comparatively
lower Young’s modulus value of 0.8 ± 0.4 TPa. It should be noted here that there are several factors affecting the observed mechanical values of CNTs, for example, conditions in experimental set up, amount of defects in nanotube samples, and nanotube synthesis approach.

Electrical properties of CNTs

A number of studies have been carried out on CNT electrical properties. The current density of nanotubes was reported by Yao et al. at the level of $10^9$ A/cm$^2$. According to this value, CNTs are better current carriers than copper.

2.1.3 Preparation of carbon nanotube dispersion

CNTs have a hydrophobic surface and tend to aggregate into large ropes or bundles naturally, leading to the difficulty in creating homogeneous nanotube distributions in ultimate CNT-based uses and, thus, low property consistency of devices in up-scaling manufacture. Dispersing nanotubes is, consequently, very crucial especially in applications that need CNTs suspended in water. Aqueous dispersion of nanotubes also allows them to be incorporated with other water-soluble materials such as CNT-based composites, giving rise to a wider variety of applications. There have been a number of approaches to disperse CNTs in different liquids as presented in this section.

Several dispersion techniques have been adopted extensively with the use of, for example, acids, surfactants, and large molecules to wrap or functionalize CNTs. These approaches, nevertheless, modify nanotube chemical structure and, thus, properties. Moreover, these processes introduce another phase into the system that maybe detrimental to eventual applications. As a result, organic solvents have sometimes been utilized as dispersant agents instead. The stability of nanotube dispersion was studied by Giordani and colleagues through the use of the solvent N-methyl-2-pyrrolidinone (NMP). Nanotube debundling was performed simply by diluting the CNT-NMP dispersion. In their work, Hipco SWNTs were sonicated in NMP by an ultrasonic tip at high power. The dispersion was then diluted and briefly further sonicated by tip, subsequently, sonicated for a long time (4 hours) in a bath sonicator at a low power, and finally briefly sonicated by a tip
again. The ultimate procedure was to centrifuge the dispersion to separate sediments from the stable dispersion. CNT bundle size decreased as nanotube content decreased and, at low content, ~70% of CNTs were individuals, as observed by photoluminescence and Raman spectroscopy respectively. AFM and absorption measurements also indicated the stability of the CNT dispersion over two weeks.

Another method involved the use of aqueous acid to oxidize CNTs and was reported by Shaffer et al.\textsuperscript{30} Their acid mixture contained 25% and 75% of nitric and sulphuric acids, respectively. CNTs were added to this acid mixture and then refluxed. The mixture was subsequently washed by water to remove excess acid. Neutralization was conducted by the use of bases to the oxidized samples as described elsewhere.\textsuperscript{31} NaOH, Na\textsubscript{2}CO\textsubscript{3}, and NaHCO\textsubscript{3} were selected in their study. The mixture was then sonicated, left for 3 days, filtered, and titrated using HCl acid. The resultant final mixture became a stable CNT dispersion in water due to inter-tube electrostatic force pushing nanotubes apart from each other. It was also found that the dispersion viscosity was directly proportional to nanotube concentration.

A preparation of CNT dispersion by means of surfactants was reported by O’Connell et al.\textsuperscript{32} Being an anionic surfactant, sodium dodecyl sulfate (SDS) forms a micelle adsorbed on nanotubes (Hipco SWNTs) by either wrapping around nanotube or lying parallel to nanotube axis.\textsuperscript{32-33} The SDS ability to bend and wrap around tube is a consequence of different ways of SDS hydrophobic tails to orient on nanotube. To prepare a CNT dispersion, CNTs were initially added to an aqueous solution of SDS by a high-shear mixing approach. The mixture was then sonicated at high power. The resultant dispersion was subsequently centrifuged to remove large aggregates. A non-ionic surfactant Triton X-100 was also employed in dispersing CNTs as recently reported by Jurewicz et al.\textsuperscript{38} To prepare nanotube dispersions, Triton X-100 was firstly mixed with deionized water by means of a magnetic stirrer. Hipco SWNTs were then incorporated to the surfactant solution using the tip sonication approach at high power. The sonication process was performed in an iced bath in order to reduce heat that may damage nanotube integrity. This technique is friendly to environment since there is no use of volatile organic compound solvents. Additionally, the resultant nanotube dispersion is aqueous, hence enabling further chemical process with a wide variety of water-soluble agents.
One example of the literature dealing with nanotube dispersion using macromolecules is the work published by Dalton and co-workers.\textsuperscript{33} The copolymer poly(p-phenylenevinylene-co-2,5-dioctyloxy-m-phenylenevinylene) or PmPV-co-DOctOPV, with the chemical structure shown in Figure 2.4,\textsuperscript{34} was adopted as a large molecule to wrap around SWNTs.\textsuperscript{35} Their nanotube dispersion preparation can be briefly illustrated that a solution of the polymer was initially prepared in toluene. The polymer solution was then mixed with SWNT powders using bath sonication method at a low power of 60 W. The resultant dispersion was left for several days to settle. Aggregates at the bottom of the dispersion were subsequently removed. It was found that the obtained dispersion was stable over months without any further sediment. Analysis of the sample suggested that an intercalation of polymer resulted in debundling of CNT ropes. In addition, individual tubes can be found in the dispersion with low CNT concentration. Rather than interacting with all nanotubes, the polymer selected tubes with a particular diameter to interact with. As a result, aggregates could be observed during settling time.

![Figure 2.4. Chemical structure of the macromolecule polymer PmPV-co-DOctOPV.\textsuperscript{34}](image1.png)

### 2.1.4 Applications of carbon nanotubes

Despite the high cost of these nanomaterials, CNTs have attracted efforts in research and development continuously over a long period of time because of their uniquely outstanding properties in many aspects. Some examples of CNT uses associated with electrical, thermal, and mechanical applications will be discussed in the following section.

*Carbon nanotubes as conductive films*\textsuperscript{36}

Ultrathin SWNT films were made by Wu and colleagues\textsuperscript{36} to investigate electrical conductivity of the films. By fabricating such thin films, they were able to make the films
transparent that could lead to a wider range of applications. Under visible light excitation, measured light transmittance is in the same order of that of commercially available indium tin oxide (ITO). They also showed the ultra thin CNT films placed on a glass substrate with the diameter as large as 10 cm. Optical transparency can be simply varied through the variation of film thickness. In particular, thicker CNT films provided lower light transmittance. Besides a clear solid glass substrate, a clear flexible substrate such as a polymer film can also be used in film deposition process, allowing flexibility of conducting nanotube films for even wider electronic applications.

**SWNTs as quantum wires**
With high electrical conductivity of SWNTs, Tans et al. connected two electrodes and electronic circuit using an individual SWNT. At room temperature, the resistance between electrodes was \( \sim 1 \, \text{M} \Omega \). This value was higher as the contact area of the CNT and electrodes increases. For four-point contact, different individual tube showed the contact resistance of 300 k\( \Omega \) and 1 M\( \Omega \) at room temperature and 4 K, respectively. A few more samples were investigated and the similar results were discovered. Furthermore, they found that between discrete electron levels, there was resonant tunnelling occurring. This indicated current transport through single molecular orbitals. From this observation, it can be implied that electrons can be transported although there are defects and structure deformation of nanotubes such as tube bending or twisting.

**SWNTs for thermal management**
Theoretically calculated thermal conductivity of SWNTs was reported as high as 6600 W/m-K at room temperature. Kim and co-workers conducted measurements at room temperature to study thermal conductivity of MWNTs and found an experimental value of 3000 W/m-K. Such high thermal conductivity is capable of being used in heat conductors. In particular, one could apply CNTs as a heat dissipator that transfers heat out of electronic circuits or devices, resulting in higher efficiency the devices could offer. CNTs are also able to conduct electrons from one place to another. Huang et al. proposed a model of an array of aligned CNT wires connected from one surface to another. The fabrication of such a device requires the use of polymer to support nanotube arrays as illustrated in Figure 2.5. However, at the two ends of the device, there are only protruding CNTs connecting two surface at different sides. For thermal conductor applications, the
authors also showed ‘in-situ injection molding’ process. This technique is able to produce CNT arrays with low thermal resistance.

Figure 2.5. Schematic presenting a model of an aligned CNT array supported by polymer matrix.

CNTs for mechanical properties
Tube buckling occurs when nanotubes are bent to high curvatures. At this state, a pattern of rippling wave forms along tube surface at the local highly-curved region. Because of elastic buckling, CNTs have extreme toughness. By using an AFM tip to draw across a nanotube, it can be demonstrated that strain energy stored in CNT is about 5 to 10 times of that stored in silicon carbide nanorods with similar diameters. In addition, the authors proposed that the ability to absorb energy enables CNTs to be used in armor application. However, the use of CNTs for mechanical applications is usually at the macro-scale. In such a big scale, CNTs require a proper matrix to reduce the amount of high-cost CNTs used in a particular product. The ultimate role of CNTs in such composites is, therefore, matrix reinforcement. Light weight CNT composites have already been utilized in some industries; for example, tennis rackets and aircraft structure.

2.2 Colloidal polymer and film formation

In order to obtain controlled nanotube arrays for flexible devices without high-cost fabrication in a clean room, one of the most promising ways to be exploited is particle self-assembly, defined as the independent arrangement of particles to form patterns or structures with no help of human beings. It has been known that latex, a colloidal dispersion of polymer particles in water, is able to self-assemble. CNTs arranged by latex microsphere assembly are also very advantageous in various sorts of applications because
of many reasons: a wide range of latex types, leading to different glass transition temperatures; latex particle sizes, resulting in different film thicknesses; and latex chemical properties, leading to various choices of chemical uses. This work here is concentrated on the investigation of thermal and mechanical properties of composites of CNTs and colloidal polymer particles.

Mostly, latex spheres in colloidal dispersion are kept apart from each other by electrostatic forces.\textsuperscript{45} When evaporation process of the liquid water phase occurs, these particles form films by particle packing, deformation, coalescence and interdiffusion. Continuous and homogeneous films form at a temperature higher than the minimum film formation temperature (MFT or MFFT). According to the definition of Eckersley et al., MFT is "the minimum temperature at which a latex cast film becomes continuous and clear. Below this critical temperature, the dry latex is opaque and powdery".\textsuperscript{46} Films cast at below MFFT contain discontinuous arrays of latex particles, thus resulting in voids which scatter light. These voids cause opacity of the films. In general, MFFT is mainly influenced by glass transition temperature (T\textsubscript{g}) of latex particles. Even though MFFT is not exactly the same temperature as T\textsubscript{g}, they are close to each other. "The definition of T\textsubscript{g} for polymers is the lowest temperature at which segmental chain motion may occur. In real terms, it is the temperature at which the material stops behaving like a glass and begins to behave like a rubber".\textsuperscript{47}

Film formation process can be generally categorized into three stages: water evaporation; particle deformation; and interdiffusion as illustrated in Figure 2.6. In the first stage, evaporation of liquids including water and solvent in dispersion causes particle packing. In addition, capillary force between particles is another factor moving latex spheres closer to each other.\textsuperscript{48} While further evaporation is taking place, latex particles are moved towards each other, resulting in a more close-packed structure. This stage happens until the polymer reaches the volume of approximately 60-70\%, depending on the ordering and particle size polydispersity. This volume percentage is near to 74\% for a close-packed structure of mono-sized particles.\textsuperscript{48}

The second stage of film formation is particle deformation. In this process, evaporation rate decreases and liquid loss almost terminates. Particles form denser packing in face centered-cubic (FCC) arrangement to fill interparticle space.\textsuperscript{44} for a particle in an FCC
array, the spherical particle shape is changed initially to “rounded polyhedral” and the rhombic dodecahedron for the last form when the radius of the “rounded polyhedral” has increased.\(^{49}\) These dodecahedral or honeycomb-like structure arrays can be even denser as the evaporation process continues to occur. This stage lasts until particles are fully deformed.

There are several driving forces for latex particle deformation. They are, for example, dry sintering, wet sintering, capillary deformation, receding water front, and Sheetz deformation.\(^{48, 53-55}\) Brown proposed that dry sintering is driven by interfacial tension.
between polymer and air and this process starts after evaporation occurs. Dry sintering contributes to film formation, at lower temperatures, when the polymer modulus is high and evaporation is comparatively higher than deformation. According to capillarity theory, particle deformation is driven by the air-water surface tension between particles. At intermediate temperatures, capillary force causes particle coalescence when this force is higher than the intrinsic force resistant to deformation. As long as this inequality exists, particle deformation is able to occur. Another driving force is wet sintering. Wet sintering occurs in soft polymers hence it is more likely at high temperatures. This process is a result of polymer-water interfacial tension.\(^5\) Based on Vanderhoff proposal, as water evaporates, particles move to be in contact, leading to subsequent deformation. Wet sintering is applicable to film deformation with the presence of slow evaporation rate or with the system of a low modulus polymer. A receding water front happens when capillary deformation is not complete. Further water receding through the film results in deformation by space filling of latex particles.\(^5\) A layer of particles deformed at the air-film interface is called a “skin”, which was proposed by Sheetz. In Sheetz mechanism, “skin” retards water evaporation. However, water diffusion through the skin causes a large osmotic pressure under the skin, leading to particle compaction.\(^5\)

In the last stage, so-called interdiffusion or crosslinking, tiny amounts of water left from the second stage continue to evaporate through small voids between particles. After these voids have disappeared, water diffuses through particle boundaries to leave the film, resulting in polymer chains crossing the interface between particles and, hence, complete interdiffusion. Film strength increases when there are chain entanglements across the interface.

When colloidal particles are forming a film and they are just about to touch each other, there are small voids between them. These voids could be filled by other materials to obtain a composite with filler embedded in a matrix. Due to tiny CNT size compared to that of latex microspheres, it is possible to add CNTs to a latex dispersion. The composite system obtained as a final result is a CNT-latex composite with highly-ordered CNT network embedded in latex matrix. As a result, controllable patterns of CNT networks can be made using latex particle assembly.\(^5\)
2.2.1 Film preparation methods of colloidal polymer particles

Deposition methods of colloidal polymer particles can be categorized into three main groups: horizontal deposition, vertical deposition, and spin-casting. Horizontal film fabrication deals with the spreading of latex dispersion onto a horizontally-placed substrate, which can be either still or movable. In a particular requirement, the substrate may be moved horizontally while the dispersion is being spread in order for a meniscus to make a film with low thickness. Additionally, the substrate may be connected to an external temperature control unit for further film annealing process.

Vertical deposition involves dipping a substrate in a latex dispersion and moving the substrate vertically out of the dispersion with a constant withdrawal rate. An advantage of vertical over horizontal deposition is that the latter provides comparatively higher number of defects and different particle packing: face-centered and body-centered structures. Highly ordered close packing of the particles can be obtained under the condition that solvent/water evaporation rate is higher than the speed of particle sedimentation. To obtain such a situation, low pressure was used during deposition process, allowing an increase of solvent evaporation rate. According to Dimitrov and Nagayama, the main driving force in particle transport processes between dispersions and a solid support is the water evaporation from the region that particle array has just been formed in. Particles are transferred onto the substrate in the convective region and close packing is a result of menisci between particles on the substrate as shown in Figure 2.7. This figure demonstrates a vertical deposition of a solid substrate into a dispersion containing colloidal particles. Another crucial parameter is water vapour surrounding the deposition setup. Essentially, unsaturated water vapour causes an agglomeration of particles, thus non-uniformity of the film surface because of excessive driving force upward along the substrate surface.
Figure 2.7. Schematic representation showing a convective assembly of colloidal particles due to solvent/water evaporation as a driving force during a vertical deposition. The figure presented here is an example for monolayer film fabrication.

Film thickness can be varied, ranging from the nano-scale up to micrometers, depending on the mean particle size. Capillary forces influence the packing order of particles and electrostatic forces contribute to the ability of particles to travel.

Another method of particle assembly deposition is spin-casting. While a substrate is rotating about a central axis, the dispersion spreads outward to the edge of the substrate, resulting in decreasing film thickness. In addition, centrifugal shear force occurring during substrate rotation helps film smoothness. Spin angular velocity and concentration of spreading material are found to be the main key in controlling film thickness. The detailed principles of spin-casting will be discussed again in section 3.2 in Chapter 3.

2.3 Carbon nanotube-colloidal polymer composites

There are several purposes of fabrication of carbon nanotube composites. One example is to improve properties of matrix such as CNTs reinforced in alumina as reported by Mo et al. According to this work, the hardness and fracture toughness of the alumina matrix were enhanced by increasing the amount of CNTs. Additionally, the purpose is also to determine properties, especially mechanical characteristics, of CNTs on their own because microscopic instruments can not be built to investigate such small scale samples. Therefore, matrix materials have been incorporated to enhance the dimension of the whole
Another aim of CNT composite studies is to control CNT patterns or networks by using matrix assembly as a CNT template. For instance, silica colloid was mixed with SWNTs by Kim et al., then the dispersion was deposited on solid substrate, and silica colloid was, subsequently, removed, resulting in a CNT network left on the substrate. There have been a number of reports dealing with CNT-polymer composites. Several of them studied polymer solutions in organic solvent rather than polymers in colloidal sphere form. In particular, Qian and colleagues obtained composites exhibiting an elastic modulus increase in the range of 36%-42% with the presence of 1 wt% CNTs, suggesting the significance of CNTs in mechanical property enhancement. However, it is difficult to blend CNT dispersions homogeneously with polymer melts because of high viscosity of the polymers. In addition, CNTs in polymer matrices were in an ordered arrangement to some extent, as observed from their transmission electron microscopy (TEM) images (Figure 2.8), but not in a highly-ordered network pattern required for some specific electronic and thermal applications.

**Figure 2.8.** Transmission electron micrograph showing homogeneous distribution of MWNTs in polystyrene polymer matrix (adapted from 67)

Here we are interested in CNT-latex particle composites with ordered nanotube networks due to their various types of applications; for example, electrical, thermal, and mechanical uses. By utilizing such a templating method, it is possible to obtain simple reproducibility of CNT networks in polymer matrix without the need of organic solvent use as media. Such latex technology was originally reported by Grunlan et al. In their work, carbon black (CB) was incorporated in poly(vinyl acetate) (PVAc) latex whose T_g is about 32°C. They found that the composite was able to reduce the percolation threshold because of comparatively larger excluded volume occupied by latex particles compared to that of the filler phase. In addition, a percolating network of CB was produced easier than other
composite systems since there is no need for using high temperature, external pressure, and other chemicals in the preparation process. The microstructure of percolating filler networks can also be engineered by changing latex particle size.\textsuperscript{66} However, colloidal particle size distribution should be narrow in order to create uniform percolated networks. More recently, Jurewicz and co-workers reported preparation method and corresponding characterization for a composite system containing SWNTs as fillers and a co-polymer as a matrix.\textsuperscript{38} They presented a long-range order of 3-D honeycomb-like networks of SWNTs as seen in Figure 2.9. During film formation, nanotubes were forced by latex particles into a continuous pathway and locked at interstitial sites of the particles during drying state. The details of composite preparation procedure will be shown in the next section 2.3.1. In addition, CNTs can be incorporated into lattices with high\textsuperscript{79} and low\textsuperscript{69-70} values of $T_g$ as reported earlier, leading to a wider applications of such CNT-latex nanocomposites. The system with CNTs and soft latex ($T_g \sim -50^\circ C$) is capable of being pressure-sensitive adhesives.\textsuperscript{69-70} One example of nanocomposites with high $T_g$ ($\sim 95^\circ C$)\textsuperscript{79},\textsuperscript{82} consisted of polystyrene polymer (PS) as reported by Yu et al. Their composite exhibited a maximum electrical conductivity of 1 S/m, which is proficient for use as electrically-conductive materials.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.9.png}
\caption{(a) Low and (b) high magnification of scanning electron micrographs of SWNT networks formed by latex self assembly.\textsuperscript{71} Inset in (a) represents cross section of the composite specimen, indicating ordered networks in 3-D. Inset in (b) is a fast Fourier transform (FFT) of the composite, demonstrating hexagonal arrangement of the nanotube networks.}
\end{figure}
2.3.1 Preparation of dispersion of carbon nanotube-colloidal polymer composites

A homogeneous dispersion of CNTs in a polymer matrix, which transfers the amazing properties of CNTs from the nano-scale to the macro-scale without changing CNT characteristics, is one of the main keys to the effectiveness of composite applications. Polymers, matrices of the composites, are conventionally mixed with CNTs by various methods depending on the polymer and CNT types. Typically, CNTs are dispersed homogeneously in solvent or aqueous surfactant solution, whereas polymers, which are in powder or other solid forms, are dissolved in a solvent to make polymer solution. Then the nanotube dispersion and polymer solution are blended by various approaches such as blender or bath sonication.\textsuperscript{72} In the first stage, the composites are still in liquid or fluid forms. When the solvent and water evaporation process occurs, composite materials are left in solid stage as, for example, bulk or thin film forms.\textsuperscript{73} CNTs can be also blended with monomers or prepolymer that are then reacted.\textsuperscript{74} Additionally, melted polymers are alternatives to fabricate CNT-polymer composites.\textsuperscript{75} Basically, polymers are heated and they are then in melted state, which is able to wet CNTs. To prepare even more uniform composites, some research groups have used functionalisation or surface modification of CNTs in order to obtain highly homogeneous nanotube dispersions. One example of such work has been conducted by Shaffer and co-workers\textsuperscript{30} as described previously in section 2.1.3. In contrast, without nanotube functionalisation, another optional approach to uniformly disperse CNTs is diluting nanotube dispersion according to the process reported by Giordani et al.\textsuperscript{29} (see details in section 2.1.3). Additionally, with the use of a high power sonicator, CNTs can also be dispersed well in solvent; as a result, uniformly distributed CNT networks as can be seen from Figure 2.8.\textsuperscript{67} This approach was performed without any functionalisation and the use of surfactants for nanotube dispersion.

Besides polymers in solution form prepared using solvents, polymers are also in colloidal form, which are latex spheres in an aqueous solution. These latex particles can be used to fabricate CNT-polymer composites as well. Because most colloidal dispersions are in water with electrostatic force between each latex particle, which makes them repel each other, there is no need to sonicate or disperse colloidal latex first. Consequently, the approach is simply to mix the colloidal polymer with an aqueous nanotube dispersion, which is usually prepared by using surfactant or polymer to modify nanotube surface chemistry. There are several practical routes to blend CNT dispersion with latex
dispersion; for example, stirrer,76 high-speed impeller,78, 88 and tip or probe sonicator.71 Blending time and output power of the sonicator or impeller speed can be varied depending on ultimate requirement of composite and on chemical properties of starting materials. Another advantage of the use of latex is that the presence of water does not dramatically change the chemical integrity of the polymer and it can be eliminated from composite by evaporation at normal ambient conditions. With this simplicity, colloidal latex is favorable for the fabrication of CNT-polymer composites and is therefore, used in the present study.

### 2.3.2 Applications of carbon nanotube-colloidal polymer composites

The superb properties of CNTs can contribute to bulk materials for various applications by blending them with other materials such as metals, fibers, ceramics or polymers, in composite form.73 One of the most common matrices being used is polymers due to their flexibility and possibility for shape control.12 In the case of CNTs on their own, their properties could be employed by, for instance, functionalization to make them chemically sensitive, doping with other chemicals, and control of their alignment in straight lines or network patterns. These arrangements could be made, in 2-D, by preparation of monolayer CNT films or, in 3-D, by fabrication of thicker films as buckypaper.77 As several research groups have been working with CNTs, a major bottleneck to their applications remains in the ability to effectively assemble them into two or three dimensional controllable structures. This problem stems from the fact that as-produced CNTs create intractable, insoluble aggregates which make processing extremely difficult.78 The degree of order in CNTs is of importance in many applications due to low total transport of carriers, which are electrons and phonons, in a random nanotube network.

Latex technology has been applied to the fabrication of highly ordered CNT networks throughout polymeric matrices. The resultant CNT-latex composites could be utilized in a variety of uses ranging from thermal, electrical, and mechanical applications. To begin with, one thermal application of CNT-latex based composites is in thermal conductors.79-80 Cai and Song fabricated MWNT-polyurethane (PU) latex composite using SDS as the surfactant to disperse MWNTs in water.79 To blend nanotube and PU dispersions, a stirrer was chosen as the instrument in composite preparation. MWNT content was varied from 0 wt % up to 7 wt % and it was revealed that, at the nanotube loading of 7 wt %, thermal
conductivity of PU was enhanced around 86%. With the similar idea of CNT networks formed by latex particle assembly, Grunlan et al. added SWNTs into PVAc latex. Gum Arabic (GA) polymer was employed as stabilizer of nanotubes in water. The dispersion of GA-SWNTs and PVAc were mixed via high-speed impeller blade. An increment of thermal conductivity of the composite compared to that of pristine latex was found at about 10%.

Another potential application of CNT-latex composite comes from thermoelectric behavior, which shows an electric potential upon temperature change. Advantages of using a polymer-based matrix are low-cost and lightweight while CNTs offer high electrical conductivity even at low concentration. Yu and co-workers used GA polymer for nanotube stabilization in water. Subsequently they blended PVAc latex aqueous dispersions with a dispersion of metallic and semiconducting single-, double-, and triple-walled nanotubes through a sonication process. The composite samples were prepared at different nanotube contents and then left to dry in molds. These composites exhibited a significant increase in electrical conductivity as CNT loading increased due to percolated networks formed throughout the composites. Thermal conductivity, on the other hand, remained constant and independent of nanotube concentration. Such electrically active but thermally inactive behavior will be promising for thermoelectric uses since the composite is electrically tunable while thermal properties do not change. In other words, high electrical and a low thermal conductivity is needed for their application of thermoelectric converters. Their measured electrical conductivity was as high as 4800 S/m whereas thermal conductivity was 0.34 W/m-K at the CNT content of 20 wt%. The same research group further investigated thermoelectric behavior and reported their results recently in 2010. In this recent work, besides the use of latex technology, they added poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) to the matrix to enhance thermoelectric efficiency. This additive helped CNTs to electrically connect each other at their junctions. As a result, electrical conductivity could be dramatically improved compared to their previous work with the value of about 40000 S/m. Thermal conductivity was still insensitive to temperature gradient, which is suitable for thermoelectric application. Nanotube type was found to affect electrical conductivity, which was highest in the case of the composite containing SWNTs. It was also discovered that PEDOT:PSS doped by dimethyl sulfoxide provided higher electrical conductivity compared to the composites fabricated using GA as the CNT stabilizer.
There is no literature associated with structure-reinforcement applications, such as buildings and bridges, of CNT-latex composites for their mechanical behaviour since such macro-scale use needs great up-scaling. However, there have been several reports on some other mechanical uses. In particular, the flexibility upon bending and recovery after being strained were demonstrated by Jurewicz et al.\textsuperscript{71} SWNT networks embedded in latex matrix were able to be strained up to \(-200\%\) and able to retain their structure after their relaxation as observed from SEM micrographs in Figure 2.10. Such composites are capable of electrical, optical, and thermal applications that require flexibility during device operation condition, for instance, photonics and electrical or thermal sensors.

