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Characterization of Carbon Nanotube/Polystyrene Composites Prepared via Microwave-Induced Polymerization

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CHARACTERIZATION OF CARBON NANOTUBE/POLYSTYRENE COMPOSITES PREPARED VIA MICROWAVE-INDUCED POLYMERIZATION

by

HUBERT AGAMASU

Under the Direction of RAFAEL QUIRINO

ABSTRACT

Carbon nanotubes (CNTs), with their excellent mechanical properties, are well suited to the production of composites with good strength-to-weight ratio. However, the use of nanotubes as reinforcement is hampered by the lack of interaction between their inert surfaces and matrices. This, coupled with the van der Waal's interactions between individual nanotubes, leads to agglomeration of CNTs in media. Functionalization is an efficient means to disperse nanotubes as well as increase their reactivity. The irradiation of CNTs with microwaves generates instantaneous, localized heating, being used in this work to trigger the rapid, thermal, free radical polymerization of styrene. Under microwaves, olefin-functionalized CNTs work as the heating source for the system, becoming the initial points for polymer chain growth during polymerization, as well as crosslink points within the polymer network. In this work, multi-walled carbon nanotubes (MW-CNTs) were covalently functionalized with three different groups: n-pentenyl, styrenyl, and phenyl. Pristine and functionalized CNTs were used as reinforcement during the production of CNT/polystyrene nanocomposites at 0.2 weight percent loading, in both conventional oven and microwave oven. The composites were characterized by thermogravimetry, differential scanning calorimetry, dynamic mechanical analysis, and tensile testing. n-pentenyl-functionalized CNTs showed the best dispersion while the addition of carbon nanotubes enhanced the mechanical properties of polystyrene. Composites from microwave-induced polymerization were more uniform than those made by conventional heating. Microwave-induced polymerization occurred five times faster than conventional heating. However, there was no statistically significant difference in mechanical properties between composites of pure and functionalized CNTs.

INDEX WORDS: Characterization, Carbon Nanotubes, Covalent Functionalization, Microwave-induced Polymerization, Nanocomposites.

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by

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MASTER OF SCIENCE

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Electronic Version Approved:

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DEDICATION

To Conrad Kakraba, for all your help in times past.

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CHAPTER 1

INTRODUCTION

1.1 Introduction and Brief History of Carbon Nanotubes

Heralded as the materials of the 21st Century [1], Carbon nanotubes (CNTs) are at the forefront of nanotechnology. A myriad of uses has been suggested for CNTs, owing to their wonderful thermal, electronic, and mechanical properties [2]. The extraordinary electrical conductivity of CNTs is attributed to the delocalized electrons created by sp^2 hybridization [3]. However, CNTs may also be semi-conducting, depending on their chirality [3]. These characteristics lend CNTs to applications such as the manufacture of biosensors and electronic components [3]. Modified CNTs are expected to influence fields such as molecular electronics [4]. Energy applications using carbon nanotubes has also been considered owing to their electrochemical stability, low mass density and excellent conductivity [4]. Carbon nanotubes are also compatible with biological tissues and have been explored for use in drug delivery [4] as well as in making scaffold for bone growth in tissue engineering [3].

Mechanically, CNTs are the stiffest of all known fibers, with Young's modulus of 1.4 TPa [2]. Their elongation to failure is 20–30%, and when stiffness is considered, the overall tensile strength turns to be over 100 GPa which is the highest for any known material [2]. This has been the motivation behind the exploration of CNTs as filler material in the production of nanocomposites [5, 23]. The use of CNTs in the manufacture of composites creates the potential for strong, lightweight materials [2]. In the aerospace industry, for instance, the excellent strength-to-weight ratio could lead to the replacement of metals by polymer composites, translating into huge fuel savings and less atmospheric pollution [6]. It is no wonder, therefore, that a great deal of the research into nanocomposites centers around the aerospace industry which holds the largest share (40%) in polymer composite manufacturing [6]. The Boeing Dreamliner 787, Airbus A350 XWB, and Bombardier CS-100, have their primary structures comprising more than 50% composites by weight [6].

Until 1985, the prevailing notion held that solid elemental carbon occurred in two different crystalline phases: diamond and graphite [7]. The work of Kroto and others in 1985 led to the discovery of a third form of elemental carbon: fullerenes. Kratschmer then succeeded in creating substantial quantities of fullerenes by arcing graphite electrodes [7]. These events would lead to an intensity in carbon research, culminating in the discovery by Ijima of “finite, carbon structure consisting of needle-like tubes” [8]. It is these “needle-like tubes” that have been christened carbon nanotubes. Ijima is, thus, credited with the discovery of CNTs, even though others like Ladushkevich and Lukyanovish had reported these structures in the mid-20th century [3].

Carbon nanotubes (CNTs) are sheets of sp^2-hybridized carbon folded seamlessly into graphitic tubes that are capped at the ends by fullerene-like carbons [9]. The imperfections in the triangular planar bonds of the sp^2-hybridized carbon lead to distortions in the hexagonal patterns, creating Stone-Wale’s defects. The folding up of these sheets into tubes is a mechanism for relieving the stress associated with this defect [10]. While carbon nanotubes are essentially seamlessly folded sheets of graphene, the curvature of CNTs leads to partial sp^3-hybridization [2], making CNTs more conductive than graphene sheets [9].

Carbon nanotubes may consist of a single folding, in which case they are referred to as single-walled carbon nanotubes (SW-CNTs). In other cases, the folding results in several nested tubes called multi-walled carbon nanotubes (MW-CNTs). Figure 1 shows both types of CNTs. However, the diversity of CNTs goes beyond the number of walls:

"Besides SW, DW [Double-Walled], and MWCNT, other CNT types include herringbone (HB), bamboo (BB), and cup-stacked (SC)-CNT as well as branched CNT. Rolled-up graphene sheets (Nano scrolls) may also be considered CNT. In contrast to the simple types, the HB-, and BBCNT have internal structures in between the tube sidewalls. CSCNT is composed by stacks of open-ended cups or cones. Additional types are in the R&D stage and may involve tailored structures such as the nanobuds, which are CNT with fullerene-like protrusions at the sidewalls, tubes with endohedral (internal) fillings of specific molecules or phases making a transition from hybrid metal-CNT to nanowire materials with the tubular space completely filled with e.g., an electrical conducting metal." [10]

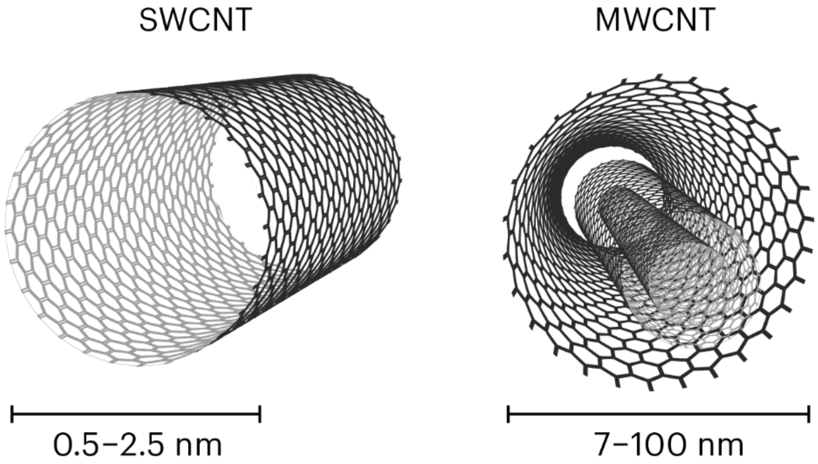


Figure1. single-walled and multi-walled carbon nanotube configurations [71].

Carbon nanotubes are also classified based on their chirality (figure 2). Chirality describes the way the sheets are rolled up. If the rolling is such that the cross section shows a zig-zag line, it is called a zig-zag configuration. Similarly, if it is rolled such that the cross section shows a “V” (called an armchair), then this is an armchair configuration [18]. In between these two extremes are various other chirality that are described using indices “n” and “m” to represent each hexagon, so that “n” represents the row number and “m” the column number (see figure 2). [11]. Hence, for a zig-zag nanotube, the CNT folds along the line which joins the first hexagon (1,0) with the (n,0) hexagon. For armchair, the CNT folds along the line which joins the (0,0) cell with (m = n) cells (1,1; 2,2; 10,10 etc.). Armchair CNTs have the properties of metals while other configurations have properties ranging from metallic to semiconducting [10].

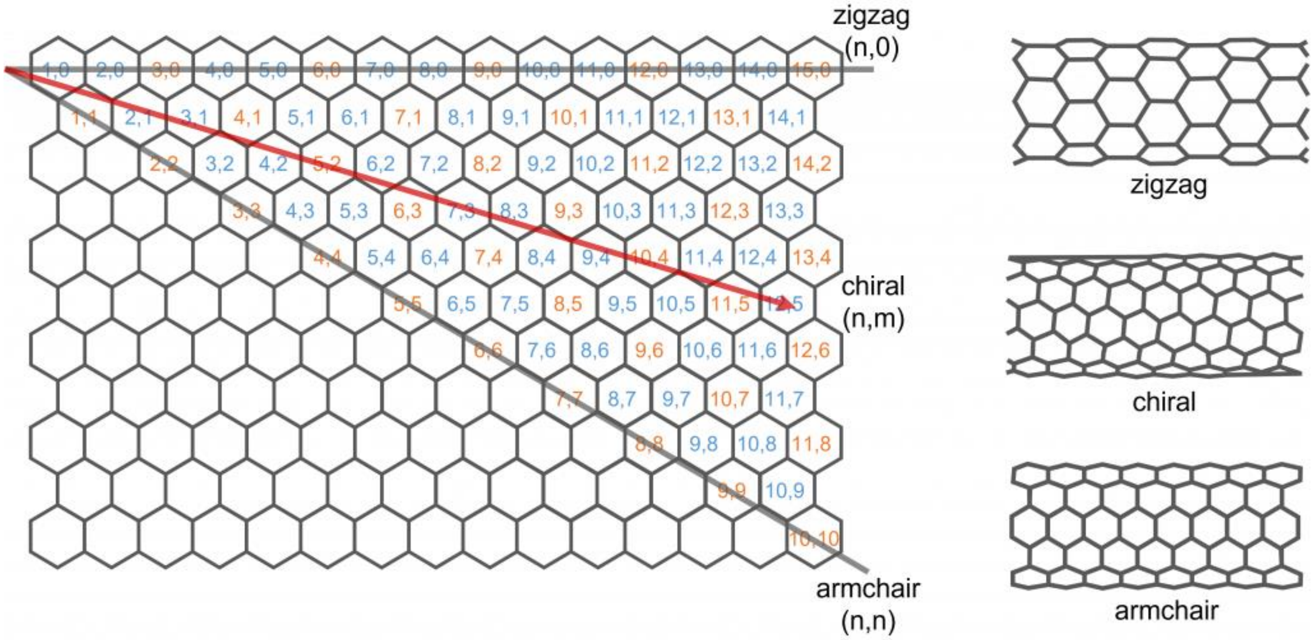


Figure 2. Chirality of Carbon Nanotubes. The inclination of the sheets during folding results in armchair, zigzag and other chirality of CNTs. [72].

1.2 Synthesis and Functionalization of Carbon Nanotubes

Carbon nanotubes may be manufactured using a variety of techniques. Prevalent among these are arc discharge, chemical vapor deposition and laser ablation.

a. Arc discharge.

Ijima used an arc discharge evaporation method like that used for fullerene synthesis. This method involves using direct current to create an arc discharge between electrodes made of graphite [8]. Two graphite electrodes are placed in a low-pressure chamber and a voltage is applied between them [10]. A low pressure, inert atmosphere is created using gases like helium or Argon [7]. The electrodes are brought closer to each other until an electrical discharge occurs, breaking down the gas into plasma [11]. The high temperature discharge which is created causes the surface of the anode to vaporize, leading to nucleation of CNTs on the cathode [10]. To obtain SW-CNTs, electrodes are doped with catalysts [10]. The yield of CNTs is dependent upon parameters such as gas pressure, current density and plasma stability. To produce MW-CNTs, the conditions are optimized so that during the arc evaporation, the amount of soot production is minimized and 75% of the evaporated carbon from a pure graphitic anode is made to deposit onto the graphitic cathode surface [7]. Arc discharge leads to the production of high-quality carbon nanotubes [3]. However, it is difficult to scale up [7]. Moreover, this method leads to the production of graphitic nanoparticles, requiring a purification step before the nanotubes could be used [7].

b. Laser vaporization.

