



UNIVERSITI PUTRA MALAYSIA

***MECHANICAL AND THERMAL CHARACTERIZATION OF
MULTISCALE CARBON NANOTUBE POLYPROPYLENE
AND EPOXY COMPOSITES***

SAEED RAHMANIAN

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**MECHANICAL AND THERMAL CHARACTERIZATION OF
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AND EPOXY COMPOSITES**

By

SAEED RAHMANIAN

**Thesis Submitted to the School of Graduate Studies, Universiti
Putra Malaysia, in Fulfillment of the Requirements for the Degree of Doctor of
Philosophy**

April 2015

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DEDICATION

To my precious Father and Mother

To my truehearted wife

To my cute son



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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

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SAEED RAHMANIAN

April 2015

Chair: Suraya Abdul Rashid, PhD

Faculty: Engineering

Different types of multiscale fillers were fabricated through growing carbon nanotubes on short fiber and microparticles. The fabricated fillers were incorporated with both thermoplastic and thermoset polymers to evaluate their reinforcing efficiency. First, dense carbon nanotubes (CNTs) were grown uniformly on the surface of short fibers to create multiscale fibers by catalytic chemical vapor deposition. Short fiber reinforced polypropylene composites were fabricated using the multiscale fibers and compared with composites made using neat fibers. Tensile, flexural and impact properties of the composites were measured, which showed evident enhancement of more than 30% in all mechanical properties compared to neat short fiber composites. SEM micrographs of composite fracture surface demonstrated improved adhesion between CNT-coated fiber and the matrix.

To evaluate the effect of multiscale fillers on thermoset matrix, CNT and CNT-short carbon fibers (CSCF) were incorporated into an epoxy matrix to fabricate a high performance multiscale composite. The multiscale composites revealed significant improvement of more than 35% in elastic and storage modulus, strength as well as impact resistance in comparison to CNT-epoxy or CSCF-epoxy composites. An optimum content of CNT equal to 0.3 wt.% was found which provided the maximum stiffness and strength. The synergic reinforcing effects of combined fillers were analyzed on the fracture surface of composites through optical and SEM.

Another multiscale filler was fabricated through growing CNT on silica microparticles. The CNT-silica fillers were incorporated within polypropylene (PP) as well as epoxy matrix. In spite of the inclusion of multiscale fillers up to 2 wt.%, the reological behaviors of nanocomposites were comparable to the pristine matrix.

An improvement by more than 35% was achieved for elastic modulus and tensile strength of nanocomposites, which was discussed by employing micromechanical modeling approaches. The strengthening effects of CNT-silica reinforcement on impact strength of PP or epoxy was revealed by impact tests and was illustrated through fractography of nanocomposites.

A micromechanical model was employed to estimate the elastic modulus of multiscale fillers reinforced composites. In this model several effective parameters on the reinforcing role of nanotubes were considered to result in an appropriate estimation.



Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PENCIRIAN MEKANIKAL DAN TERMAL KOMPOSIT POLIPROPILENA DAN EPOKSI NANOTIUB KARBON BERBILANG SKALA

Oleh

SAEED RAHMANIAN

April 2015

Penyelia: Suraya Abdul Rashid, PhD

Fakulti: Kejuruteraan

Beberapa jenis pengisi berbilang skala telah dihasilkan melalui penumbuhan nanotub karbon pada gentian pendek dan mikropartikel. Pengisi yang dihasilkan telah ditambah dengan polimer termoplastik dan termoset untuk menguji kecekapan pengukuhan. Pertama, nanotub karbon padat (CNTs) telah dihasilkan dengan sekata pada permukaan gentian pendek untuk membuat gentian berbilang skala dengan pemendapan wap kimia berpemangkin. Komposit polipropilena yang diperkukuhkan dengan gentian pendek telah dihasilkan menggunakan gentian berbilang skala dan dibandingkan dengan komposit yang dibuat dengan gentian kemas. Ciri-ciri ketegangan, kelenturan dan impak komposit telah diukur dan menunjukkan peningkatan jelas ciri-ciri mekanikal melebihi 30% berbanding dengan komposit gentian pendek kemas. Mikrograf SEM permukaan patah komposit yang dibelah menunjukkan pelekatan yang lebih baik antara gentian yang disalut CNT dengan matriks.