![Figure 2.10. SEM micrographs representing SWNT networks: (a) being strained to 200\% and (b) without strain applied after strained up to 200\% (adapted from \textsuperscript{38}). It can be noticed that nanotube networks in (b) retain their morphology to be somewhat like hexagonal structure as they used to be before external tensile loading was applied.](image)

An obvious practical mechanical application of nanotubes with colloidal polymer particles is adhesives. Wang et al.\textsuperscript{69} functionalized SWNTs using hydrophilic poly(vinyl alcohol) (PVA) via sonication and incorporated this PVA-SWNT dispersion into poly(butyl acrylate) (P(BuA)) latex. After centrifugation process of mixture dispersion, resultant supernatant was collected for composite preparation. The composites were found to be stiffer compared to pristine latex. In addition, they showed that no matter what the debonding velocity was (10 or 100 \(\mu m\ s^{-1}\)), the composite with higher SWNT contents could be able to suffer higher stress and strain at failure. An observed increase in energy dissipation in the adhesive is the contribution of frictional sliding at the interface between CNTs and latex. The frictional force of sliding nanotubes along the interface with the matrix during debonding leads to an energy dissipation mechanism during adhesive
debonding. Wang and colleagues continued to study advantages of CNT-latex adhesives over conventional adhesives. In their experiments, water was added to several nanotube stabilizers: SDS, Triton X-100, poly(vinyl alcohol) (PVOH), and poly(vinyl pyrrolidone) (PVP). Then these solutions were blended with MWNTs and, subsequently, P(BuA) latex. It was reported that the polymer stabilizer with high molecular weight was mandatory in strengthening the interfacial region of nanotubes and their latex matrix. This is because polymer sits on nanotube surface and could form entanglement with the matrix. The polymer also causes sliding of nanotubes relative to their matrix. A study to determine interfacial strength between CNTs and a soft polymeric matrix \((T_g \sim -50^\circ C)\), which related to mechanical strength of the composite, was performed by Wang et al. In their work, MWNT dispersions were mixed with poly(butyl acrylate-co-acrylic acid) (poly(BuA-co-AA)) with poly(vinylpyrrolidone) (PVP) as a CNT dispersant polymer. The authors looked at the effect of chain molecular weight and density of dispersant polymer, which was adsorbed at the interface, on bulk mechanical property. It was found that interfacial strength increases with the nanocomposites containing higher molecular weight and density of adsorbed polymer. Sliding friction between the polymer matrix and polymer adsorbed at the interface is an explanation for this observation. The authors then suggested that mechanical properties of the nanocomposites can be tuned by using different adsorbed polymers.

Electrical applications of the composite with CNTs and latex matrix were widely published. A few examples are those reported by Jurewicz et al. and Wang et al. In the former work, composite preparation was similar to that described previously. Relatively, high electrical conductivity was shown at 0.1 S-cm\(^{-1}\) at low CNT loading because of percolated paths of nanotube networks. More interestingly, after the composite was strained and then relaxed, it was found that the composite still showed electrically conductive behaviour although the value decreased down to 0.04 S-cm\(^{-1}\), which was a consequence of network damage because of load transferred from latex matrix to nanotube bundles. The authors proposed that possible application of such nanocomposites is for stretchable electronics.

Wang and colleagues, with the similar sample preparation procedure as they previously used, demonstrated that their SWNT-latex adhesive has an advantage over conventional
adhesives that use metallic flakes and particles as fillers that cause an increment in storage modulus and viscosity. Another disadvantage of such metallic fillers is the low transparency of the final adhesives. Prominent electrical conductivity, coupled with optical and mechanical properties, therefore makes this novel CNT-latex adhesive promising for a wide range of applications.
References


Chapter 3

Materials, sample fabrication, and characterization techniques

This chapter basically describes the materials and methodology utilized in all of the present studies in Chapters 4, 5, and 6. The chapter begins with the main materials used: carbon nanotubes and latex, including their composite dispersion preparation. Subsequently, sample fabrication will be described in detail for each experimental investigation. In the characterization technique part, theoretical principles of each instrument used will be provided.

3.1 Materials

3.1.1. Carbon nanotubes

Both SWNTs and MWNTs were utilized in the present studies. Multi-walled type contains various CNT diameter sizes ranging from small to very large whereas SWNTs have lower diameter distribution. SWNTs applied to this work were synthesized by the high-pressure CO conversion (HiPCO) method and used as received from CNI Nanotechnologies, TX, USA, which is later merged with Unidym Inc., without any further purification. HiPCO is the technique of carbon nanotube synthesis performed by flowing CO gas as a carbon precursor in a heated chamber with the atmosphere of Fe(CO)₅ which contains iron catalyst. MWNTs (> 95% carbon purity) were produced by catalytic carbon vapour deposition and were used as produced from Nanocyl, Sambreville, Belgium.
3.1.2. Latices

CNTs can form rather more uniform networks when embedded in latex particles compared to the situation of being distributed in a homogeneous polymer. Consequently, in this study, polymers in colloidal form were employed to prepare composite dispersions. Because of the limited amount and availability of the latex from the supplier, the same latex could not be used throughout the whole current studies. As a result, there were three different latices being used in the current work. All of them were co-polymers and based on the similar polymer, butyl acrylate (BA). The latices were made by emulsion polymerization by DSM NeoResins, the Netherlands. In Chapter 4, the latex used was made from a copolymer of BA, methyl methacrylate, and methacrylic acid (BA/MMA/MAA). Two types of latices were applied in the study in Chapter 5. The so-called “hard latex” with Tg of 21°C is a co-polymer of styrene (St), BA, and acrylic acid (AA). Another latex with Tg of -50°C is a co-polymer of 2-ethyl hexly acrylate (2EHA), BA, ethyl acrylate (EA), and MMA. In Chapter 6, the latex was a random co-polymer consisting of BA, MMA, MAA, and acetoacetoxyethyl-methacrylate (AAEM). The physical properties of these polymers, categorized by chapter, are summarized in Table 3.1.

Table 3.1. Physical properties of colloidal polymers utilized in this work

<table>
<thead>
<tr>
<th>Latex monomer composition</th>
<th>Chapter 4</th>
<th>Chapter 5</th>
<th>Chapter 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid content (%)</td>
<td>BA/MMA/MAA</td>
<td>St/BA/AA</td>
<td>2EHA/BA/EA/AAMMA</td>
</tr>
<tr>
<td>Mean particle size (nm)</td>
<td>48.9</td>
<td>270</td>
<td>295</td>
</tr>
<tr>
<td>Glass transition Temperature (°C)</td>
<td>20</td>
<td>21</td>
<td>-50</td>
</tr>
</tbody>
</table>
3.1.3. Composite dispersion preparation

Dispersions of SWNTs and MWNTs with all colloidal latices were prepared according to diagram shown in Figure 3.1. It is noted here that the quantities of materials in the following procedure can be varied depending on desired amount of composite dispersion.

![Diagram of composite dispersion preparation](image)

**Figure 3.1.** Diagram describing the procedure to prepare the composite dispersion

The composite dispersion was prepared by blending homogeneous CNT dispersion with the latex which is in a liquid state. Triton X-100, a non-ionic surfactant \( \text{C}_{14}\text{H}_{22}\text{O}(\text{C}_{2}\text{H}_{4}\text{O})_{n} \), was utilized to homogeneously disperse CNTs in deionized water with
the weight ratio of 1.0 g water to 0.01 g Triton X-100 to 1 mg SWNTs. Ultrasonication was applied to the dispersion preparation due to its high power output enabling for uniform dispersion. The probe sonicator used, a Branson Sonifier model 150D, (Branson Ultrasonics Corporation, Danbury, CT, USA) was subsequently employed for nanotube debundling due to nanotube behaviour to aggregate with the use of ice in a water bath to ensure that the dispersion is not too hot to damage nanotube integrity. The resultant homogeneous nanotube dispersion was then sonicated with latex using lower power, which is enough to make a homogeneous composite dispersion due to the ability of the surfactant, in CNT dispersion, to make CNTs well dispersed in an aqueous colloidal latex dispersion.

3.2. Thin film fabrication

Bulk composite specimens can be prepared by applying the dispersion onto a mold. The dimensions of the samples are controlled through the mold size and volume of the dispersion, which is more straightforward compared to the preparation of thin film samples. This section is therefore focused on the details of thin film fabrication.

Usually, thin films are on the order of the wavelength of light, which causes interference colors observed by the human eye. Those films whose thicknesses are higher than such range are called thick films. There are several approaches developed to prepare thin films, for example, sputtering, molecular beam epitaxy (MBE), spin coating, Langmuir-Blodgett (LB), dip coating, etc. Different techniques have been chosen to prepare thin films depending on how much thickness accuracy is required for specific applications. MBE is the most accurate method among these techniques. However, not all of them are simple enough to be performed in ambient condition or at room temperature and pressure. Sputtering and MBE must be conducted in an advanced clean room with high or ultra high vacuum because it uses atomic level deposition, which makes film fabrication of latex not applicable since typically colloidal particles range from nano to micrometer in size. On the other hand, such a complicated instrumental system is not required for some chemical film preparations, i.e., spin coating, LB, and dip coating. However, the difficulty in LB and dip coating, especially for vertical deposition, is that materials need to wet the substrate and attach very well on the substrate. Otherwise, the first film layer cannot be deposited on substrate, resulting in non-uniformity of following film layers.
Spin coating

Although LB, dip coating, and spin coating are all effective ways of thin film fabrication, spin coating is a widely adopted technique for film deposition among these methods because it is a simply repeatable and rather fast procedure yet able to provide the uniformity of resultant films over a large area.\(^1\) Compared to other techniques, spin coating can eliminate non-uniformity of films due to high angular spin speed, spreading materials uniformly about the spin axis. In addition, films with controllable qualities and film thickness can also be managed by simple spin speed and time variation. To prepare spin cast films, briefly, the coating material in a liquid state is applied usually by dropping at the center of the rotation axis of a substrate that is previously horizontally attached at the center of a spin rotor, as illustrated in Figure 3.2.\(^3\)

![Figure 3.2](image)

**Figure 3.2.** Schematic illustration of spin coating process: (a) dispense, (b) ramp-up and spreading, (c) constant angular spin speed \(\omega\) and drying\(^2\)

The substrate is rotated with a certain speed and spin time. Centrifugal forces take the excess suspension or solution off the substrate in the radial direction, resulting in a liquid film on the substrate at first. Subsequently evaporation process of solvent or water in the liquid film causes the formation of a solid film on the substrate. Nevertheless, the drying step for thick films under a high angular speed is sometime necessary to improve stability because evaporation lasts longer for a thicker film. If the drying process is not performed for thick films, the uniformity of films can be destroyed when removing them out of the spin coater. In the present work, a constant spin speed of 5000 rpm was used in this drying process to ensure that the speed is not too high which can cause a significant thickness decrease.
Film thickness control by spin coating technique

Owing to various specific requirements for different applications, for example, thick films for adhesive study or thin films for electrical investigation, film thickness control is one of the most crucial issues being realized in film fabrication. This simple technique, spin coating, is undoubtedly one of the most effective candidates for film scalability. There are some parameters affecting film qualities, in particular, angular spin speed, spin time, concentration and viscosity of spreading solution or particle dispersion, and chemical interaction wetting between coating material and substrate. The contribution of the angular spin speed to film thickness can be presented as the following equation.³

\[ h = k\omega^a \]  

(3.1)

In this equation, \( h \) refers to film thickness, \( k \) and \( a \) are constants, and \( \omega \) represents angular spin velocity. Based on equation (3.1), the value of \( a \) in most case is negative, meaning that film thickness is decreased as higher spin angular speed is applied. Excess material is ejected from the substrate in the axial direction by a centrifugal force which is a function of \( \omega \). In addition, with similar spin parameters, spin time and coating material viscosity are also significant factors controlling film thickness as shown in the equation (3.2).⁴

\[ h = h_0[1 + \{4(2\pi f)^2/3 v\eta_0^2\}t]^{1/2} \]  

(3.2)

where \( h_0 \) is initial film thickness, \( f \) refers to spin frequency, \( \nu \) is kinematic viscosity or viscosity per unit density of the coating material, and \( t \) represents spin time. A longer spin time allows a longer time for centrifugal forces to pull fluid or particles away from the rotation axis, resulting in the spreading into thinner layers. According to equation (3.2), a lower kinematic viscosity also contributes to thinner films. Another crucial factor contributing to film thickness is the concentration of coating material as reported by Schubert et al.⁵ The dependence of film thickness on dispersion concentration, \( c \), is presented in the following relationship.

\[ h \sim \frac{c^2}{1 + \text{const.}*c} \]  

(3.3)
It is more likely from this dependence that coating materials with high concentration are prone to have high thickness when other spin conditions are kept identical. Moreover, the homogeneity of a film can be improved by substrate treatment or suspension functionalization in order for particles in suspension to be adsorbed well on the substrate over larger surface areas. A hydrophilic suspension will not spread on a substrate with dirt or oil on it, leading to de-wetting of coating material on the substrate.

3.3. Characterization techniques

In the present work, pristine latex and composite samples were investigated using several techniques for specific investigations. In particular, measurements were carried out to determine chemical composition by Raman spectroscopy, topography by AFM, film thickness through ellipsometry, micro-and nano-morphology by SEM, and thermal conductivity via differential scanning calorimetry (DSC). The following sections will be attributed to the principles of each characterization technique.

3.3.1. Raman spectroscopy

To observe the presence of CNTs, one of the most sensitive techniques widely applied is Raman spectroscopy. This can even detect some information from samples with very low percentage of CNTs in polymer matrix. SWNTs are Raman-active materials due to the electronic and phonon state confinement in one dimension, which results in van Hove singularities in the nanotube density of state.

When monochromatic light hits a transparent material, scattered light comes out with the frequency almost similar to that of incident frequency, which is actually elastic scattering. Such phenomenon is known as “Rayleigh scattering”. On the other hand, in the situation called “Raman scattering”, there are some scattered discrete light with frequencies higher and lower than that of monochromatic as well and this is called inelastic scattering. This latter type of light scattering was experimentally found firstly in 1928 by Raman and Krishnan. Raman scattered signal, however, is extremely weak as it is only one photon in every $10^6$ to $10^8$ photons scattered but vibrational and rotational energy levels can be
known from this scattering. Most photons scatter according to Rayleigh scattering, resulting in its highest intensity of scattered light.

There are two vibrational states in Figure 3.3: \( m \) and \( n \). The state so-called \( m \) is the one in which ground-state electrons are. However, if excited electrons emit energy lower than that of the absorbed energy, they are in a vibrational state \( n \). Virtual states do not really exist. They are excited states. Rayleigh scattering is an elastic process; no energy change is generated after excited electrons return to the ground state. In contrast, Raman scattering called “Stokes” and “anti-Stokes” are inelastic processes. As it is unlikely for anti-Stokes process to occur, Raman scattering typically analyses the Stokes spectrum. A Raman spectrum in spectroscopy is regularly presented with two axes given as intensity and wavenumber, the displacement of spectra from the Rayleigh line. The Rayleigh line is then always at the wavenumber of 0 cm\(^{-1}\). The wavenumber axis, the one along horizontal axis, has the units of cm\(^{-1}\), which is not an SI unit. It is also well known to use “Raman shift” instead of using wavenumber to label this axis. The vertical axis is given as intensity, the difference of energy density between \( m \) and \( n \) states in Figure 3.3. The unit of intensity axis is usually provided in arbitrary units (a.u.). An example scheme of a Raman spectrum is illustrated in Figure 3.4. Nowadays, a laser is usually used as light source for Raman system because it is a high-power source that is able to provide monochromatic light and the laser beam size can be focused to shine on a tiny spot on a sample.
Figure 3.4. Raman spectrum of SWNTs synthesized by HiPCO method\textsuperscript{11}

Basically, SWNTs have some specific spectral features: G-band, first order Raman scattering coming from graphite at around 1582 cm\textsuperscript{-1}; D-band, second order Raman scattering with a weak Raman signal at around 1350 cm\textsuperscript{-1}; radial breathing mode (RBM), another first order Raman mode of nanotubes in the range of 100-500 cm\textsuperscript{-1}; and the G' band, another second order Raman scattering at around 2700 cm\textsuperscript{-1} of wave number.\textsuperscript{6} According to their peak positions, it can be noted here that the G' band is an overtone of the D band. Second order Raman scattering can be either the events of two-phonon scattering or the event of one-phonon and one-elastic scattering.

The strongest Raman spectra are from G-band and RBM modes for SWNTs.\textsuperscript{6} RBM is a unique mode that can be found in SWNTs only. As a result, this mode is an indicator of the presence of SWNTs in a sample. Its name “Radial breathing mode” comes from nanotube behavior. Particularly, all carbon atoms move in radial direction at the same time due to bond stretching, which is like breathing of the tube. The frequency of RBM mode (\(\omega_{\text{RBM}}\)) is inversely proportional to tube diameter (\(d_i\)) as stated in equation (3.4), where \(C\) is 248 cm\textsuperscript{-1} for for individual SWNT on a silicon dioxide substrate.\textsuperscript{1,11}

\[
\omega_{\text{RBM}} = \frac{C}{d_i}
\]

(3.4)

The main parts of a Raman spectrometer in the present work are shown in Figure 3.5.\textsuperscript{12} Their corresponding functions according to the numbers marked in the figure are as follows:
1. Sample stages that are connected to AFM probe for Raman measurement of samples with significantly low Raman intensity.

2. Objective lenses enhance weak Raman signal.

3. Photomultiplier tube (PMT) unit is used to obtain fast confocal laser (Rayleigh) image.

4. Avalanche photodiode (APD) is used to count single photons. Charge-coupled device (CCD) detector is sensitive for charge movement, which can subsequently be converted to output signal.

5. Polarization optics for excitation laser and light scattered/reflected.

6. Software to control all components of the instrument such as lasers, gratings, polarizers, and pinhole.

7. Confocal Raman images are created at the same time as AFM topography and phase images using the same software.

---

**Figure 3.5.** Schematic representation of components of a Raman spectroscope (adapted from \(^\text{12}\))

Theoretically, there are several factors causing a variation in Raman intensity as follows:\(^7\)
1. **Raman scattering**: Raman scattering is directly proportional to the number of incident photons from a light source. The higher intensity the light is, the higher amount scattering occurs; hence, the higher Raman intensity is. For the specimens that provide tiny Raman scattering, a laser with high power of light is used to increase scattering events.

2. **Diffraction grating efficiency**: In a Raman spectrometer, most diffraction gratings are blazed at 5000 Angstroms. The grating efficiency is maximum at the blaze wavelength, as seen in Figure 3.6 that the efficiency is highest at 5000 Angstroms. At wavelengths lower or higher than this blaze wavelength, efficiency of the grating decreases. The blaze wavelength can be varied. For example, in the Raman system designed for a helium-neon laser, a grating blazed at 6500 Angstroms is used because its efficiency is highest in the range of helium-neon laser wavelength.

![Figure 3.6. A plot showing relative efficiency as a function of wavelength (adapted from 7)](image)

3. **Photomultiplier tubes**: A photomultiplier tube is a detector for Raman light coming out from the spectrometer. Its efficiency is reduced at the wavelengths \( \geq 4000 \) angstroms. An efficiency decrease of photomultiplier tube together with grating deficiency can result in low intensity of Raman signal and could lead to a decrease of sensitivity up to 100 times.

4. **Width of spectral slit or pinhole**: Spectral slit width should be kept unchanged during a spectral scan. To have such a situation, it is necessary to vary the actual slit width according to the light spectra to have this value constant.

5. **Discrimination**: In a Raman optical system, there is background light that is not intended to exist, called “stray light”. The discrimination is a measure of stray light level occurring in the instrument. Since the Raman signal is very weak, stray light
level should be kept minimum. By using a double monochromator, the stray light level could be reduced approximately a square root of the level present in the system with a single monochromator. Discrimination is, then, briefly how effective it is to detect the signal above the stray light.

The purpose of Raman spectroscopy in this work is to verify the existence of SWNTs in composite films. It is a technique appropriate for CNT and CNT-polymer composite samples due to very high sensitivity to Raman signals emitted from nanotubes with low response to polymers. As a result, it is possible to distinguish CNTs from polymer. Nanotube networks can also be revealed by a Raman mapping procedure which was conducted by selecting the outstanding peaks of CNTs and detecting these signals while spatially scanning. Moreover, polarized Raman spectroscope will be performed to investigate deformation of nanotube networks embedded in latex matrix. Specifically, the maximum Raman intensity will be revealed when nanotube bundles are aligned parallel to the direction of the polarization direction of the incident light.$^{13}$

The Raman instrument in this study was an NTEGRA Spectra (NT-MDT Co., Moscow, Russia). Lasers used as light sources for the spectroscopy were red, with a wavelength of 633 nm, and a blue laser (473 nm).$^{14}$

3.3.2. Atomic force microscopy

To investigate the topographies of polymer films in two and three dimensions, atomic force microscopy (AFM) was exploited to the polymer film surface due to its high spatial resolution down to nano-scale level, operating temperature at ambient conditions, and various software functions for surface analysis. These useful operations are, for example, a scale bar for particle size measurement, and fast Fourier transform (FFT) analysis for the study of particle packing patterns formed in a sample. AFM also offers an accurate topography analysis due to the use of a photodiode detector system, which is very sensitive to the difference in surface morphology. The AFM operation is based on force between the AFM tip and sample atoms without the use of electron beam, leading to no need of sample surface treatment like gold coating in SEM technique that may change surface topography.
AFM is a mechanical imaging technique used to image topography in three dimensions by means of interaction between the AFM probe and a sample surface. Besides topography, AFM also reveals physical surface properties, for example, hardness and softness. During a scan process, a sharp probe is fixed while a sample stage, attached on scanner, is moving underneath it, or vise versa. Scanner movement generates a two-dimensional line profile as shown in Figure 3.7. By integrating these lines, a three-dimensional image can be created.

Figure 3.7. A scheme demonstrating AFM imaging of a three-dimensional sample

An AFM consists of three main components: a computer, a stage, and control electronics. The computer is used to adjust control electronics suitable for probe and sample as well as display obtained imaging. The stage normally comprises of a sample holder and a scanner, which is able to move in three dimensions. Control electronics manage scanner movement and convert mechanical change of cantilever to electrical signal, and vice-versa according to input received from the computer.

The AFM imaging procedure can be briefly explained as following: A laser beam hits the top of a cantilever under which there is a probe. Sample is moved by a scanner in the x-y plane in a way that makes the probe scan over the desired area. Because there is always a repulsive force between the atoms of the AFM tip and the specimen surface, different heights of the sample surface cause probe bending, resulting in a change of the deflected laser beam projected on different quadrants of a photodiode. A feedback loop is used, during the scan process, to maintain a constant deflection of the cantilever by adjusting the vertical position. The photodiode, lastly, detects changed laser signal and sends the signal to electronic component for further surface analysis.
Figure 3.8. Illustration of (a) AFM operation with the inset showing atomic interaction between probe tip and sample and (b) an actual tip attached on a cantilever. The scale bar in (b) is 50 μm.\(^{17-18}\)

The graph shown in Figure 3.9 represents the relationship between van de Waals force and separation distance between AFM tip and sample atoms for each operational mode.\(^{19}\) When the tip and sample surface are apart from each other less than a few Angstroms, the interaction between them is repulsive force as they are too close to each other. In non-contact mode, the separation ranges from tens to hundreds of angstroms and it is attractive van de Waals interaction. Intermittent mode has the fluctuation between these separation regions.

Figure 3.9. A graph presenting attractive and repulsive forces in AFM contact, intermittent contact, and non-contact modes (adapted from \(^{19}\))
There are three modes of AFM operation, contact, intermittent contact, and non-contact modes as shown in Figure 3.10. Fixed deflection is applied in contact mode operation. In contrast, the tip oscillation amplitude is fixed and the probe is vibrating near its resonant frequency during surface scanning in intermittent contact mode. This AFM mode enhances signal/noise ratio due to the modulation of the signal measured. For non-contact mode, signal detected is from the weak attractive van der Waals force between the atoms of tip end and sample surface. The amplitude of tip oscillation is maintained below the mean distance between the tip and sample. As a result, the tip does not contact the sample surface. However, a contact mode is able to offer the highest resolution imaging among these three modes. In such an operation, a repulsive force of around $10^{-9}$ to $10^{-8}$ Newton is kept constant. The operation for high resolution requires high sharpness of AFM tips, accuracy of the control unit, a vibration protection unit, and low noise level in the feedback system.

Figure 3.10. AFM scanning modes: (a) contact, (b) non-contact, and (c) intermittent contact modes

Phase imaging is a measure of the relative phase of the signal driving cantilever and the phase that the photodiode monitors pixel by pixel. A combination of all these pixels gives rise to an AFM phase image corresponding to a particular scan area. Phase images are indicative of difference in properties of material; for example, viscoelasticity, chemical composition, hardness or softness, and electrical or magnetic contrast of sample surface. Contrast in phase images stems from heterogeneity of surface or other materials deposited on top of the surface under ambient conditions. Consequently, topography and phase images do not necessarily have similar features. Base on this principle, phase contrast imaging is useful in distinguishing different phases of, for instance, co-polymer materials that have identical topography as seen form an example in Figure 3.11.
In this study, all samples were investigated by intermittent contact mode because in contact mode it is more likely for the probe to stick to a soft polymer surface, causing the distortion of the real topography. This mode, in addition, provides high signal/noise ratio. To prepare samples for AFM, firstly one deposits a latex dispersion on a solid substrate and then lets the film dry. The obtained film is ready to be studied by AFM immediately without any further treatment. All AFM micrographs were obtained by an NT-MDT Atomic Force Microscope (NT-MDT Co., Moscow, Russia) in the air and at room temperature. Silicon cantilevers (ATEC-NC, Nanosensors, Switzerland) were used throughout the present study with the spring constant of about 45 N/m and resonant frequency of about 330 kHz.

3.3.3. Ellipsometry

Ellipsometry is a technique using polarized light to investigate thin film optical properties. Its detector measures the ratio of incident and reflected amplitudes, psi ($\Psi$), and phase difference caused by reflection, delta ($\Delta$). These measured values relate to the ratio of the Fresnel reflection coefficients, $R_p$ and $R_s$ for p- and s- polarized light, as shown in equation (3.5) below. By measuring both amplitude and phase changes, it is undoubtedly highly sensitive to film surface characteristics.

$$\frac{R_p}{R_s} = \tan(\Psi) e^{\iota \Delta}$$

(3.5)
These coefficients depend on the angle of incidence and film refractive index. The p-direction lies in the incident plane, which is the plane consisting of incident, reflected, and normal vector perpendicular to sample surface. The s-direction is perpendicular to the p-direction. The p-direction, the s-direction, and wave propagation direction are perpendicular to each other corresponding to a Cartesian coordinate system. They can be represented as Figure 3.12.

![Figure 3.12](image)

**Figure 3.12.** Schematic illustration showing the p- and s-directions

In this work, ellipsometry has been applied to investigate optical properties of pristine polymer and CNT-polymer composite films. A variable angle spectroscopic instrument (J. A. Woollam Co., Inc., Lincoln, NE, USA) with a rotating analyzer configuration was applied to the study. The instrument has an incident wavelength in the wide range of 200 nm to 1200 nm and an angular range from 0° to 90°. In this study, operating wavelengths were in the range of 400 to 800 nm. It allows a highly sensitive detection of film thickness change of 0.1 nm. By analyzing optical data, it reveals some physical characteristics of thin films including thickness, refractive index, and expansivity, etc. Thermal expansivity can be measured using a heating stage (Linkam Scientific Instruments Ltd., Surrey, England) installed on the sample stage of an ellipsometer. This heating stage is able to increase temperature from room temperature, approximately 21°C, up to 150°C and decrease temperature with controllable rate. All ellipsometric experiments were conducted in the air at different temperatures and heating rates depending on what was being studied. Heating rates used in Chapter 4 were varied from 0.2°C/min to 10°C. Films to be investigated by ellipsometry were on silicon wafer because the instrument detects elliptically polarized light reflected from samples. Other substrates, such as glass or mica, cannot reflect much light, resulting in no, or too weak, signal reflected to the detector. However, one limitation
for sample preparation is that film must not be too thick. In other words, film thickness should not be more than the penetration depth of light.

Ellipsometry cannot provide film properties immediately after a scan. A model consisting of substrate and material layers needs to be first created and subsequently applied to compare experimental and generated data. If these data fit well to each other, as can be determined by a low mean square error (MSE), as shown in equation (3.6), one may terminate the process of data fitting.

\[
MSE = \frac{1}{2N-M} \sum_{i=1}^{N} \left[ \left( \frac{\Psi_i^{\text{mod}} - \Psi_i^{\exp}}{\sigma_{\Psi_i}} \right)^2 + \left( \frac{\Delta_i^{\text{mod}} - \Delta_i^{\exp}}{\sigma_{\Delta_i}} \right)^2 \right] = \frac{1}{2N-M} \chi^2 \quad (3.6)
\]

where \( N \) is the number of \((\Psi, \Delta)\) pairs, \( M \) represents the number of variable parameters in the model, \( \sigma \) is the standard deviation of the experimental data points, and \( \chi^2 \) is presented for comparison. However, in the data analysis procedure, if MSE is still high, new fit parameters need to be changed from initial guessing values. The iterative process of data analysis is briefly presented in Figure 3.13.