This method is similar to arc discharge, with a pulsed laser replacing the high voltage. The reaction chamber consists of a quartz tube [11]. A piece of graphite target is irradiated with a pulsed laser, at high temperature and in an inert atmosphere [7]. This leads to the vaporization of the graphite, forming CNTs on a cooled substrate [10]. The use of pure graphite produces MW-CNTs while the use of catalysts results in SWCNTs [11]. Laser ablation leads to high quality CNTs, but this method is expensive and also difficult to scale up [3].

c. Chemical vapor deposition

The previous two methods discussed so far require high temperatures and short reaction times. Chemical vapor deposition is different in that it requires low temperatures and longer reaction times [7]. Chemical vapor deposition is the preferred method for industrial production of CNTs [10]. The reaction system consists of a quartz tube enclosed in a furnace. Hydrocarbons such as carbon monoxide, methane and acetylene are used as feedstock in the presence of metal nanoparticles which act as catalysts. [3]. The reaction mixture consisting of hydrocarbons and inert gas is passed over heated catalyst [11] (Figure 3). The carbon then precipitates out of the nanoparticles, forming CNTs [7]. The morphology of CNTs produced depends on the type and size of catalysts used [11]. While this method is commercially viable, the CNTs produced are of lower quality, compared to previously mentioned methods [3].

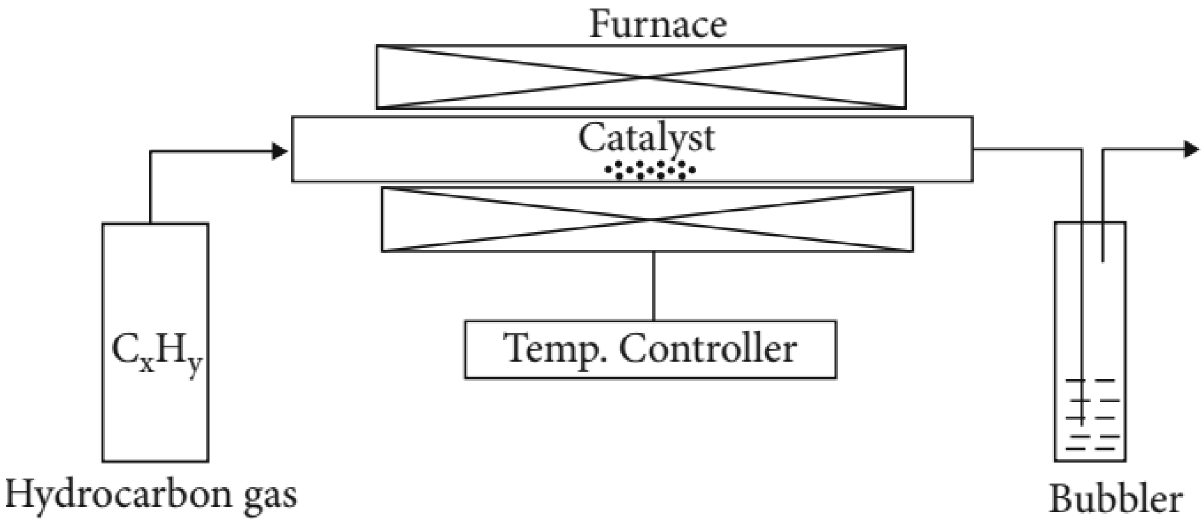


Figure 3. Chemical Vapor Deposition. Hydrocarbon gas is passed over a catalyst bed [11].

Defects may be created during the synthesis, purification, and functionalization of carbon nanotubes. These defects have a substantial effect on mechanical, electronic and optical properties of CNTs [2,9]. However, they also increase the reactivity of carbon nanotubes by creating points of attachment for molecules or atoms. Defects are categorized into vacancy, interstitial, and stone-Wales's defects. Vacancy defects are created by missing atoms. This leads to the three dangling bonds which may rehybridize, forming a pentagonal ring with neighboring atoms and a single dangling bond [10]. Vacancy defects are produced during the synthesis of carbon nanotubes [9]. Interstitial defects occur when carbon atoms are trapped within the CNTs. Stone-Wales defects are the consequence of bond rotations which affect four hexagons, changing two into pentagons and two into heptagons. For this reason, the Stone-Wale's defect is also referred to as the 5-7-7-5 defect [9].

Important qualifications for fillers in polymer composites include excellent physical properties, good aspect ratio, particle size, particle orientation and dispersibility of filler within the polymer matrix [14]. Carbon nanotubes outdo all other materials in many of these areas. As previously mentioned, they have the highest tensile strength of any known material, best electrical conductivity, and highest thermal conductivity and great aspect ratio [4,2]. A major drawback in the use of carbon nanotubes as fillers, is the difficulty in dissolving or dispersing nanotubes in solution [4, 21]. Nanofiller dispersion in the polymer matrix is very important, since it affects the mechanical and thermal properties [16]. However, carbon nanotubes have inert surfaces that interact little with media.

Figure 4. (a) SEM image of agglomerated carbon nanotubes (x 9500). (b) Settling Test for virgin CNTs.

Added to this, there are considerable van der Waal’s forces between the individual carbon sheets. Although considered to be weak intermolecular forces, van der Waal’s become significant at the nanoscale due to the large surface area per unit mass of materials on this scale [14]. These forces, coupled with the chemical inertness of CNTs, cause them to agglomerate, forming bundles in solution (see figure 4 a) [15]. CNTs in a liquid medium, therefore, tend to settle at the bottom of the container (Figure 4b). The success of CNT reinforcement, therefore, will depend on the exfoliation of the bundles, leading to homogeneity of its dispersion in media and the consequently, better interfacial compatibility with the matrix [13,54]. Functionalization, which is the modification of CNTs by the attachment of moieties to their surfaces, is a means to achieve these. The moieties alleviate the chemical inertness of carbon nanotubes and foster interaction between CNTs and the medium. This helps to counteract the long-range van der Waal’s forces of attraction, leading to better dispersion. [2]. Load transfer, the ability to transfer mechanical loading to two adjacent fillers [22], is crucial to the mechanical properties of composites [58]. The presence of functional groups on the side walls of CNTs increases the chemical reactivity between the filler and matrix [5, 16, 18].

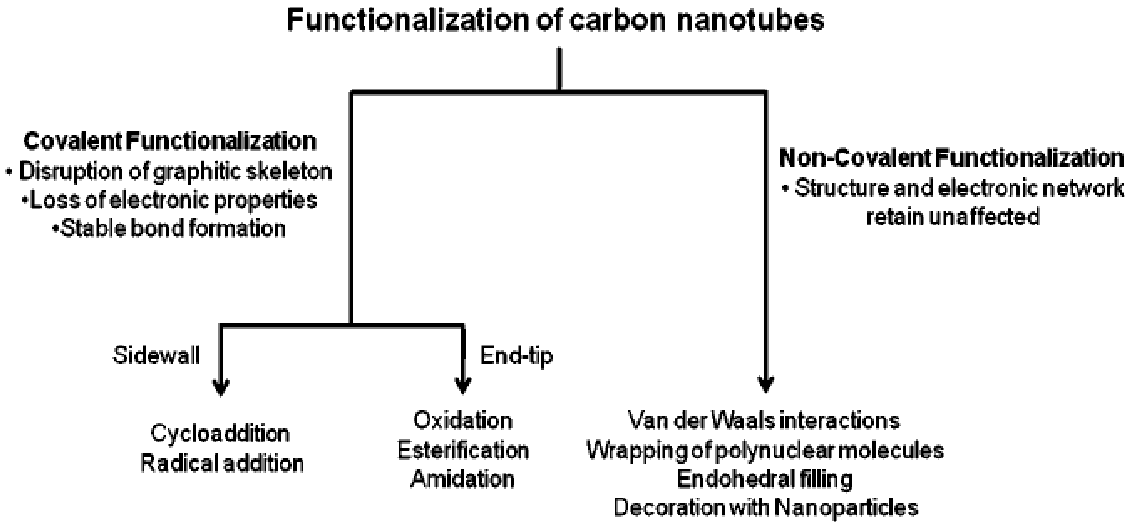


Figure 5. Different approaches to functionalization [18].

Functionalization can be exohedral or endohedral [4]. Endohedral functionalization involves placing material on the inner surface of nanotubes. This is usually done during production of nanotubes or by opening and filling the nanotubes. One advantage of this method is that protective carbon layers prevent oxidation of the encapsulated nanoparticles [4]. However, this method is not useful in dispersing CNTs since the functional groups are not attached to the outer surface. Exohedral functionalization involves attaching materials to the outer surface of CNTs and is employed in dispersing CNTs in solution. This comes in two forms: covalent and non-covalent functionalization.

In covalent functionalization, covalent linkages are formed between functional groups and carbon nanotubes. Examples include the use of fluorination to solubilize CNTs [4]. CNTs have also been functionalized with hydrogen in gas phase reactions, using low temperatures and a dry process that maintained the chemical and physical properties of CNTs [4]. Another method of covalent functionalization is electrophilic addition of chloroform in the presence of Lewis acids. Metal complexes such as Vaskas compounds are also used in the functionalization of CNTs with application in molecular electronics and metallo-organic chemistry [4]. This is especially important because this could add new functionality to nanotube surfaces, making them more reactive [20]. Covalent functionalization leads to the formation of stable bonds between CNTs and molecules [18]. However, it engenders degradation of the mechanical structure and electronic properties of the nanotubes [18, 46].

Non-covalent functionalization on the other hand, involves the adsorption of materials onto the surfaces of CNTs without the formation of chemical bonds. Methods include the use of surfactants with sonication to exfoliate the nanotubes. [4]. Polymers are also wrapped around CNTs as a means of functionalization. [4]. Non-covalent functionalization has the merit of not altering the mechanical and electronic properties of the CNTs [18]. However, no chemical bonds are formed. Also, this method does not remove impurities from the tubes. For this latter reason, covalent functionalization is preferred for biological applications [20].

Characterization of functionalized nanotubes in terms of position and bonding of moieties is done via transmission electron microscopy, tunneling microscopy, Raman spectroscopy and Fourier transform infra-red spectroscopy (FTIR) [17, 24]. New absorption bands in FTIR spectrum confirm the successful grafting of groups. Thermogravimetric Analysis (TGA) is also used in characterizing functionalized CNTs [19,21]. TGA involves heating the functionalized CNTs until degradation of moieties occurs and estimating the percentage loss in weight. The suspension of functionalized nanotubes in solvents is also indicative of successful functionalization [19].

1.3 Microwave Synthesis

In the last twenty years, the production of synthetic polymers was 280 million tons [25]. The conventional way of synthesizing polymers is the use of heat ovens that convert electrical energy into thermal energy. Using this method, energy is transferred from the surface of the substrate into the interior. This leads to longer heating cycles and large input of energy. Moreover, heating beyond the maximum rate of reaction leads to thermal degradation of the material [25].

Given the problems associated with the conventional heating process, Belkhir and others summarize the need for alternate synthesis methods that would (a) improve the properties of the material (mechanical, thermal, rheological, optical, and chemical properties) and optimize of the processes involved in polymer chemistry or transformation to achieve gains in time and cost, and compliance with the ecological requirements [26]. Microwave heating promises to be a solution to most of these problems.

Microwaves are electromagnetic radiation with a frequency range of 300 MHz to 30 GHz. A typical commercial microwave uses a frequency of 2450 MHz. This frequency range has been deliberately chosen to avoid interference with telecommunication devices. [27]. Microwave heating is caused by conductive losses, dielectric losses and magnetic losses. In order to understand the advantages of microwave synthesis over conventional heating, it is important to understand how microwave heating occurs.

The response of a dielectric material to an electromagnetic field is encapsulated in the equation.

$$D = \varepsilon E \qquad (1)$$

Where E is the applied field, ε is the dielectric constant and D is the electric displacement, accounting for both free and bound charges in the material [26]. In the absence of an electromagnetic field, these dipoles are randomly aligned. However, when an electromagnetic field is applied in the vicinity of the dipoles, they experience a net torque that tends to align them in a position of minimum energy, to wit, in the direction of the field [see figure 6]. If there is a reversal in the field direction, the dipoles are again aligned so that they lie parallel to this new direction of the field. In the case where this field oscillates- as is the case with field associated with electromagnetic waves- the dipoles are forced to oscillate in tandem with the field. The dipoles are unable to keep up with the rapidly oscillating fields, resulting in a phase lag between the field and the dipoles [29]. This phase lag leads to energy dissipation via inertial, frictional, elastic and other molecular interactions [29, 30]. As similar effect is observed in ionic substances [6, 28]. The dielectric constant ε may then be expressed in terms of real and imaginary parts ε' and ε'' . [6]. ε' represents the polarizability of the material (or its ability to store electromagnetic energy) while ε'' represents its ability to dissipate energy. The loss factor (tan δ) is then defined as

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} \qquad (2)$$ [29].