Bagi menilai kesan pengisi berbilang skala pada matriks termoset, CNT dan CNT-gentian karbon pendek (CSCF) telah ditambah ke dalam matriks epoksi untuk menghasilkan komposit berbilang skala yang berprestasi tinggi. Komposit-komposit tersebut menunjukkan peningkatan lebih daripada 35% dalam modulus elastik dan simpanan, kekuatan dan daya tahan impak berbanding dengan komposit CNT-epoksi atau CSCF-epoksi. Kandungan optimum CNT yang bersamaan dengan 0.3 wt.% didapati memberi kekerasan dan kekuatan yang maksimum. Kesan pengukuhan sinergistik pengisi-pengisi yang telah digabung dikaji dengan menganalisa permukaan patah komposit yang dibelah menggunakan SEM dan mikroskopi optikal.

Sejenis lagi pengisi berbilang skala telah dihasilkan melalui penumbuhan CNT pada mikropartikel silika. Pengisi CNT-silika telah digabung dengan polipropilena (PP)

dan matriks epoksi. Walaupun dengan penambahan pengisi berbilang skala sebanyak 2 wt.%, ciri-ciri reologi nanokomposit adalah hampir sama dengan matriks tanpa sebarang tambahan. Peningkatan melebihi 35% telah dicapai untuk modulus elastik dan kekuatan ketegangan nanokomposit yang diperoleh dengan menggunakan pendekatan secara pemodelan mikromekanikal. Kesan pengukuhan CNT-silika pada kekuatan impak PP atau epoksi telah ditunjukkan dengan ujian impak dan digambarkan melalui patahgraf nanokomposit.

Model mikromekanikal telah diggunakan untuk menganggar modulus elastik komposit yang diperkukuh dengan pengisi berbilang skala. Dalam model ini, beberapa parameter yang berkesan dalam peranan pengukuhan nanotiub telah dipertimbangkan untuk memberi anggaran yang tepat.



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Engineering
Putra Malaysia
examiner)

Leman, PhD
Professor
Engineering
Putra Malaysia
examiner)

Wu, PhD
Engineering
University
and Technology
examiner)

Zulfahrain Z
Professor
Sci

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This thesis was submitted to the Senate of Universiti Putra Malaysia has been accepted as fulfillment of the requirement for the degree of Doctor of Philosophy. The members of supervisory committee were as follow:

Suraya Abdul Rahid, PhD

Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Chairperson)

Rizal Bin Zahari, PhD

Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Member)

Edi Syams Zainudin, PhD

Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Member)