![Figure 3.13. Diagram explaining ellipsometry data analysis procedure](image)

To analyze experimental data in this work, firstly a model of the sample was formed using silicon as a substrate with the thickness of 1 mm. Thin silicon dioxide layer was then chosen to be first material layer for each simulation. The thickness and index of refraction
of this layer were measured independently. The neat polymer or composite film was modeled with a Cauchy equation due to its wide applicable range to dielectrics and semiconductors, except metals. In the Cauchy method, the index of refraction $n$ and extinction coefficient $k$ are dependent on wavelength $\lambda$ as presented in equation (3.7) and (3.8) below.\(^{23}\) Equation (3.7) enables the refractive index over a range of wavelengths to be described with only a few parameters. The number of unknown parameters can be kept low. The complex index of refraction is then given by equation (3.9).

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$$ \hspace{1cm} (3.7)

$$k(\lambda) = a e^{\beta(12400(\frac{1}{\lambda} - 1))}$$ \hspace{1cm} (3.8)

$$n = n + ik$$ \hspace{1cm} (3.9)

where $A, B$ (μm\(^2\)), $C$ (μm\(^4\)) are constants, $\alpha$ represents extinction coefficient amplitude, $\beta$ is exponent factor, and $\gamma$ refers to band edge. For some samples, surface roughness, a layer consisting of 50% material film and 50% voids, and thickness non-uniformity, which is normally applied for films with unparallel interfaces, were used with the Cauchy layer in order to reduce the MSE and improve the fit. Typically, films with high transparency were analyzed by varying $A, B, C$ without $k$ consideration. The constant $C$ was frequently neglected due to the value close to zero because of the $\lambda^4$ term. Nevertheless, sometimes, $k$ has to be determined when films were not highly transparent to obtain better fit. Essentially, SWNTs used in this work are able to absorb light in the visible region, which is in the same wavelength range as the light emitted from the source.\(^{25}\) In-situ or real-time study of film properties can also be performed using dynamic analysis. Such operation measures generated and experimental data of samples over time, leading to the possibility to determine several film properties, such as glass transition temperature. Furthermore, by further analyzing generated data, thermal expansivity is able to be known as well.
3.3.4. Scanning electron microscopy

Scanning electron microscopy (SEM) is an imaging technique using an electron beam to scan on a sample surface. A microscope consists of two main parts: control console, a unit used to control electron beam; and microscope column, which has an electron gun, magnetic lens for electron path control, and detectors. These components are schematically illustrated in Figure 3.14. The wavelength, or energy, of electrons depends on applied accelerating voltage, ranging from 1 – 30 keV in general operation and up to 60 keV, whereas samples are at earth potential. Electron beam size for a thermionic emission source is typically ~ 6 nm. However, a probe size as tiny as ~ 3 nm can be achieved using a higher intensity of emission source. The resolution of the microscope is in the range of nanometers to micrometers. Theoretically, the smaller the electron beam, the higher resolution achieved provided that the aberrations, the effect in which electrons of different energy are focused to different plane, of the condenser lens are low. Resolution is limited by the electron beam size. In particular, it is not possible to have resolution lower than the electron beam size. A certain depth of focus is created when electron beam hits a sample surface and this depth is called "interaction volume". Signals generated from the interaction between the electron beam and sample interaction volume are secondary electrons, backscattered electrons, Auger electrons, and x-ray fluorescence. Information obtained from these key signals can be summarized as shown in Table 3.2. However, important emitted signals to be detected are secondary and backscattered electrons because they provide topography differences.

<table>
<thead>
<tr>
<th>Signal</th>
<th>Obtained Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>Backscattered electrons</td>
<td>Topography, composition, crystallography</td>
</tr>
<tr>
<td>Secondary electrons</td>
<td>Topography, voltage, magnetic and electric field</td>
</tr>
<tr>
<td>Absorbed specimen current</td>
<td>Topography, composition</td>
</tr>
<tr>
<td>Auger electrons</td>
<td>The identity of the emitting atoms</td>
</tr>
<tr>
<td>X-Ray fluorescence</td>
<td>Elementary analysis of samples</td>
</tr>
</tbody>
</table>

Table 3.2. Specimen information analyzed from each emitting signal

60
Figure 3.14. Schematic drawing showing SEM components

Scanning electron microscopy is an effective sample analysis for the study of surface topography of thin films and morphology of latex particles and nanotubes in films. By comparison of sample with a bar scale on an SEM image, the technique also provides dimensions of samples. The instrument utilized in this work was a Hitachi S-4000 field-emission scanning electron microscope. The applied operating voltage was in the range of 5 kV to 20 kV. Sample preparation in this characterization can be divided into two groups which are with and without gold coating on the sample surface. The thickness of the gold coating layer was 1 nm; hence, real topography was not significantly changed. The purpose of the coating is to make a non electron-conductive surface to be more electron conductive to obtain noise-free SEM images. For example, for a composite film, if nanotube networks are studied, the film does not have to be coated by gold due to much higher electron conductivity of nanotubes compared to that of polymer. On the other hand, if polymer topography is expected to be seen, the film has to be coated by gold. However, care must be taken in varying the incident voltage for polymeric specimens because high-energy electrons can cause a topography change by, for example, melting. Unlike AFM sample preparation using sticky tape to attach a sample to a sample holder, SEM sample preparation requires the use of conductive glue. Therefore, silver paint has been utilized instead to make the sample holder to be electronically conductive in this study. Copper tape was also utilized as a glue in the case of samples on silicon wafer, and this is practical since the wafer is conductive of electrons.
3.3.5 Differential scanning calorimetry

Differential scanning calorimetry (DSC) is a technique measuring a difference in heat flow through a sample and reference material against time or temperature. Both the sample and reference are connected to a temperature controlled unit. In this technique, a difference in energy is measured rather than temperature whereas the operation principle of differential thermal analysis (DTA) is to measure temperature. Therefore, DSC is more practical in measuring; for example, heat of reaction and transition and specific heat compared to DTA technique.

Figure 3.15. A representation of DSC sample holder, which has a reference pan and a sample pan on the left and right, respectively.

Sample, red colour in Figure 3.15, is put in the sample pan while reference pan is an empty pan. Reference and sample pans are identical to eliminate other factors affecting thermal analysis. DSC working principle can be briefly described that heat flows through both reference and sample via a heat plate, which has pans on top of it. Heat is then transferred from a heat plate to reference and sample pans at the same time and, ultimately, to reference and sample materials. Thermocouples underneath the heat plate subsequently measure the heat required to keep the sample at the same temperature as the reference that is directly proportional to the difference in heat flow. Thus, heat flow through the sample and reference can be determined.

In the present study, DSC is operated to determine the glass transition temperature of materials. At transition temperature, some amount of energy is absorbed in a phase transformation (latent heat), which is shown in the form of a dramatic change in heat
flow. As a result, $T_g$ is in this range of apparent heat flow difference. From Figure 3.16, $T_g$ can be found using the software accompanied with a Q1000 differential scanning calorimeter (DSC) (TA Instrument, New Castle, USA). With an aid of derivative heat flow (right vertical axis), the temperature at which there is a great change in heat flow can be simply determined. The software then finds a point on the heat flow curve at about the middle of heat flow difference and reports this as the $T_g$ of the sample.

![Heat flow curve and its corresponding derivative showing data from a conventional DSC. Red curve refers to heat flow profile and blue line corresponds to derivative heat flow. $T_g$ of this particular sample is found at 32.90°C.](image)

**Figure 3.16.** Heat flow curve and its corresponding derivative showing data from a conventional DSC. Red curve refers to heat flow profile and blue line corresponds to derivative heat flow. $T_g$ of this particular sample is found at 32.90°C.

**Modulated DSC**

In DSC, there is a limitation in analyzing complex transitions with overlapping thermal events. Modulated DSC (MDSC), or Temperature MDSC, was created to solve this problem. The difference between DSC and MDSC is that, in MDSC, the operating temperature profile is a sinusoidal temperature modulation, which is a fluctuation in temperature, using a linear heating rate (heating or cooling). As a result, MDSC is not only
able to provide total heat flow information, which is the only information DSC can offer, but also the reversible (heat capacity element) and non-reversible (kinetic element) are able to be shown.

In MDSC, time-dependent sample temperature $T(t)$ is a function of temperature at the beginning $T_0 (K)$, linear heating rate (or cooling rate) $\beta (K/min)$, and time $t (min)$ as shown in equation (3.10).

$$T(t) = T_0 + \beta t$$

(3.10)

A sinusoidal temperature modulation is applied additionally to a constant linear heating profile. If the temperature modulation has an amplitude $A_T (\pm K)$, and a modulation frequency $\omega (s^{-1}) = 2\pi/p$, where $p (s)$ represents the period of modulation, the equation (3.10) can be rewritten as follows:

$$T(t) = T_0 + \beta t + A_T \sin \omega t$$

(3.11)

An example of this combination of constant heating rate profile and sinusoidal temperature profile is presented in Figure 3.17.

In DSC or MDSC, the total heat flow $Q (J)$ is a function of time $t (s)$, heat capacity of the sample $C_p (J/K)$, and the kinetic heat flow. The total heat flow can be shown as the following equation.

$$\frac{dQ}{dt} = C_p \beta + f(T,t)$$

(3.12)

The first term on the right, $C_p \beta$, of this equation represents the reversing heat flow. The term $f(T,t)$ is for non-reversing heat flow. The equation (3.12) can alternatively be rewritten as follows:

Total heat flow = (reversing heat flow) + (non-reversing heat flow)

(3.13)

Examples of reversible and non-reversing events are shown in Table 3.3.
Table 3.3. MDSC data signals obtained from reversing and non-reversing heat flow

<table>
<thead>
<tr>
<th>Reversing heat flow</th>
<th>Non-reversing heat flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat capacity</td>
<td>Evaporation</td>
</tr>
<tr>
<td>Most melting</td>
<td>Crystallization</td>
</tr>
<tr>
<td>Glass transition</td>
<td>Enthalpic recovery</td>
</tr>
<tr>
<td></td>
<td>Decomposition</td>
</tr>
<tr>
<td></td>
<td>Thermoset cure</td>
</tr>
<tr>
<td></td>
<td>Protein denaturation</td>
</tr>
<tr>
<td></td>
<td>Starch gelatinization</td>
</tr>
</tbody>
</table>

Figure 3.17. An example of heating profile in an MDSC experiment with two heating profiles applied to reference and sample: a constant linear and a sinusoidal heating profiles. In this particular experiment, the modulation period of 80 s, modulation amplitude of 1°C, and linear constant heating rate of 3°C/min were used.
Typical DSC measures only the total heat flow whereas MDSC can distinguish each component in equation (3.12). The resultant information on time, modulated heat flow, and modulated heating rate are used in the interpretation of the data obtained. To reveal typical DSC data, deconvolution of MDSC data is required to be performed. Different thermal behaviours of a sample, such as glass transition, cold crystallization, and fusion, are able to be detected in an overlapping thermal event in MDSC experiment.
References


Chapter 4

Thermal Expansion of Single Walled Carbon Nanotube-Colloidal Latex Composite Monolayer Thin Films

The beginning of this chapter provides relevant background about thermal expansion. Then it will provide experimental details on how nanocomposite films were prepared and then report results on their thermal expansivity.

It will be shown that incorporation of SWNTs in a colloidal polymer film results in the formation of belt-like nanotube networks surrounding each polymer particle in the film plane. Particle sintering as temperature scales up is prohibited by this nanotube network. The mismatch of thermal expansivity of SWNTs and latex matrix is the reason causing the expansion of the polymer only while nanotube networks comparatively do not expand. While being heated above their T_g, polymer particles are squeezed out in out-of-plane direction only due to the confinement of in-plane belt-like nanotube networks. The consequence is an increased expansion in the direction normal to the film plane. The maximum enhancement of thermal expansivity of 200% has been found when the percolating CNT network is formed. We believe that this is the first time that the “squeezing effect” has been studied at the nano-scale.

4.1 Background

4.1.1 Introduction to thermal expansion of materials

Thermal expansion is the phenomenon in which materials have a dimensional change due to a temperature change at constant pressure.\(^1\) Thermal expansion characteristic is typically measured as a coefficient of thermal expansion (CTE) or simply expansivity whose unit is the inverse of temperature, i.e., K\(^{-1}\). This coefficient can be either positive or negative,
meaning that materials can either increase or decrease their dimensions with an increase in temperature. The reason of positive and negative expansivity is as follows:

(i) **Positive expansivity**: Materials with this behavior expand upon increasing temperature. As temperature scales up, atoms have higher thermal energy and vibrate more vigorously, resulting in farther average distance between them due to their greater kinetic energy. Material expansion can also be described using an asymmetric potential well as shown in Figure 4.1. It is seen that atoms have an equilibrium spacing, \( r_0 \), defined as the minimum in potential energy. Atoms gain higher potential energy from increasing temperature. To retain an equilibrium state, these two atoms need to follow the dashed curve in Figure 4.1 with increasing temperature and higher energy levels. Hence the mean value of \( r \) increases.\(^1\)

![Figure 4.1. Asymmetric potential well of adjacent atoms in solids.](image)

The shape of the potential well can be varied depending on chemical bond strength between atoms. Figure 4.2 demonstrates the potential wells with strong and weak bonding. Strong bonding prohibits vigorous atomic vibration that causes long inter-atomic distance due to the attractive force between them. Therefore, thermal expansion is relatively low. In contrast, weak bonding allows atoms to vibrate with longer vibration distance as attractive force between them is low, resulting in longer inter-atomic distance and, hence, the final outcome is higher thermal expansion.
Figure 4.2. Potential wells of atoms with high (solid line) and low (dashed line) chemical bonding between them.\(^1\)

(ii) **Negative expansivity:** In reality, atomic vibration happens not only in 1-D but also in other two dimensions. If the vibration in a particular direction is greater, the vibration amplitude in another direction has to be smaller. Material contraction is the consequence of the prominence of this vibration along the direction with a smaller amplitude of motion.\(^1\)

Generally, solid materials tend to expand as temperature is increased. Thermal expansions happening in one, two, and three dimensions are called linear, area, and volume thermal expansion, respectively. Linear CTE, \(a\), is defined as a length change per unit length, \(L\), per temperature, \(T\), change at a given tension, \(r\). Volume expansion, \(\beta\), refers to a volume change per unit volume, \(V\), per temperature change. For volume expansion, \(\beta\) at a given pressure, \(P\), is expressed as following equation.\(^2\)\(^3\)

\[
\alpha = \frac{1}{L} \left( \frac{dL}{dT} \right)_r 
\]  \hspace{1cm} (4.1)

\[
\beta = \frac{1}{V} \left( \frac{dV}{dT} \right)_P 
\]  \hspace{1cm} (4.2)

Usually, the coefficient of volume expansion is three times that in the linear case.\(^2\)\(^3\) This relation can be derived as follows:
Polymers have expansivities higher than most other materials, such as ceramics and metals. The expansion of polymers is not necessarily linearly proportional to temperature change. In other words, the CTE for a polymer depends on the temperature range over which it is measured.

**Thermal expansion and the glass transition temperature**

At glass transition temperature ($T_g$), thermal expansion of polymer is not continuous. This discontinuity is therefore indicative in determining polymer's $T_g$. Consequently, the value of thermal expansion can be utilized to identify glassy and liquid phases as shown in Figure 4.3. From this figure, $T_g$ can be determined by drawing two straight lines passing through linear regions of glass and liquid. The intersection of these two lines is $T_g$. Below $T_g$, molecules cannot undergo long-range motion but are frozen in place. Polymer bonds are rigid and strong at the temperature below $T_g$, resulting in high viscosity. In this case, polymer is in glassy state.

![Figure 4.3](image)

**Figure 4.3.** Phase transition between glassy and liquid states, which have different values of thermal expansion (adapted from ⁶).
In contrast, at temperatures above $T_g$, higher kinetic energy enables molecular motion. Structural relaxation in this temperature range results in a decrease in viscosity and an increase in thermal expansion. Figure 4.3 shows how the volume increases with temperature for a glassy polymer. There is one expansivity in the glassy state and a different, higher expansivity in the rubbery (liquid) state at higher temperatures.

4.1.2 Review of thermal expansion of carbon nanotube composite materials

Single-wall carbon nanotubes have been incorporated into a polymer matrix by several research groups to fabricate composites with promising applications in structure design and electronic packaging. The composite materials and devices designed for thermal applications can be controlled. Particularly, composite thermal expansion can be tuned by changing the filler’s aspect ratio, size, shape, volume fraction, and distribution. Unlike the investigations on mechanical and electrical properties of bulk material systems, the reports on thermal expansion of novel nanocomposites is rather limited.

The computational study of Wei et al. through molecular dynamics (MD) simulations enable them to predict the density of a polyethylene (PE) polymer-CNT composites as a function of temperature. They observed a more-rapid decrease of composite density as temperature increases compared to the case of PE without CNTs. This means a considerable thermal expansion enhancement of SWNT-polyethylene composite above its $T_g$. It was reported that, with a SWNT content of 8 vol.% in the polymer host, a 142% increment in thermal expansion coefficient was found at temperatures higher than 400 K. Their explanation of this report is an equivalent increase in the excluded volume of the embedded CNTs as a function of temperature. Another study has shown that the thermal expansion of a nano-composite above its $T_g$ can be tuned by different nanotube functionalization method. Apart from the case of pristine SWNTs in the composite, the maximum enhancement of thermal expansion in this work was up to 50% at temperature higher than its $T_g$ through the oxidized SWNTs incorporated into the epoxy matrix.

Not only are researchers interested in an increased material thermal expansion, but some of them also developed composites with low thermal expansion. SWNTs were added to a polyacrylonitrile polymer to reduce the polymer’s thermal expansion by Guo et al. The
outcome was a much lower thermal expansivity of the composite at temperature above its \( T_g \) compared to thermal expansion of the polymeric matrix, as it was found that thermal expansions are \( 108 \times 10^{-6} \, ^\circ\text{C}^{-1} \) and \( 0.6 \times 10^{-6} \, ^\circ\text{C}^{-1} \) for neat polymer and the composite, respectively. A related report on the contribution of SWNTs to a decrease of thermal expansion was presented by Xu et al.\textsuperscript{11} Based on their work, the composite thermal expansion was reduced when the SWNT amount was higher. Essentially, a SWNT volume fraction of 0.49 contributed to a decrease of 35% of thermal expansivity which was explained by the low thermal expansivity of SWNTs compared to that of the polymer matrix. However, they stated that their technique is practical for the composites containing polymer in powder form only. Thermal expansion manipulation of polymers was reported by Duc et al. with a completely different approach.\textsuperscript{12} In their materials system, polymer was filled in between fingers of a rigid comb made up of silicon. It was reported that, when constrained in the in-plane direction along the comb fingers, the out-of-plane thermal expansion is enhanced. This “squeezing” process can be explained by the concept that the total thermal expansion of a constrained block is the sum of the regular thermal expansion in three dimensions for the free polymer.

Among rather limited literature on thermal expansion of CNT-polymer, none of them, however, relates to the use of latex as a matrix for CNT fillers. In addition, most of them require high CNT loadings to achieve pronounced thermal expansion of composites. In the present work, the same principle as that proposed by Duc et al. has been applied. Particularly, instead of using two rigid microscopic plates to introduce a squeezing effect, here we utilize self-assembly of honeycomb-like SWNT networks to constrain polymer matrix expansion in a particular direction. The manipulation of thermal expansion at the nanoscale can be accomplished via a simple self-assembly method which offers super-enhancement of expansion perpendicular to the plane of the film.
4.2 Film Preparation

4.2.1 Experimental details

Effect of substrate treatment on film uniformity

Substrate treatment is the removal of dust particles or contaminants on a substrate. Cleaning a surface usually increases the surface energy. In that case, water will wet the surface, enabling a water-based coating material to attach and spread on the substrate well during film deposition.

To study the substrate treatment effect, silicon wafers were utilized due to their high flatness, electron-conductive property for further SEM analysis, and optical reflectivity, suitable for ellipsometry. The aim of the study was to search for an approach to increase hydrophilicity of the silicon substrates for better attachment between the substrate and the dispersion. Such investigation was performed through a contact angle measurement whose related theory is schematically explained in Figure 4.4.

![Figure 4.4](image)

**Figure 4.4.** Schematic showing tensions acting on a triple interface of gas (G), liquid (L), and solid (S). In this figure, a drop of liquid is placed on a solid surface.

Shown in Figure 4.4, contact angle, $\theta$, is the angle between liquid-solid interface and a tangent drawing from the triple interface to liquid-gas interface. When a liquid drop is applied on a surface, the triple interface moves along the solid surface to the position that tensions acting on it are in equilibrium. At the equilibrium position, the relationship between all tensions at the triple interface can be written as equation (4.4) and it is called Young's equation.\(^1\)

$$\gamma_{GS} = \gamma_{LS} + \gamma_{GL} \cos \theta$$  \( \text{(4.4)} \)
Different substrate treatment methods as described in the following list.

- **UV-ozone cleaning**
  A treatment for organic contamination removal by the absorption of short-wavelength UV light of contaminants which results in their disassociation. Ozone breaks down any organic contaminants and they generate CO$_2$ and H$_2$O molecules which are able to desorb from the surface.$^{14}$

- **Ethanol rinsing**
  A method able to remove polar ions or molecules due to OH$^-$ group polarity, resulting in more wettability of water-based materials to spread on substrates.

- **KOH/ethanol solution cleaning**
  The solution can oxidize contaminants and hydrolyze SiO$_2$ layer to leave an SiOH surface. Through this method, SiO$_2$ layer can be partially removed.$^{15}$ OH$^-$ group in SiOH can form hydrogen bonding to water, leading to high wettability of aqueous coating materials. In this study, the concentration of 1 M of KOH in ethanol was used.

- **Poly(ethylenimine) (PEI) solution cleaning**
  A cleaning solution with positive charged ions which are able to attract negatively charged ions or molecules of coating materials, latex particles in this case, to themselves.$^{13}$ In this study a 37 wt% of PEI in aqueous solution was used.

- **Piranha solution cleaning**
  A method of organic contaminant removal using a chemical etching from its strong oxidizing property.$^{12}$ In this study, the solution was prepared by a mixture of 95% H$_2$SO$_4$ and 30% H$_2$O$_2$ with the ratio of 3:1 by volume at 100°C.

To perform such experiments, a 1 µL drop of deionized water was applied to each treated substrate. With the use of such tiny volume of the water on each substrate, the effect of water drop weight on contact angle can be eliminated. An optical camera was used to capture the side view of substrates to measure their contact angles. Finding a contact angle can be performed by Kruss software accompanied with Kruss contact angle measurement instrument (Kruss Co. Ltd., Hamburg, Germany). Side view images of the substrates with a water drop on each of them were shown along with their contact angles in Figure 4.5.
Figure 4.5. Contact angle measurement for substrates treated by different methods:
(a) no treatment; (b) UV/ozone cleaner (30 min); (c) UV/ozone (30 min) + ethanol (30 min) + water rinsing; (d) UV/ozone (30 min) + ethanol (overnight) + water rinsing; (e) UV/ozone (30 min) + KOH/ethanol solution (30 min, 100°C) + water rinsing; (f) UV/ozone (30 min) + KOH/ethanol solution (overnight) + water rinsing; (g) UV/ozone (30 min) + PEI (30 min) + water rinsing; (h) UV/ozone (30 min) + PEI (overnight) + water rinsing; and (i) Piranha solution (15 min) + water rinsing.

The software basically generates two tangents at two sides of a liquid drop and creates a curve which fits to these two tangents. The angle between a tangent and a substrate surface is the contact angle. Based on the contact angle measurement, the silicon substrates without any treatment have large contact angles. This result stems from an organic material or some dust particles on the substrates and the surface being pure SiO₂, making it highly hydrophobic. However, UV-ozone treated substrate is the one with highest hydrophilicity with the contact angle of only 17.1 degrees. It can be also observed by naked eyes, during the experiment, that the water drop spreads on the substrate more widely and quickly than on the substrates cleaned by other different methods. This result reflects that UV-ozone cleaning is very efficient to make the substrate more hydrophilic yet simple with no need to use any chemical cleaning procedure. As a result, all substrates to be used from this point on have been treated by UV-ozone cleaner before a film deposition procedure.
4.2.2 Primary characterizations of materials and films

Characterization of SWNTs

Raman spectroscopy has been applied to SWNTs received from CNI Nanotechnologies (TX, USA). The instrument used was an NTEGRA Spectra (NT-MDT Co., Moscow Russia). Because SWNTs are very light, they can fly in the air easily when placed on a sample stage. As a result, they were prepared as a solution form in acetone. The solution was then dropped on a substrate and left to dry.

![Raman Spectra](image)

**Figure 4.6.** Typical Raman spectra of SWNTs excited by 633 nm-laser source in this work.

Figure 4.6 shows SWNT typical modes. The Raman modes, as described in section 3.3.1. of Chapter 3, which are RBM mode, D-band, G-band, and G'-band, are in the range of 150-350, 1300-1400, 1500-1600, and 2600-2700 cm⁻¹, respectively, which correspond to those in Figure 3.4, Chapter 3. These peaks suggest that CNTs utilized are truly the single-walled type without the presence of multi-walled type, which has a different Raman spectrum profile.

Characterization of pristine polymer film

The initial investigation of BA/MMA/MAA latex topography has been performed using a drop-casting deposition method. The details of this latex can be seen from Table 3.1 in Chapter 3. As-received latex dispersion was dropped on a silicon substrate over the area of
2 x 2 cm² and left to dry in ambient conditions without any further annealing. AFM images were obtained from intermittent contact mode and are demonstrated in Figure 4.7.

**Figure 4.7.** AFM images illustrating the film topography of BA/MMA/MAA latex used in this work: (a) height (20x20 μm²), (b) phase (20x20 μm²), (c) 3D height (5x5 μm²), and (d) FFT analysis of (a).

Over a large scan area, 20 x 20 μm², the latex spheres arrange themselves in an almost perfect hexagonal array with a few interstitial sites between them as shown in Figure 4.7 (a) and (b). The honey-comb arrangement has been confirmed through Fast Fourier Transform (FFT) analysis shown in Figure 4.7 (d). In Figure 4.7 (d), there exist six dominant bright dots arranged in the hexagon-like pattern. Such results reflect high capability of this latex for being a good template for highly-structured CNT networks.

This work, however, has initially been focused on thermal properties of monolayer composite films. Consequently, the drop-casting approach is not suitable for monolayer film fabrication because the obtained films tend to be thicker than a monolayer thickness. This leads to the advent of spin coating to be employed later in this study.
Characterization of SWNT-latex particle composite films

In the investigation of the composite films, the suspension with 0.5 wt% of SWNTs in latex dispersion was selected to make films for Raman spectroscopy and AFM investigations because it was found that the suspension of 1 wt% SWNTs in the latex is obviously viscous which may cause comparatively higher non-uniformity. Therefore, the concentration of 0.5 wt% was chosen. It is noted here that wt% is the weight as a percentage of the total polymer weight, excluding water and the weights of any other surfactants or solvents.

To verify the existence of SWNTs in the composite films, a drop of 0.5 wt% SWNT-latex dispersion was applied to a UV-ozone treated substrate and spin cast for 10 seconds at a spin rate of 3 k rpm for initial study. With very high sensitivity of the technique to CNTs, Raman signals emitted from the composite sample are revealed even though the nanotube concentration is extremely low compared to the amount of latex matrix. The spin cast film, however, is thin; hence, Raman signals given off from the silicon substrate, as seen at around 520 cm⁻¹, are also detected with rather high intensity compared to the Raman spectrum of SWNTs. RBM mode, D-band, G-band, and G'-band of the CNTs can be observed at the Raman shifts of around 200, 1350, 1600, and 2700, respectively. These Raman spectral peaks at the same wavenumbers as those in Figure 4.6 indicate the presence of SWNTs.