The higher the loss factor, the greater the microwave absorption of the medium and vice versa [42]. Solvents with loss factor of 0.5 or more are said to be good absorbers, those with loss factor between 0.1 and 0.5 are moderate absorbers and those below 0.1 are poor absorbers [42].

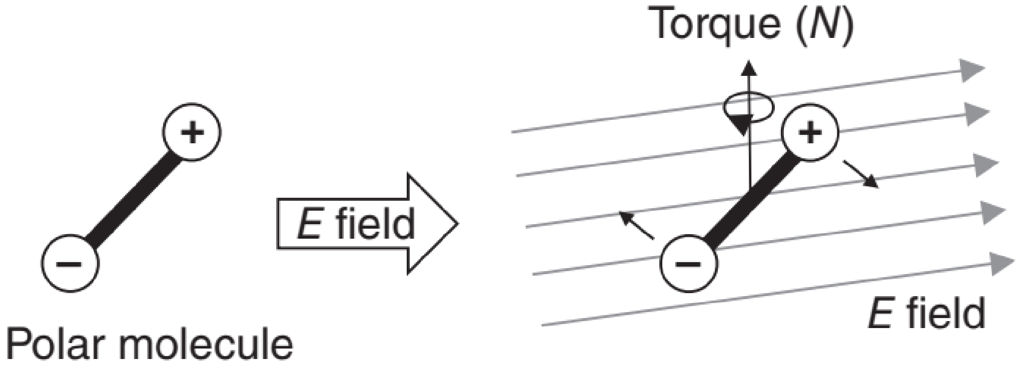
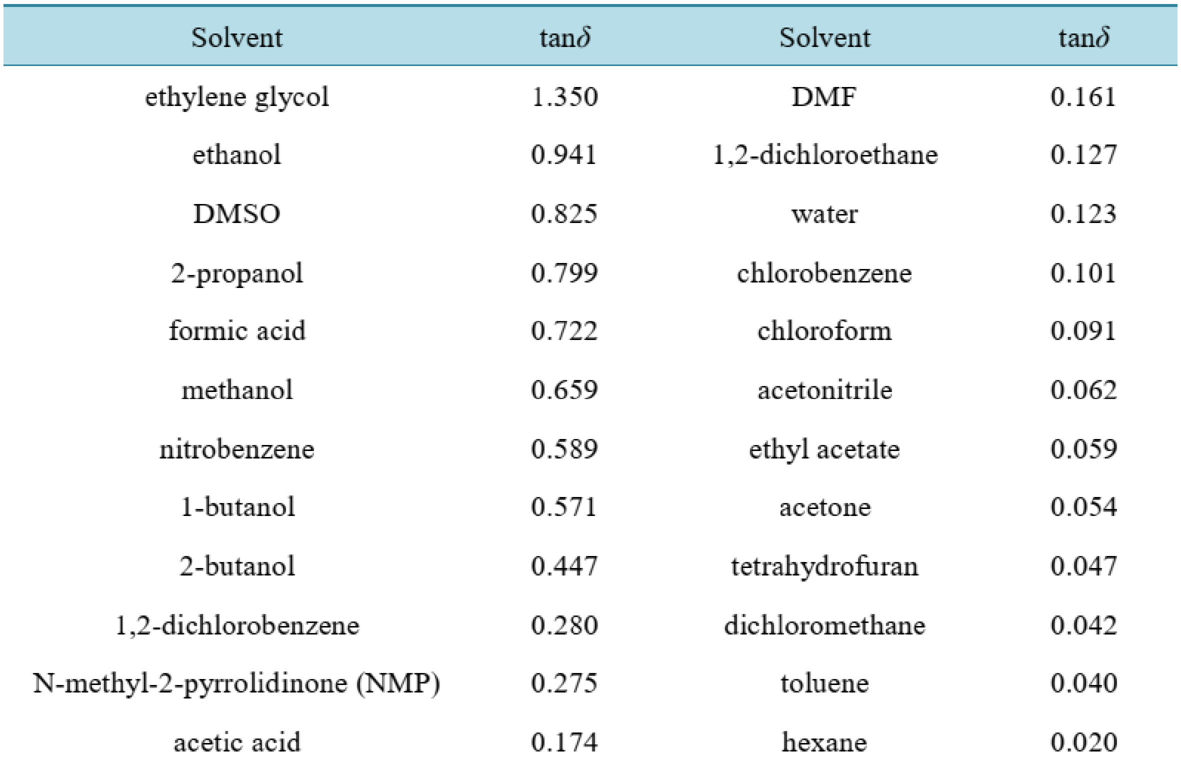


Figure 6. A dipole in an electromagnetic field [28]. The field exerts torque, causing the dipole to align with the field.

Table 1. Loss Factor for different materials at 2.45 GHz and 20 °C [26]



Solvent	tanδ	Solvent	tanδ
ethylene glycol	1.350	DMF	0.161
ethanol	0.941	1,2-dichloroethane	0.127
DMSO	0.825	water	0.123
2-propanol	0.799	chlorobenzene	0.101
formic acid	0.722	chloroform	0.091
methanol	0.659	acetonitrile	0.062
nitrobenzene	0.589	ethyl acetate	0.059
1-butanol	0.571	acetone	0.054
2-butanol	0.447	tetrahydrofuran	0.047
1,2-dichlorobenzene	0.280	dichloromethane	0.042
N-methyl-2-pyrrolidinone (NMP)	0.275	toluene	0.040
acetic acid	0.174	hexane	0.020

In materials of non-negligible conductivity, further heating may occur because of thermal activation of electrons [28]. This is known as conductive heating or Joule heating and may account for the intense heating of the highly conductive CNTs [28]. Overall, the microwave power absorbed is given as

$$P_{abs} = (2\pi f\mu\tan\delta+\sigma)E^2 \qquad (3)$$

for an electric dipole and

$$P_{abs} = (2\pi f\mu\tan\delta+\sigma)H^2 \qquad (4)$$

for a magnetic dipole. [26]

where symbols have their usual meanings.

Another parameter associated with microwave heating is the penetration depth (or skin depth, in metals) which measures the attenuation of electromagnetic waves in medium. Penetration depth is defined as the distance from the surface at which the magnitude of the field drops by a factor of 1/e (36.8%) [28]. Good conductors like metals tend to have poor penetration depth and end up reflecting most of the radiation that is incident on them. These materials are said to be opaque to microwaves [28]. Such materials are used to shield microwaves. When the penetration depth is larger than the dimensions of the material, it practically becomes transparent to microwaves [30]. An example of such a transparent system is styrene in a microwave vial. In-between these two are materials that absorb microwave energy and cause heating. Carbon nanotubes in particular have been reported to be good absorbers of microwave energy with a concomitant release of intense heat [38].

Dielectric properties are dependent on a combination of electrical permittivity and dielectric permeability, and these may be affected by temperature, moisture and the mode of preparation of composites [6].

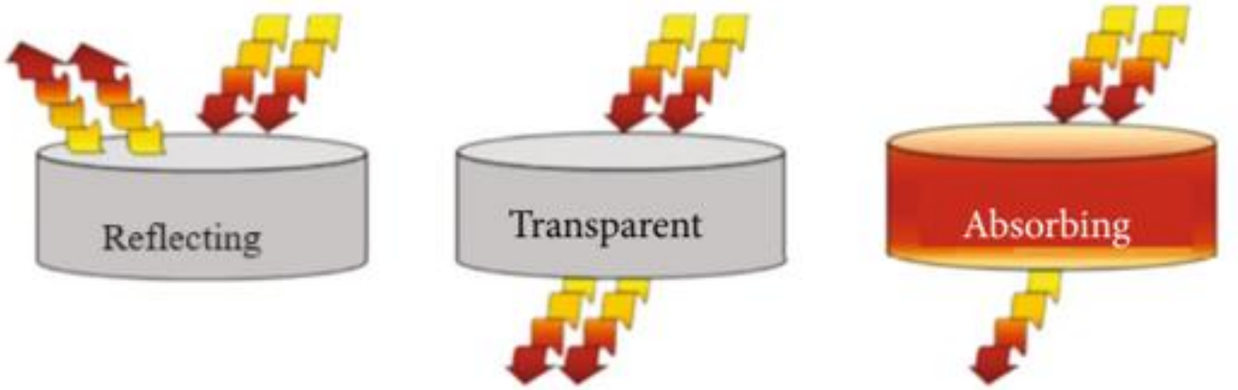


Figure 7. Interactions of matter with Electromagnetic Waves [Adapted from 28].

It has also been suggested that microwave fields contribute some kind of non-thermal phenomenon that affects parameters such as the glass transition range [31, 35]. Tomovska and others attributed the increased molecular weight and increased reaction rate of microwave-induced polymerization to the microwave effect in free radical polymerization [26]. This microwave effect is considered a consequence of the dielectric effect [36]. Others are more critical, arguing that there is insufficient evidence to distinguish the thermal from microwave effects [33, 35].

1.4 Merits and Demerits of Microwave Synthesis

Conventional heating (CH) proceeds mainly via conduction, radiation and convection of heat from the oven, through the surface into the substrate. The material, thus, is warmer on the surface and is cooler as one moves deer within. In microwave heating (MH), the EM energy travels into the material and initiates instantaneous heating from within the volume of the substrate. This direct heating leads to an inverse temperature profile where the material is warmer inside than outside. This phenomenon, known as volumetric heating, leads to uniformity in the heating process [30]. This may be an important parameter for living polymerization techniques that provides polymers with narrow molar mass distributions [32]. Volumetric heating makes microwave heating a faster process, compared to conventional oven heating [29]. However, this increased reaction rate is said to occur only in the early stages of the reaction [31]. It has also been demonstrated that increasing the power of microwave irradiation decreases the time taken to achieve a given yield [33]. Energy consumption is also drastically reduced in MW synthesis, compared to conventional heating [29]. Moreover, volumetric heating ensures uniformity in heat distribution since heating is not concentrated at any point but occurs simultaneously in all parts of the system [6]. By using dielectric nanomaterials with varying efficiencies, it is possible to tune the volumetric heating process and achieve optimum heating under any circumstance [6].

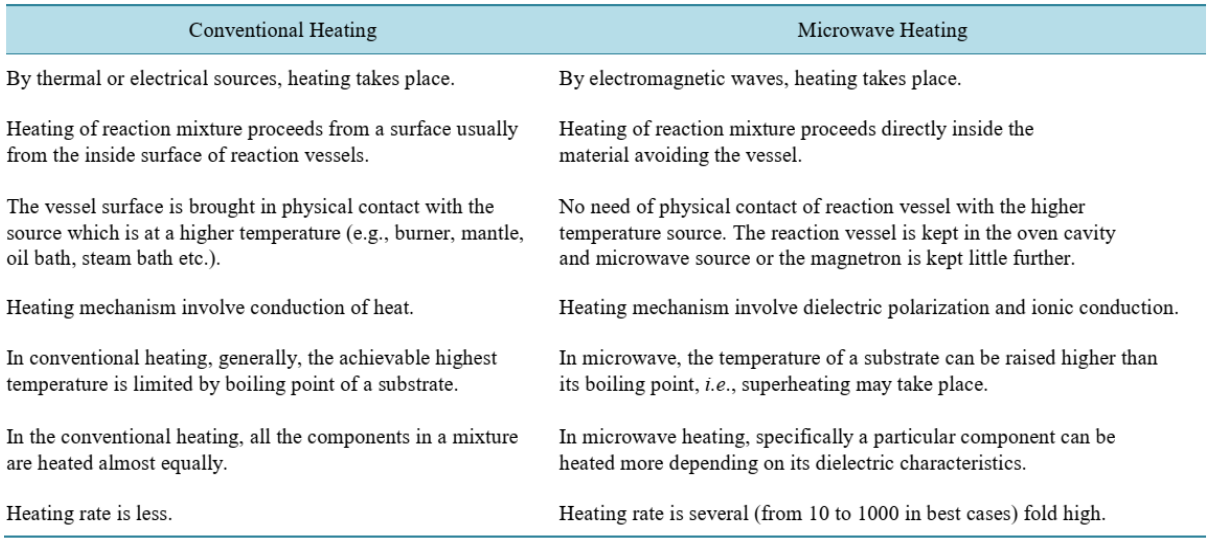
Another advantage of microwave heating is selectivity. Given that some polymer materials are more sensitive to microwaves than others, MW affords the opportunity to selectively heat materials [33]. The literature also shows that effective absorption of microwaves leads to higher boiling points in liquid reactants, the so-called superheating effect. This is responsible for the higher yields associated with microwave polymerization [33]. Finally, microwave heating improves the overall properties of composites during curing. Mechanical characterization of composites made of graphene nanoribbons in thermoset polymers revealed that the composites cured via microwave showed better compressive strength, yield stress and toughness in comparison to conventionally cured counterparts [30]. Microwave-induced synthesis has, thus, found application in numerous fields of chemistry including but not limited to ring-opening polymerization, controlled radical polymerization, semi-conducting polymerization, click chemistry polymerization, metal-catalyzed, cross-coupling polymerization, and synthesis of polymer nanocomposites [36]. It has also been demonstrated that the selective heating of fibers by microwave radiation and the subsequent transfer of heat from fiber to matrix by conduction helps to strengthen the fiber-matrix interface [35]. While there are other wavelengths in the EM spectrum capable of heating, microwave is preferred because it penetrates the matrix efficiently without posing any health hazards [35].