BUJANG BIN KIM HUAT, PhD

Professor and Dean
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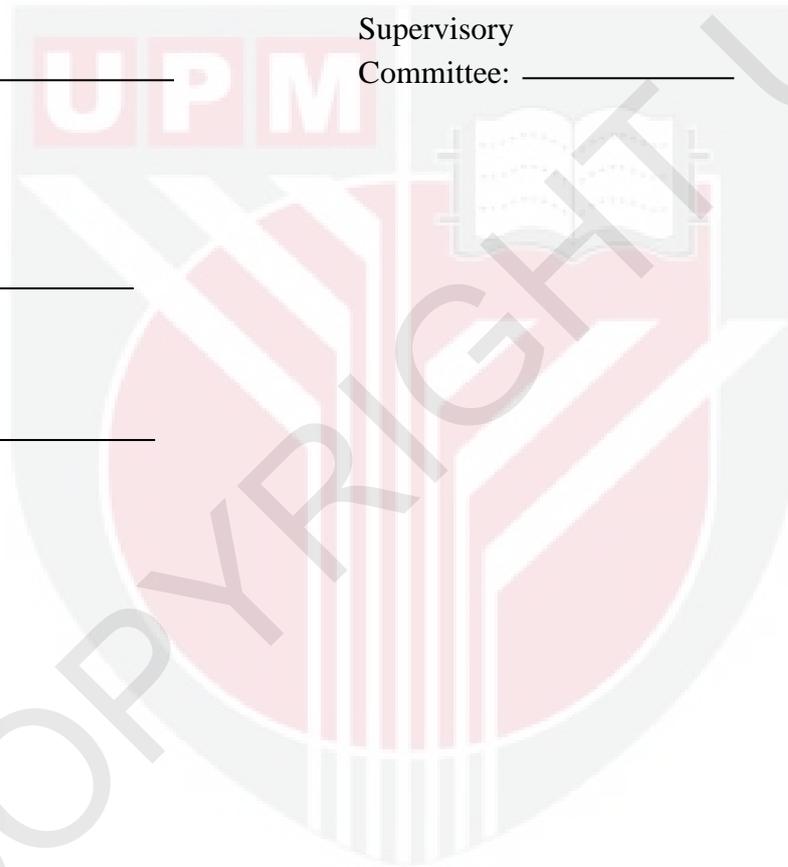


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LIST OF ABBREVIATIONS

1-D	Uni-dimensional
2-D	Two-dimensional
3-D	Three-dimensional
CF	Carbon fiber
CF/Epoxy	Carbon fiber reinforced epoxy
CF/PP	Carbon fiber reinforced polypropylene
CNT	Carbon nanotube
CNTs	Carbon nanotubes
CNT-CF	Carbon nanotube coated carbon fiber
CSCF	Carbon nanotube grown short carbon fiber
CNT-SC	Carbon nanotube grown silica particle
CVD	Chemical vapor deposition
DMA	Dynamic mechanical analysis
EDA	Ethylenediamine
EDX	Energy dispersive x-ray
FTIR	Fourier transform infrared spectra
GF	Glass fiber
HMD	Hexamethylene diamine
HT	Halpin- Tsai equation
IFSS	Interfacial shear strength
LSG	Large silica gel
MWCNT	Multi-walled carbon nanotubes
NCF	Neat carbon fiber
NE	Neat epoxy
PAN	Polyacrylonitrile
PAMAM	Poly (amido amnie)
PEI	Polyethyleneimine
PMMA	Poly methyl methacrylate
PP	Polypropylene
POSS	Polyhedral oligomeric silsesquioxane
RoM	Rule-of-mixtures
SDS	Sodium dodecylsulfate
SDBS	Sodium dodecyl benzene sulfonate
SEM	Scanning electron microscope
SFFT	Single fiber fragmentation test
SFRC	Short fiber reinforced composite
SiC	Silicon carbide
SSG	Small silicagel
SWNT	Single-walled carbon nanotubes
TEM	Transmission electron microscope
TGA	Thermogravimetric analysis



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LIST OF SYMBOLS

d_f	Fiber diameter
E_{eq}	Equivalent modulus
$E_{ }$	Longitudinal modulus
E_{\perp}	Transverse modulus
E_c	Young's modulus of composite
E_f	Young's modulus of the fiber
l_c	Critical fragment length
r_{CNT}	Radius of carbon nanotube
V_f	Volume fraction
W_f	Weight fraction of filler
W_M	Weight fraction of matrix
ε	Strain
σ	Stress
σ_f	Ultimate fibre strength



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CHAPTER 1

INTRODUCTION

1.1 Background

The expressions nanoscience and nanotechnology point to the ability to investigate, to measure, to accumulate, to manipulate and to distinguish the matter on a dimensional scale lower than 100 nanometers, thus to molecular status. However, nanotechnology is still in the early phase of their advancement and it is interesting to exploit and employ the methods of nanosciences for the manufacture and use of materials, equipment and systems with magnitudes to the molecular level. Working in this field, it is possible to prepare products with characters greatly improved or with completely new properties. In fact, operating to nanosize level, the material offers diverse opportunities from those surveyed when working on macrosize dimensions. The application fields of nanotechnology are very large, and they can persuade many productive divisions such as, the transportation means, the food industry, information technologies, telecommunications and the automobile industry and the aerospace, through the development and the employment of new or improved materials.