Figure 4.8. Raman spectrum of the composite sample made from 0.5 wt% SWNTs in latex.
The SWNT networks are buried under the latex particles and are not be able to be observed when investigated using AFM. This structure, however, can be seen through the latex by a Raman mapping operation. The G-band in Figure 4.8 is selected for the Raman mapping. Different regions of a sample surface provide different G-band intensities. By detecting such differences, the instrument is able to relate the emitted signals to the presence of SWNT networks to construct a map. The brighter regions reflect higher G-band intensities in the composite films and hence higher SWNT concentration. The black regions, consequently, are probably the latex particles.

**Figure 4.9.** Raman image (10x10 μm²) showing G-band distribution in the 0.5 wt% SWNT-latex composite film. The region circled shows the networks formed in hexagonal structure.

Figure 4.9 discloses the distribution of SWNTs over the scan area. Small bright lines form a hexagonal-like structure, indicating the hexagonal network formation of SWNTs in the film. However, there are several dark large regions in the image, reflecting that the networks are not perfect. This indicates non-uniformity of the film. The average diameter of each hexagon is in the range of 200 to 300 nm, which spans the average diameter of the pristine latex particles (262 nm). This result, therefore, supports the idea of SWNTs wrapping around latex particles. The characterization of the composite film suggests that the spin-coating technique, with suitable spin conditions, can be an efficient film preparation method which is able to provide long-range ordered SWNT networks.
Effect of film preparation conditions on film topography

In the spin coating process of latex, the parameters affecting film topography or thickness are spin time and speed at a given concentration of a material to be applied. Suspension volume does not matter for the deposition as long as the film covers the whole substrate surface prior to spinning. The excess dispersion volume is ejected off of the substrate by centrifugal forces. In terms of time, it is found that 10 s is adequate to make films dry whereas a shorter time, 5 s, is too short providing wet films at the end of the spin process. Therefore, in the spin-coating approach, the time to be utilized for spinning was 10 s. Spin speed, however, is the major parameter to vary film thickness, as it is known from equation (3.1) that the higher spin speed applied, the higher centrifugal force pulling latex spheres on the substrate along the axial direction, and the lower film thickness obtained. Therefore, highly-ordered monolayer films of SWNT-latex particles can be fabricated through the variation of spin speed.

Based on Figure 4.9, the nanotube networks are not quite uniform in two dimensions meaning that latex particle arrays are not a perfect monolayer. Thus, higher spin speeds, which are higher than 3 k rpm, have been employed to obtain higher centrifugal forces spreading latex particles on the substrate outwards along the axial direction.

The dispersion used in this study was 0.5 wt% SWNT-BA/MMA/MAA in Triton X-100 solution and the substrates were UV-ozone cleaned silicon wafers. With the spinning time of 10 s, high angular spinning speeds up to 9 k rpm were varied from 4 k rpm with 1 k rpm step increase. After the prepared films dried, their topographies were then investigated using AFM without any further annealing as shown in Figure 4.10.
Figure 4.10. AFM height images of the composite films spin cast using different spin speeds, as indicated on each image. All images are 20 μm x 20 μm.

Average surface roughness values of the films in Figure 4.10 are presented in Table 4.1.
Table 4.1. Average surface roughness values of composite films at different spin rate

<table>
<thead>
<tr>
<th>Spin rate (rpm)</th>
<th>Average surface roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>18.4</td>
</tr>
<tr>
<td>5</td>
<td>19.3</td>
</tr>
<tr>
<td>6</td>
<td>26.0</td>
</tr>
<tr>
<td>7</td>
<td>30.3</td>
</tr>
<tr>
<td>8</td>
<td>41.5</td>
</tr>
<tr>
<td>9</td>
<td>57.6</td>
</tr>
</tbody>
</table>

It is obviously seen that low spin speeds provide film surfaces with low average roughness required for monolayer film fabrication. The explanation for this is that when higher spin speeds are applied, the particle arrays tend to be smaller in grain size with more cracks, due to higher forces pulling the particles along the spin axis. However, the slow spin speed of 4 k rpm provides large regions of non-uniform particle arrays. The trend of grain size is smaller as the spin rate increases. In addition, it can be observed that cracking regions are larger when higher spin rates were applied. Grain size could be related to the time of spin-coating as well. However, in the present study, this parameter was kept constant, which was able to provide dried films. These results reflect that, for the deposition of such dispersions on a cleaned silicon substrate, the optimal spinning speed to be used for further studies should be 5 k rpm as it offers the largest particle grain size of up to around 4x4 μm² with low average roughness.

**Ellipsometry studies on film thickness**

Film thickness is being investigated in this section through ellipsometry due to its high sensitivity and accuracy. The purpose of this study is to verify whether prepared films are monolayer or not and to study the effect of spin speeds on the film thicknesses.
Film thicknesses studied by ellipsometry under ambient temperature

Silicon is known to have a native oxide layer, SiO\(_2\). Every silicon wafer in the current work was covered by thin SiO\(_2\) layer, which was also considered as another film layer. Therefore, the experiment to determine SiO\(_2\) layer thickness using spectroscopic ellipsometry was primarily performed for later polymer composite film investigations. \(\Psi\) and \(\Delta\) over the incident wavelengths ranging from 400 to 800 nm were recorded during a spectroscopic scan of bare silicon wafer as shown in Figure 4.11.

![Figure 4.11. Model fit (red lines) compared to experimental \(\Psi\) and \(\Delta\) data (green dashed lines) of a silicon substrate at three angles of incidence of 60°, 65°, and 70°.](image)

The generated data are well fit to the experimental data as can be seen that they almost perfectly overlap for \(\Psi\) data even though the \(\Delta\) data are noisy. The fit of this model provides a silicon dioxide layer thickness in the range of 24.2±4.2 Å with high reliability of the low MSE (equation 3.5), of 1.412. Therefore, the SiO\(_2\) thickness value of 25 Å will be used later for all silicon substrates as a fit parameter in the slab model (equations 3.7 and 3.8).

In contrast, composite films consisting of latex particles have their non-uniformities. To obtain reliable fits, thickness non-uniformity has been fit as another fit parameter. In the Cauchy model (equation 3.7), refractive indices of transparent latex-based films are also considered; as a result, A and, sometimes, B also have to be fit. Surface roughness is another fit parameter used in the model due to rough surfaces of films containing latex particles. The lowest possible number of fit parameters is used at the beginning of the fit procedure. The addition of more fit parameters is applied later on in order to obtain a
minimal MSE. By applying such fitting methods, resultant film thicknesses and thickness non-uniformities as a function of spin speeds are obtained (see Figure 4.12). In addition, $A$ values (equation 3.7) which are the main parameter contributing to refractive index are presented in Figure 4.13.

Figure 4.12. Spin speed dependence of composite film thicknesses (blue) and thickness non-uniformity (red).

Figure 4.13. Values of the Cauchy parameter, $A$, for composite films spin cast at different spin speeds.
**Figure 4.14.** Model fit (red solid lines) compared to experimental Ψ and Δ data (green dashed lines) of the film spin cast at 9 krpm. The spectroscopic scan was made at three angles of incidence of 60°, 65°, and 70°.

The results here are from the fits with MSEs less than 20 for all film samples. Such MSEs are acceptable, as seen from the fits in Figure 4.14, for films containing latex particles although it is comparatively higher than the MSE of the previous silicon dioxide layer study. Actually, MSE also depends on the number of unknown parameters. The result in Figure 4.12 agrees with equation (3.1) in that as higher spin speeds have been applied, higher centrifugal forces pull latex particles along the substrate, resulting in thinner films and a decrease in thickness non-uniformity. Figure 4.13 indicates that A values, which are proportional to the refractive indices, decrease as high spin speeds were used. In turn, refractive index is proportional to the film density. Denser films have a higher refractive index. The important point to notice here is that all films, which were made from different spin speeds, are monolayer as can be seen that their film thicknesses are less than the latex particle size (262 nm). The thickness of the film spin cast at 4 k rpm is also less than the latex particle size. This may stem from the hydrophilicity of the UV-ozone cleaned substrate, which encourages wetting of the polymer. Also, ellipsometry measures the average thickness of the composite films containing interstitial sites between latex particles and cracks. These defects reduce average film thicknesses to be lower than the latex particle size. Furthermore, all spin speeds are able to make monolayer composite films; nevertheless, the most appropriate speed to be utilized in this work is 5 k rpm because of the largest grains of latex particle arrays as previously suggested by AFM images in Figure 4.10.
Film thickness investigation through scanning electron microscopy

The films to be used for thermal expansivity in the next part are studied again through SEM to confirm the obtained ellipsometry results that the films are really a monolayer. In doing this, SEM measurement is operated to present a side view of the samples. Also, SEM on the top view of the films is performed to observe the order of SWNT networks embedded in the films as shown in Figure 4.15.

![Figure 4.15. SEM micrographs demonstrating (a) the cross-section of a composite monolayer containing 1 wt.% of SWNTs, (b) a high resolution SEM image representing the belt-like structure of CNTs equatorially surrounding latex spheres, and (c) a low-magnification micrograph showing long range ordering of honeycomb-like SWNT networks.](image)

The observed thickness (~180 nm) in Figure 4.15 (a) support ellipsometry results in that the films in this study are monolayer as seen that the thickness is less than 262 nm, which is the latex particle size. The thickness of the spin-cast films is reduced approximately one third of the mean latex particle size. This significant thickness reduction is due to the high affinity between polymer and substrate during deposition. The colloidal particles are able to spread uniformly throughout the substrate to maximize contact with the surface. UV-ozone cleaning effectively makes silicon substrate hydrophilic. Therefore, wetting effect
occurs and this contributes to a decrease of interparticle voids. Shearing during spin-coating induces ordering and the formation of 2D colloidal crystals. A close view in Figure 4.15 (b) clearly presents nanotube bundle networks that act like belts circling latex particles. The similar network structure can be seen in the long-area micrograph (Figure 4.15 (c)) as well. Comparatively higher secondary electron generation around CNTs is the reason that SEM is able to reveal a high contrast between CNTs and the polymer matrix.

4.3 Thermal Expansivity

4.3.1 Experimental details

The first study on thermal expansivity is the investigation of effect of SWNT amount in the composite films on thermal expansivity. In this study, the amounts of SWNTs are varied to be lower and higher than 0.5 wt%. For the films with concentrated CNTs, the transparency is likely to be lower. In other words, a greater amount of the incident light can be absorbed in the film. Therefore, the extinction coefficient (k) has also to be fit in the ellipsometry data analysis, leading to the fits of extinction coefficient amplitude, \( \alpha \), and exponent factor, \( \beta \), in the Cauchy model (equation 3.8). In addition, thickness non-uniformity and surface roughness are also fit because, in some film regions, nanotubes make film surfaces non-uniform.

According to previous AFM and ellipsometry studies, optimal parameters have been found for spin-coating method and it has been verified that this technique can provide monolayer uniform latex-based films. Therefore, spin coating has been adopted for monolayer film preparation. As it is known that SWNTs have very high thermal conductivity, this could affect polymer film properties dramatically. Ellipsometry was employed to measure the thermal expansivity.

To study the temperature dependence of film thicknesses as different amounts of SWNTs are in the composite thin films, all dispersions used contain the same amounts of deionized water, Triton X-100, and latex dispersion. The only one parameter to be varied is SWNT amount. Composite dispersions were deposited on UV-ozone cleaned silicon wafers using a spin coater with a spin speed of 5 krpm and spin time of 10 s. A dynamic ellipsometry
scan using six wavelengths (500, 550, 600, 650, 700, and 750 nm) and a fixed angle of incidence of 70°C were applied to obtain experimental data while the films were heated from room temperature to 60°C at a heating rate of 2°C/min. The data of Ψ and Δ versus time were measured. The heating procedure was performed according to the following steps:

1.) The films were heated from room temperature (approximately 20°C) to 60°C at the heating rate of 2°C/min.
2.) Temperature was maintained constant at 60°C for 10 minutes.
3.) The films were cooled down from 60°C until the temperature was at around room temperature.
4.) The films were heated to 60°C using the heating rate of 2°C/min.
5.) Step 2 was then repeated.
6.) The films were cooled down from 60°C until the temperature was at around room temperature.

Procedures 4, 5, and 6 were performed in order to observe the reproducibility of film behavior. Figure 4.16 shows the heating procedure while conducting a dynamic ellipsometry scan.

The results obtained show initial thicknesses at the beginning time all being less than the latex sphere size, indicating that all samples are monolayer films. However, it is extremely difficult to fabricate films with exactly the same thickness. Consequently, film thicknesses are normalized, by dividing by the initial thickness, for a set of comparable data.

![Figure 4.16. Heating profile used during dynamic scan.](image-url)
Studies of the effects of heating temperature and heating rate on composite film thermal expansivity followed procedures similar to those in this section. The varied parameters are only heating temperature and heating rate, respectively, in each investigation.

4.3.2 Results and discussion

Effect of SWNT amount in the composite films on thermal expansivity.

Thicknesses of all films were measured as a function of time. However, the initial film thicknesses were not exactly identical. To compare an increase of film thicknesses, all thicknesses were the normalized by corresponding initial thickness of each film sample. Figure 4.17 presents normalized film thicknesses as heat treatment (Figure 4.16) was applied.

![Figure 4.17](image)

Figure 4.17. Normalized thicknesses of heated and cooled composite films with different SWNT amounts as indicated. The heating profile defined in Figure 4.15 has been applied with the heating rate of 2°C/min.
According to Figure 4.17, the film without SWNTs behaves differently from the composite films in that the latex film, while being annealed to 60°C, has decreasing thickness. Such behavior can be explained by particle sintering or coalescence when the latex particles tend to be in a liquid-like phase. In particular, there is the flattening of latex film surface occurring. At this state, the film is thinner as seen from the graph. For the second expansion during the second heating, increasing temperature causes a film thickness rise, suggesting that the latex particles completely coalesces during the first heating because they do not coalesce any further. Latex behavior in the second expansion agrees with the thermal expansion principle as shown in equation (4.1) previously. Based on this equation, a volume increase is proportional to a temperature change. Likewise, volume decreases while temperature has decreased, thus resulting in a thickness decrease.

All generated data are well fit to experimental data as seen in the ellipsometric $\Psi$ and $\Delta$ data of a dynamic scan in Figure 4.18, which suggests highly reliable results. Nevertheless, at the highest percentage of SWNTs, the MSE is found to be higher which may come from higher film non-uniformity owing to the presence of more CNT bundles embedded in the film.

![Figure 4.18. Ellipsometric $\Psi$ and $\Delta$ of model (solid red and black lines) and experimental (green and blue circles) data from the film made by 0.5 wt% SWNTs in BA/MMA/MAA as it was heated, cooled, heated, and cooled, respectively, from room temperature to 60°C at 2°C/min. Wavelengths used are 550 and 700 nm. Experimental and generated data clearly show a good accordance to each other.](image)

The expansion behavior of the film containing 0.1 wt% of SWNTs is different from that of the latex film in that there is no apparent flattening process occurring while the film is being heated. Instead, thermal expansion is observed. SWNT networks wrapping around
latex particles are the possible reason for this phenomenon. Hexagonal nanotube grids act like “belts” surrounding latex particles in the film plane and prevent latex particles to touch each other, thus, while being heated, particles can expand in out-of-plane direction only without lateral thermal expansion. It is the latex that expands rather than CNTs because SWNTs have a considerably low range of thermal expansion, on the order of $10^{-6} \text{ K}^{-1}$, compared to the CTEs of typical polymers, with their CTEs in the range of $10^{-4} \text{ K}^{-1}$. Therefore, SWNT networks are considered to be fixed in shape while the polymer expands vertically. The predicted shape of each expanded particle is probably an ellipsoid with the long axis pointing up as demonstrated in Figure 4.19.

![Figure 4.19](image)

**Figure 4.19.** Carbon nanotube belts encircle latex particles in a hexagonal array in a composite film with the thickness of about 180 nm. The nanoscale belts prohibit polymer expansion in the film plane; as a result, thermal expansion is enhanced in normal direction.$^{15}$

The film samples with SWNT amounts ranging from 0.3 to 1.0 wt% have different characteristics compared to the latex film and 0.1 wt% SWNT film. As the films are heated in the first annealing, polymers expand normally to the film plane much more with higher SWNT loads, resulting in higher thickness increases. These thickness changes are the behaviors invoked from SWNT networks wrapping around latex particles as shown in Figure 4.20 (a). Higher amounts of SWNTs form a continuous belt-like confinement; thereby, latex particles are under a restriction to expand laterally. Consequently, an increase in film thickness is more evident in the films containing higher nanotube loads (Figure 4.20 (b)). It can also be observed here that the final thicknesses, at the time around 120 minutes, are higher than the initial ones. To delineate this observation, an assumption has been established. SWNT networks make latex particles to expand vertically. When these particles reached their high thicknesses at high temperature, the particle top parts are above nanotube arrays (Figure 4.20 (b)). At higher temperature, the polymers have lower viscosity, resulting in significant lateral spreading to cover cracks and voids in the film.
Consequently, during the annealing process, the uniformity in surface morphology of the composite film is higher than pure latex.

![Figure 4.20. The model to explain temperature-dependent behaviors of the composite films.](image)

Upon cooling, the film surface contracts linearly because polymer is squeezed out and stays on top of CNT networks. This behavior is similar to polymer film without any constraint in expansion. Squeezed-out polymer causes irreversible expansion and contraction. Specifically, the polymer is not able to return to its original thickness. As annealing progresses, the same behavior can be observed. In particular, the film exhibits normal linear thermal expansion because there are no “walls” to restrict expansion anymore.

Based on Figure 4.17, thickness increase has its own limit as demonstrated in the case of the 1.4 wt% sample. At such high CNT content, excess CNTs form thicker belt networks and encircle more volume of colloidal polymer particles. Therefore, polymer thermal expansion is restricted and cannot be higher than the film with 1 wt% nanotubes. A smaller thickness decrease at the end of the first annealing and a small thickness increase in the second round are probably due to high amount of heat absorbed in the film, which keeps the film in expanding state. The final thickness, however, is in a similar trend to films containing lower amounts of nanotubes. This behavior can be explained by the spreading of the latex.
In order to support this proposed idea, AFM and SEM investigations have been applied to the latex film and 1 wt% SWNT composite film before and after the heat treatment to 60°C.

![AFM height images of the latex film: (a) before, (b) after heat treatment to 60°C, and (c) height profiles of the green lines across particles in (a) and (b)](image)

**Figure 4.21.** AFM height images of the latex film: (a) before, (b) after heat treatment to 60°C, and (c) height profiles of the green lines across particles in (a) and (b)

Figure 4.21 presents higher flatness of the latex film after film annealing. The peak-to-valley height of the film has been decreased significantly owing to latex sintering process. In contrast, Figure 4.22 reflects a lower flatness of the composite film. The flatness of the latex film is more evident than in the composite film case because SWNT belts prohibit latex sintering. However, the composite film is still flatter compared to the original film before heating since there is particle spreading happening during its heating. SEM micrograph (b) in Figure 4.22 reveals SWNT networks in the heated film with a small disruption in hexagonal structure due to the latex vertical expansion. After this “squeezing
effect" at 60°C, nanotube networks still remain their structure almost similar to that before being heated as seen in the SEM micrograph in Figure 4.22 (b).

Figure 4.22. AFM height images (left) showing film topography and SEM micrographs (right) presenting SWNT networks of the composite films: (a) before and (b) after heat treatment to 60°C, and (c) height profiles of the green lines in (a) and (b) (left). AFM image sizes are 5x5 μm² and the scale bars in SEM images are 3 μm.
After the first film expansion, subsequent film thickness changes consisting of contraction, expansion, and contraction happen. The thickness/temperature paths are similar to hysteresis loops with different loop widths depending on the type of sample. It is noted here that, in this study, “reversible process” is used for film thermal expansion that has initial and final film thicknesses at nearly the same value. Particularly, the thermal expansion of the film made by 0.1 wt% SWNTs is called a reversible process (Figure 4.23). Film expansion processes for all other films with different nanotube percentages, including the sample without nanotubes, are called irreversible processes. Presenting the results in Figure 4.16 as normalized thicknesses against temperature, as displayed below in Figure 4.23, can show film expansion reversibility more evidently.

In Figure 4.23, there is a sintering, or film flattening, of the latex sample (Figure 4.23 (a)) and expansions only in the composite films (Figure 4.23 (b)-(g)), as seen in the first expansions. The films expand more in their first expansions when there are greater SWNT amounts in the films. The reasons for these results are as described previously. The hysteresis loops in all film samples show reversible expansion behaviors after their first expansion. This result confirms polymer collapse after the high expansion state because there are normal expansions and contractions of the polymer occurring afterwards. In the second heating, the widths of all hysteresis loops are small, reflecting that the polymer in each film sample has almost identical thickness at the same temperature.

Reversibility and irreversibility behaviors from our composite systems with different nanotube amounts can be applied to various applications. For example, the irreversible thickness change property can be used in food packaging industries. In particular, it can be a temperature sensor indicating how a bag of frozen fish has been kept. If it was in the temperature higher than a suitable temperature, the sensor, which is the composite material, will change its color, etc. For the composites with a reversible processes, they could be utilized in a temperature sensor in a building, for example, and it can be used many times later in the future.
Figure 4.23. Normalized thicknesses of films containing different weight percentages of SWNTs in BA/MMA/MAA during heat treatment to 60°C: (a) 0 %, (b) 0.1 %, (c) 0.3 %, (d) 0.5%, (e) 0.75%, (f) 1.0%, and (g) 1.4 %. The chronological order of the heat-cool-heat-cool procedure is represented by red-blue-orange-green arrows, respectively. Red circular dots indicate the beginnings of thermal expansion process.
Compared to other previous work, the finding in this study agrees with the work reported by Lee et al.\textsuperscript{15} According to their work, CTE in the direction normal to the plane of the composite increases due to the fillers squeezing the matrix upwards in the two-phase composite system containing a significant CTE difference between the fillers and the matrix. In our composite system, the linear CTE of SWNTs is on the order of $10^{-6} \text{ K}^{-1}$, whereas $10^{-4} \text{ K}^{-1}$ for the volume CTE of poly(methyl methacrylate)-based polymer. This phenomenon can be explained by the equation as follows:

\[
\bar{e}_y = (\alpha_f - \alpha_m) \Delta T \delta_{ij}
\]

where $\bar{e}_y$ refers to thermal strain in a certain direction, $\alpha_f$ is the linear CTE of fillers, $\alpha_m$ is the linear CTE of a matrix, $\Delta T$ is a temperature change, and $\delta_{ij}$ is the Kronecker delta, which is 1 if $i=j$ and 0 if $i\neq j$. Based on the above equation, temperature change and CTE difference of the fillers and matrix in the composite lead to a thermal strain squeezing the matrix out. Furthermore, thermal expansion is more apparent for the system with a huge CTE difference between the fillers and matrix than the thermal strain of the system with a lower CTE difference.

**Thermal expansivity of the composite films**

CTEs can be calculated using equation (4.1) previously described. Values are shown in Table 4.2 and Table 4.3 for the first and second heating as a function of SWNT concentration. The results are presented graphically in Figure 4.24.

**Table 4.2. Thermal expansivity from the first thermal expansion**

<table>
<thead>
<tr>
<th>SWNT Load (wt.%)</th>
<th>Thermal Expansivity ($10^{-4} \text{ K}^{-1}$)</th>
<th>CTE Error ($10^{-4} \text{ K}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>film flattened</td>
<td>0.09</td>
</tr>
<tr>
<td>0.1</td>
<td>5.8</td>
<td>0.15</td>
</tr>
<tr>
<td>0.3</td>
<td>9.1</td>
<td>0.87</td>
</tr>
<tr>
<td>0.5</td>
<td>14.5</td>
<td>1.92</td>
</tr>
<tr>
<td>0.75</td>
<td>17.2</td>
<td>1.76</td>
</tr>
<tr>
<td>1.0</td>
<td>19.6</td>
<td>0.43</td>
</tr>
<tr>
<td>1.4</td>
<td>18.8</td>
<td>1.61</td>
</tr>
</tbody>
</table>
Table 4.3. Thermal expansivity from the second thermal expansion

<table>
<thead>
<tr>
<th>SWNT Load (wt.%)</th>
<th>Thermal Expansivity ($10^{-4}$ K$^{-1}$)</th>
<th>CTE Error ($10^{-4}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.9</td>
<td>0.09</td>
</tr>
<tr>
<td>0.1</td>
<td>5.8</td>
<td>0.08</td>
</tr>
<tr>
<td>0.3</td>
<td>6.3</td>
<td>0.23</td>
</tr>
<tr>
<td>0.5</td>
<td>5.7</td>
<td>0.06</td>
</tr>
<tr>
<td>0.75</td>
<td>5.6</td>
<td>0.16</td>
</tr>
<tr>
<td>1.0</td>
<td>7.0</td>
<td>0.16</td>
</tr>
<tr>
<td>1.4</td>
<td>2.7</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Figure 4.24. Thermal expansivity of the latex composite (▲) and polymer melt composite (○) films from the first expansion. Two horizontal dashed lines indicate that CTEs of the composite containing high SWNT amount are approximately three times of polymer CTE.

It is noted here that CTE in Figure 4.24 for the latex film without SWNTs is presented for the second heating. It is adopted in this way because, for the first heating, there is a flattening process happening instead of thermal expansion. As clearly seen, CTE tends to increase dramatically with nanotube loads in the range from 0.3 to 0.8 wt% and seems to be steady at SWNT weight percentage higher than 1 wt%. This behavior resembles electrical percolation threshold as reported elsewhere due to more complete nanotube networks formed as a confinement for polymer lateral expansion. Composite film spin coated from solution was also prepared and studied to compare the effect of nanotube
network order on thermal expansivity. Polymer melt was incorporated to 1 wt% SWNTs because this nanotube content provides highest CTE in the case of latex composite. CTE of two composite systems without nanotubes added show similar CTE. At 1 wt% SWNTs, polymer melt composite exhibit a CTE of $9.1 \times 10^{-4} \text{ K}^{-1}$, which is significantly lower than the CTE of the latex composite film. This result can be explained that CNTs in polymer melt do not form continuous networks. As a result, polymer is able to expand laterally along the film plane. The expanded volume, therefore, does not have to expand in out-of-plane direction only.

The experimental results of the present work correspond to the theoretical finding of Wei et al. in that, with the SWNT presence in the bulk polymer, SWNT-polymer composite samples have CTEs much higher than the CTE of the pristine bulk polymer. The difference in the materials system used by Wei et al. and the current work is that SWNT-polyethylene composite with random CNT networks were used in their simulation. They reported a 142\% increase in CTE but, from our finding, the composite films in this work have even higher thermal expansion behavior. CTE has increased more than 200\% for the composite film fabricated using 1 wt% SWNT-BA/MMA/MAA dispersion.

Not only do the experimental results correspond to prior work but they also agree with the basic principle of volume thermal expansion. In particular, it can be observed that the CTE ($\alpha$) of 1 wt% sample is approximately three times that of linear CTE of the latex film without nanotubes, as presented by two horizontal dashed lines in Figure 4.24. To explain this result, the model of fixed nanotube networks wrapping around latex particles is adopted. Typically, bulk materials, when being heated, with no boundary confinement expand their volume in three dimensions. With the same amount of heat or energy they obtain, the materials expand their volume equally in three dimensions. In the circumstance that they cannot expand laterally, they, instead, expand vertically three times to reach similar volume thermal expansion in no boundary case. In the latex film without nanotubes, polymer particles spread and flatten in a sintering process. In its second expansion, polymer expands vertically only, with the CTE of $5.9 \times 10^{-4} \text{ K}^{-1}$, because the latex already completely expands and leaves no more space for itself to fill in on the lateral plane. Therefore, it is found that the CTE of BA/MMA/MAA with the presence of Triton X-100 surfactant is $5.9 \times 10^{-4} \text{ K}^{-1}$. With the existence of SWNT networks, the latex cannot expand laterally. To expand with a similar CTE in three dimensions, it expands vertically
with, roughly, three times of $5.9 \times 10^{-4} \text{ K}^{-1}$ for volume thermal expansion. The tendency of thermal expansivity seems to be constant at higher CNT loads. This indicates that, for volume thermal expansion of the latex, there is a limit of expansion, which is three times of linear CTE. It has been also found that CTEs of all composite films from the second expansion are in the same range of the CTE of the latex film without nanotubes. These CTE values are in the range of 5.6 to 7.0 $\times 10^{-4}$ K$^{-1}$, except the film with high non-uniformity such as the 1.4 wt% sample. The similarity of their second expansions corresponds to our assumption in that, during annealing procedure, the latex particles spread over the substrate and cover nanotube networks. The resultant materials are, therefore, a layer of the latex polymer without nanotubes on top part of their surfaces. Such a layer then expands with normal linear CTE of the polymer when heated.