Microwave polymerization also comes with tremendous energy savings. In a comparison between microwave and conventional curing, Rao and co-researchers reported energy savings of about 80% and a reaction rate that was about 8 times higher than conventional polymerization. [34]. It has also been demonstrated that increasing microwave power increases the reaction rate [37].

While microwave energy may be used to synthesize polymers, it may also be useful in degrading polymers [37]. In a study geared towards microwave recycling, the effect of microwave radiation on the interfacial adhesion properties between epoxy and carbon fibers in a carbon composite material was investigated. It was observed that carbon fiber surface deterioration occurred due to extreme exposure to microwave at temperatures of 600 °C under 100 W power [37]. This unveils the potential of microwaves to be used for recycling polymers. The key advantage of chemical recycling via microwave is the ability to recover monomers in their pristine form, consequently, recycled materials maintain their original properties, in contrast to mechanical recycling [40]. Accordingly, Frisa-Rubio and his team developed a heated reactor to carry out the depolymerization of polyamide-6 (PA6), polyamide-6,6 (PA66) and polyurethane (PU) using microwave (MW) technology as the heating source [40].

Microwave heating, however, has its own disadvantages. It was previously mentioned that dipolar heating is caused by the rapid oscillation of dipoles electromagnetic field, resulting in phase lag as the dipoles struggle to keep up with the field frequency. This phase lag makes microwave heating material and geometry dependent, resulting in heating delays in thick materials or those with complex geometry. The temperature gradient which exists in conventional heating affects the material characteristics, thus, tends to change the microstructure and mechanical properties [30]. In view of this some authors have suggested a combination of conventional and microwave heating [37]. Microwave shielding may also occur, in which materials beyond the penetration depth are not heated by microwaves [6]. Arching is another phenomenon which occurs when the absorption is higher compared to the dissipation, resulting in partial transmission of energy through the material. For high microwave exposure, this release can be high, making arching a high possibility. [6]. Moreover, microwave heating is unsuitable for non-polar substances with very low loss factor, resulting in the use of high wattage [37]. In such cases, susceptors may be used to heat up the monomers indirectly [25]. Another limitation of Microwave polymerization has to do with temperature measurements. The externa infra-red sensor used in systems like CEM Discover microwave does not accurately measure the temperature of the system. This makes it difficult to compare microwave polymerization to conventional heating [31]. The table below summarizes the differences between microwave and conventional heating.

Table 2. A comparison between Microwave heating and conventional heating [42].



Conventional Heating	Microwave Heating
By thermal or electrical sources, heating takes place.	By electromagnetic waves, heating takes place.
Heating of reaction mixture proceeds from a surface usually from the inside surface of reaction vessels.	Heating of reaction mixture proceeds directly inside the material avoiding the vessel.
The vessel surface is brought in physical contact with the source which is at a higher temperature (e.g., burner, mantle, oil bath, steam bath etc.).	No need of physical contact of reaction vessel with the higher temperature source. The reaction vessel is kept in the oven cavity and microwave source or the magnetron is kept little further.
Heating mechanism involve conduction of heat.	Heating mechanism involve dielectric polarization and ionic conduction.
In conventional heating, generally, the achievable highest temperature is limited by boiling point of a substrate.	In microwave, the temperature of a substrate can be raised higher than its boiling point, *i.e.*, superheating may take place.
In the conventional heating, all the components in a mixture are heated almost equally.	In microwave heating, specifically a particular component can be heated more depending on its dielectric characteristics.
Heating rate is less.	Heating rate is several (from 10 to 1000 in best cases) fold high.

It is worth noting that despite the advantages of microwave-induced heating over conventional heating, the former is not a mature field. Tejas itemizes the reasons for this as follows: (a) lack of tools (microwave transparent) for use in the process (b) high initial investment on industrial microwave applicators, (c) process requires costlier consumable materials as compared to conventional processes (d) size of the applicators is usually significantly smaller unless customized, (e) heating behavior of complicated tool geometries is often required to be verified before commercial use, stressing the importance of process monitoring and simulation tools (f) hot spots and electrical arcing can result from selective microwave coupling to fibers (g) close monitoring and process parameters control is required to produce a uniformly cured laminate (h) difficulty in achieving uniform electromagnetic field inside the cavity (i), less pressure application during fabrication of the composites and (j) concern on the leakage of microwaves during microwave processing [30]. However, some stride has been made in the manufacture of industrial scale microwave ovens for testing purposes. The most prevalent one is the HEPHAISTOS developed by Karlsruhe institute of technology [35]. This model uses a hexagonal applicator to create a uniform microwave field. [35]. It produces no arcing and does not require microwave-transparent materials to work in the chamber.

1.5 Instrumentation

At the core of the microwave oven is the magnetron where electromagnetic waves are generated. This generation may be continued or pulsed [39], with frequencies from 1 to 40 GHz and power efficiency of 85%- and 5000-hours life span [41]. Microwaves are generated in the vacuum tubes which are mostly magnetrons or klystron [25]. In the magnetron, a cylindrical cathode is situated close to a circular anode [41]. The anode contains cavities that are designed to resonate at a particular frequency. Magnetic and electric fields are applied to the electrodes such that the fields are perpendicular to each other. Electrons ejected from the cathode move towards the anode and are forced by the perpendicular magnetic field to assume a curved path, setting up a space circulation [41]. The resonant cavities accelerate and decelerate the electrons, causing them to move around the cathode at microwave frequencies. [39]. There is a difficulty in using conductors to transport MW radiation that is above 3 GHz [25]. For this reason, wave guides - metal tubs with rectangular cross section - are used to transport the microwave from magnetron to the cavity [42]. The material to be heated is placed in a cavity lined with metallic walls such that, once microwaves enter the cavity, multiple reflections are set off from the walls, creating standing waves [41]. These standing waves have maximum power at antinodes and minimum at nodes. This creates uneven power distribution, hence, the need for a turntable or stirrers in microwaves [41].

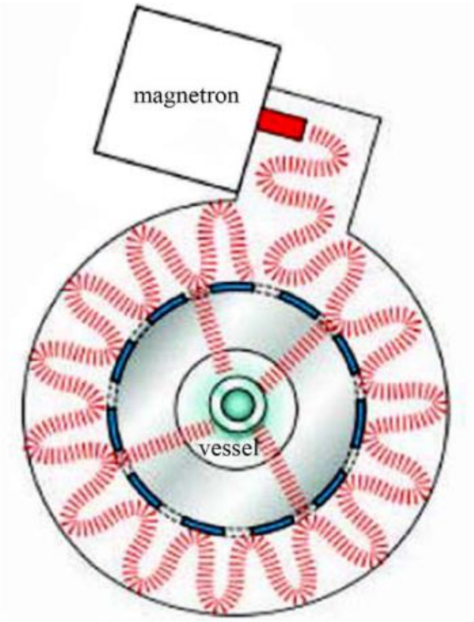


Figure 8. Microwave instrumentation. Microwaves are produced inside a magnetron and transported by waveguides [42].

Single mode versus multimode

A microwave apparatus may be monomodal (single mode) or multimodal (multi-mode). In a monomodal apparatus, waves having the same amplitude, but different directions of travel, are made to interfere, creating standing waves with points of constructive interference (antinodes) and points of destructive interference (nodes) [25]. The design is such that the cavity that contains the sample coincides with the antinode of the standing wave where energy is maximum. This ensures efficient heating. Single mode has a high rate of heating and is suited to small scale applications. However, only one sample may be run at a time [42]. In multimode reactors, Radiation is sent into the reaction cavity and dispersed, avoiding standing waves [25]. Multiple samples can be irradiated at the same time. The domestic microwave oven is an example of a multimodal oven. The propagation of radio waves in multimode is such as to generate as much chaos as possible, leading to dispersal of energy [42]. While many samples can be heated by this method, it leads to difficulty in temperature control.

The CEM Products represent one of the common microwave systems. The magnitude of microwave power available is 300 W. The Discover Series of single-mode microwave synthesizers is available with a variety of options and accessories, including automation. The synthesizers are used for research scale reactions with volumes up to 75 ml. The applicator consists of two concentric cavities with aperture ensuring the coupling. It can operate at atmospheric conditions using open vessels and standard glassware (1 ml to 125 ml) or at elevated pressure and temperature using sealed vessels (0.5 ml to 10 ml sealed with a septum [73].

1.6 Polymer Nanocomposites

Polymers are among the most important materials-if not the most important-of the 21st century, making up 80% of the output of the chemical industry [25]. They are found in nearly every industry including sports, food, transportation, and health. Polymers are made up of smaller repeating units covalently linked in a process called polymerization. They hold some unique advantages that set them apart from other materials. Their raw materials, mostly obtained from crude oil distillation, are relatively cheaper than metals or ceramics. Also, they are chemically inert, making them very useful in chemical reactions. An equally important feature is the wide range of properties that polymers display for any given property. This is a consequence of their variable molecular structure [43]. An example is the wide range of Young’s modulus, as seen on the materials selection chart (Figure 9). This translates to a wide range of applications for polymers. Though this range is clearly lower than other materials such as metals and ceramics, polymers compensate by having lower densities. Hence, when a strength to weight ratio is defined, polymers compete favorably with metals in some cases.

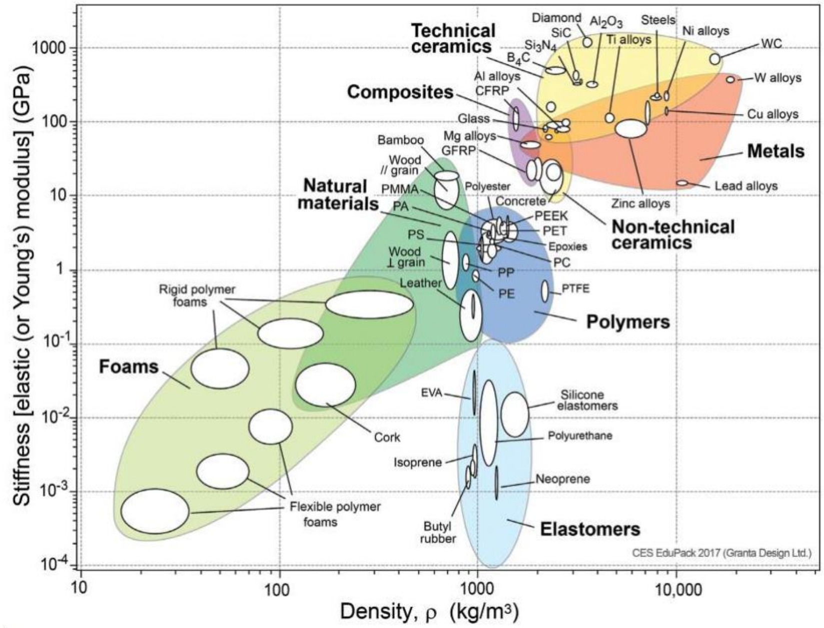


Figure 9. Materials selection chart. Polymers are the only synthetic materials in the upper quadrant, representing high tensile strength and low density [12].