Looking at nanoscience from a chemical view, a material body interacts with its surrounding environment according to its surface characteristics. Therefore, higher surface area of material body results in higher interfacial zones with large number of physical phenomena. The enhancement of surface by reducing the body dimension is shown in Figure 1.1. As easy to understand, the nanosize particles provide an extremely high surface area in comparison to macro/micro size one with equivalent volume. Indeed a great raise in chemical reactivity is achieved merely by declining the system characteristic dimensions from macro/micro to nano-scale.

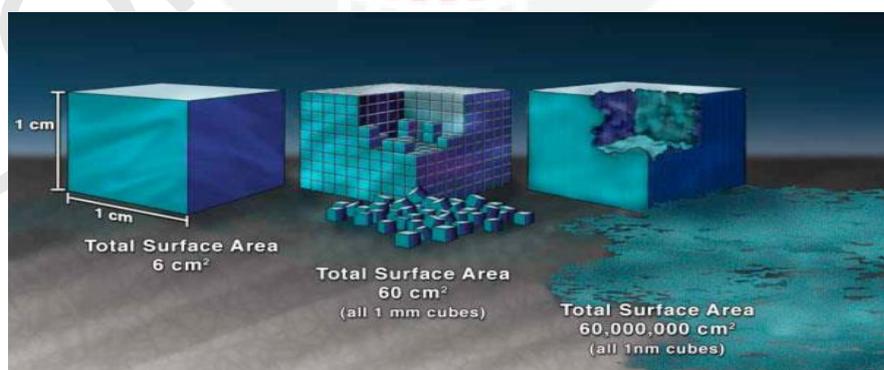


Figure 1.1 The morphological revolution of the nanostructures: enhancement of the surface area by going to nanosize
(Source: Chatterjee, 2012)

The significance of carbon in “macrosize materials world” is obvious for a long time, thus it is simple to understand the big efforts in promoting carbon nanostructured materials. In the mid-1980s, carbon science and technology were accelerated by the discovery of a former all-carbon molecule, fullerene and followed by the discovery of carbon nanotubes in 1991 (Grady, 2011). Carbon nanotubes (CNTs) are derived from graphite sheet with a tubular form which comprised graphite cylinders normally closed at both ends with caps consisting pentagonal rings. CNTs are available in the forms of single, double or multi walled. In general, CNTs possess a diameter of a few nanometers with length can enlarge up to several centimeters. Different shapes of carbon nanoparticles derived from the graphene structure are presented schematically in Figure 1.2.

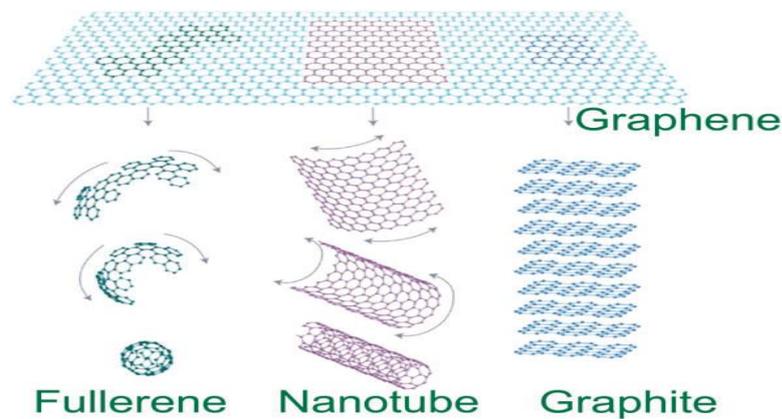


Figure 1.2. Graphene is a 2-D of carbon structure. It can be formed into 0-D fullerene, 1-D nanotubes and 3-D graphite
 (Source: Geim et al., 2007)