The finding that the composite CTE is three time of the polymer case can also be described mathematically as follows:

For a temperature increase of $\Delta T$, we can rewrite the equations of linear (equation (4.1)) and volume (equation (4.2)) thermal expansion as shown in equations (4.5) and (4.6), respectively.

$$\Delta L_z = \alpha L_z \Delta T$$

(4.5)

$$\Delta V = \beta V_0 \Delta T$$

(4.6)

Where $\Delta L_z$ represents a change of film thickness in the direction normal to the film plane, $L_z$ is initial film thickness. For the volume case, $\Delta V$ is a change in volume and $V_0$ is initial volume before annealing process.

In addition, we know that

$$\beta = 3\alpha$$

(4.7)
The restriction of polymer thermal expansion in the film plane causes no equatorial expansion; therefore, $\Delta A \approx 0$. As a result, the polymer can expand in the out-of-plane direction only. We then have

$$\Delta V \approx A \Delta L_z$$  \hspace{1cm} (4.8)

Equation (4.7) can be inserted in equation (4.6) and then

$$\Delta V \approx 3\alpha(V_0)\Delta T = 3\alpha(AL_z)\Delta T \approx A\Delta L_z$$ \hspace{1cm} (4.9)

Therefore,

$$\Delta L_z = \frac{3\alpha L_z\Delta T}{A}$$ \hspace{1cm} (4.10)

Compared to $\Delta L_z = \alpha L_z\Delta T$ in the linear thermal expansion of the polymer case (equation 4.5), it is found that composite CTE in confined condition is three times the polymer CTE in the unconfined case.

In order to investigate whether a percolation-like behaviour is present in the variation of the thermal expansion with CNT content or not, the equation associated with electrical percolation threshold, equation (4.11), is adopted.\textsuperscript{19-20}

$$\sigma = \sigma_0 (\phi - \phi_c)^t$$ \hspace{1cm} (4.11)

Where $\sigma$ and $\sigma_c$ are electrical conductivities of composite and filler, respectively. $\phi$ is filler concentration and $\phi_c$ represents the filler concentration that forms the percolative filler network. In this equation, $\phi > \phi_c$. For thermal expansion investigation, determination of $\phi_c$ can be performed by taking a derivative of the data in Figure 4.24 and the peak of the derivative is chosen as a good estimate of $\phi_c$. The exponent $t$ depends on system dimensionality and is similar in macroscopic system.\textsuperscript{21} Thermal expansivity and its associated derivative are then plotted in Figure 4.25.
Figure 4.25. Thermal expansivity of the latex composites from the first expansion (●) and their associated thermal expansivity (α).

From figure 4.25, it can be seen that the peak of the derivative thermal expansivity is at CNT weight fraction of 0.3 (wt. %) and this value is assigned as φ. Thermal expansivity, α₀, of SWNTs is ~7.5 x 10⁻⁶ K⁻¹.22 α of the composites can be found in table 4.2. Using equation (4.11) for the composites containing SWNTs above percolation region, the exponent t can be calculated and shown in table 4.4.

Table 4.4. The exponent values, t, of the SWNT-latex composite thin films

<table>
<thead>
<tr>
<th>SWNT Load (wt.%)</th>
<th>Thermal Expansivity (10⁻⁶ K⁻¹)</th>
<th>Exponent, t</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>19.6</td>
<td>-15.60</td>
</tr>
<tr>
<td>1.4</td>
<td>18.8</td>
<td>57.96</td>
</tr>
</tbody>
</table>

It was found previously in the literature that t ≈ 2 for the three-dimensional composite systems23-24 and t ≈ 1 - 1.33 for the ones with two dimensions.25 The calculated exponent t values in table 4.4 do not correspond to the theoretical calculation in any case. As a result,
it can be concluded that the percolation behavior in the present study is not valid in the variation of thermal expansion with SWNT content.

**Effect of heating temperature on composite film thermal expansivity**

The heating process in the previous study has been performed from room temperature to 60°C at the rate of 2°C/min for composite films containing different amounts of SWNTs. However, their thickness changes may depend not only on SWNT loads but also on maximum heating temperature because volume thermal expansion depends proportionally on a temperature change as predicted by equation (4.2). To study such effects, all films are heated at the similar heating rate of 2°C/min. The films with the nanotube of 1 wt% were chosen to be utilized because such a load shows the highest fractional thickness change and the composite dispersion is not too viscous which may result in film non-uniformity and ellipsometry fits with a high MSE. Normalized thicknesses measured over annealing time as the maximum heating temperatures have been varied are plotted in Figure 4.26.

![Figure 4.26](image.png)

**Figure 4.26.** Thickness change of the composite films heated to different temperatures at 2°C/min.

All generated data were fit to the experimental data with MSEs in an acceptable range for films consisting of latex spheres. The composite films, as heated to different temperatures, show different characteristics as discussed in the explanations that follow.
Unlike normal latex film flattening reported elsewhere,\textsuperscript{26-27} the composite films in this work show unusual expansion behavior. Particularly, the films have increasing thicknesses instead of film flattening when they are heated to 40°C. Figure 4.26 shows greater thickness increase with higher temperatures. Increasing and decreasing with comparatively low thickness change for the first expansion are the behavior of the composite film. However, squeezing effect is not destroyed after heating to 40°C. Therefore, it is found that the film has higher thickness during the second expansion. Thickness decreases in both the first and second expansions are only small drop because, at such temperature, the temperature difference between 40°C and room temperature is 20°C. The composite film can collapse at such temperature. Similar to the films heated to higher temperatures, irreversible film thickness change occurs as well.

The film heated to 60°C shows a collapse behavior with higher thickness drop at the end of each expansion which are caused by a higher temperature difference between 60°C and room temperature. Likewise, the films heated to 90 and 120°C have the same graph shape as that of the film heated to 60°C. The only one difference among them is that it has a higher thickness change due to a higher temperature increase. It can be noticed that the thickness drop at the end of the first and second expansions for films heated to 60, 90, and 120°C are almost identical, indicating that all of them decrease their thicknesses equally from their highest thicknesses. At an extremely high temperature, 150°C, the composite film also demonstrates an irreversible behavior. However, at such high temperature, the latex tends to be in a liquid phase, with much lower viscosity, rather than a solid phase, resulting in film flattening as seen from the valley of the graph. It can reach the same maximum thickness again due to a higher temperature difference. The general tendency of Figure 4.26 indicates that a higher temperature increase causes higher thickness increase as observed in the graphs with the maximum heating temperatures of 40, 60, and 90°C. However, according to the 90, 120 and 150°C graphs, there is a limit of thickness rise no matter how high the maximum heating temperature is. The limit suggests that composite film made from 1 wt% SWNTs in BA/MMA/MAA can expand approximately 12 percent.

In addition, for the first heating, the slopes of all graphs in Figure 4.26 also indicate that thermal expansivities of the composite heated to different temperatures are similar to each other, except at relatively high temperature where the composite tends to have a slightly lower CTE.
The film topography and SWNT networks of the composite films are investigated using AFM and SEM for the films before and after heating to different temperature as shown in Figure 4.27.

![AFM height images](left) and SEM micrographs (right) of the composite films heated to (a) 120°C, and (b) 150°C, and (c) height profiles of the green lines in AFM images (a) and (b) of Figure 4.22 and 4.27.

**Figure 4.27.** AFM height images (left) and SEM micrographs (right) of the composite films heated to (a) 120°C, and (b) 150°C, and (c) height profiles of the green lines in AFM images (a) and (b) of Figure 4.22 and 4.27.
As observed from the AFM images, there is a higher flatness of the composite films when heated to higher temperature. The reason for this is that polymer viscosity decreases with temperature increase. Therefore, liquid-phase latex can spread faster on substrates after polymer collapse. Under latex surface, nanotube network structure is destroyed due to the polymer movement as illustrated by the SEM images (Figure 4.27). These AFM and SEM results support each other, i.e., AFM shows greater flatness when films were annealed to higher temperatures, meaning that there is more movement of the latex which causes more SWNT network destruction. The irreversibility of film swelling and deswelling can be displayed by plotting the thickness-temperature graphs in Figure 4.28.

Figure 4.28. Thickness-temperature dependence of 1 wt% SWNT films heated to different temperatures: (a) 40°C, (b) 60°C, (c) 90°C, (d) 120°C, and (e) 150°C. The chronological order of the heat-cool-heat-cool procedure is presented by red-blue-orange-green arrows, respectively. Red circular dots indicate the beginnings of thermal expansion process.
It has been found that all film samples exhibit irreversible thickness changes, as it is seen that the final thicknesses are higher than the initial ones. The tendency, however, after the first expansion seems to be almost reversible, reflecting normal latex expansion behavior of collapsed polymer films. In Figure 4.28 (c), there is an apparent decrease in thermal expansion at the temperature around 100°C for the first expansion, indicating that latex particles have reached the limit of the "squeezing" effect. This CTE decrease verifies the assumption of film collapse.

**Effect of heating rate on composite film thermal expansivity**

It has been found that the amount of SWNTs and heating temperature affect film thickness changes as the composite films are annealed. Another parameter that might result in such a phenomenon is heating rate. To investigate this influence, the SWNT load and maximum heating temperature are maintained constant at 1 wt% and 60°C, respectively, for different heating rates. The experimental data are measured during dynamic ellipsometry scans. The annealing procedure has been carried out according to Figure 4.16 but dynamic scan time are varied dependent on how fast each film is heated. Thicknesses are analyzed and normalized thicknesses are then plotted in Figure 4.29.

![Figure 4.29. Thickness change of the composite films heated by different heating rates when heated up to 60°C.](image)

At the low heating rate of 0.2°C/min, the composite film expands slowly with increasing thickness lower than those of films annealed at higher heating rates. This result can be
described that latex, when heated, is in a viscous phase, which is able to flow through holes or interstitial sites of SWNT networks to cover substrate underneath the nanotube grids. In contrast, such phenomenon does not happen for the films heated using much higher, on the order of ten times, heating rates because these high rates cause a rapid expansion of the latex before particle sintering becomes significant.

The composite films heated through 2 and 5°C/min, on the other hand, show higher thickness increases. In addition, it can be observed from the slopes of the first expansions that thermal expansivity of the one heated at the rate of 5°C/min is higher than that heated by 2°C/min. However, at higher heating rate, 10°C/min, the film seems to exhibit “inertia” behavior, i.e., a thickness rise happening is smaller than in the cases of the films heated at 2 and 5°C/min. This appearance is due to too short time for the latex and SWNTs to absorb heat energy. Thus, in the high heating rate process, the absorbed heat for latex expansion is less than the heat absorbed for the expansion with lower heating rates. Small decreases at the end of first expansions of the films heated at 5 and 10°C/min stem from this “inertia” property, which is stimulated by too high heat deceleration. It is noted that there is error in the data because faster cooling rates could not be achieved through natural cooling in air. During the second expansions, their thicknesses increase further using the heat previously stored in the materials.

All composite films show irreversible thickness changes, as illustrated below in Figure 4.30, suggesting latex collapse and spreading processes during the heat treatment.
Figure 4.30. Thickness-temperature dependence of 1 wt% SWNT films heated at different heating rates: (a) 0.2, (b) 2, (c) 5, and (d) 10°C/min. The chronological order of the heat-cool-heat-cool procedure is presented by red-blue-orange-green arrows, respectively. Red circular dots indicate the beginnings of thermal expansion process.
4.4 Conclusions

Film preparation

Thin composite films of SWNTs in the matrix of BA/MMA/MAA latex have been prepared and characterized for the investigation of their thermal properties. Thin film fabrication was conducted starting from the study of different substrate cleaning routes. The outcomes suggest that the cleaning technique offering highest convenience and the least time consumption is UV-ozone cleaning as can be seen from its minimum contact angle compared to other cleaning methods. From this finding, UV-ozone cleaning has been then adopted to all silicon wafer substrates for these studies.

SWNT dispersion has been prepared using a combination of surfactant dispersants and the adoption of high output power sonication to ensure that the dispersions obtained are truly homogeneous. Nanotube-latex dispersions have been also blended by the sonication system. Spin-coating has been subsequently utilized in producing thin films owing to the high reproducibility with low time consumption of the technique. Optimal parameters have been developed to make monolayer films. AFM results suggest that, for the spin time of 10 s, 5 k rpm is the appropriate spin rate because it provides composite films with high smoothness and large continuous latex particle array grains with the largest grain size of up to 4 μm x 4 μm. Resultant films are then investigated by means of ellipsometry to determine the film thicknesses. The results obtained from generated data show film thicknesses lower than latex particle size, confirming that the fabricated films are monolayers.

Thermal expansivity

Thermal properties of composite films were subsequently studied. Thermal expansivity investigations have been then performed by dividing different conditions during heat treatment process into three sections: the effect of SWNT amounts, the effect of heating temperatures, and the effect of heating rates on film thickness changes.
According to the ellipsometry results, it has been found that, when heated, SWNT percentage in the latex matrix significantly causes film thickness to increase and leads to a considerable increase of the composite CTEs. This phenomenon can be described by the constraint or squeezing effect. In particular, with the comparatively low linear CTE of SWNTs, ordered hexagonal nanotube networks are embedded in latex matrix. They undergo very low expansion. On the other hand, the latex matrix can expand much more than the nanotube grids. Consequently, the matrix has to expand in the out-of-plane direction into free space because it cannot expand laterally with the presence of the networks wrapping around latex particles. It is interestingly found that higher amounts of SWNTs offer higher CTEs and higher thickness increases due to more complete SWNT network confinement embedded in polymer matrix. However, the CTE of the composite system cannot increase any further beyond the value at around 1 wt% SWNT content. The plateau in the thermal expansivity graph demonstrates the limit of its thermal expansion. The latex CTE is about three times greater in the direction normal to the film plane, with the existence of fixed nanotube networks. The expansion and contraction of the composite are not a reversible process and it can be seen that the final thicknesses after a heat treatment is higher than the initial thicknesses. This implies the spreading of the polymer with reduced viscosity when heated and squeezed. The finding in this work corresponds to the report of Wei et al. in that SWNTs embedded in a polymer matrix enhance the CTE of the composite. Moreover, the results from this study also agree with the work reported by Lee et al. Essentially, the constraining effect is able to increase linear CTE, in the direction perpendicular to film plane, of a composite system containing fillers and a matrix.

Heating temperature has been found to be another parameter affecting composite film thickness change. With similar SWNT percentage and heating rate, higher heating temperatures evidently cause higher thickness increases for the first expansion. Thermal expansivities observed from their slopes are almost identical except the one at higher temperature that CTE decreases slightly due to the limit of the squeezing effect.

When heated to a similar temperature, the composite films with the same SWNT content behave differently as different heating rates are applied. A low rate causes a comparatively low CTE and thus lower thickness increase. This result can be explained by the low-viscosity latex flowing through nanotube networks and spreading on the substrate. Likewise, an extremely high heating speed provides a low film thickness rise because of
very short time for the materials to absorb heat energy for latex expansion. At the heating rates in between low and high ones, thickness increases are enhanced because the composites have enough time to absorb and store heat for their expansions.

The application of the high CTE composite system could be in a thermal actuator that requires a great dimension change. Furthermore, the idea of reversible/irreversible processes could be applied in temperature sensor industries. In particular, for some other polymers, their thickness changes, when heated to a certain temperature, provide colour variations due to different light refractions observable to human eyes.
References


Chapter 5

Thermal Conductivity of Carbon Nanotube-Colloidal Polymer Composites

Interestingly unique properties of CNTs are able to enhance thermal expansivity of the composite of SWNTs-colloidal polymer as previously shown in the last chapter. Because thermal conductivity of CNTs is very high,\(^1\) when incorporated into polymeric materials, CNTs may increase thermal conductivity of the composite. There have been a number of publications on thermal conductivity of CNT-polymer composites, which will be discussed in the literature review later. However, there are a limited number of reports on thermal conductivity of CNT composite materials using latex as a matrix. Using our latex technology that can offer a method to achieve highly-ordered CNT networks may, again, enhance thermal properties of the polymer host. Therefore, thermal properties of the composites are investigated in this chapter.

The present chapter will determine another novel route to improve thermal conductivity, \(\kappa\), of CNT-latex composites via the use of latex self assembly as a template to control CNT network formation. The particular CNT networks prepared by this latex technology are highly ordered in a hexagonal close packing fashion as seen in 2-D. By using latex with comparatively high \(T_g\) that can form CNT segregated networks, \(\kappa\) can be enhanced beyond that of the composite containing low-\(T_g\) latex which creates random CNT networks. This technology also offers ultra-low thermal percolation thresholds in the range of 0.05-0.10 wt\% CNTs. SWNTs have been found to provide higher \(\kappa\) enhancement in such a particular composite compared to MWNTs. The ordered nanotube networks are able to be further controlled and tuned for various needs. Particularly, one can simply change CNT type, CNT content, latex \(T_g\), latex particle size, and surfactant for CNT dispersion. This latex processing is simple, economical, up scalable, and reproducible; hence, it will offer another promising way of composite fabrication for thermal applications.
5.1 Background

5.1.1 Introduction to thermal conductivity of materials

Introduction to conduction

Heat conduction is a consequence of atomic or molecular motion in a random pattern. It is energy transfer in a medium due to an energy gradient. To describe heat transfer by conduction, Fourier's Law, first stated in 1822, is usually adopted. This law demonstrates the relationship between thermal conductivity, heat transfer rate, temperature, and physical dimensions of particular matter. In other words, Fourier's Law states the relationship between heat flow and temperature gradient. Consider a cylindrical rod in Figure 5.1.

\[
q_x = \alpha \frac{A \Delta T}{\Delta x}
\]

This relationship can be applied to different materials such as metals and polymers. With the equal \(A\), \(\Delta T\), and \(\Delta x\), the parameter \(q_x\) is varied for different materials. To convert the above proportionality into an equation, a constant for each material must be placed in.
and this constant is called thermal conductivity ($k$), which has units of W/m-K. The following equation is then obtained.

$$q_x = KA \frac{\Delta T}{\Delta x} \quad (5.2)$$

The heat transfer rate can be derived from determining $q_x$ at a very small $\Delta x$ or, particularly, taking $\Delta x \to 0$. Hence, the heat transfer rate is as follows:

$$q_x = -KA \frac{dT}{dx} \quad (5.3)$$

In order for $k$ to be positive, the minus sign is always added to equation (5.3) as heat is transferred from the region with higher to lower temperature. Heat flux ($q_x^*$) is defined as $q_x$ per unit area as shown in equation (5.4), which is actually a modified Fourier’s Law. This law is applicable for all states of matter: solid, liquid, and gas.

$$q_x^* = \frac{q_x}{A} = -K \frac{dt}{dx} \quad (5.4)$$

It can be seen that heat flux is a direction-dependent quantity. In other words, $q_x$ is a vector having its direction perpendicular to cross-sectional area $A$. Heat flow always moves normally through a surface with a similar temperature or, essentially, an isothermal surface. To write heat flux in the general case in 3-D, the del operator $\nabla$ is introduced to Fourier’s Law as follows:

$$q^* = -K \nabla T = -K \left( \hat{i} \frac{\partial T}{\partial x} + \hat{j} \frac{\partial T}{\partial y} + \hat{k} \frac{\partial T}{\partial z} \right) \quad (5.5)$$

Alternatively, Fourier’s Law can be rewritten as equation (5.6) and (5.7). Where $n$ represents a direction normal to an isothermal surface.

$$q_n^* = -K \frac{\partial T}{\partial n} \quad (5.6)$$
Therefore, heat flux can also be rewritten in $x$, $y$, and $z$ directions as shown in equation (5.8).

\[ q^* = \hat{i} q^* x + \hat{j} q^* y + \hat{k} q^* z \quad (5.7) \]

\[
q^*_x = -K \frac{\partial T}{\partial x} \quad q^*_y = -K \frac{\partial T}{\partial y} \quad q^*_z = -K \frac{\partial T}{\partial z} \quad (5.8)
\]

**Introduction to thermal conductivity**

The rate that heat is transferred by diffusion can be determined by thermal conductivity measurements. When heat transport is higher, then a material’s thermal conductivity is higher. From equation (5.8), we have equation (5.9) as thermal conductivity in $x$ direction.

\[ K_x = -\frac{q^*_x}{(\partial T / \partial x)} \quad (5.9) \]

In an isotropic, linear material, $\kappa_x = \kappa_y = \kappa_z \equiv \kappa$ since heat transport is independent of direction. Intermolecular spacing in a given material contributes to thermal conductivity. In particular, matter with short atomic separation lengths tends to have higher heat conduction. Consequently, thermal conductivity of gases and liquids is much greater than that of solids because molecular collisions are random and average atomic separation length of fluids is considerably larger than intermolecular spacing of solids.\(^3\)

A solid consists of a lattice, which is a periodic arrangement of atoms. In this regard, two factors governing thermal conductivity are conduction from free electron flow and lattice vibrational waves, which are called phonons when lattice vibrations are considered as packets of quantized energy. Lattice waves are always present in all types of materials. Because there are a large amount of free electrons in metals, these free electrons have a dominant contribution while phonons dominate in semiconductors and non-conductor materials.
Thermal conductivity is a function of specific heat per unit volume $C$, the average speed of sound $\bar{c}$, and mean free path of heat carrier $\lambda_{\text{mfp}}$ as shown in equation (5.10). The mean free path is the average distance that a carrier travels before it hits another carrier or a defect. In metals, electron conduction is dominant, thus $C \equiv C_e$ and $\lambda_{\text{mfp}} \equiv \lambda_e$, where $\lambda_e$ is electron mean free path. Additionally, $\bar{c}$ is replaced by average electron velocity. For the case of semiconductors or non-conductor materials, $C \equiv C_{\text{ph}}$ is phonon specific heat, $\bar{c}$ is the mean speed of sound, and $\lambda_{\text{mfp}} \equiv \lambda_{\text{ph}}$ represents phonon mean free path.

$$K = \frac{1}{3} C \bar{c} \lambda_{\text{mfp}}$$

(5.10)

$$K = k_e + k_{\text{ph}}$$

(5.11)

Based on equation (5.10), the longer that the mean free path of a heat carrier is, the higher is the thermal conductivity. In addition, increasing temperature leads to more vigorous vibration of heat carriers; therefore, there is a shorter average mean free path. Consequently, the final outcome is a reduction in thermal conductivity. Mean free path is relevant to boundary effects as explained in the next topic.

*Boundary effects on solids in micro- and nanoscale*

Boundary effects are more important in some applications that require small dimensions of a solid, for example, uses in microelectronics. At this small scale, thermal conductivity is different from that of bulk materials at the macroscale. In the same material with a pronounced difference in thickness, heat carriers are more likely to collide with a solid's boundaries in the case of a thin film, thus varying propagation direction of the carriers. This mechanism is equivalent to reducing net distance that heat carriers travel. This phenomenon is called carrier scattering. In contrast, boundary effects are less prominent in thick films since carriers can travel through a longer path before they hit boundaries. As a result, bulk solids offer higher thermal conductivity compared to ultra-thin solid films. Comparing thermal conductivity of bulk solids to that of thin films, it can be written as
\[ K_{\text{normal}} < K_{\text{in plane}} < \kappa \]  

(5.12)

Where \( K_{\text{normal}} \) is \( \kappa \) in normal direction to the film plane, \( K_{\text{in plane}} \) represents \( \kappa \) in the film plane, and \( \kappa \) means bulk thermal conductivity.

Not only can heat carriers be scattered by boundary effects but they also scatter because of dopants that may be distributed throughout the bulk solid. At the micro- and/or nanoscale, grain boundaries are another crucial factor affecting thermal conductivity. In particular, the carriers have a shorter distance to travel before collisions with grain boundaries. Smaller grain boundaries, consequently, cause lower thermal conductivity. This effect is even more important in nanostructured materials as they have significantly small grain boundaries. However, the incorporation of materials with extremely-high thermal conductivity could overcome this limitation and provide promising composite materials with satisfactory thermal conductivity.

**Temperature effect on phonon scattering**

In an infinite perfect single crystal, lattice vibration is highly harmonic and phonons are able to migrate without any resistance. Apart from this condition where phonons vibrate with greater amplitudes and no longer in harmonicity, phonons are likely to collide with each other. More collisions result in lower thermal conductivity as the temperature scales up. This explanation is applied to describe insulator behaviours at high temperature.

Point defects and impurity atoms are crucial factors contributing to phonon scattering even at low temperature. The fact that lattice defects have an effect on carrier mean free path can be applied in thermal conductivity measurements to investigate lattice imperfections. At such low-temperature conditions, phonon collision is not dominant but the collision with a solid’s surface or grain boundaries will be important. As a result, at low temperature, this causes an increase of thermal conductivity with temperature as \( T^3 \). The maximum thermal conductivity is at some intermediate value, which is between low and high temperature. Therefore, the proportionality of thermal conductivity and temperature can be shown in Figure 5.2 and be written as follows:
at high temperature, \[ \kappa \propto T^1 \] (5.13)

at low temperature, \[ \kappa \propto T^3 \] (5.14)

Figure 5.2. Thermal conductivity as a function of temperature. There are two temperature ranges: low and high temperature where \( \kappa \propto T^3 \) and \( \kappa \propto T^{-1} \), respectively (adapted from 4).

5.1.2 Review of thermal conductivity of carbon nanotube composite materials

Polymers materials have relatively low thermal conductivity compared to metals and carbon-based materials such as diamond and graphite. Polymers are most often insulators with no free electrons. They are also amorphous, so there is less phonon transport when heated. To enhance \( \kappa \) of polymers, additives with high \( \kappa \) are needed to incorporate into polymer composite fabrication.

Among materials known, a material with a markedly high \( \kappa \) is CNTs whose \( \kappa \) is reported, at room temperature, theoretically at about 6600 W/m-K for individual (10, 10) SWNTs and 3000 W/m-K for individual MWNTs as found experimentally. Such exceptionally high \( \kappa \) values of CNTs can be described that it is the contribution of long phonon mean free paths and perfect seamless order of carbon atoms along the tube. The simulation study in Berber et al.'s work was performed by equilibrium and nonequilibrium molecular dynamics using carbon potentials. For the \( \kappa \) measurement of isolated MWNTs, Kim and co-workers made micro-device that is able to suspend an individual MWNT without any
contact with substrate underneath. Heat flow was measured through this suspended nanotube. Although there are several studies in the literature, these investigations based on bulks or bundles or ropes of CNTs. As a result, obtained $\kappa$ values are from tubes with different lengths and diameters. The bulk samples also cause a complication in $\kappa$ study since there are a great amount of tube-tube junctions which act as heat obstacles. The real $\kappa$ values were then not able to be obtained. Being a high-$\kappa$ material, CNTs have been incorporated into polymeric materials to fabricate composites with the expectation that they can enhance $\kappa$ of the host. MWNTs are relatively low-cost and widely available. However, although SWNTs require a more difficult manufacturing process due to specific growth conditions, which causes lower availability, and a relatively higher production cost, they have been still employed as inclusions due to their theoretical high $\kappa$ value. The way of using such carbon–based materials is to apply them as a heat sink, heat conductor, or heat spreader, including thermoelectric material for the case of possible insulator applications.