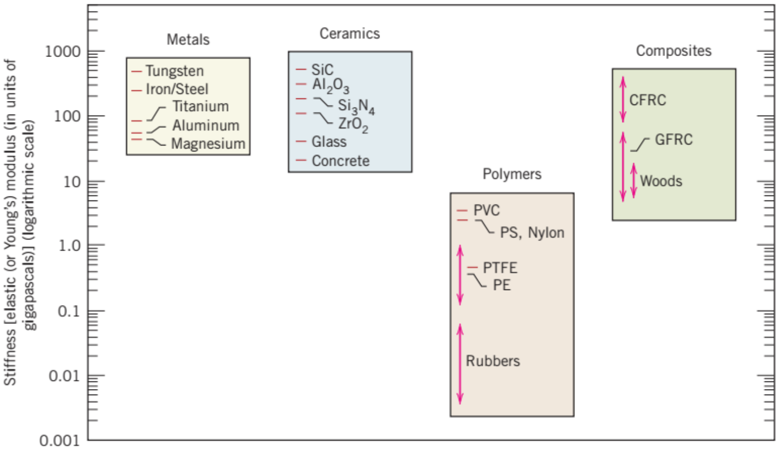


Figure 10. Bar chart of stiffness at room temperature for different materials. [12].

Clearly, if Young’s modulus of polymers could be increased considerable, then they would certainly overlap with some metals such as aluminum (see fig 10). Consequently, these metals could be replaced by lighter, cheaper polymers of equal strength [45]. This is especially important in the aerospace industry where strength to weight ratio is critical [6]. The traditional method of reinforcing the properties of polymers is by the incorporation of other materials with desired properties [45]. This results in the production of a polymer composite.

A composite material consists of two distinct phases that are combined such that the properties of one are transferred to the other. Polymer nanocomposites (PNCs) may be defined as a mixture of two or more materials, where the matrix is a polymer, and the dispersed phase has at least one dimension smaller than 100 nm [49]. The reinforcing material is known as a filler or dispersed phase while the reinforced material is the matrix. Wood is an example of a natural composite and clay building blocks mixed with hay are early examples of manmade composites.

Traditional fillers require high loading for modest property enhancement, causing problems in melt flow and processing due to the high viscosity of the filled materials. Furthermore, the high density of traditional fillers also leads to heavier composites. Finally, the lack of interfacial interaction between the filler and the polymeric matrix leads to weak interfacial adhesion and results in failure. For this reason, smaller particles are preferred as fillers. [48]. It’s been observed that smaller particle size is a necessary requirement, and very likely the predominant requirement, for the reinforcement of composites [48]. The reinforcement of micro fillers could be attained using smaller loadings of nanofillers. Nanofillers in the range of 3%–5% by weight achieves the same reinforcement as 20%–30% of micro sized fillers [48]. This gives nanocomposites have an advantage over conventional composites and. For this reason, nanoscale materials have emerged as the most attractive candidates for reinforcing polymers.

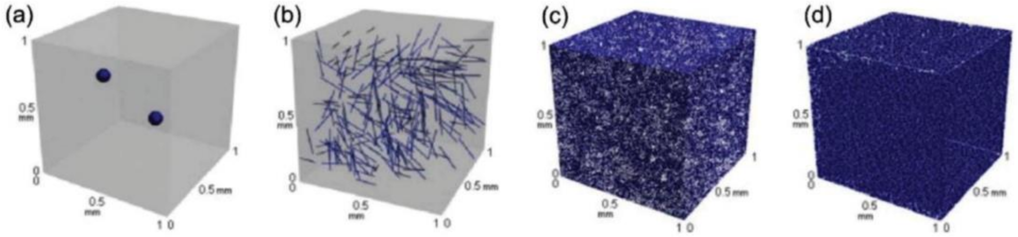
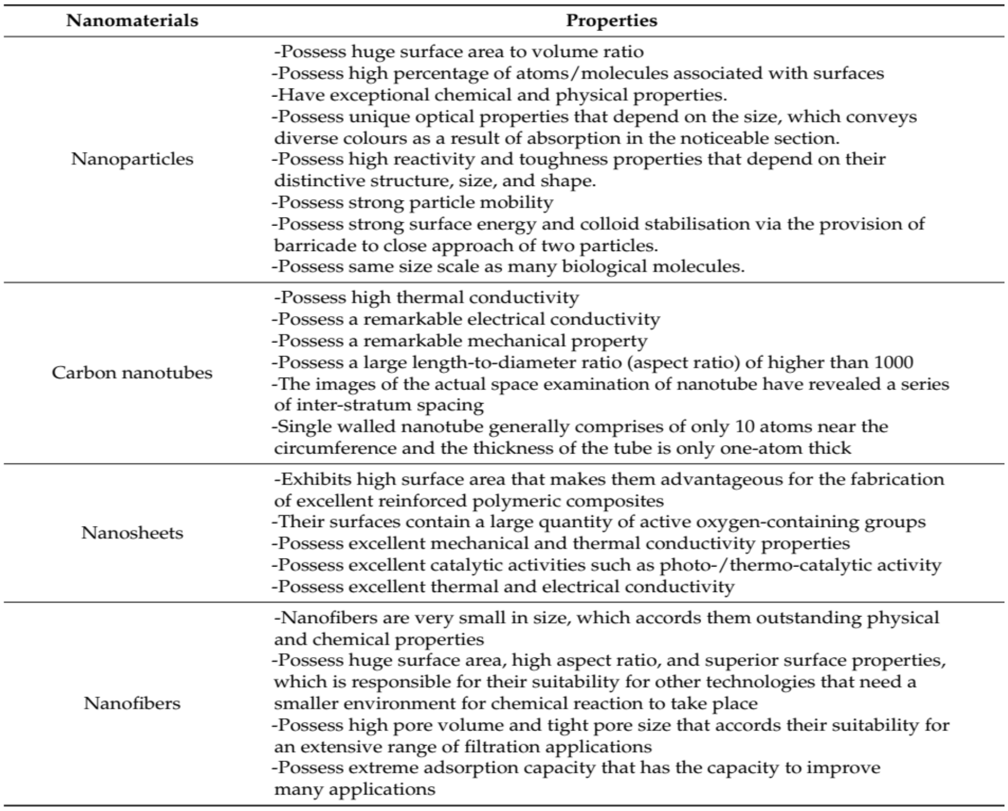


Figure 11. Distribution of micro and nano fillers in matrix. (a) Aluminum oxide (b) carbon fiber, (c) graphene nanoplatelets and (d) carbon nanotubes [48].

Nanofillers are fillers that have have at least one dimension in the nanometer range. Nanofillers may be zero dimensional (silver, nickel, gold, palladium, copper, and iron), one-dimensional (nanorods, nanofibers, nanowires, nanotubes) or two dimensional (graphene, silicates and nanosheets) [46]. Others include clays, nanocellulose and halloysite [49]. Their nano-level properties differ from their macroscopic ones. For instance, while bulk gold is very stable, gold nanoparticles are highly reactive and are used as catalysts [45]. The properties imparted by nanofillers to a polymer matrix, therefore, may be substantially different from the traditional materials from which they are made.

Table 3. Common fillers for nanocomposites and their properties [48].



Nanomaterials	Properties
Nanoparticles	-Possess huge surface area to volume ratio -Possess high percentage of atoms/molecules associated with surfaces -Have exceptional chemical and physical properties. -Possess unique optical properties that depend on the size, which conveys diverse colours as a result of absorption in the noticeable section. -Possess high reactivity and toughness properties that depend on their distinctive structure, size, and shape. -Possess strong particle mobility -Possess strong surface energy and colloid stabilisation via the provision of barricade to close approach of two particles. -Possess same size scale as many biological molecules.
Carbon nanotubes	-Possess high thermal conductivity -Possess a remarkable electrical conductivity -Possess a remarkable mechanical property -Possess a large length-to-diameter ratio (aspect ratio) of higher than 1000 -The images of the actual space examination of nanotube have revealed a series of inter-stratum spacing -Single walled nanotube generally comprises of only 10 atoms near the circumference and the thickness of the tube is only one-atom thick
Nanosheets	-Exhibits high surface area that makes them advantageous for the fabrication of excellent reinforced polymeric composites -Their surfaces contain a large quantity of active oxygen-containing groups -Possess excellent mechanical and thermal conductivity properties -Possess excellent catalytic activities such as photo-/thermo-catalytic activity -Possess excellent thermal and electrical conductivity
Nanofibers	-Nanofibers are very small in size, which accords them outstanding physical and chemical properties -Possess huge surface area, high aspect ratio, and superior surface properties, which is responsible for their suitability for other technologies that need a smaller environment for chemical reaction to take place -Possess high pore volume and tight pore size that accords their suitability for an extensive range of filtration applications -Possess extreme adsorption capacity that has the capacity to improve many applications

1.7 Synthesis of Nanocomposites

a. Melt-mixing.

This method is suited to thermoplastics, especially those which are insoluble. It is quick and cheap to carry out [48]. The matrix is heated to high temperatures above its melting point [50]. The filler material is then added, and the mixture is subjected to shearing forces [51]. An extruder or Banbury mixer is used to disperse and mix the CNTs with the matrix [48]. During mixing in the melt state, the strain that the polymer applies on the particles depends on its molecular weight and weight distribution [49]. This technique supports many polymers, requires no solvent and has little environmental effects [50]. The transfer of strain from the polymer to these new agglomerates leads to stronger shearing, which breaks them into individual particles. This process depends fundamentally on time and on the chemical affinity between the polymer and the surface of the nanoparticles [49]. In order to enhance polymer intercalation, filler may first be mixed with low molecular weight compatibilizer before the addition of high molecular weight polymer [50]. The melt blending is well matched with several industrial operations, such as extrusion and injection molding [49]. Other benefits of this technique are enhancement of the heat stability, improvement of mechanical properties, and low cost-effectiveness [49]. A limitation is the use of high temperatures, which can damage the modified surface of the nanofillers. [49,51].

b. Solution Mixing

This is the most common method used for composites, owing to its simplicity [49]. Solution mixing entails intensive agitation/refluxing to aid the mixing of polymers in a solvent. The use of solvent helps to exfoliate carbon nanotubes within the polymer matrix [48]. The filler is first dispersed into a solvent using sonication, stirring, or mixing. The polymer is then dissolved in the solvent, followed by mixing the polymer solution with filler suspension under mechanical stirring and/or sonication [46]. The filler/polymer composites are formed by removing solvent via evaporation or precipitation or casting the suspension into a film [50].

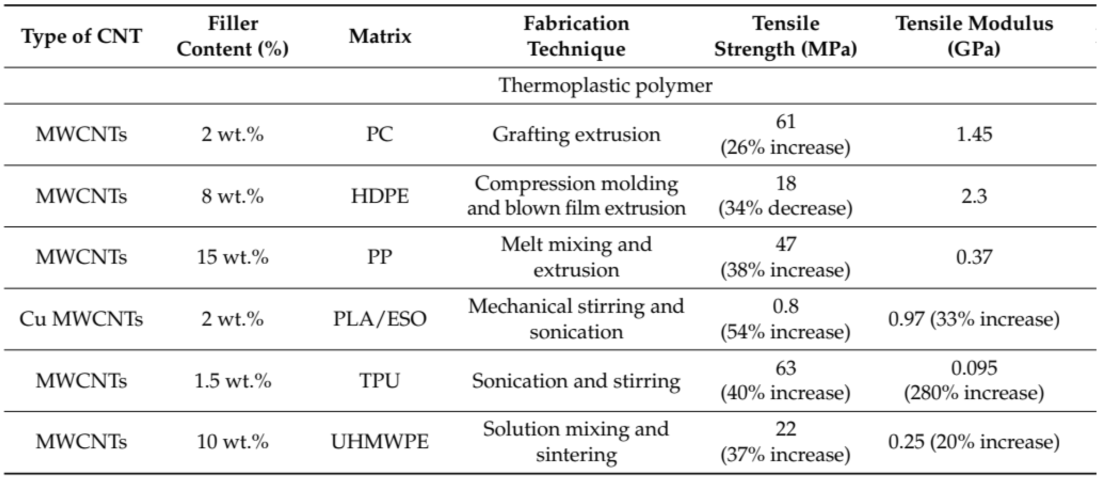
The solubility of the polymer determines the solvent used. While two different solvents may be used for filler and polymer, these must be miscible [50]. Also, solvents with low boiling point are preferred to those with high boiling point as the latter does not fully vaporize at lower temperatures and gets trapped in the solid polymer composite. [48]. Ultrasonic irradiation, magnetic stirring or even shear mixing can be used to disperse the nanofiller within the polymer [49]. In this method, when the solvent evaporates, the nanoparticle remains dispersed into the polymer chains. The produced nanocomposite can also be obtained as a thin film [49].