Carbon nanotubes have attracted the interest of many scientists worldwide. The combination of tiny dimensions, high strength and the outstanding physical properties of their structures make them a unique element with a whole range of favorable applications. The combination of a particular structure and topology endows CNTs with prominent mechanical properties such as high stiffness, strength, elastic deformability jointed with stability, low density and special surface chemistry. Considering covalent bonds of carbon-carbon as one of the strongest link in nature, afterward a structure established on a perfect arrangement of such bonds, which are directed along the axis of the nanotubes can construct an exceedingly strong material.

The theoretical and experimental works on individual nanotubes have confirmed an elastic modulus as high as 1000 GPa, which is equal to the in-plane stiffness of defect free graphite. Moreover, the tensile strength of individual nanotubes was estimated about 300 GPa theoretically and close to 50 GPa experimentally, which is still ten times higher that carbon fiber stiffness (Breuer et al., 2004; Coleman et al., 2006).

1.2 Significance of Study

Polymer composites with fillers mixed in thermoplastic and thermoset matrices are taken into account as an important group of materials because of their wide range of applications. In comparison to the incorporation of microscale additives, nanofillers, with their tiny size, establish a very small inter-particle space which influences the polymer matrix characteristics even at very diluted filler concentrations (Thostenson et al., 2001). Polymer nanocomposites came into industrial consideration with the detection at Toyota research center in the 1980s. In that research, via addition of a small portion of nanofiller to PA6 impressive improvement was recorded in modulus, strength, gas barrier properties and heat distortion temperature (Mittal, 2011).

Nanocomposite is defined as a class of multi-phase material in which one of the components is dispersed in another one in nanometer level. Conventional fillers incorporated within polymers have often been employed to decline cost or improve material properties needed for particular applications. Ceramic fillers such as alumina or silica are typically utilized to increase the elastic modulus in epoxy resins with reducing the cost. However, the disadvantage is that inclusion of such rigid particles further decreases the ductility in the initially brittle epoxy. On the other hand, soft filler particles, such as rubber, can be employed to toughen the epoxy resin matrix, but they subsequently reduce the stiffness.

Well-dispersed nanofillers are able to improve elastic modulus and strength, and to keep or even enhance ductility since they are much smaller than the crucial crack size for polymer matrix and require not initiate failure. Moreover, achievement of the desired properties by the incorporation of large amounts of traditional fillers often results in diminishing the weight-savings acquired in utilizing low-density polymers. Polymeric nanocomposites have been demonstrated to present unique combinations of electrical, thermal and mechanical properties at low filler weight fractions.

The mechanical performance of carbon nanotubes is exciting because CNTs are considered as the “extreme” fibrous carbon ever made. The conventional carbon fibers with approximately fifty times the strength to density ratio higher than steel, are tremendous load-bearing reinforcing components in composites. Carbon fibers have been employed as reinforcing element in lightweight, high strength and performance composites. It can typically be found in a range of products from costly tennis rackets to aircraft and spacecraft body parts. Therefore, nanotubes should be perfect potential candidates for structural applications.

The tiny size of nanofillers leads to some factors that discern nanocomposites from conventional composites. First of all, nanofillers have small mechanical, electrical and optical defects in contrast to micron size fillers. The inclusion of nanofillers within a polymer matrix does not necessarily result in a reduction in the ductility of the polymer and in some cases can enhance it. Secondly, even though many properties of a reinforcement material are supposed to be intrinsic, they are often valid above a critical length scale. While the nanoparticles decline below this size, the characteristics of the particles can change considerably from the bulk material.

Third, the small size of the fillers creates an exceptionally large interphase region in the composites. For instance, the surface area of a 10mm fibrous carbon is more than 100 times larger than that of a 1nm single-walled nanotube with the similar total volume. In addition, the inter-particle spacing decreases such that at small volume fractions of filler.