With these promising applications of CNTs in mind, there have been several efforts in exploring novel routes to improve $\kappa$ of CNT-filled polymer composite systems. For instance, one elaborated means is to grow highly aligned CNTs on a substrate and inject polymer to the already-prepared aligned-CNT layer. $\kappa$ enhancement via this fabrication method is much higher than that from ordinary dispersed CNTs but its mass-production is rather difficult. More recently, nanotube junctions were made connected by the addition of poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) to the SWNT-polymer composite by making use of the additive’s conducting characteristics. This composite is viable for being a material for thermoelectric application since $\kappa$ has not been improved considerably at low CNT concentration.

For simpler pathways to the fabrication of composites for thermal applications, Biercuk et al. made randomly arranged SWNT networks in an epoxy matrix and found the percolation threshold of their composite in the range of 0.1-0.2 wt.% SWNTs. The increase in $\kappa$ is 70% for 1 wt.% SWNTs. However, through this composite fabrication method, solvent is required to dissolve epoxy and it must therefore be eliminated afterwards at high temperature. Another investigation on CNT-epoxy composites was published by Moisala et al. For their composite system, the thermal percolation threshold was below 0.1 wt.% MWNTs with the $\kappa$ enhancement of around 14% at MWNT loading of 0.5 wt.%. Again,
high temperature (140°C) in a vacuum oven is mandatory for the film curing process, making it a high energy-consumption production for up-scaling assembly. Cai and Song disclosed another composite system using MWNTs and polyurethane. According to their work, an increase in $k$ of about 210% was found using 3 wt% MWNTs. The percolation region was between 0.5 and 3.0 wt.% MWNTs. However, this threshold might be possibly reduced to lower percolation if nanotube networks were more ordered. In particular, the composite with random CNT networks embedded has a large volume for nanotubes to sit in; therefore, tube overlapping regions that act as percolated paths are not necessary created. In contrast, in the composite system containing particulate matrix, nanotubes are only accommodated to interstitial sites between these particulates. As a result, CNTs have nowhere to go and more likely to connect to each other and create percolated paths.

Another route performed at room temperature, latex self assembly, was introduced. Latex consists of colloidal polymer particles dispersed in water. CNTs can be added to latex if the CNTs are dispersed in water. There is no use of organic solvent. As a result, annealing such composites at high temperature is not required. Additionally, the ability to control filler arrangement is feasible via a variation of latices with different glass transition temperature ($T_g$). Particularly, more ordered CNT networks can be produced using a latex matrix with a $T_g$ close to room temperature because there is no interdiffusion happening between latex particles for the composite fabrication at ambient temperature. Therefore, CNTs cannot go inside the hard latex particles and they are left outside to wrap around latex particles. In contrast, CNTs are able to move inside the soft latex particle, resulting in random CNT networks formed. The mechanism of such an assembly was shown elsewhere. Briefly, CNTs are dispersed in an aqueous phase. During the water evaporation process, CNTs are accommodated in interstitial voids between latex particles. Short bundles of CNTs then connect to each other and form longer segregated networks due to inter-tube van der Waals interaction and tube entanglement. An increment of 10% in $k$ was found in poly(vinyl acetate) latex and SWNT composites with a percolation threshold of 0.59-1.64 vol.%. The possible reasons for this low $k$ enhancement are interfacial thermal resistance and the degree of nanotube rope order as homogeneous nanotube networks could dissipate heat well throughout the bulk composite. Polystyrene latex was also used as a matrix as reported in the work by Peters et al. In this communication, high SWNT amounts were added to the latex. $k$ could be augmented significantly at a high nanotube weight fraction. However, $k$, including percolation
threshold, at low SWNT loading was not revealed. Poly(vinyl acetate) latex was studied again by Yu et al.\textsuperscript{10} through the combination of single-, double-, and triple-walled CNTs as fillers for the latex matrix. It was shown that emulsion particles pushed CNTs to interstitial sites between polymer particles. Although there was a certain degree of CNT network arrangement, based on this report, there was a small increase in $\kappa$ at low CNT content up to 5 wt.%. In contrast to previous works, CNT weight fraction of 0.5 provided lower $\kappa$ for a particular composite system. To obtain higher $\kappa$, more CNTs have to be added at a higher loading, which was 10 and 20 wt.%.

Based on this literature, latex technology is comparatively simple, economical, nontoxic, and reproducible. In addition, $\kappa$ could be possibly increased if the CNT network formation is more controllable. It has proved practical to arrange CNTs controllably between latex particles. Long-range order of CNT networks have been successfully fabricated by Jurewicz et al.\textsuperscript{15} The composite exhibits high elasticity which is promising for a wide range of mechano-thermal applications. Essentially, CNT networks are able to relax back to be almost the same structure as those before being strained. SWNTs are also perfect for being a latex filler because they are comparatively much smaller than the matrix. Their high aspect ratio\textsuperscript{17} also makes them applicable to entangle, form ropes, and finally form long continuous networks. We report here the use of latex self assembly to fabricate highly ordered CNT segregated networks and compare the $\kappa$ increase of the composites containing random and segregated CNT networks using latices with high and low $T_g$, to be called "hard" and "soft" latices respectively, for both SWNTs and MWNTs. The focus of the present work will be on the impact of the highly-ordered hexagonal CNT arrays with an ultra-low CNT content on $\kappa$ enhancement.

5.2 Experimental details

5.2.1. Materials and sample preparation

SWNTs were synthesized by high-pressure carbon monoxide method (HiPco\textsuperscript{®}) and were used as received from Unidym, Inc., CA, USA. MWNTs (95+\% carbon purity) were produced by catalytic carbon vapour deposition and were used as produced from Nanocyl, Sambreville, Belgium. An aqueous solution of 1 wt.% non-ionic surfactant, Triton-X100
(Fisher Scientific, Leicestershire, UK) was used to disperse CNTs. For the composite dispersion with 0.5 wt% CNT/latex, the CNT dispersion was prepared at 1 mg/ml of CNT/deionised water weight fraction through iced-bath probe sonication at the output power of 20 Watts for 10 minutes. The amounts of the latex, water, and surfactant were kept similar to those used in this 0.5 wt.% dispersion for all other composite dispersions. The only one varied parameter was CNT content, which were 0, 0.01, 0.05, 0.1, 0.25, and 0.5 wt.% (Figure 5.3) compared to polymer weight. The so-called “hard latex” is a co-polymer of styrene (St), butyl acrylate (BA), and acrylic acid (AA) with a solids content of 40 wt.%, average particle size of 295 nm, and T_g of 21°C. “Soft latex” in the present work is a co-polymer of 2-ethyl hexyl acrylate (2EHA), butyl acrylate (BA), ethyl acrylate (EA), and methyl methacrylate (MMA) with the solids content of 60 wt.%, average particle size of 190 nm, and T_g of -50°C. The composite dispersion of CNTs and latex were blended using the same process as that used for making CNT dispersion but with a lower output power of 10 Watts.

5.2.2 Analysis

Atomic force microscopy (AFM) measurements were performed on an NT-MDT system (Moscow, Russia) using intermittent mode. Scanning electron micrographs (SEM) were taken by a Hitachi S-4000 at an accelerating voltage ranging from 6 to 15 kV without specimen surface modification.

A Q1000 differential scanning calorimeter (DSC) (TA Instrument, New Castle, USA) was applied for all modulated DSC (MDSC) at the modulation amplitude of 1°C, modulation period of 80 seconds, and a heating rate of 3°C/min from -100 to 60°C. Thin (<0.5 mm) specimens were prepared by drop casting the composite dispersion on a rectangular PTFE trough as shown in Figure 5.4 (a). The composite thin film was left for 4 days at room temperature to dry and then cut into a circular shape with a diameter of 5 mm (Figure 5.4 (b)) to fit the DSC pans. For the preparation of thick (>3 mm) specimens, the composite dispersion was also dropped in 5 mm-diameter cylindrical holes in a PTFE block (Figure 5.5 (a)) and left for 4 weeks at room temperature. The resulting thick specimens are presented in Figure 5.5 (b).
Figure 5.3. Composite dispersions of SWNTs and hard latex. The SWNT concentrations from left to right is 0, 0.01, 0.05, 0.10, 0.25, and 0.50 wt.%, respectively.

Figure 5.4. (a) a rectangular PTFE trough used to make thin samples. (b) obtained thin specimens with SWNT concentrations from left to right of 0, 0.01, 0.05, 0.10, 0.25, and 0.50 wt.%, respectively. The diameter of each thin specimen piece is 5 mm.

Figure 5.5. (a) a PTFE block for the preparation of thick specimens. (b) thick specimen pieces with SWNT contents from left to right of 0, 0.01, 0.05, 0.10, 0.25, and 0.50 wt.%, respectively.

To calculate thermal conductivity, the equation (5.15), as derived elsewhere, was used.¹⁸
\[ K = \frac{8LC^2}{C_pMd^3P} \]  

(5.15)

where \( k \) is in units of W/m-K, \( L \) is sample thickness (m), \( C \) is apparent heat capacity of the sample (J/K), \( C_p \) is sample specific heat (J/g-K), \( M \) is sample mass (g), \( d \) is sample diameter (m), and \( P \) is modulation period (s).

Because there is normally heat loss from a specimen to the ambient, to obtain \( k \) with high precision, a thermal conductivity calibration constant was determined according to equation (5.16)\(^\text{16} \). The actual \( k \) value was then calculated using equation (5.17) as follows:

\[
D = (k_o k_r)^{0.5} - k_r
\]  

(5.16)

\[
K = \frac{[K_o - 2D + (K_o^2 - 4DK_o)^{0.5}]}{2}
\]  

(5.17)

where \( D \) is a thermal conductivity calibration constant, \( k_o \) and \( k_r \) are the observed and true reference material conductivity (W/m-K), respectively. \( k \) is the thermal conductivity of unknown specimens. In the present work, polystyrene was used as a reference material with the literature \( k_r \) value of 0.14 W/m-K.\(^\text{19} \) Polystyrene samples were prepared by cutting a polystyrene block into thin (< 0.5 mm) circular pieces and thick (> 3 mm) cylinders.
5.3 Results and discussion

Heat flow profiles as a function of temperature at different amounts of CNTs for all composites are shown in Figure 5.6 and the average $T_g$ values of four different types of the composites are summarized in Table 5.1. The average $T_g$ value of each composite is calculated from 6 different CNT contents: 0, 0.01, 0.05, 0.1, 0.25, and 0.5 wt.%. 

(a) 

(b)
Figure 5.6. DSC thermograms presenting the $T_g$ of all composites with varying CNT concentrations: (a) MWNT-soft latex, (b) MWNT-hard latex, (c) SWNT-soft latex, and (d) SWNT-hard latex. Note: 0% in all graphs means no CNTs were added to the sample. All concentrations have an identical amount of Triton X-100 and polymer.
Table 5.1. Average glass transition temperature of pristine latices and their composites

<table>
<thead>
<tr>
<th></th>
<th>Soft latex</th>
<th>Hard latex</th>
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<tr>
<td></td>
<td>Pristine (No CNTs and Triton)</td>
<td>Pristine (No CNTs and Triton)</td>
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<tr>
<td></td>
<td>MWNTs and Triton added</td>
<td>MWNTs and Triton added</td>
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<td></td>
<td>SWNTs and Triton added</td>
<td>SWNTs and Triton added</td>
</tr>
<tr>
<td>$T_g$ (°C)</td>
<td>-50</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>$-50 \pm 0.5$</td>
<td>$13 \pm 0.8$</td>
</tr>
<tr>
<td></td>
<td>$-51 \pm 0.4$</td>
<td>$12 \pm 0.7$</td>
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The trend of Figure 5.6 is that, for each composite type, samples having the same amount of surfactant exhibit a similar $T_g$. With the presence of CNTs and surfactant, both soft and hard latices have a lower $T_g$ as seen in Table 5.1. A decrease of $T_g$ in the composite containing hard latex is a consequence of Triton-X 100 surfactant plasticization where the surfactant is present between latex particles. However, this prominent $T_g$ drop is not clearly observable in soft latex case. In all cases, $T_g$ barely depends on CNT concentration as seen from standard deviation (error) in Table 5.1 that $T_g$ variation after adding CNTs to the matrix is less than 1°C. The $T_g$ difference of soft and hard composites is about 62°C, which allows different patterns of latex particle arrangement at room temperature (~20°C), and thus different CNT network formation as shown elsewhere.\textsuperscript{14}
Figure 5.7. AFM height (left) and phase (right) images of the composite made by (a,b) 0.5 wt.% SWNT-soft latex dispersion and (c,d) 0.5 wt.% SWNT-hard latex dispersion. Random arrangement of SWNTs has been shown clearly in (b). In (d), the marked areas reveal SWNT bundles between latex particles. (e) SEM micrograph of 0.5 wt.% SWNT-hard latex composite showing highly ordered hidden SWNT networks.
The AFM height image in Figure 5.7 (a) demonstrates topography of the composite containing 0.5 wt.% SWNT in the soft latex composite. Figure 5.7 (b), phase image, shows more evidently nanotube networks embedded in the matrix of the specimen. CNTs randomly orient in the host without any pattern because latex is able to coalesce at room temperature, which is the temperature at which all samples were prepared. More CNT loading contributes to further overlapping and longer percolated paths that are created through bundle formation and entanglement as illustrated in Figure 5.8. Besides side by side attraction between tubes, one end of a short nanotube attracts one end of another tube by van der Waals interaction and so on while forming bundles. In addition, other intermolecular forces, such as pi stacking, also contribute to tube-end attraction. Mechanical twisting and wrapping around other tubes’ ends also increase percolated path length. However, the CNT distribution throughout the soft composite is not uniform on the long-range scale, hindering electron transfer during SEM operation. Charging effects on the specimen surface then occurred and made surface SEM investigation not possible.

Figure 5.8. 2-D schematic representing nanotube bundles of composite systems with soft and hard latexes as CNT concentration increases. Longer percolation paths form at higher CNT loading. Note: the size of the schematic is not scaled for nanotube size.
In contrast, in the case of hard latex, polymer particles do not coalesce significantly at room temperature. As a result, polymer hard spheres are still able to exist and push CNTs throughout the dispersion while they form hexagonal close packing. With the restriction that CNTs have no place to go, latex particle arrangement drives CNTs to interstitial sites between latex spheres. AFM height and phase images show the composite topography in Figure 5.7 (c) and 5.7 (d), respectively. Hexagonal close packing of polymer particles can be observed which is a good indicator of being a proper matrix to form dodecahedral nanotube networks between them in 3-D. The phase image reveals SWNT bundles in some local places at different locations, reflecting the uniform density of filler distribution. Under this phase AFM investigation, both the matrix and inclusions are disclosed at the same time. Figure 5.7 (e) confirms the presence of highly arranged nanotubes between matrix particles by showing SWNT networks in the latex host of the composite made from 0.5 wt.% SWNTs in hard latex. It can be observed that SWNTs form hexagonal networks whose hexagon size is roughly similar to the polymer particle size of pristine latex (295 nm). This confirms that CNTs wrap around matrix particles. The regular distribution of hidden SWNTs across the sample can be also observed, suggesting percolated path formed throughout the composite bulk. The networks enable better electron transport in the material and this is the reason why such a sample is practical for SEM measurement. At low SWNT amounts, nanotube networks do not spread throughout the whole composite but there are some connected paths which will be confirmed from its thermal conductivity later on. Adding a higher amount of CNTs to the latex creates more complete nanotube networks over larger areas. However, at comparatively higher CNT concentration, excess CNTs go to latex interstitial places and bridge the networks more, similar to those in Figure 5.8, as well as form thicker nanotube bundles as shown elsewhere.14

Heating profiles used in the MDSC of representative samples, 0.5 wt.% SWNT-hard latex and 0.5 wt.% SWNT-soft latex, are shown in Figure 5.9. Heat flow curves (red) indicate the Tg values of the composites at around 13 and -50°C, respectively. At these transitions, heat capacity changed, as reflected in the change in the heat flow and was used as glass transition. Modulated temperature sinusoidal curves (blue) indicate temperature oscillation heating process applied in the present study on one side of the sample in open aluminium pans.16
To determine all $\kappa$ values, initially MDSC was performed on a polystyrene sample. The resultant $\kappa$ obtained from this reference specimen is 0.16 W/m-K while the literature value is 0.14 W/m-K. These two values were then used to correct for the heat loss effect. $\kappa$ as a function of CNT content at different temperatures (below, above, and further above $T_g$), with the calibration constant incorporated, of CNT-composites is shown in Figure 5.10. The tendency is that $\kappa$ decreases at very low CNT loading, then rises up to its maximum value during the region of thermal percolated path formation, and finally decreases again with the presence of more CNTs. At higher nanotube concentration in the present study, $\kappa$ tends to be either constant or decreasing.

Figure 5.9. Heating profiles showing heat flow at a selected temperature region close to $T_g$ of the composites and temperature variation profile applied to different samples: (a) 0.5 wt.% SWNT-soft latex and (b) 0.5 wt.% SWNT-hard latex.
Figure 5.10. Thermal conductivity of (a) MWNT-soft latex, (b) MWNT-hard latex, (c) SWNT-soft latex, and (d) SWNT-hard latex as a function of the CNT content at two different temperatures of 20°C and 40°C.
A drop at low CNT loading can be seen in the present work and was actually found in the literature earlier. At low CNT amounts embedded in the latex matrix, there are more free spaces between latex particles because low concentration of CNTs cannot fill up those spaces. These free volumes could be occupied by air which is in fact an obstacle for heat transfer between the matrix and CNTs. Additionally, this decrease may also come from thermal interfacial resistance. Particularly, at such low CNT content, percolated nanotube networks cannot be formed. Thus, there are only discontinuous pathways that heat is not able to travel on seamlessly. These networks, as a result, hinder heat flow between polymer particles; thus, has been reduced as observed in Figure 5.10 (a-d) at 0.01 wt.% CNTs. As heat flows across interfaces, there is an inharmonicity of lattice vibration of CNTs, surfactant, and latex matrix. Essentially, the interfacial thermal resistance is the result of the overlap of the phonon density of states of each material at specific interfaces. A lower mismatch of phonon reflection and transmission in material layers contributes to lower interfacial thermal resistance or, in other words, lower phonon wave packet scattering at the interface, leading to higher thermal conductivity.

However, more CNT loading contributes to a sharp change in up to a maximum at CNT content of 0.05 wt.% (0.10 wt.% for MWNT-hard latex case) due to continuous thermally conducting pathways. This percolation threshold of the composite with 0.05 wt.% SWNT-hard latex exhibits high thermally conductive behaviour and its percolation threshold is markedly lower than those reported earlier, indicating a success of the novel route to fabricate 3-D thermally percolated CNT networks for thermal management. The resultant higher value also suggests that nanotube continuous networks can be formed completely through such a technology at ultra-low CNT content. The decrease of at higher CNT loading could be from more phonon scattering occurring, which implies that CNT networks are the path for phonons to scatter at the same time as heat is transferred since more CNTs create higher interface. This effect is even more evident at the highest nanotube amount in the composite containing SWNTs and hard latex. This may tell us that, in the SWNT-hard latex system, the continuous percolated paths, which are CNT networks, are highly ordered in hexagonal arrangement and are most complete, compared with the other three composite cases. As a result, there is the highest decrease in at high CNT loading due to the greatest phonon scattering. Alternatively, the decreasing trend of for all composites as high CNT contents were added can be explained that of individual CNTs can be reduced because of interaction between adjacent tubes in
bundles. This effect is obvious in the case of the composite with segregated SWNT networks. Essentially, higher CNT amount are accommodated in latex particle interstitial sites, hence forming bigger bundles. However, this tendency is not strong in the case of the composites containing random CNT networks since more CNT amount can be distributed randomly throughout the latex host as they do not have to sit at particular places, such as in matrix interstitial sites. Furthermore, the relatively constant or decreasing $\kappa$ at high CNT concentration suggests that there is no need to add more CNTs in such a latex-based composite system. Instead, only a low CNT content should be added to the latex in order to maximize $\kappa$, which is desirable for lower-cost material manufacture.

In the MWNT composite case, it has been found that thermal percolation threshold is higher, 0.10 wt.% MWNTs for hard latex host. It is surprising that adding MWNTs to soft latex drops $\kappa$ rather than contributes to a $\kappa$ increase. Additionally, when compared between SWNT and MWNT composites containing soft and hard latexes, it has been found that SWNTs offer higher $\kappa$ which is in agreement with that reported elsewhere for the composite made from a polymer melt but our composites show lower percolation thresholds for both SWNT and MWNT cases. The potential reason is that MWNTs themselves possess comparatively lower $\kappa$ compared to SWNTs. Coupled with the fact that all MWNTs form bundles that increase the interfacial region in the composites, $\kappa$ in the present work is essentially decreased. Comparing between composites with the same type of CNTs but different types of latex matrix, hard latex yields a higher $\kappa$ enhancement because it is able to create more continuous CNT networks formed between its polymer particles.

Phonons govern heat transport in non-metallic materials. At increasing temperature, phonons vibrate more vigorously; therefore, $\kappa$ is dependent on temperature. By plotting $\kappa$ as a function of temperature, it can be shown more clearly the effect of temperature on $\kappa$. 

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As seen from Figure 5.11, apart from the SWNT-hard latex composite system in (d), $k$ is comparatively constant. However, in the SWNT-hard latex composite, $k$ increases as temperature is increasing for all composites except the one with 0.5 wt.% SWNTs, which has a lower $k$ at higher temperature. This reflects that the SWNT content up to around 0.25 wt.% is still able to enhance $k$ for such a particular composite. The results here are particularly interesting for the hard composites containing SWNTs as $k$ increases significantly. A comparison of thermal conductivity is made of the composites with a nanotube content of 0.05 wt.%, where $k$ is maximum, for both SWNT-soft and SWNT-hard latex cases, has been made in Figure 5.12.
Figure 5.12. Temperature dependence of thermal conductivity presented as (a) a value normalized by the -80°C value and (b) enhancement percentage of the composites consisting of random and segregated SWNT networks. The black dashed lines connected between data points are a guide to observe the slope.

Normalized $\kappa$ values in Figure 5.12 (a) are calculated by dividing $\kappa$ value at each temperature by that at -80°C in order to see the trend of $\kappa$ as temperature scales up from this particular temperature. Enhancement percentage of $\kappa$ in Figure 5.12 (b) is calculated by dividing the difference of $\kappa$ values between the composites with 0.05 wt.% and without SWNTs, at each temperature, by $\kappa$ values of the composites with no nanotubes and multiplying by 100. From Figure 5.12 (a), it is observed in the case of 0.05 wt% segregated SWNT networks that the linear fits before and after $T_g$ range have quite an identical slope (0.0055 and 0.0058 °C⁻¹), indicating the applicability of the composite material for $\kappa$.
improvement below and above its $T_g$. Furthermore, $\kappa$ also increases almost linearly as a function of temperature. This temperature-dependent thermal behaviour can be described using phonon thermal conductivity theory since phonons are dominant for heat conduction in semiconducting materials compared to the contribution of electrons.\textsuperscript{23} In this regard, as temperature rises, heat carriers or phonons have a shorter mean free path because all phonons vibrate more vigorously, leading to a higher probability of phonon collision. Accordingly, $\kappa$ decreases in accordance with equation (5.10).\textsuperscript{23}

Based on the equation (5.10), it can be understood that thermal conductivity is inversely proportional to temperature as seen in Figure 5.11 (a-c) at temperature below $T_g$. The decrease in $\kappa$ is even more pronounced for the composite consisting of MWNTs (Figure 5.11 (a, b)) due to higher number of encircled walls that act as reflection and scattering interfaces for phonons. Particularly, SWNTs offer higher $\kappa$ due to their longer phonon mean free path.\textsuperscript{2a, 25} In contrast, the trend of decreasing $\kappa$ at higher temperature (below $T_g$) cannot be observed for the case of the composite containing segregated SWNT networks. Essentially, latex particles soften and become more liquid like at higher temperatures, thus enabling more intimate contact between SWNTs and latex matrix. Consequently, a higher amount of heat can be transferred through the interfacial regions. A comparison of the SWNT composites with hard and soft lattices (Figure 5.11 (c) and (d)) shows that the composite containing hard latex has higher $\kappa$. One potential reason for this is that there are CNT networks throughout the bulk in the case of hard-latex composite.

Being shown in Figure 5.12 (b), throughout investigating temperature between -80 and 60°C, $\kappa$ enhancement of the 0.05 wt% SWNT composite containing random nanotube networks is consistently low (5.12–12.28%) and tends to decrease when the composite increases in temperature. On the other hand, $\kappa$ enhancement is up to 61.60% at 50°C for the composite with segregated nanotube networks at the same SWNT content. $\kappa$ enhancement increases rather linearly over the experimental temperature range which includes the $T_g$ of the composite. A small drop in $\kappa$ at around the polymer's $T_g$ (~20 and -40°C) can be observed not only in SWNT composites in 5.12 (a) but also actually in all specimens as shown by Figure 5.11 (a-d). In Figure 5.12 (a), for the pristine soft and pristine hard latex, $\kappa$ reduces up to $T_g$. This could be the consequence of more phonon scattering and air voids between latex particles. Similarly, in 0.05 wt.% SWNT-soft latex, at below $T_g$, as temperature is rising, latex tends to become softer and introduces a higher modulus difference...
compared to CNTs. As a result, the Kapitza resistance scales up, hence a decrease in \( \kappa \). Kapitza resistance is an interfacial resistance due to a modulus difference between a filler and matrix in a composite. This resistance is more pronounced with the presence of higher modulus difference. In such three composite systems (Figure 5.11 (a-c)), there is less ordered nanotube networks, compared to the case of Figure 5.11 (d), acting as thermally percolated paths that absorb heat from polymer matrix and this is the reason for high modulus difference at high temperature. At temperature around \( T_g \), latex particles deform and pack more closely. This process reduces air voids whose \( \kappa \) is comparatively low. Therefore, \( \kappa \) of the whole composite system tends to increase from this temperature upward. Nevertheless, in the case of 0.05 wt\% SWNT-hard latex composite, the contributions of high \( \kappa \) from SWNTs themselves and the comparatively more complete percolated paths of CNTs networks could probably overcome Kapitza interfacial resistance effect. Therefore, an increment in \( \kappa \) can be observed at all temperatures apart from its \( T_g \) range. In other words, \( \kappa \) enhancement is mainly due to the presence of CNT networks wrapping around polymer particles and this prevents the mechanism for latex to become softer, as heat is transferred very well through the networks, and Kapitza resistance could not be significant.

It is interesting to compare the maximum \( \kappa \) enhancement of all different four types of the composites quantitatively at room temperature (~20°C) which might be feasible for thermal management applications at ambient condition. At the percolation region of 0.05 or 0.10 (for MWNT-hard latex) wt.% CNTs, \( \kappa \) enhancement percentage at 20°C is illustrated in Figure 5.13 where segregated SWNT networks offer highest \( \kappa \) improvement. In Figure 5.13, we can categorize the composites into two main groups: the composites with soft latex and those with hard latex. In soft latex systems, CNT networks have their arrangement in a random fashion; consequently, there is large interfacial area resulting in higher interfacial resistance and thus lower \( \kappa \). A comparison between the MWNT- and SWNT-composites with hard latex indicates that the one with SWNTs offers higher \( \kappa \) enhancement. The possible explanation for this is that SWNTs have very high \( \kappa \); therefore, heat can be transferred better through their networks compared to the case of MWNT composite. Less amount of heat is left in the latex host, resulting in lower modulus difference between the fillers and the matrix. This causes lower Kapitza resistance of SWNT composite compared to that of the MWNT composite.
Figure 5.13. Maximum $k$ enhancement percentage at 20°C of different composites: MWNT-soft latex, SWNT-soft latex, MWNT-hard latex, and SWNT-hard latex.