The benefits of using solution mixing include reduction in the permeability of gases and easy operation [49]. However, it is limited to soluble polymers [48].

c. In-situ polymerization

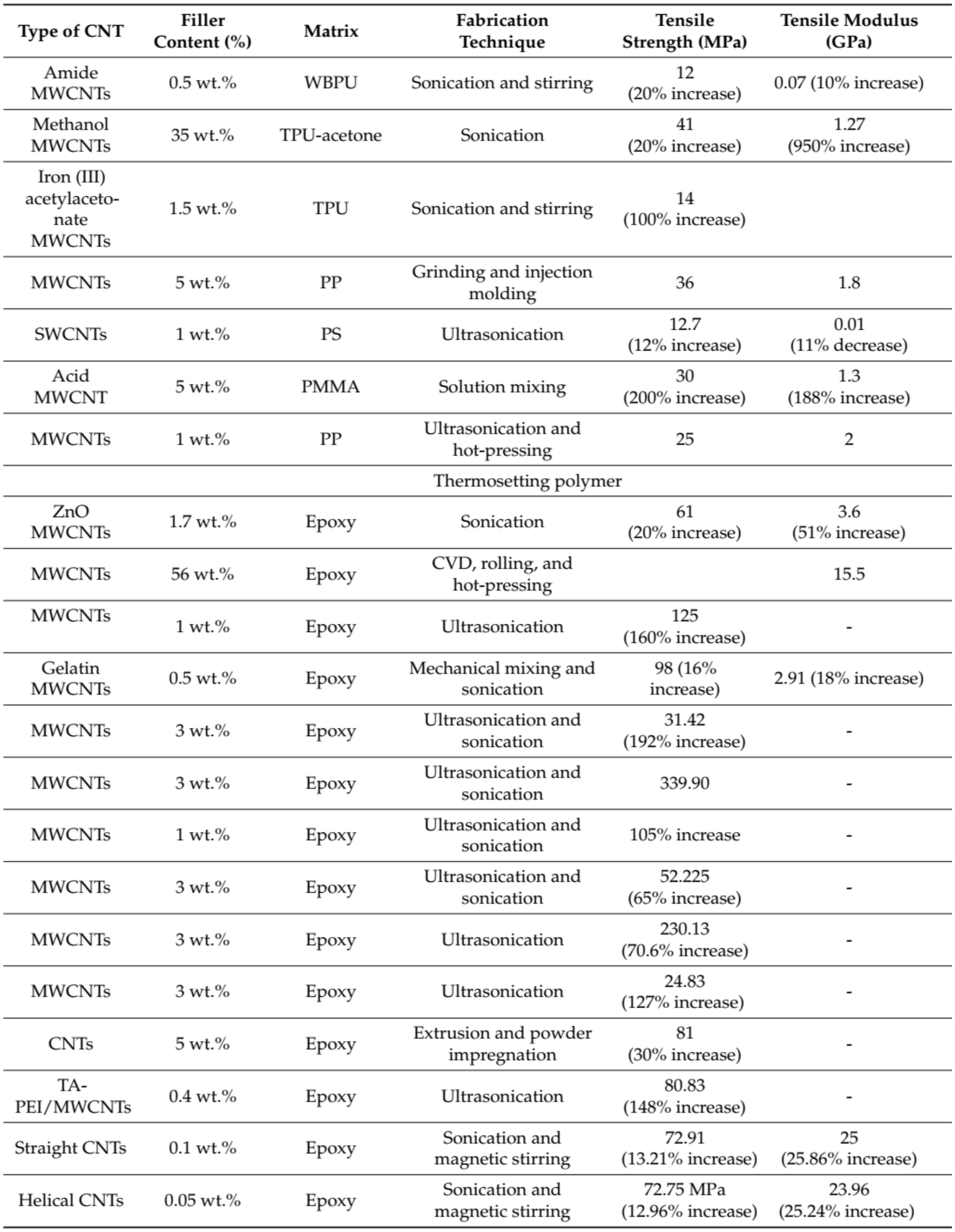
In-situ polymerization involves the production of the polymer chains in the presence of nanofillers so that reinforcement is achieved during polymerization. The efficient dispersion of carbon nanotubes in polymers is one factor that makes this type of polymerization attractive [50]. During in-situ polymerization, the nanofiller must be properly dispersed in the monomer solution before the polymerization process starts, ensuring the polymer will be formed between the nanoparticles [50]. This is particularly true for insoluble polymers. The method may be used for polymers that cannot be produced by solution or melt processing. In-situ polymerization can also be used as a method for noncovalent functionalization of carbon nanotubes, specifically, polymer wrapping. Organic modifiers may be used to help the dispersion of the nanoparticles [49]. In-situ polymerization is superior in terms of the ability to process high filler-loading nanocomposites, facilitate dispersion of filler within a polymer matrix, and affect excellent intimacy between filler and matrix polymers. [48]. Bulk polymerization, a form of in-situ polymerization, involves mixing monomer and initiator in a heated reactor under stirring in a protective atmosphere [48]. Emulsion, another variant, is used to produce latex particles with a wide variety of desired properties. Emulsion polymerization involves emulsification of a monomer with poor solubility in a continuous phase (e.g., water), forming an oil-in-water emulsifier in the presence of a surfactant [46]. When using this method, it is possible to apply higher loadings of nanofillers without agglomeration, have better performance of the final products, expand to the solvent-free form and have covalent bond among the nanoparticle functional groups and polymer chains [49]. Also, renewable additives like cellulose, chitin, starch, and lignin, can be made into composites during polymerization of commonly used organic monomers.[50]

Table 4. Mehcanical properties of nanocomposites [48]



Type of CNT	Filler Content (%)	Matrix	Fabrication Technique	Tensile Strength (MPa)	Tensile Modulus (GPa)
Thermoplastic polymer					
MWCNTs	2 wt.%	PC	Grafting extrusion	61 (26% increase)	1.45
MWCNTs	8 wt.%	HDPE	Compression molding and blown film extrusion	18 (34% decrease)	2.3
MWCNTs	15 wt.%	PP	Melt mixing and extrusion	47 (38% increase)	0.37
Cu MWCNTs	2 wt.%	PLA/ESO	Mechanical stirring and sonication	0.8 (54% increase)	0.97 (33% increase)
MWCNTs	1.5 wt.%	TPU	Sonication and stirring	63 (40% increase)	0.095 (280% increase)
MWCNTs	10 wt.%	UHMWPE	Solution mixing and sintering	22 (37% increase)	0.25 (20% increase)

Table 4 (continued)



Type of CNT	Filler Content (%)	Matrix	Fabrication Technique	Tensile Strength (MPa)	Tensile Modulus (GPa)
Amide MWCNTs	0.5 wt.%	WBPU	Sonication and stirring	12 (20% increase)	0.07 (10% increase)
Methanol MWCNTs	35 wt.%	TPU-acetone	Sonication	41 (20% increase)	1.27 (950% increase)
Iron (III) acetylacetonate MWCNTs	1.5 wt.%	TPU	Sonication and stirring	14 (100% increase)	
MWCNTs	5 wt.%	PP	Grinding and injection molding	36	1.8
SWCNTs	1 wt.%	PS	Ultrasonication	12.7 (12% increase)	0.01 (11% decrease)
Acid MWCNT	5 wt.%	PMMA	Solution mixing	30 (200% increase)	1.3 (188% increase)
MWCNTs	1 wt.%	PP	Ultrasonication and hot-pressing	25	2
			Thermosetting polymer		
ZnO MWCNTs	1.7 wt.%	Epoxy	Sonication	61 (20% increase)	3.6 (51% increase)
MWCNTs	56 wt.%	Epoxy	CVD, rolling, and hot-pressing		15.5
MWCNTs	1 wt.%	Epoxy	Ultrasonication	125 (160% increase)	-
Gelatin MWCNTs	0.5 wt.%	Epoxy	Mechanical mixing and sonication	98 (16% increase)	2.91 (18% increase)
MWCNTs	3 wt.%	Epoxy	Ultrasonication and sonication	31.42 (192% increase)	-
MWCNTs	3 wt.%	Epoxy	Ultrasonication and sonication	339.90	-
MWCNTs	1 wt.%	Epoxy	Ultrasonication and sonication	105% increase	-
MWCNTs	3 wt.%	Epoxy	Ultrasonication and sonication	52.225 (65% increase)	-
MWCNTs	3 wt.%	Epoxy	Ultrasonication	230.13 (70.6% increase)	-
MWCNTs	3 wt.%	Epoxy	Ultrasonication	24.83 (127% increase)	-
CNTs	5 wt.%	Epoxy	Extrusion and powder impregnation	81 (30% increase)	-
TA-PEI/MWCNTs	0.4 wt.%	Epoxy	Ultrasonication	80.83 (148% increase)	-
Straight CNTs	0.1 wt.%	Epoxy	Sonication and magnetic stirring	72.91 (13.21% increase)	25 (25.86% increase)
Helical CNTs	0.05 wt.%	Epoxy	Sonication and magnetic stirring	72.75 MPa (12.96% increase)	23.96 (25.24% increase)

1.8 Previous Work

Microwave synthesis has gained a lot of attention in the literature, spanning a wide array of reactions that include microwave-induced polymerization [36]. This interest can be largely attributed to the reputation of microwave heating as a faster, energy efficient method of chemical synthesis. [77]. The frequency of the microwaves was found to be integral to the mechanical properties of composites, with lower frequencies giving better interlaminar sheer stress [77]. Heating rate has also been observed to increase significantly in microwaves when nanofiller concentration was increased [75]. The increased heating rates also enhanced the compressive and flexural strengths of the composites [76]. However, this had a detrimental effect on the tensile and interlaminar strength [76].

Carbon nanomaterials have also been reacted with polymeric materials under conditions of microwave heating. Pristine CNTs were heated under microwave irradiation, along with polypropylene (PP) [83]. PP was molten by the heat generated by CNTs, and a well-formed CNTs network was built under proper microwave treatment period, after which hot pressing was carried out, resulting in the formation of conductive PP composites. The pressing temperature and CNT loadings were found to significantly enhance the conductivity of polypropylene.

In other instances, microwaves have been used to functionalize carbon nanotubes [79]. Zhang and coworkers successfully grafted polylactic acid onto carbon nanotubes, increasing their functionality and dispersion [80]. Another interesting work, which bears closer semblance to this research was conducted by Kim and his group [81]. In this work, graphene nanoribbons were functionalized with poly (propylene oxide) and used to reinforce thermoset polymers.

Long, in his M.A. thesis, explored the use of pure and functionalized CNTs in conventional oven polymerization but there was no appreciable difference in mechanical properties [52]. Hulette carried this further by comparing these oven samples to those made by microwave-induced polymerization [53]. However, the microwave composites were eventually cured in the conventional oven, casting some doubts on a meaningful comparison of the two methods. Further research was done by Thomas to find the optimum conditions for curing the composites in microwave and this resulted in more solid composites which were still too soft to be molded. Moreover, settling tests from previous works [52, 53] indicated that functionalization was unsuccessful. Building on these previous works, this current research has been able to successfully functionalize CNTs and produce fully cured composites in the microwave, making their comparison with oven composites more meaningful. The CNT loadings have also been increased from 0.1% to 0.2%.

1.9 Objectives of Study

a. Functionalization of Carbon Nanotubes

An important motivation for the use of graphene nanoribbons as an alternative to carbon nanotubes is the difficulty in functionalizing the latter [81]. The ability to functionalize CNTs. thus, has been a limiting factor to the exploitation of their excellent properties. The first part of this research aims to modify the surface properties of CNTs via covalent functionalization. The use of reactive Grignard reagent is expected to create covalent linkages with carbon nanotubes. n-pentenyl, being the most reactive of the moieties, is expected to give higher functionality to CNTs, enabling more efficient interaction with medium and, hence, better dispersion. This should manifest in better suspension during the settling tests and a higher percentage mass loss thermogravimetry of functionalized carbon nanotubes.

b. Composites containing Pure and Functionalized Carbon Nanotubes

The processing method adopted for a nanocomposite has implications for the thermal and mechanical properties of the material formed. It is expected that the functionalization of carbon nanotubes would enhance the overall properties of the composites they form. Covalent functionalization of carbon nanotubes should make them more evenly dispersed in a polymer matrix, leading to better interaction with matrix and hence, more efficient transfer of properties in comparison to pristine nanotubes. These covalently bonded moieties are also expected to take part in the polymerization process, resulting in polymer chains that are covalently bonded to CNTs (figure 12). Since the interaction between the matrix and filler is critical to properties of the composite, this covalent bonding should most likely increase load transfer. It is, thus, expected that composites made from functionalized carbon nanotubes will show enhanced thermomechanical properties in comparison to those made from pristine carbon nanotubes.