1.3 Problem Statements

The outstanding properties of CNTs can be exploited by the addition of such nanofillers within a polymer matrix to fabricate nanocomposites. Various polymer matrices can be utilized along with such carbon nanofillers to fabricate interesting composites that are investigated in this present work. Several methods have been introduced to manufacture polymer nanocomposites while the capability of nanofillers dispersion is a critical parameter to tune their properties.

The most main application of CNTs regarding their mechanical properties would be as reinforcements in composite materials. In spite of the evident advantages of CNTs incorporation within a polymer matrix, fabrication process of nanocomposites involves some particular feature, distinctive from traditional composites. The major problem includes obtaining a good interface between CNTs and the polymer matrix as well as achieving proper load transfer from the matrix to the CNTs, during loading. This problem originates essentially from two reasons. First, CNTs possess a smooth atomic structure with roughly the same diameters and length as polymer chains. Second, CNTs are almost formed into aggregates that act differently in reaction to a loading, in comparison to individual CNTs (Ma et al., 2010).

Proper dispersion/distribution of CNTs should be provided to obtain improved mechanical properties of the nanocomposite. Large surface area of nanotubes can potentially create physical interactions and entanglements which form aggregations of CNTs. The aggregations reduce the reinforcing efficiency of nanotubes because of restriction on load transfer to all CNTs, declining effective aspect ratio and creating local stress concentrations. Furthermore, the orientation and waviness of nanotubes play a critical role in the ultimate properties of the nanocomposites (Bose et al., 2010).

In view of the preceding, a huge effort has been done to establish suitable conditions for the well-dispersion of CNTs and subsequently, transfer of mechanical load to nanotubes in a polymer matrix. Various approaches of CNTs chemical treatment have been confirmed quite successful in attaching functional moieties which afford superior nanotube dispersion, as well as effective wetting of CNTs with polymer matrices (Bose et al., 2010; Ma et al., 2010). Another method of chemical modification has been introduced as grafting of macromolecules onto the CNTs surface. Indeed, the attachment of a whole polymer chain is supposed to have superior influence on the CNTs characteristics and their affinity to polymer matrices in contrast to the addition of functional groups (Bose et al., 2010; Ma et al., 2010).

In addition to modifying the chemical affinity of CNTs to polymer matrices, a variety of dispersing strategies, also assist in the efficient processing to form CNT/polymer nanocomposites with increased mechanical properties. These dispersion strategies include solution processing, bulk mixing, melt mixing and in situ polymerization (Andrews et al., 2004; Grady, 2011). Solution processing is used as the most common method at small scales to prepare CNT–polymer composites. In this method, CNTs powder is dispersed in a liquid medium through intense stirring and sanction, then mixed with a polymer or polymer solution. The extra solvent will evaporate in a controlled manner under vacuum condition to form a CNT-polymer blend. In bulk mixing, the nanofillers are blended in polymer matrix via local burden of high pressure. High energy ball milling and three roll milling with microsize gap are two common approaches in this category while the former often shorten the nanotube length (Dai, 2006).

On account of the fact that thermoplastic polymers become softer when heated over their melting point, melt processing has been the preferred methodology for the fabrication of CNT-thermoplastic based composites. Moreover, the technique is relevant for polymers with insolvability behavior in common solvents. The process factors and accordingly the shear stresses should be tailored to attain an optimum dispersion feature within the extrusion, which ultimately would be subjected to a consequent shaping step, such as hot pressing, for the fabrication of the final parts. Apart from other methods, in situ polymerization of monomers in the presence of CNT has been performed for the production of functional composites. The main preference of this technique is that it fabricates polymer grafted tubes, blended with free polymer chains (Koerner et al., 2005; Pham et al., 2008; Tang et al., 2003).

It is evident from the literature that although the mentioned chemical process possesses a positive effect on nanofillers dispersion, this route disrupts some inherent characteristics of CNTs. Furthermore, these methods involve the immense consumption of chemical solvents, especially environmentally unfriendly strong acids. Therefore, the worth of achieving improvements by treatments of CNTs, in contrast to the treatment cost is seriously in doubt.