By looking at Figure 5.10, 5.11 and 5.12, it is apparent that $k$ can be varied by changing CNT type, CNT content, latex matrix $T_g$, and temperature at which $k$ is measured. Such composites provide a range of $k$ that is tuneable. Additionally, $k$ may be altered to other ranges by changing latex matrix particles size and type. More interestingly, their percolation thresholds may be reduced by adding smaller latex particles to the existing composite systems as reported previously.\(^{24}\)

$k$ experimentally found from these composites is still much lower than the theoretical $k$ of SWNTs and MWNTs. By coating around nanotubes, the surfactant used to disperse CNTs in water blocks heat transfer between the polymer matrix and CNTs.\(^{25}\) Moreover, heat transfer is hindered at the connection between individual nanotubes.\(^{26}\) $k$ from the composite containing CNT bundles is also lower than that with individual nanotubes.\(^{2}\) Kapitza resistance is an essential possible reason of such an observation and is even more important factor in CNT-polymer composites because interfacial area is especially high due to nanotube’s small radius. From the opposite point of view, however relatively high $k$ enhancement in the present work on CNT-polymer composites may come from the surfactant used. Particularly, the surfactant absorbing on CNTs influences polymer chain orientation in each latex particle; therefore, heat flow between nanotube and the polymer...
host through the interface can be increased\textsuperscript{29} as it is known that heat transport is more pronounced in crystalline compared to amorphous materials.\textsuperscript{23} Based on latex technology reported here, to improve $\kappa$ in CNT-latex composites, one could use a latex that do not have particle deformation at room temperature. By doing so, latex particles would not deform to be dodecahedrons completely but they would have their particle shape much like spheres which allow free spaces for CNTs to sit in. Air voids that could be formed can then be eliminated by heating the composite. In polymer-melt composite systems with coalescence of polymer, there is only small or even no free volume for CNTs to occupy. Hence, CNT surfaces and polymer surfaces are in close contact, resulting in a considerable modulus or stiffness difference and, consequently, a decrease of $\kappa$ because of high Kapitza resistance.\textsuperscript{5} In addition, CNTs form bundles with tube-tube interfacial area inside the bundles; therefore, the CNT-latex interfacial area is lower than polymer melt composite case. With these contributions, the modulus mismatch would not be very high, leading to an improvement of $\kappa$. 
5.4 Conclusions

A comparison of thermal conductivity of polymeric composites with random and segregated carbon nanotube (CNT) networks has been made for both single-walled (SWNT) and multi-walled (MWNT) types. The control of nanotube network ordering has been achieved using latices with different glass transition temperature. Due to the excluded volume that polymer particles occupy, it has proved successful for latex technology to make percolation threshold significantly low in the range of 0.05-0.10 wt.% CNTs. Segregated networks offer a higher thermal improvement compared to the random case for both SWNTs and MWNTs. Such enhancement is the contribution of heat transfer governed by phonon scattering in materials. With random CNT networks, there are numerous disconnected junctions for heat carriers, impeding heat transport throughout the material. For the same type of latex used, the composites with SWNTs exhibit higher thermal conductivity, compared to MWNT cases, with the maximum enhancement of about 55% at room temperature and more CNTs are not necessary to be incorporated into the matrix because thermal conductivity drops at concentration above its percolation threshold. It is amazing that thermal conductivity of the latex cannot only be enhanced but also reduced when MWNTs have been included in the latex in a random fashion. With the ability to tune thermal conductivity via the variation of CNT type and content, latex host type, and surrounding temperature, such a composite could be a potential candidate for a wide range of thermal applications; for instance, polymer-based heat conductor or dissipater.
References


In this chapter, the composite of single-walled carbon nanotubes (SWNTs) and colloidal polymer under tensile load will be studied to understand the role of SWNTs as a filler material. A monolayer of the composite is investigated using Raman spectroscopy. The thickness of the composite monolayer being in the nanoscale range which negates the possibility to do tensile measurements on a single monolayer specimen. To mitigate these problems, it is necessary to have a thick polymeric substrate for this composite monolayer to sit on. The substrate, additionally, has to consist of identical colloidal polymer particles as in the composite monolayer so that, while being strained, both polymer substrate and composite monolayer stretch as much equally as possible.

In order to know how much the colloidal polymer can be stretched, tensile mechanical properties of latex substrates will be studied initially. Subsequently, the composite monolayers, which is deposited on top of the polymer substrate, will be investigated by means of different characterization techniques.

6.1 Background

There are several aspects to material mechanical properties: shear, bending, torsion, compression, tensile, creep, and stress relaxation behaviours. In this section, some general concepts of mechanical properties of polymers are provided, which are concentrated on tensile properties as we are only interested in carbon nanotube (CNT) role in nanotube-colloidal polymer composite under applied tension strain.
6.1.1 Tensile properties of materials

Stress and strain

A body is in a state of stress when there are external forces applied on it.\(^2\) There are two types of forces that can apply to a body: body forces, such as gravitational force which is proportional to the body’s volume; and surface forces, which are applied by neighbouring material and these forces are proportional to the surface area of the contact part. Generally, surface forces are much more prominent than body forces, thus it can be written as the following relationship with SI unit being Nm\(^2\). Stress, \(\sigma\), is defined as force, \(F\), acting per unit area, \(A\). At failure, the stress is known as the tensile strength. In addition, specific strength or tenacity is defined as strength divided by density.\(^1\)

\[
\sigma = \frac{F}{A}
\]  

(6.1)

![Figure 6.1. A force is applied on a surface at an angle \(\theta\) to the normal direction to the surface plane.](image)

In the general case, the force \(F\) does not have to be applied normally to the surface with an area \(A\) as shown in Figure 6.1. If the angle between force direction and the direction normal to the surface is \(\theta\), the force component applied in the surface plane is called ‘tangential’ or ‘shearing’ stress, \(\tau\), acting per unit area and can be written as follows:

\[
\tau = \frac{F \sin \theta}{A}
\]  

(6.2)
The stress acting perpendicularly to the surface is called 'contractile' or 'tensile' stress $\sigma$. The relation of tensile stress, surface area, and force acting normally to the surface is shown in equation (6.3).

$$\sigma = \frac{F \cos \theta}{A}$$ (6.3)

When a body is stressed, there is a change in body dimension, which is the consequence of particle separation at the molecular scale. The term 'strain' is used to define the change in size of a body.

**Tensile strain**

Forces applied on a body with unstretched length, $l_0$, cause a change in dimension of the body to its new length, $l$. The ratio of the dimension change to original length can be described as tensile strain, $\varepsilon$, as defined in equation (6.4).

$$\varepsilon = \frac{l - l_0}{l_0}$$ (6.4)

**Hooke's Law**

Hooke's Law is used to describe the stress-strain relationship for an elastic solid. It was first found experimentally and reported by Hooke in 1660 that, under applied strain, a body has its strain directly proportional to stress as in the following relationship.

$$\varepsilon \propto \sigma$$ (6.5)

In other words, this can be rewritten as equation (6.6).

$$\sigma = \text{constant} \times \varepsilon$$ (6.6)

A term 'modulus of elasticity' or 'Young's modulus' is used to define the constant in the above equation. In the Hookean region, where stress is proportional to strain, the Young's modulus (E) is actually the slope of the load-elongation curve. Stiff or hard materials have high E. On the other hand, materials with low E are categorized as soft materials. This
modulus is temperature dependent and is typically inversely proportional to an increase of
temperature. Based on equation (6.1) and (6.6), it can be rewritten engineering stress, or
specific stress, or conventional stress, as follows:

$$\sigma = \frac{F}{A_0} = E \frac{(l-l_0)}{l_0}$$  \hspace{1cm} (6.7)

Under applied strain, a change in length of a body is happening at the same time as a
change in cross-section. For elastic deformation, it is found that the term so-called
‘Poisson’s ratio’ ($\nu$) is constant, which is defined in equation (6.8).

$$\nu = \frac{(\Delta A / A_0)}{(\Delta l / l_0)}$$  \hspace{1cm} (6.8)

Where $\Delta A$ represents change in lateral dimension, $A_0$ is original lateral dimension, $\Delta l$ is
change in length, and $l_0$ represents original length. For a incompressible solid, $\nu = 0.5$. 3

Due to the change in cross-sectional area as the body is strained, stress applies on different
sizes of surface area as the body has changing dimension. Therefore, two terms are defined
for stress as follows:

conventional stress = \left(\frac{F}{A_0}\right)  \hspace{1cm} (6.9)

true stress = \left(\frac{F}{A_t}\right)  \hspace{1cm} (6.10)

Where $F$ is load at any extension, $A_0$ represents original area of cross-section, and $A_t$ is area
of cross-section under that load. Equation (6.9) is used for the case of cross-section that has
constant area while equation (6.10) is applied for the body with changing cross-sectional
area. However, for a low amount of strain, conventional and true stresses are similar to
each other. Another term relating to a true stress is called ‘stretch ratio’ ($\lambda$) or elongation
ratio expressed in equation (6.11). 1
Polymers can behave both as a viscous liquid and as a glassy solid depending on the conditions in which they have been processed. In particular, they may be soft or rigid depending on temperatures, applied strain rate, and strain amount. As a result, polymers are categorized as viscoelastic materials because they exhibit both the viscous properties of liquids and elastic properties of solids. Elastic and viscoelastic behaviours of polymers are shown in stress-strain curve in Figure 6.2. Area inside curve is the energy dissipated. Polymers with elasticity expand and contract linearly and in proportion to applied force. Polymers showing plasticity behaviour can be strained linearly at the beginning and further applied force contributes to non-linearly dimension increase. Upon relaxation, the polymers do not return to their initial dimension. For those with viscoelasticity, polymers exhibit similar behaviour to that of plasticity polymers but, at the end of relaxation, they can return to their original dimension.

\[ \lambda = \frac{l}{l_0} = 1 + \varepsilon \]  

(6.11)

**Figure 6.2.** Polymer behaviours upon loading and unloading cycle applied: (a) elasticity, (b) plasticity, and (c) viscoelasticity. Areas under the curves in (b) and (c) are energy dissipation.
Polymer behaviour at different temperatures is shown in Figure 6.3, which is the external load applied to a polymer specimen as a function of elongation or strain.\(^4\)

Figure 6.3. Polymer elongation behaviours under load applied at different temperatures. Temperature is increasing from A to B, C, and D, respectively. A: brittle fracture, B: ductile failure, C: necking, and D: rubber-like behaviour.\(^4\)

In Figure 6.3, temperatures become consecutively higher at A, B, C, and D, respectively. Polymer behaviours at different conditions can be separately considered as follows:

(i) Curve A: This curve shows load-elongation behaviour of a polymer at the temperature considerably lower than its \(T_g\). At this state, polymers are brittle and fractures can be formed. Therefore, the polymers are only able to suffer low applied strain only. Their failure normally happens at low elongation (about 10\%). This curve normally has a Hookean region, where load is linearly proportional to elongation, at the beginning of the curve.\(^1\) In other words, when load is removed, a material is able to return to its original dimension.

(ii) Curve B: At temperature slightly lower than the polymer’s \(T_g\), polymers behave like metals as they show ductility. Particularly, a yield point can be seen before their failure. When stress is removed, some deformation is permanent.

(iii) Curve C: As temperature scales up to slightly below the polymer’s \(T_g\), polymers exhibit metal-like behaviour as a yield point is present before
the stress level decreases to a constant stress region. Polymers also show a rubber-like state as stress applied is constant while strain increases. This region is called necking, which is associated with a thinning, where deformation can occur for about 300-1000%. After this necking region, further strain applied attributes to a polymer's stress increase until failure.

(iv) Curve D: At higher temperatures, polymers exhibit rubber-like behaviour and are able to undergo higher strain under a lower stress as seen in the case of curve D. Ruptures for this condition typically occur at high elongation of about 30-1000%.

Figure 6.3 can be also rewritten as stress and strain for vertical and horizontal axis, respectively. The area under the stress-strain curve indicates a material's toughness or work-to-break, which is defined as energy that the material can absorb from an external load before its failure. Therefore, brittle materials may possess low toughness. In contrast, ductile materials that exhibit necking behaviour are comparatively tougher than brittle materials due to their greater elongation region that increases the area under stress-strain curve.

6.1.2 Review of Raman spectroscopy studies of carbon nanotube composites under applied mechanical load

In the early 1990's, CNTs were first discovered and reported by Iijima et al. There have been several studies focusing on the synthesis and characterization of the materials to thoroughly understand their properties. With their uniquely high toughness, CNTs have been utilized as reinforcing materials in polymer matrices. To investigate the efficiency of CNT reinforcement, a method to monitor load transfer from the matrix to CNTs needs to be established. Raman spectroscopy is a technique sensitive to the vibrational modes of CNTs. It can be utilized to investigate CNT characteristics in a polymer matrix, CNT dispersion in the matrix, interaction between CNT fillers and the polymeric host, and the phase transition of polymers in the presence of nanotubes. The technique is also applicable to the monitoring of strained CNTs because, under strain, bond length, and thus inter-atomic force constants, between carbon atoms changes, resulting in
the change of tube interaction and different modes of vibration, thus a change in Raman signal emitted.\textsuperscript{12} Not only can Raman spectroscopy provide us with information about load transfer\textsuperscript{13} but such a principle can also be applied in ultra thin strain sensor applications for civil infrastructures.\textsuperscript{14}

With regard to the test specimen factors affecting high performance in matrix reinforcement is directly related to the degree of homogeneity in distribution of CNTs in the matrix. Standard means of preparing CNT-polymer composite specimens is blending CNT dispersions with a solution of polymer in solvent or polymer melt.\textsuperscript{12-13, 15} The resulting nanotube distribution in the polymer matrix is rather non-uniform with random directions of CNT orientation, resulting in Raman signals averaged from all tube orientations. Due to their randomly oriented arrangement, CNTs, at low content, do not form continuous networks throughout the whole bulk specimen. The networks can be more connected or continuous only when they are stretched or compressed, resulting in possible instability of mechanical properties as well as thermal and electrical properties under load applied. The approach to creating ordered continuous inclusion arrays in the matrix has been therefore developed later on.

There are a number of publications relating to Raman spectroscopy investigations of CNT-polymer melt composites.\textsuperscript{11, 13, 16-21} Ajayan et al. reported the mechanics of SWNTs embedded in epoxy matrix under a low magnitude of applied strain (~1.25%). Systematic downward shifts of G'-band was found as the composite was strained. The proposed explanations for this Raman shift are two folds: SWNTs are pulled out from their bundles and nanotubes carry external tensile load until they break. They described the possible reason as being the former. In particular, if each individual SWNT is strained, the G'-band shift would be more considerable while the shift is less than 2 cm\textsuperscript{-1} in their work. Additionally, the energy used to break individual nanotubes (~7 eV, where 1 eV = 1.602 x 10\textsuperscript{19} Joules, to break a covalent carbon bond) is higher than that (tenths of 1 eV) operating in a slippage mechanism. Therefore what happens in the composites is the sliding of individual SWNTs in the bundles, resulting in the limitation of load transfer from the polymer matrix to nanotube inclusions. It is also described that debundling of nanotubes upon tension causes the reduction of the stresses in the axial direction and contributes to increasing inter-tube spacing. The stiffness change of the bonds between SWNTs due to these mechanics then results in altered vibrations in the out-of-plane direction.
The composite of SWNTs and poly(vinyl alcohol) (PVA) was studied Wang et al. as well.\(^{19}\) In their work, they determined the reinforcing role of SWNTs in the polymer matrix and confirmed that nanotubes enhance the strength of the composite. Polarized Raman spectroscopy showed a high degree of orientation observed by the Raman intensity of the G-band was decreasing as the angle between the strain and polarization directions approach 90°. Low strains up to 0.9% were applied in two types of composite samples with random and highly ordered CNT orientation. Their results are in accordance with Ajayan's work witnessing that tensile stress causes a G'-band shifts to lower wave number. A linear downshift of this Raman mode is found in the elastic deformation region. In addition, it was stated that the steeper slope of G'-band Raman shift reflects better load transfer from the polymer matrix to nanotubes. The magnitude of their Raman shift was different from that of Ajayan's composite system, which may be due to different materials used that result in varied inter-tube interaction forces in nanotube bundles and the interaction between the nanotubes and the PVA host.

Load transfer from the polymer matrix to reinforcement materials was also studied by Zhang et al.\(^{17}\) In their work, the material under investigation was a composite of poly(vinyl alcohol) (PVA), poly(vinyl pyrrolidone) (PVP), sodium dodecyl sulfate (SDS), and SWNTs. Correlating mechanical properties with G'-band shift was again employed to monitor load transfer. The combination of these composite constituent makes load transfer feasible. Essentially, a downward Raman shift of about 15 cm\(^{-1}\) at ~45% strain was observed. This result shows a good agreement with Ajayan and colleagues in that the tensile load leads to a downshift of the G'-band. They describe that the G'-band shift curve has similar features as stress-strain curve. By applying comparatively higher strain to the composites, the downshift found in this work is higher than those in the reports of Ajayan et al. and Wang et al.

The similar trend of G'-band downward shift under applied stress was experimentally found by Zhao et al. as well.\(^{11, 15c}\) The composite of SWNTs and polyurethane acrylate (PUA) was investigated. In their findings, there were two regions of Raman wave number shift: the downshift with a high rate at low applied strain (up to 1.5% strain) and comparatively constant wave number region when higher strain was applied. Frogley et al., who were in the same research group with Zhao, also reported their results on a Raman study of SWNT-PUA composites.\(^{19}\) Again, a similar trend of Raman wave number
downshift was observed. In particular, the shift is linearly proportional to the strain applied till 1.5% strain and remains relatively constant under further tensile load. In these studies, there were transitions that shear stress cannot be transferred from the polymer matrix to nanotubes anymore. After this transitions, Raman wavenumbers were therefore constant.

In addition to studying Raman wave number shift of G'-band mode, the stress-strain behaviour can be assessed through the relative Raman intensity of the radial breathing mode (RBM) as well, since both G'-band and RBM are sensitive to strain. In other words, compressive and tensile stresses cause a change in resonance conditions, thus markedly modifying the associated resonant RBM frequency distribution. Their study reported in 2007 shows the relative intensity of peaks at 234 cm\(^{-1}\) and 268 cm\(^{-1}\) for a composite of SWNTs and epoxy. As the composite goes to a higher temperature, the peak intensity at 234 cm\(^{-1}\) decreases comparatively to the one at 268 cm\(^{-1}\). The explanation of this observation is that increasing temperature of the composite generates compressive stress on the nanotube bundles. Under this environment, vibrational frequency of atoms in nanotubes is close to resonance conditions for the peak at 268 cm\(^{-1}\) while it is further away in the case of 234 cm\(^{-1}\).

None of these literature studies illustrates the recovery of the composites using Raman spectroscopy. In this work we will use Raman spectroscopy to elucidate information about the stress-transfer and nanotube-polymer interactions in out CNT-colloidal polymer monolayers. Information is obtained even at strains of up to 250%. Stress-induced modifications to the Raman spectrum undergo complete reversibility after straining indicating almost-perfect recovery of composite.

Colloidal polymer or latex has been used as a template for the arrangement of numerous materials, including metal photonic crystals and CNTs. Recently, we reported a successful route of fabricating long-range CNT networks using latex particle assembly as a CNT network template. Such highly ordered networks are perfect for the Raman study of CNTs under strain as the networks become very well aligned along a particular, i.e. drawing, direction. With the technology to make monolayers of colloidal polymer with segregated SWNT networks wrapping around the particles, we previously made thermal actuators (see Chapter 4) which was built on the same technology we used before to make the bulk composite. In this chapter, the mechanical properties of composite
monolayer will be presented. We show that the networks are elastic although some in certain cases their behaviour is non-affine. Using a combination of Raman spectroscopy, scanning electron microscopy (SEM), and atomic force microscopy (AFM), we explain such elasticity by inter-tube van der Waals force and slippage in nanotube bundles. Raman measurements also reveal efficient load transfer from the polymeric template to nanotubes.

6.2 Experimental details

6.2.1 Materials

(a) Latex: The emulsion polymerized latex (NeoResins, the Netherlands) used in this work was a random copolymer consisting of butyl acrylate (BA), methyl methacrylate (MMA), methacrylic acid (MAA), and acetoacetoxyethyl methacrylate (AAEM) with the molar ratio of 36.7:50.3:3:10, respectively.

(b) CNT dispersion: High pressure carbon monoxide (HiPeo) synthesized SWNTs (Unidym Inc., CA, USA) were used as received for SWNT dispersion. To prepare a nanotube dispersion, deionised water was first mixed with a non ionic surfactant, Triton X-100 (Union Carbide Corp., TX, USA), in the weight ratio Triton X-100: water of 1:100 using a stirrer at 30°C for 20 minutes. SWNT powders were added to the solution (1 mg SWNTs: 1 g water) and probe-sonicated (Branson Sonifier 150, Branson Ultrasonics Corp, Danbury, CT, USA) for 10 minutes at an output power of 20 Watts.

(c) Composite dispersion: The prepared SWNT dispersion and as received latex dispersion were blended by probe sonication at 10 Watts for 10 minutes to obtain a composite dispersion.

6.2.2 Sample preparation

Because the thin composite film cannot be prepared as a free-standing specimen, there must be a substrate, with almost exactly the same mechanical property, underneath the monolayer film. The fabrication process in this work was as a result performed by coating thick latex substrates with a dispersion of SWNTs and the latex used as the substrate. A schematic representation of the brief procedure for sample preparation is shown in Figure 6.4.
Details of all procedures of sample preparation are as follows:

(a) Latex substrate preparation: To prepare a substrate for the composite monolayers, the latex dispersion was blended with an aqueous solution of Triton X-100
with the similar concentration of Triton X-100 used for a particular SWNT dispersion. The mixtures were then blended using a brief stir, poured into a polytetrafluoroethylene (PTFE) trough, and left at room temperature (22°C) for a few days to become dry polymer films. The film was subsequently cut into small pieces with the size of approximately 2.5 x 20 x 0.4 mm³.

(b) Coating composite monolayers on latex substrate: The SWNT-latex monolayers on latex substrate were fabricated by spin coating the composite dispersion on top of the substrate at the spin speed of 2 krpm for 10 seconds under room temperature.

(c) Stretching samples: The small pieces of substrates with SWNT monolayers on top were subsequently strained under a tensile load using a tensile apparatus (MicroSystems Texture Analyzer, Godalming, UK). The velocity of the strain deformation used was 0.5 mm/s. At the required strain, a sticky tape, which was attached on a metal stub, was attached to the stretched substrate while being drawn on the apparatus. The two ends of specimen were then cut and kept fixed at the back of the metal stub using another sticky tape to ensure that specimen relaxation is not allowed.

6.2.3 Analysis

AFM height and phase images were taken from an atomic force microscope (NT-MDT, Moscow, Russia) in intermittent contact mode with the use of gold cantilever. The force constant of the cantilever is 1.45-15.1 Nm⁻¹ and the resonant frequency is in the range of 87-230 kHz. The degree of order for latex particle arrangement was found using Fast Fourier Transform (FFT) analysis in NT-MDT SPM software. A Hitachi S-4000 field emission scanning electron microscope was used to take SEM images at an accelerating voltage of 4-6 kV without any metal coating. All Raman measurements were performed using a 473 nm excitation laser on the upright system of an NTEGRA Raman spectroscope (NT-MDT, Moscow, Russia) equipped with a 100x objective lens at room temperature. For each specimen, Raman spectra were taken three times to obtain the average value of Raman peak positions. However, to ensure that the laser does not damage the specimens, the adjacent Raman measurements were conducted after the previous one has been finished for a few minutes.
6.3 Results and discussion

6.3.1 Characterization of topography and mechanical properties of latex substrate

AFM was performed on a latex substrate specimen to investigate the order, topography, and latex bead arrangement pattern.

![AFM micrographs showing (a) topography and (b) phase of the unstrained latex substrate with no strain applied. (c) Stress-strain behaviours of the latex substrates made using the same amount of Triton X-100 as those used in 0.5 wt% (—) and 1 wt% (—) SWNT-latex monolayer fabrication.](image)

Figure 6.5. AFM micrographs showing (a) topography and (b) phase of the unstrained latex substrate with no strain applied. (c) Stress-strain behaviours of the latex substrates made using the same amount of Triton X-100 as those used in 0.5 wt% (—) and 1 wt% (—) SWNT-latex monolayer fabrication.

Figures 6.5 (a) and 6.5 (b) demonstrate AFM images of latex particles with almost perfectly ordered packing on the surface of the specimen. Each particle deforms from a sphere to a dodecahedron in the bulk, which appears hexagonal at the surface and packs with neighbour particles, forming a honeycomb-like pattern. With such a degree of order,
this latex is undoubtedly a promising template that could provide highly ordered networks of SWNTs embedded between latex particles which will be shown later on.

As can be seen 0.5 wt% of SWNTs provides a complete continuous nanotube networks in 3-D. Low SWNT amounts (0.5 and 1.0 wt% compared to latex solid weight) were added to be added into the latex matrix. The surfactant concentration (1 g/ml) in water is adopted which is similar to the recipe used previously. As a result, surfactant content has been prepared to be the same as those used in 0.5 and 1.0 wt% SWNT-latex composites. The substrates, with the presence of Triton X-100, were strained on a tensile apparatus from the original length to failure in order to find ascertain the stress-strain relationships. Stress-strain curves in Figure 6.5 (c) indicate the different mechanical behaviour of latex substrates with these two surfactant amounts. There is a high yield point in 0.5 wt% Triton X-100 sample, indicating that this substrate is plastically deformed and tougher than the sample containing 1 wt% Triton X-100 which has a lower area under the stress-strain curve. The substrate with a higher amount of Triton X-100 has a lower yield point and shows higher strain before failure, as seen from the longer plastic deformation region, due to more plasticization of the surfactant. It can be seen that the latex substrate containing a higher amounts of Triton X-100 possesses higher strain at failure as it can be strained up to almost 300 %. Therefore, this higher surfactant concentration was used to prepare SWNT-latex composite monolayers throughout this study. However, the maximum strain to be applied on the monolayer with this higher amount of Triton X-100 will be 250% since this strain is below the breaking point. The substrate coated by a monolayer of 1 wt% SWNT-latex composite was strained to different degrees: 50%, 100%, 150%, and 250% to monitor its mechanical behaviour.

6.3.2 Characterization of SWNT-latex composite monolayer with and without strain applied

Composite monolayer without strain applied
Figure 6.6. AFM (a) topography and (b) phase images, respectively, of 1 wt% SWNT-latex monolayer on polymer substrate. (c) SEM micrograph of 1 wt% SWNT monolayers on the latex substrate in (a) and (b). Note: SWNT bundles can be observed on the sample surface in (a) and (b).

AFM height and phase images of 1 wt% SWNTs in Figure 6.6 disclose identical hexagonal closed packing of latex particles shown previously in Figure 6.5. However, in some local regions, SWNT bundles can be revealed between latex particles and this is an indication that nanotubes are really accommodated at the latex interstitial sites. This observation corresponds to the SEM result in Figure 6.6 (c). Particularly, each hexagon size is roughly the same as that of latex hexagonal particles in Figure 6.6 (a) and (b). It is clearly seen that SWNT networks are highly ordered and uniformly distributed throughout the composite monolayer, enabling Raman and polarized Raman investigations effective for the strain-dependence study.

*Composite monolayer with strain applied*
The topography and corresponding phase images of the composite monolayer under strain is shown in Figure 6.7.

**Figure 6.7.** AFM topography (left) and phase (right column) images of 1 wt% SWNT-latex composite monolayers on top of the latex substrates strained to (a, b) 0%, (c, f) 100%, (g, h) 150%, and (i, j) 250%. (c) G-band mapping Raman image of the monolayers in (a). (d) close-up image of the selected area in (a) showing the ordered hexagonal SWNT networks embedded in latex matrix.
It can be seen from AFM micrographs that the composite monolayer is still ordered and the distribution is modified due to the deformation of the latex particles along the drawing direction. A few bundles of SWNTs are also revealed between latex particles in some regions of the specimen surface. Figure 6.7 (c), a Raman map of tangential mode (G-band) intensity, also shows hexagonal-like arrays of the composite in long-range order while the corresponding Figure 6.7 (d) is the close-up of Figure 6.7 (c), showing the size of hexagonal arrays whose size is nearly identical with that of latex hexagons. Nanotube orientation under 50% strain is displayed in Figure 6.7 (e) and 6.7 (f). This thin drawn composite layer cannot be investigated by SEM, especially at higher degree of strain applied, because thin SWNT networks on latex substrate are not electronically conductive enough, resulting in charging effect. The reason for this is more likely that, under this deformation, the percolation is reduced which leads to charging. In addition, tiny Raman signal is also detected.