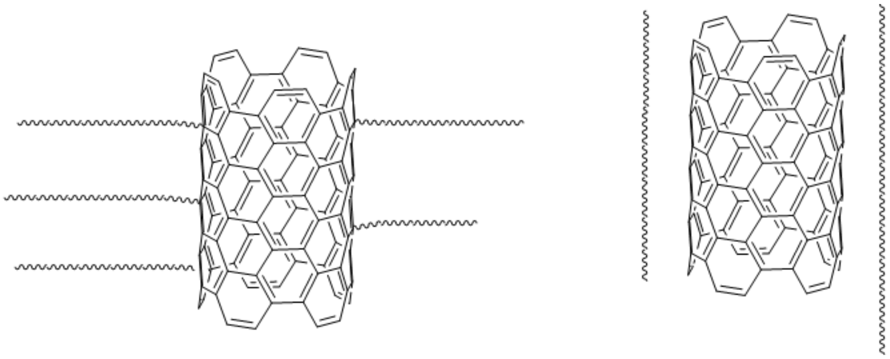


Figure 12. Polymer chains growing from CNTs. These chains are covalently linked, as opposed to CNRTs being buried within polymer chains.

c. Reaction Rates for conventional Heating (CH) and Microwave Heating (MH).

Conventional polymerization starts from the molecules on the outside of the vial and proceeds towards the interior, leading to longer reaction time. The volumetric nature of microwave heating polymerization is expected to make this process faster than conventional heating. It is hoped that Microwave composites will be polymerized at a rate which is higher than conventional composites.

d. Selectivity of Microwave Heating

The selectivity of microwave heating guarantees that when carbon nanotubes are mixed with a non-polar monomer such as styrene, two different processing techniques would be observed for microwaves and for conventional heating. The selective heating of carbon nanotubes over polystyrene in microwave ensures that the functional groups of CNTs receive priority as initiators of polymerization. This microwave-induced polymerization is expected to increase the proportion of polymer chains that are covalently bonded to carbon nanotubes, leading to better load transfer in microwave composites. MH composites are, therefore, expected to have better mechanical properties compared to CH composites. The use of functional groups as initiators in microwave-induced polymerization also promises control of molecular weight by varying the amount of functional CNTs used in the reaction.

The goals of the research can be summarized as follows:

- Determination of the effect of different moieties on the dispersion of carbon nanotubes.
- Comparison of the thermal and mechanical properties of carbon nanotubes made under microwave and conventional heating.
- Investigation of the kinetics of microwave and conventional oven polymerization.

- Investigation of properties of composites made from functionalized and unfunctionalized carbon nanotubes.
- Comparison of the mechanical and thermal properties of composites containing different loadings of CNTs.

CHAPTER 2

FUNCTIONALIZATION OF CARBON NANOTUBES

2.1 Materials

a. Carbon Nanotubes

Carbon nanotubes used in this experiment were procured from Sigma Aldrich and were multiwalled. Multiwalled carbon nanotubes were expected to have higher mechanical strength owing to the presence of multiple tubes. The purity was reported as (95%+). This was confirmed by the fact that there were no metal residues during thermogravimetry of the nanotubes. The inner and outer diameters were 5-10 nm and 10-20 nm respectively with an average length of 0.5 to 200 µm. Carbon nanotubes were chosen owing to their superior mechanical properties and their intense heating in microwave [38]. The chirality of tubes could not be ascertained from the manufacturer.

b. Styrenyl

Styrenyl: Styrenyl is a colorless and odorless liquid that is very volatile. It is the basic building block of polystyrene, a commodity plastic. The production of styrene starts with the alkylation of benzene (an unsaturated hydrocarbon obtained from crude oil) with ethylene to produce ethylbenzene. Once that is done, the ethylbenzene is put through a very precise dehydrogenation process by passing ethylbenzene and steam over a catalyst like iron oxide, aluminum chloride, or lately, a fixed-bed zeolite catalyst system to get a very pure form of styrene [55]. Styrene undergoes chain polymerization under the catalysis of a free radical initiator such as benzoyl peroxide. Styrene polymerizes at room temperature and so needs to be refrigerated when not in use. It is also a suspected carcinogen and needs to be handled with care [54]. The choice of styrene is due to its availability. It also has a low microwave loss factor and is transparent to microwaves. This guarantees selective when carbon nanotubes are added to styrene in a microwave.

c. Phenyl

Phenyl is a cyclic group of atoms with the formula C_6H_5. Phenyl moiety used in this experiment is obtained from its Grignard reagent, phenylmagnesium bromide. This is prepared by the reaction of bromobenzene with magnesium. Phenyl is included in the research because phenyl-functionalized CNTs are stable and unreactive and are included as a reference for investigating the effects of functionalization on the properties of carbon nanotubes.

d. n-pentenyl

This is a univalent radical derived from pentenes by the removal of a hydrogen atom [56]. n-pentenyl has been chosen because it is highly reactive and is expected to bond more efficiently to the carbon nanotubes.

2.2 Procedure

To ensure efficient exfoliation of CNTs and increase their reactivity with monomers, covalent functionalization was carried out with three different functional groups, styrenyl, phenyl and n-pentenyl. Covalent functionalization was carried out using Grignard reagents prepared from each of the moieties. Grignard reagents are organomagnesium compounds with the general formula R-Mg-X where X is a halide and R is an alkyl or aryl group. They are formed by reacting magnesium with aryl or alkyl halides. The use of Grignard reagent was to create covalent linkages between aryl groups and aromatic carbon rings, a hitherto unexplored method of functionalization. However, moisture easily deactivates Grignard reagents, preventing the formation of new carbon-carbon bonds from the carbonyl. For this reason, the glassware involved in the rection, the CNTs and magnesium had to be dried for 24 hours in a conventional oven, under vacuum and at a temperature of 88 C. Thes glassware include the following:

- A 100 ml, 3-neck, round-bottom flask.
- A 500 ml, round bottom flask containing carbon nanotubes.
- 2 glass syringes
- Reflux condenser.
- Pressure-equalizing funnel.

The required amounts of CNTs and reagents were calculated beforehand [see Appendix A]. The nanotubes were weighed and placed into the 3-neck flask before drying. The magnesium was crushed into fine powder to maximize surface area, before being dried in the oven. On the day of the reaction, the flask containing the CNTs was taken out and capped to prevent the entry of moisture. It was then pressurized using a nitrogen line. Dried Tetrahydrofuran (THF) was added to the CNTs, and the mixture sonicated for 90 min to exfoliate the CNT bundles.

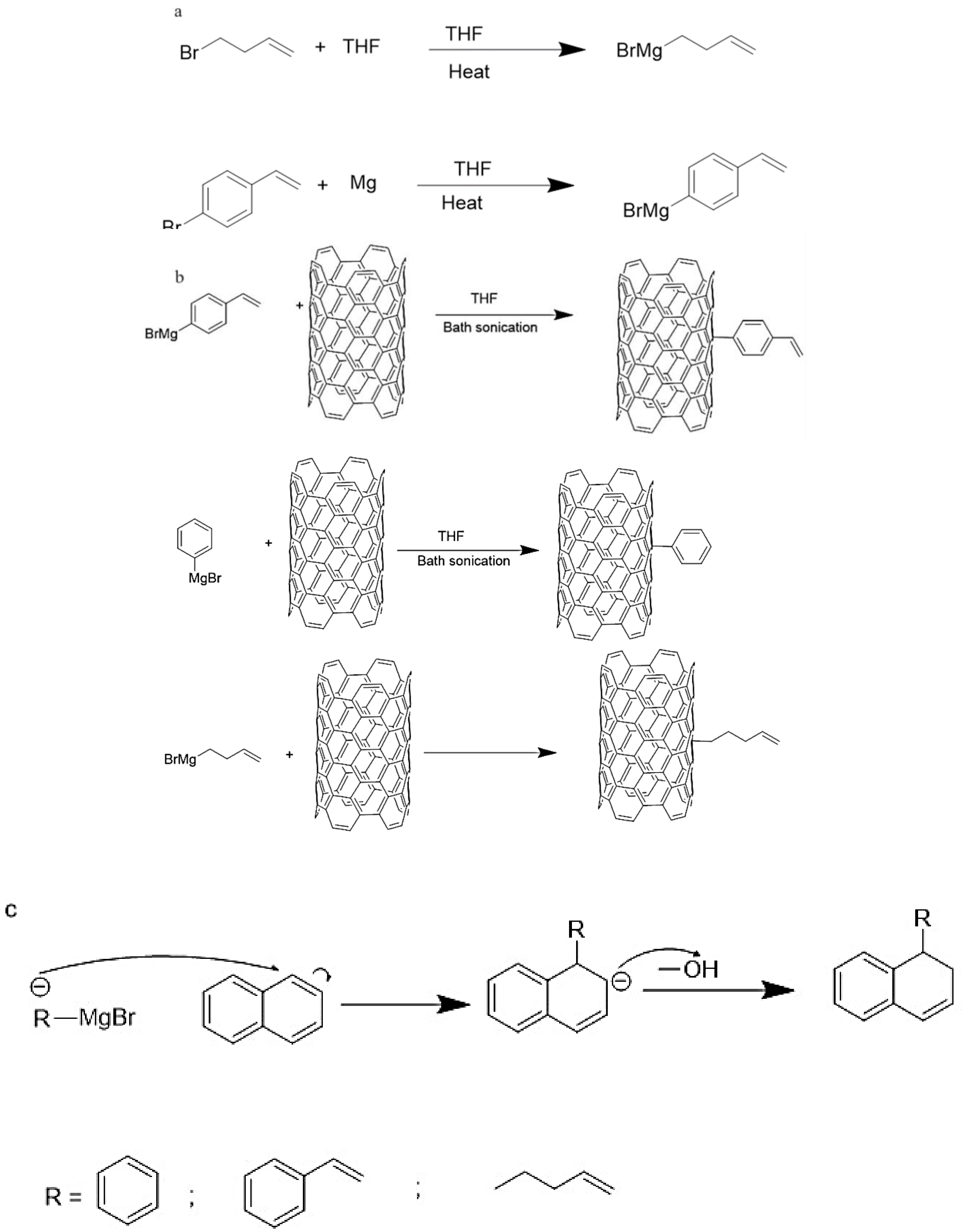


Figure 13. Functionalization of CNTs. (a) preparation of pentenylmanesium bromide and styrenyl magnesium bromide. (b) Preparation of styrenyl- CNTs, phenyl- CNTs and n-pentenyl- CNTs (c) mechanism of functionalization: R attacks aromatic carbon, transferring the double bond to the adjacent carbon which abstracts a hydrogen from methanol, stabilizing the ring.

The 100 ml flask containing magnesium was capped at the two ends while a capped thistle funnel was placed on the middle neck. Bromostyrene was added to pressure-equalizing funnel. 15 ml of THF was added to the Bromo styrene and the mixture was slowly added to the magnesium while heating and stirring with a stir bar. 15 ml was initially added to activate the magnesium and the rest slowly to prevent coupling. When the magnesium totally disappeared, the stirring and heating was turned off. The styrenylmagnesium bromide was then added slowly to the CNTs in the sonication bath and the mixture is sonicated for a further 90 minutes, causing the Grignard to react with and functionalize the CNTs. The mixture was swirled once or twice during the sonication and heated for the last 30 minutes. At the end, the CNT mixture was taken out and ethanol added to quench the reaction. A filtration system was set up with a membrane glass funnel resting in a conical flask which is connected to a vacuum pump. A wet Teflon filter paper was placed on to the glass membrane and a glass container is fixed on top of it. The mixture then poured onto the filter paper and filtered while stirring gently. The CNTs were washed with acetone which removed magnesium salts. Isopropyl and hexanes were used to wash the nanotubes, removing unreacted material. The carbon nanotubes were then scooped into a vial, weighed, labeled, and placed in the vacuum oven to dry. This procedure was repeated for phenylmagnesium bromide and pentenylmagnesium bromide. In the end, four categories of CNTs were obtained: pristine or pure CNTs (pu-CNTs), phenyl-functionalized CNTs (ph-CNTs), n-pentenyl- functionalized CNTs (pe-CNTs) and styrenyl-functionalized CNTs (st-CNT) CNTs. Phenylmagnesium bromide was bought and not prepared in this research.

2.3 Settling Test

5 mg of each CNT type (phenyl, styrenyl, n-pentenyl) was weighed and placed into a 20 ml vial. 5 grams of styrenyl was then added resulting in .2 wt % mixtures of CNT and styrene. The vials were then sonicated for 30 minutes after which they were made to stand for about two hours. It was expected that efficient dispersion would result in the suspension of carbon nanotubes in solution while poor dispersion would result in the settling and clumping of carbon nanotubes. Settling test, thus, is a measure of the effectiveness of functionalization [57].