In addition to the mentioned methods, some very recent studies demonstrated ‘grafting CNTs on microparticles’ as an effective way to fabricate nanocomposites. Growing CNTs on microfibers or microparticles seems more practical and economically performable to tailor dispersion of nanotubes through conventional manufacturing apparatus (Dichiara et al., 2012; Li et al., 2013; Zeng et al., 2008). Whereas other efforts require chemical or physical treatment of nanofillers or polymer prior to the mixing process. Furthermore, by growing nanotubes on microfiller, a multiscale filler will be fabricated which can offer the advantages of both nanosize and microsize fillers.

In this doctoral research, the author have attempted to introduce some multiscale fillers through growing CNTs on different microfillers. These microfillers include: short glass fiber, short carbon fiber and silica mesoporous particles. CNTs are grown onto the surface of these substrates fabricating an isotropic structure referred to as

multiscale fillers. The grown nanotubes create an interphase region between polymer matrix and microfiber, which are expected to improve the stress transfer. Since the CNTs are attached to the microfiller, it is anticipated that the multiscale fillers will disperse within the matrix by use of the conventional mixing process. Resolving the dispersion problem by introduction of multiscale fillers is a preferred approach compared to chemical treatment methods because of low cost, relative simplicity, preserving the intrinsic properties of CNTs as well as adapting capability to the conventional manufacturing process.

Both thermoset and thermoplastic polymer are used as composite matrix to identify the advantages of CNTs-microfillers. Epoxy resin as a thermoset and polypropylene as a thermoplastic matrix are employed to investigate the reinforcing efficiency of multiscale fillers. Both types of multiscale fillers which were CNTs-short fiber and CNTs-silica, were incorporated with epoxy and polypropylene via common mixing techniques. It is expected that such method addresses the dispersion problem of CNTs and subsequently improves the mechanical properties of the polymer nanocomposites. In addition, CNTs-silica particles are studied regarding the rheological behavior of nanocomposites to demonstrate another advantage of multiscale fillers during processing.

1.4 The Aim and Objectives of Study

The main aim of this study was to investigate the effects of several CNT-multiscale fillers on the problems associated with nanotubes dispersion and to improve the mechanical properties of polymer nanocomposites.

To achieve this aim, the following specific objectives have been pursued:

- (a) To characterize the morphology and quality of CNT grown on short fiber as a multiscale filler.
- (b) To characterize the morphology and quality of multiscale filler produced by growing CNT on silica microparticles.
- (c) To investigate the reinforcing effects of both short fiber and silica multiscale fillers on mechanical properties of polypropylene nanocomposites produced through common manufacturing process.
- (d) To identify their reinforcing effects of both short fiber and silica multiscale fillers on mechanical properties of epoxy nanocomposites.
- (e) To study the reinforcement efficiency of produced CNT-microfiller reinforcements through employing micromechanical modeling approaches.

1.5 Scope of Work

The scope of work is schematically shown in Figure 1.3. In addition, micromechanical modeling was performed to investigate their prediction ability of elastic modulus of multiscale composites.