Raman spectroscopy study of tangential mode (G-band)

Polarized Raman is a powerful technique for investigating the alignment of CNTs in a given composite. In this measurement, the 150%-strained specimen with 1 wt% SWNT networks on top is selected as the sample and placed on a Raman sample holder at a fixed position while the polariser of the instrument is rotated to different angles.

As shown in Figure 6.8 (a), the G-band peak, centred at 1589.45 cm\(^{-1}\), has lower intensity as the polariser is rotated to be perpendicular to the monolayer drawing direction. However, Figure 6.8 (b) indicates that the intensity found in the present study is not proportional to \(\cos^4\theta\) according to the previous report,\(^{25-26}\) where \(\theta\) is the angle between drawing direction and the polarization direction of the laser. The total Raman intensity of CNTs is a combination of the intensity from nanotubes at each angle (equation 6.12\(^{25}\)). The law expressing the \(\cos^4\theta\) dependence is actually for the Raman study of one-dimensional materials but, in the current work, the study is on nanotube bundles form arrays of distorted hexagons under strain and this is the reason for a disagreement of this law and experimental results.
Where \( I(\psi) \) is the total Raman intensity, \( \psi \) is the angle between fibre orientation and the orientation of incident polarized light, \( c \) is a parameter providing maximum Raman intensity when \( \theta = 0 \), \( F(\theta - \psi, \Delta) \) represents a distribution function of angular width determined by \( \Delta \). It is seen obviously that incident polarized light along CNT orientation gives rise to highest Raman intensity.

\[
I(\psi) = \int_{\psi - \pi/2}^{\psi + \pi/2} cF(\theta - \psi, \Delta) \cos^4 \theta d\theta
\]  
(6.12)

**Figure 6.8.** (a) Polarized Raman of 150%-strained 1 wt% SWNT/latex monolayers as the polarization direction and specimen-drawing direction are in angle of 0°, 15°, 30°, 45°, 60°, 75°, and 90° to each other. (b) Normalized Raman intensity of all peaks in Figure 6.8 (a) as the angle between strain and polarization directions, \( \theta \), varies.
To determine whether the monolayer on the substrate undergoes affine deformation or not, the AFM anisotropy of the strained bare substrate and composite monolayer has been calculated at the same tension from 20 latex particles. AFM anisotropy is defined as the ratio between the long axis to the short axis of each hexagonal latex bead. The experimental AFM anisotropy of a monolayer is plotted in Figure 6.9 against the extension ratio ($\lambda$), which is the ratio between final and initial length of a specimen. There is a slope of $1.24 \pm 0.10$ on this log-log plot. In addition, to compare to the values derived theoretically, $\theta$ which is a half of an angle at a corner of a hexagonal particle along the long axis is inserted in equation (6.13)** and plotted in the same graph as experimental Raman anisotropy.

$$\text{Raman anisotropy} = \frac{1 + \cos \theta}{2 \sin \theta}$$

(6.13)

where $\theta$ in the present work is the averaged value from AFM images obtained experimentally.
Figure 6.9. AFM and Raman anisotropies of specimens strained to different extension ratios: AFM anisotropy of the latex substrate with similar amount of Triton X-100 used in 1 wt% SWNT/latex dispersion (○), AFM anisotropy of monolayers made from 1 wt% SWNT/latex dispersion (△), Raman anisotropies of 1 wt% SWNT monolayers derived from equation (6.13) (□) and from the experiment (○). A comparison of AFM anisotropies is presented by black dashed line (the present work) and grey solid line (Jurewicz et al.’s work\textsuperscript{27}).

Affine deformation is used when macro deformation is equal to particle deformation in a material under strain applied. In other words, a deformation is called affined when molecular level strain is identical to strain applied in macroscopic scale. Jurewicz and colleagues\textsuperscript{23} explained that, if the particle volume is conserved under external strain applied, the ratio of dimensions of ellipsoidal particle along major to minor axis follows a power of 1.5 as derived briefly by Figure 6.10 and equation 6.14. It can be seen that the monolayer in this study is non-affine as the slope of the AFM anisotropy is not equal to 1.5. Nonetheless, the substrate and the composite monolayer provide equivalent AFM anisotropy, suggesting an accordance of the deformation of latex substrate and composite monolayer.
Figure 6.10. Schematic showing affine deformation of a particle. R and \( \lambda \) represent the radius and extension ratio of the particle, respectively.

Under particle deformation mechanism, volume conservation makes the particle radius \( R \) to be \( \lambda R \) and \( R/\lambda^{1/2} \) for major and minor axis, respectively. The ratio between the major to the minor axis can then be written in equation 6.14. This affine deformation ratio is therefore proportional to extension ratio \( \lambda \) to the power of 1.5.

\[
\frac{\lambda R}{R/\lambda^{1/2}} = \lambda^{3/2}
\]

(6.14)

Non-affine behaviour for the composite can be explained as follows: Latex particles form dodecahedral structure. With the imperfection in shape that each dodecahedron has, facets of each dodecahedron are not identical. Under tensile stress, forces acting on these facets are then not uniform, resulting in facet position shifts. The facets are not initially stable. As a result, they rearrange themselves, leading to residual strain gradients being applied to surrounding particles. This causes the movement or slippage of the particles instead of ideal affine deformation during external strain applied. Besides single particle slippage, there are also several other possible slippage mechanisms: the slippage of particle rows and the slippage of the crystalline grain boundaries.

Molecular orientation of SWNT networks has been investigated through Raman anisotropy measurement. The ratio of G-band intensities where the laser polarization direction is parallel and perpendicular to strain direction is defined as the experimental Raman anisotropy. These values from the experiment at each tension for the 1 wt% SWNT specimen are plotted as black dots in Figure 6.9. It can be seen that the anisotropy from Raman experiment and that derived geometrically match each other at most strain percentages. The difference of AFM anisotropy in the present work and that in Jurewicz et
al.'s work could be because different types of latex were used, causing a different interaction between particle-particle as well as particle-surfactant/CNTs.

*Raman spectroscopy study of the second order of tangential mode (G'-band) wavenumber shift*

The Raman shift of G' band has been previously used as an indicator of polymeric matrix-CNT load transfer and nanotube mechanical deformation.\(^\text{10, 12, 15c}\) This G' band shift is more obvious and apparent compared to shifts associated with RBM. In the present work, three measurements have been taken for the averaged wavenumber, ranging from 2672 to 2680 cm\(^{-1}\), at each strain and then plotted in Figure 6.11. The experiments are performed on specimens made using 1 wt% SWNTs. The features of the monolayer drawn beyond its failure (so called “relaxed” samples in this report) is also shown for comparison.

According to Frogley et al., SWNTs under higher compression tend to have higher G' band wavenumbers\(^\text{19}\) because nanotubes are compressed and are closer to each other. This results in increased attractive forces between tubes and causes a modification to the relative atomic vibrations, thus an associated shift in modal frequency.\(^\text{16-17}\) In this report, nanotube bundles are stretched and the opposite outcome, i.e. a downshift is observed. The results reported here agree with previous work in that tensile stress causes a G'-band downshift of SWNTs.\(^\text{16-17, 20-21, 23, 33}\) However, the magnitude of the shift depends on the interaction between nanotubes and surrounded polymeric host. There is an effect on both individual nanotubes and bundles, causing a higher compression force from the surrounding latex matrix on the radial direction of tubes. The effect of tension along tubes overcomes that of radial compression for the G' mode as this mode does not correspond with the tubes axial vibration. Therefore, an up shift due to compressive stress has not been revealed for the G' investigation.
Figure 6.11. $G'$-band shift of SWNTs in the composite as the monolayers, made using 1 wt% SWNT dispersion, are strained at different tensions ($\circ$). Wavenumbers of relaxed monolayers of the same specimen after drawn to failure ($\bullet$). Blue dashed lines are eye guides which are linear fit of the data points at 0, 50, 100% strain and at 100% up to higher strain. The schematic is for side view of (a) nanotube bundles with no strain applied, (b) stretched tubes in the bundles under tension, and (c) loose bundles due to nanotube slippage. Grey arrows represent the direction of strain applied to the bundles. Yellow arrows display the slippage of individual SWNT.

It can be also observed from the curve that the downshift is linearly proportional to the tension up to 100% strain. This implies that the applied tensile stress is transferred to individual SWNTs at the beginning up to around 100% strain and, subsequently, tube slippage happens within the bundles, causing a slight downshift as described schematically in Figure 6.11 (a-c). The lower slope, at 100 - 250% strain, stems more likely from
lower deformation of CNT bundles as a certain amount of applied tension is shared to nanotube slippage mechanism rather than the mechanism of deformation along axial direction alone.\textsuperscript{22} For the $G'$ peak positions of the relaxed sample, the 1 wt\% SWNT specimen shows elastic behaviour even after drawing to tensile loads as high as 250%. This wavenumber recovery is the contribution from van der Waals force between nanotubes in the bundles.\textsuperscript{30-31} The density of individual nanotubes is high enough to create an attraction force between the tubes that pulls themselves back into the bundles again. This observation corresponds with the results reported by Wood \textit{et al.}\textsuperscript{22} in that CNT bundle deformation behaves mechanical reversibility and elasticity.

Before nanotubes slip past each other, SWNTs can be strained up to approximately 100 % which is found to be considerably higher than the strain value (5.3\%) reported by Yu \textit{et al.}\textsuperscript{37} The reason for this is that tensile load is not only applied on local nanotubes but it has also been shared between SWNTs and latex templates in the composite monolayers homogeneously due to the long-range uniformity of hexagonal CNT networks that work as tension or energy dissipators.\textsuperscript{32} In addition, the findings here can also be described in the same way as Farr's work.\textsuperscript{33} Particularly, the bundle or rope formation of individual tubes strengthens the whole system and improves the ability to suffer higher tensile load. In bundle formation, SWNTs sometimes twist around each other as wire rope.\textsuperscript{34-35} Compared to a straight bundle, twisted or woven nanotube bundles exhibit significantly higher tensile load transfer.\textsuperscript{34,36} The nanotube bundles in the present work are likely to be formed as tight rather than loosely packed bundles since all nanotubes are accommodated to latex particles' interstitial sites. Under such a restriction in space CNTs can reside in, short-range van der Waals forces between tubes gather nanotubes together and form as bundles.
Raman spectroscopy study of relative intensity change in radial breathing mode (RBM)

Figure 6.12 demonstrates the dependence of strain on the relative intensity of RBM modes, the first order Raman mode stemming from an axial vibration of nanotubes in the range of 100-500 cm\(^{-1}\). The peak shift of the RBM is not as apparent as the case of the G' band but the relative intensity of the peaks at around 201 and 227 cm\(^{-1}\) has changed and can be observed. The intensity of the peak at 227 cm\(^{-1}\) is fixed constant in order to see the intensity change of the peak at 201 cm\(^{-1}\). As the SWNT networks are under higher tensile load, the peak positioned at 201 cm\(^{-1}\) tends to attenuate as seen quantitatively from Table 6.1 and Figure 6.13. Van der Waals interaction between tubes could contribute to the “aggregation peak” positioned at 227 cm\(^{-1}\). Nanotubes in the bundles have strong van der Waals force at all states no matter how strain applied. Under strain, van der Waals force is probably “turned on”, suggesting that the tubes must be closer to each other as they undergo higher compressive stress from latex particles surrounded. This is why the “aggregation peak” has increasing intensity under higher applied strain. Additionally, the decrease of the peak centered at 201 cm\(^{-1}\) is the result of the compressive stress from the matrix that prohibits tube axial vibration. The individual tube slippage, however, in this case does not affect tube radial vibration significantly and, therefore, should not be the potential explanation for this RBM observation.
Figure 6.12. RBM of 1 wt% SWNT as a function of strain: 0%, 50%, 100%, and 150%. Schematic explains schematic illustration for top view of (a) nanotube bundles with no strain applied, (b) nanotube bundles under compressive stress from surrounding latex matrix, and (c) the bundles at higher compressive stress under higher strain applied on the composite. Grey arrows represent the direction of compressive stress applied from the matrix and the arrow size represents the amount of compressive stress applied.
Table 6.1. Raman intensity ratio of RBM peaks at 201 to 227 cm\(^{-1}\).

<table>
<thead>
<tr>
<th>Strain (%)</th>
<th>Intensity ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.92</td>
</tr>
<tr>
<td>50</td>
<td>1.33</td>
</tr>
<tr>
<td>100</td>
<td>1.07</td>
</tr>
<tr>
<td>150</td>
<td>0.23</td>
</tr>
</tbody>
</table>

Another way in explaining such an observation on RBM relative Raman intensity can be expressed according to Eklund et al.\(^{31}\) In particular, the peak positioned at 201 cm\(^{-1}\) disappearance can be described that a distortion of nanotube bundles in radial direction (Figure 6.14) because of compressive stress causes a reduction of the electronic resonance in the Raman scattering. Under such a compression, there is a decrease in bond lengths between carbon atoms on nanotube surface, leading to resultant bond stiffening and, thus, a change in Raman vibration.
Figure 6.14. Schematic representing a hexagonally distorted cross section of a nanotube bundle due to axial compressive stress from surrounding polymeric matrix. Arrows are applied compression.

Investigation of composite monolayer relaxation after being drawn to failure

AFM cannot provide much information about the SWNT networks of unstrained specimen since nanotubes are buried in interstitial sites between latex particles. However, this characterization technique is surprisingly useful in studying the nanotube networks drawn to failure. In particular, Figure 6.15 reveals hidden nanotube bundles after the composite monolayer is broken at its failure compared to the original specimen with no strain applied.

High resolution AFM images obviously show disruption to the packing of discrete nanotube bundles. Only a few tubes can be seen in ring-like confirmations wrapping around latex particles for the unstrained monolayers (Figure 6.15 (a, b)). For the monolayer after failure, most nanotubes are still in their original sites, between latex particles as observed from Figure 6.15 (c, d). Nevertheless, some coil-like tubes are unveiled on the monolayer surface which have apparently been displaced from the original interstitial sites surrounding latex particles. The same explanation can be adopted here to understand the AFM results. Van der Waals forces between neighbour tubes are high as nanotubes form bundles. Therefore, this force pulls back the tubes, and thus latex particles, to be at almost their original configuration. On the other hand, over some local regions, tensile load overcomes intertube van der Waals interaction, resulting in the break down of the bundles. Individual nanotubes are no longer in the bundles and remain at the length to which they were drawn as if they have a length memory. When the monolayers are relaxed back to no-
strain condition, these tubes cannot fit the same sites, thus forming as bending bundles (S-shape or coil-like) out of the latex interstitial places.

Figure 6.15. High resolution AFM topography (left) and phase (right column) images: (a, b) unstrained 1 wt% SWNTs and (c, d) “relaxed” 1 wt% SWNTs.
6.4 Conclusions

The technology for preparing ordered SWNT-polymer composite monolayers has been developed using the assembly of colloidal latex particles as the template for SWNT network formation. The latex is applied as the template because they form a highly ordered hexagonal structure in which nanotubes can sit. The mechanical property of the latex mixed with Triton X-100 surfactant shows elasticity which is suitable for the latex being used as a substrate for nanotube-latex composite monolayer for mechanical property study of the role of SWNTs as reinforcing materials. Polarized Raman measurement has proved a good alignment of stretched nanotube networks embedded between latex beads even at high tensile stress up to 250%. AFM anisotropy suggests that the composite monolayer and latex substrate are strained almost equally. Likewise, experimental Raman anisotropy tends to agree with that derived theoretically for affine deformation. Thanks to Raman sensitivity of SWNTs to tensile and compressive stresses, a G'-band shift and RBM relative intensity variation can be observed. The initial tensile load contributes to the strain of the nanotubes up to a certain tension and further tensile stress results in the slippage of nanotubes passing each other, i.e., debundling of individual SWNTs from their bundles. While being strained, nanotubes at the same time are pressed axially from the latex host, resulting in the prominence of the aggregation peak. The monolayer exhibits elastic behaviour, i.e. SWNTs are able to move back in place between latex particles, because there is a strong van der Waals force pulling nanotubes back to the bundles when the specimen is relaxed.
References


Chapter 7

Summary and Future Work

7.1 Summary

The present study has been performed to fabricate and characterize a nanocomposite system containing CNTs and colloidal polymer. There were three main property investigations of the composite: thermal expansion, thermal conductivity, and mechanics of the composite under tensile strain.

In the study of thermal expansivity of the composite, the best method to prepare hydrophilic substrates was initially researched. UV-Ozone cleaning was found to be a reproducible and simple route to introduce a high degree of hydrophilicity to a silicon wafer substrate. The CNT-latex composite dispersion was then prepared by blending a dispersion of surfactant-dispersed CNTs with a latex dispersion. The composite films were made as a particle monolayer, whose thickness is about 180 nm, on a substrate since the composite is aimed to be used in nano-scale applications. Spin coating was applied to prepare thin films because this technique is fast, simple, and up-scalable. Actuation behaviour of the films has been monitored using ellipsometry as it is non-invasive and very sensitive in detecting small film thickness changes. Upon annealing, the composite films exhibit thermal expansion behaviour while the pristine polymer film shows film flattening. Thermal expansivity of the composites can be more pronounced with increasing content of CNTs in the films. Such a phenomenon resembles electrical percolation. In particular, higher amounts of CNTs forms more complete nanotube networks between latex particles. Because the CTE of SWNTs is much lower than that of polymeric materials, CNT networks act like rigid belts encircling each colloidal particle in the film plane. With this confinement, the polymer is not able to expand laterally along the film plane. During heating, the polymer is forced to expand in the direction normal to the film plane only, resulting in a significant enhancement of CTE of the polymers. CTE in the confined case, which is in a CNT-latex composite, has been found to be approximately three times that of
the CTE in the unconfined case. Essentially, an isotropic material expands in three dimensions but, under restriction that allows polymer to expand in only one direction, a volume increase in the other two dimensions has to be transferred to the direction with no confinement. As a result, a three times increase in linear thermal expansion has been observed in the film thickness of nanocomposite films in the present study.

Thermal properties have been further studied with a focus on thermal conductivity of the CNT-polymer composite systems containing segregated and random CNT networks. The segregated CNT arrays were made by using high $T_g$ latex as the composite's matrix. On the other hand, latex with a low $T_g$ was used to create random networks. The particles are able to coalesce at room temperature; therefore, nanotubes can go inside latex particles and form random networks that are not ordered throughout the composite. Heat can be transported throughout the composite via a uniform segregated path, hence exhibiting high thermal conductivity. In contrast, phonon transport is hindered by numerous disconnected junctions in the composite containing random nanotube networks, leading to resultant low thermal conductivity. It has been also found in the present work that SWNTs offer higher composite thermal conductivity compared to the MWNT case. This observation may be described by the intrinsic ultra-high thermal conductivity of SWNTs. Thermal conductivity cannot only be enhanced but also can be reduced as well when MWNTs were incorporated into soft latex. These results demonstrate the ability to tune thermal conductivity by changing the polymer matrix’s $T_g$, nanotube content, and nanotube type. The composite system containing segregated SWNT networks offers more than 50% enhancement in thermal conductivity and this is found to be higher than the cases of the composite with random SWNT arrays, the composite with MWNT random networks, and the composite with MWNT segregated networks. Another advantage of using latex technology is that the percolation threshold can be achieved at extremely low CNT content (0.05 – 0.10 wt%) due to colloidal assembly that accommodates CNTs in an ordered fashion within their comparatively large excluded volume.

Furthermore, mechanical properties of CNT-latex composites have been investigated. The study was concentrated on the role of CNTs in composite recovery after it is strained. Similar latex technology has been adopted to prepare composite monolayers on latex substrates. Initially, it was found that surfactant allows latex films to accommodate large applied strain. The composite monolayer deformation under a tensile load has been found
to be uniform as observed from AFM micrographs. However AFM can show only uniform
deformation of colloidal particles. To investigate CNT network deformation, polarized
Raman measurement has been performed. For a strain of 150%, a composite monolayer
containing 1 wt% SWNT exhibits a decrease in G-band intensity, reflecting highly oriented
nanotube networks along the tensile load direction. In addition, Raman and AFM
anisotropies are in accordance, implying that tensile stress applied on the macroscopic
scale can be actually transferred to nanotubes in the nano-scale. High downshift rate of G'-
band at low strain suggests that SWNTs in their bundles are strained since this Raman
mode is associated with atomic vibration along the axial direction. Further strain applied
results in slippage of individual nanotubes. It is not a tube-breaking process because the
energy used to break CNTs is much higher than the energy employed in sliding nanotubes
past each other. After the composite monolayer is drawn past the failure and let go, the G'-
band spectrum moves back to almost the same wavenumber as the composite before being
strained. This result implies the recovery of composite although it is drawn up to more than
250%. The explanation of this recovery is the back slippage of SWNTs to their original
position in the bundles because of the attractive van der Waals interaction between tubes.
While nanotubes slide back to their bundles, they pull the whole nanotube networks back
as well and, hence, colloidal particles that are surrounded by nanotube networks. The
dimension in the direction perpendicular to tensile load direction is decreasing as higher
strain is applied to the composite monolayer. In particular, there is higher compressive
stress applied on the radial direction of nanotube bundles. Being associated with atomic
vibration in the radial direction, RBM signal change has been detected as a change of
relative intensity of the main RBM peaks. The explanation is that, in the direction
perpendicular to strain direction, there is higher compressive stress applied on the
composite, thus higher stress applied on the radial direction of aligned nanotubes, while the
composite is under higher strain. This higher compressive stress applied in the radial
direction of nanotubes causes a restriction of atomic vibration in this particular direction.
7.2 Future Work

Nowadays, there are several available techniques to prepare monolayer films on a solid substrate. One interesting method is wet-chemical film deposition in vertical direction since it is up-scalable, simple, and economical as the process can be conducted at room temperature and pressure. Well-know techniques are, for example, Langmuir-Blodgett and dip-coating. Applying these methods with optimized dipping parameters to CNT-latex composite dispersions, one will be able to fabricate composite monolayer films with highly ordered packing of polymer particles. Compared to the vertical dipping methods, spin-coating has a drawback of material waste as most composite dispersion is dispersed by centrifugal force at high spin speed.

The future work for the study of composite coefficient of thermal expansion could be varying colloidal polymer size to confirm the proposed thermal expansion model with rigid nanotube belts. Particularly, bigger latex particles could be added to the nanotube dispersion and the measurement should be aimed to determine an incremental response in thermal expansivity. Eventually, the relationship between colloidal particle size and thermal expansivity may be created in order to search for an optimal particle size that could offer the highest thermal expansion of the CNT-latex composite films. However, it was found elsewhere that small latex particles (~50 nm) are not able to create continuous honeycomb-like structure of CNTs. The possible reason for this relates to the large persistence length and the limitation of CNT flexibility to encircle nanospheres. Therefore, utilizing small polymer particles instead of big ones or adding the small particles to the big ones would reduce thermal expansivity because nanotube belts could not be perfectly formed. In particular, polymer does not have to expand in only one particular direction. A restriction in utilizing the present composite system is due to its non-reversible actuation behaviour as observed that the film thickness before and after annealing is not identical. To enable the composite for wider actuation applications, thermally-reversible polymer covered by a plasticized shell could be used instead of the latex used in the current study. In such a core-shell structure, polymer chains could return to their original structure as the temperature is decreasing. CNT belts will act like an obstacle for polymer particles to expand in the film plane. The polymer and its shell will expand upon annealing and contract while cooling with similar initial and final thicknesses. This idea can be illustrated in Figure 7.1.
Figure 7.1. Schematic representation of CNT composite film containing a core-shell structure polymer. The shell is expandable while being heated and contractible while being cooled. The polymer particle consists of thermally expandable and contractible chains. At the final state (polymer-chain relaxation), film thickness is similar to that before heating.

Thermal conductivity of a composite depends on properties of both matrix and filler. Changing a composite’s constituents will definitely cause a different thermal conductivity. The future work for this study is to vary colloidal particle size, which will alter the density of CNT networks in a unit volume of composite. Different observations will be obtained due to a change of the ability to conduct heat per unit volume. Furthermore, denser nanotube networks may result in a variation of phonon mean free path that can contribute to phonon scattering. In our previous report, it was found that the use of non-ionic surfactant, Triton X-100, offers a nearly perfect CNT honeycomb-like structure. However, as described previously in chapter 5, Kapitza resistance contributes to a great reduction of thermal conductivity. By absorbing on nanotubes, different types of non-ionic surfactants should cause increasing or decreasing thermal conductivity and this could be another future work associated with tuning thermal conductivity through choices of
materials at interface between filler and matrix. In addition, using longer nanotubes will also affect heat carrier mobility because phonons are able to travel through long tubes continuously without any obstacles at nanotube junctions, hence having higher thermal conductivity compared to the case of the composite containing short CNTs. Besides the incorporation of CNTs and colloidal polymer, such latex technology could be further applied in other composite systems. One carbon-based nanomaterial that possesses markedly high thermal conductivity is graphene, whose thermal conductivity is experimentally measured about 5300 W/m-K. Comparing this value to experimentally found thermal conductivity of individual SWNTs, which is about 3500 W/m-K, it can be seen that graphene is a promising nanomaterial to be incorporated into latex matrix for thermal management.

Elasticity of the composites is another advantage of the CNT-latex system in the current work, as elastic and recovery properties lead to wider mechanical applications. Essentially, one could have a stretchable material with high thermal conductivity and thermal expansivity. Carbon nanotube content higher than 1 wt% used in the present work could be applied to the latex matrix in order to study the dependence of CNT content and maximum strain before failure. In addition, varying CNT content in the composite will also provide the information about higher or lower Raman wavenumber shift. More obvious Raman shifts will be useful in stress/strain detectors for some applications; for example, stress self-monitoring of building infrastructure. One practical future work that could be performed in our laboratory is a comparison of the maximum strain of two different nanocomposite systems: composites containing CNT segregated networks fabricated by latex and composite with random CNT orientation made with a polymer melt. With an identical amount of CNTs in the matrix, the same sonication time and power, and a similar film fabrication method, the composite system that could undergo higher applied strain will be revealed. The one with higher strain before failure tells us that higher tensile load can be transferred from polymeric matrix to CNTs and this nanocomposite material is applicable to mechanical applications that need material high strength. The predicted trend is that our composite with CNT segregated networks will exhibit the ability to undergo a higher tensile load because CNT networks distribute throughout their latex host. As a result, the external load is transferred homogeneously to the filler phase. Moreover, nanotube networks via latex assembly are in bundles. Besides the energy to strain nanotubes, some additional energy is required to debundle tube entanglements in the
bundles. In contrast, the tensile load can be transferred to local regions of random CNT arrays because the networks do not distribute orderly throughout the matrix. Therefore, nanotube filler phase is locally broken and tensile load could not be transferred significantly to nanotubes anymore. A comparison on using long and short nanotubes is another practical future work as long tubes are prone to cause more tube entanglement. Latex particle size variation could also be a potential future work to investigate the ability of the composite to respond to tensile stress. Particularly, large colloidal particle size offers a low density of CNT networks per unit volume, resulting in possible lower strain at failure that the material could suffer. Ultimately, stress transfer depends on the interface between filler and matrix. Future work could be performed to study whether there is slippage at the interface or not.
7.3 Publication List Associated with The Work of This Thesis

7.3.1. Publication from Chapter 4 of this thesis: Thermal Expansion of Single Walled Carbon Nanotube-Colloidal Latex Composite Monolayer Thin Films


7.3.2. Publications from the work performed with colleagues


References