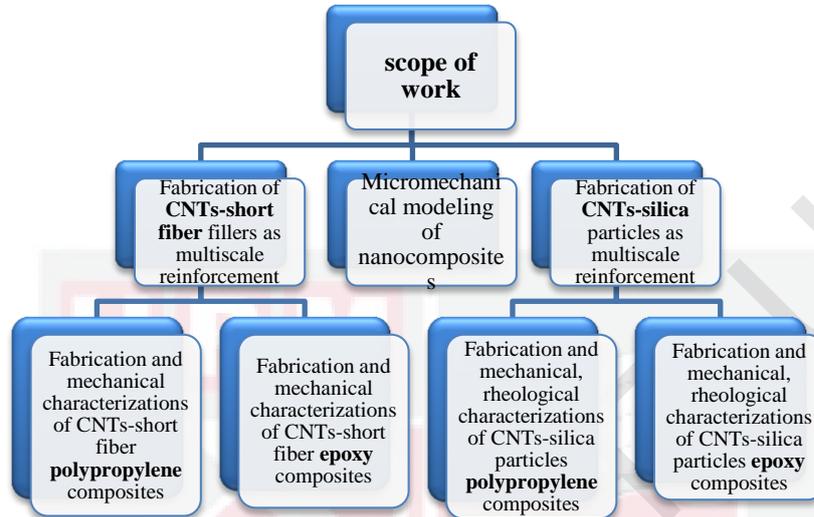


Figure 1.3. Schematic representation of scope of work

As shown in Figure 1.3, the synthesis of two types of multiscale fillers will be discussed. Among various methods of nanotube synthesis, CVD has shown the most promise for industrial-scale deposition, because of its price/unit ratio, and its capability of growing nanotubes directly on a desired substrate. Therefore, CNT-short fiber was synthesized through CVD process and incorporated within polypropylene as well as epoxy matrix. Mechanical and thermal characterizations were carried out to investigate the effects of CNT-short fiber reinforcements. The work continued by the introduction of CNT-silica as another type of multiscale filler. The mixing of CNT-silica particle within polypropylene and epoxy matrix provided multiscale composites which were characterized mechanically and thermally. Micromechanical models were employed to study the reinforcement efficiency of the produced fillers.

Among different types of polymers, epoxy resin and polypropylene were selected as a thermoset and thermoplastic polymers respectively. Epoxy has always been the preferred choice as the matrix for advanced composites due to its excellent properties and its suitability for various processing techniques. Epoxy as a thermosetting polymer often possesses strong mechanical properties as well as high temperature and chemical resistance. It has a wide range of industrial applications, including metal coatings, use in electronic and electrical components, high tension electrical insulators, fiber-reinforced plastic materials, and structural adhesives commonly used in boat building.

Polypropylene (PP), also known as polypropene, is a thermoplastic polymer used in a wide variety of applications including packaging and labeling, textiles (e.g., ropes, thermal underwear and carpets), stationery, plastic parts and reusable containers of various types, laboratory equipment, loudspeakers, automotive components, and polymer banknotes. A polymer made from the monomer propylene, PP is rugged and unusually resistant to many chemical solvents, bases and acids. Research is ongoing with PP as makers experiment with different methods for synthesizing it. Some of these experiments yield the promise of exciting new types of plastic, with new consistencies and a different feel from the fairly rigid version that most people are used to. Mixing CNT within PP has been introduced as a new technique to provide a new nanocomposite with some mechanical and thermal advantages.

1.6 The Outline of the Thesis

Chapter 2 includes a literature review of properties of CNTs, methods used to produce CNTs, grafting approaches of CNTs on several substrates with special emphasis given to short fiber and microparticles, dispersion methods of CNTs as well as mechanical properties of polymer nanocomposites as a result of mixing CNTs.

In chapter 3, the methodology employed to fabricate CNTs-short fiber and CNTs-silica fillers as the reinforcement of nanocomposites are discussed. Manufacturing process of nanocomposites and mechanical and rheological analysis methods are also explained. The characterization techniques of both multiscale fillers and nanocomposites are discussed.

Chapter 4 reports the morphology and characterizes the quantity and the crystallinity of the CNTs grown on short fibers under certain growth parameters. The effects of CNTs-short fiber reinforcements on the mechanical properties of polypropylene and epoxy matrix are presented. The relationship of mechanical improvements with microstructural characters of nanocomposites is discussed. This chapter continues by reporting the characteristics of CNTs-silica, morphology and effective parameters on the synthesis. This is followed by reporting the enhanced mechanical properties obtained as a result of incorporating CNT-silica microparticles into the epoxy and polypropylene matrix. The rheological behaviour of epoxy suspensions containing multiscale particles and CNT-silica polypropylene composites are compared with pure polymers.

Chapter 5 concludes the research finding and provides suggestions for the future work.

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