The vials were then made to stand for 24 hours. Figure (20) shows the results of settling test after 24 hours. pe-CNTs showed a higher level of dispersion in solution and maintained this for 24 hours whereas all other moieties settled after two hours. This may be attributed to the higher reactivity of n-pentenyl, compared to the other moieties. Being sp^3-hybridized, n-pentenyl has a lower s-character which means its electrons are more loosely held, compared to other moieties. The electrons, thus, readily take part in chemical reactions with the CNTs. The bonding of the reactive n-pentenyl to the CNT surface increases interaction between CNTs and styrene monomers. This effectively counteracts the van der Waal’s forces and exfoliating CNT ropes in styrene, leading to better suspension.

Moreover, the pi-stacking interaction between the aromatic rings of phenyl and styrenyl results in attraction between nanotubes bearing these group. This may also explain the agglomeration observed in these samples. Because of this superior dispersion, pe-CNTs were used to represent functionalized CNTs in subsequent comparison of composites.

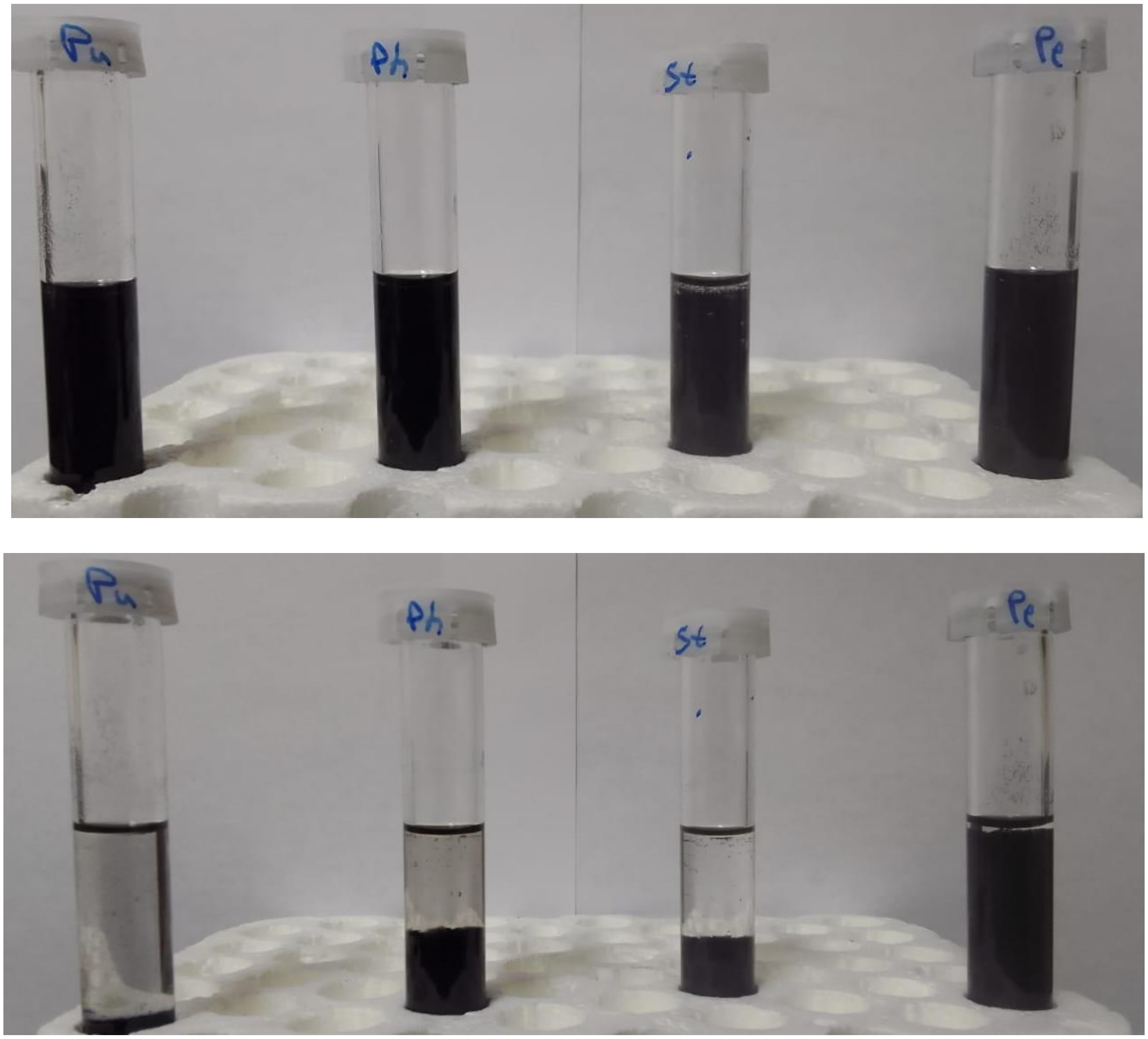


Figure 14. Settling test for functionalized CNTs. n-pentenyl-functionalized CNTs show better dispersion than other samples. From left to right: pure CNTs (pu-CNTs), phenyl CNTs (ph-CNTs), styrenyl CNTs (st-CNTs) and n-pentenyl CNTs (pe-CNTs).

2.4 Thermogravimetry of Carbon Nanotubes

Thermogravimetric analysis of pure carbon nanotubes provides another layer of evidence for functionalization [60, 61,62]. The graph shows mass loss around 200 °C and at 600 °C. The loss at 600 °C is indicative of the degradation of carbon nanotubes and is common to both functionalized and unfunctionalized carbon nanotubes [63]. (figure 22). The loss of material at 300 °C is only seen for functionalized nanotubes, strongly suggesting that this is a defunctionalisation step at which functional groups are coming off the carbon nanotube.

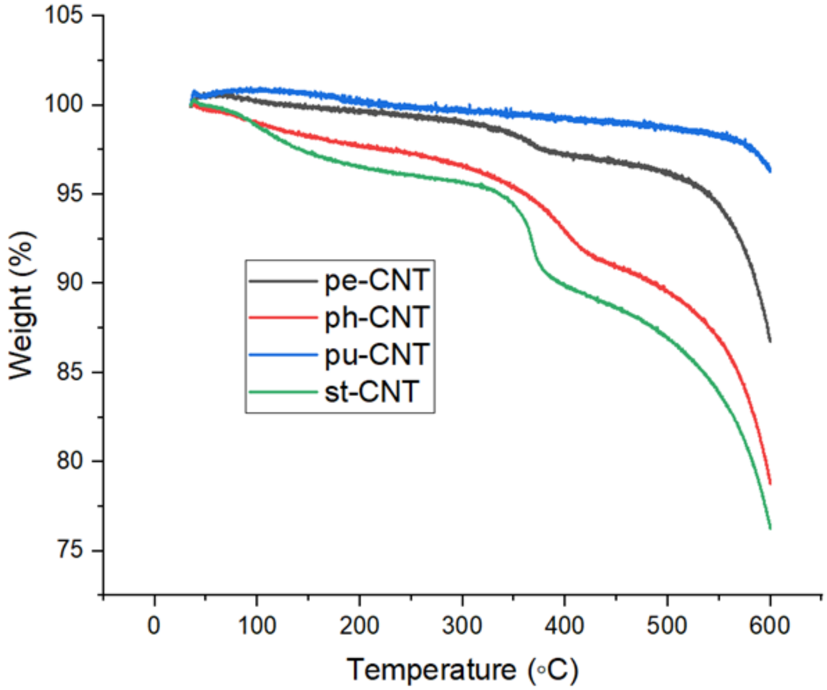


Figure 15. TGA of fucntionalized CNTs showing a mass loss around 400 ℃

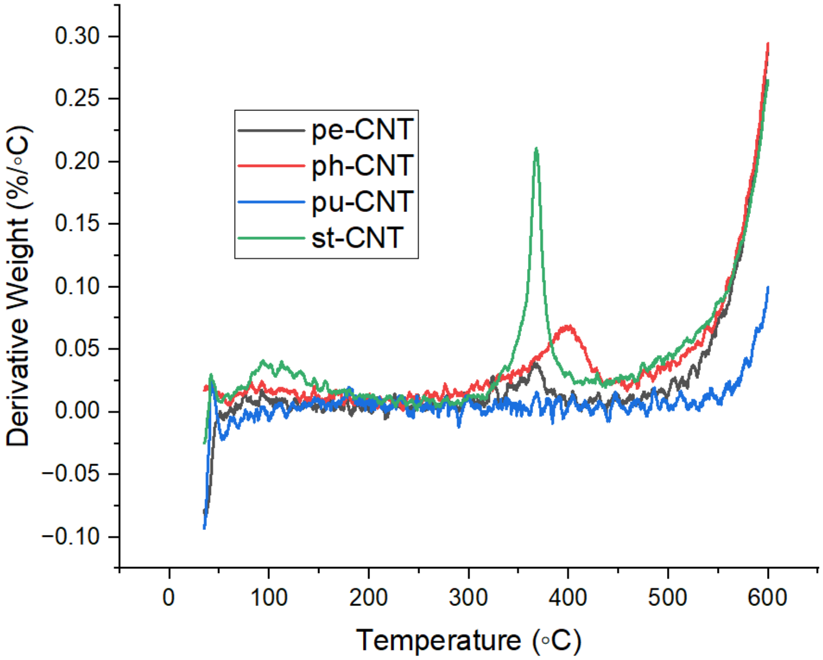


Figure 16. DTG of functionalized CNTs. Functionalized CNTs show earlier decomposition, compared to pure CNTs.

While the previous analysis confirms the functionalization of CNTs, it does not answer the question of whether this functionalization is covalent or a mere adsorption of moieties to the carbon nanotube surface. An interesting feature that may offer some evidence is the shift in the onset of degradation of carbon nanotubes (figure 23). This is indicative of the extent of interaction between nanotubes and functional groups. In the case where nanotubes are simply physically adsorbed onto CNT surface, the decomposition of such moieties would not affect the structural integrity of the nanotubes. However, If the moieties were covalently bonded then their decomposition weakens the CNT structure, resulting in lower degradation onset. This explains why the degradation onset for functionalized CNTs is considerably lower than that of pure CNTs and may be taken as supporting evidence for covalent functionalization.

CHAPTER 3

POLYMERIZATION AND SAMPLE PREPARATION

3.1 Polymerization

Samples were prepared as was done for the settling test and placed in a conventional oven. Heating

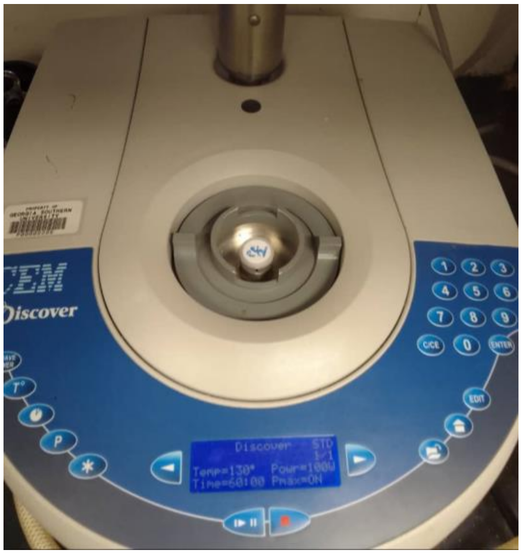


Figure 17. Polymerzation techniques. Microwave polymerization (left). Metal blocks are used to speed up the rate of heat transfer in conventional polymerization (right).

Similar vials were made again and polymerized in both oven and microwave. The oven temperature was set to 130 ℃ for ten hours. CEM Discover microwave was used for microwave polymerization. Similar vials were prepared, and the solution transferred into special microwave vials. These were then polymerized in the microwave 100W power for two hours at 130 ℃ . The vials were then broken, and the polymer composites retrieved. Since the microwave heating is continuous for only an hour, the ample was cooled for 30 minutes and heated again for another hour.

3.2 Molding

A Carver ® mold was turned was set to a temperature of 200 ℃, following the work of Hulette [53]. The plates were wrapped in aluminum and sprayed with Sprayon ®, a dry film-releasing agent, to prevent the polymer from sticking to the aluminum foil. Polymer was placed between the mold and set into the machine. When temperature reached 200 ℃, a pressure of 0.5-1 TPa was applied to the composite to flatten it. The machine was then switched off and water turned on to cool the sample for 5 minutes. In the case of conventional composite, the molding process was used to melt-mix the samples in order to obtain uniform wafers of composite material. A dog bone was then used to cut out specimen from each disc, in preparation for characterization.

Figure 18. Specimen preparation. a. Molding of composites b. A conventional oven composite taken from vial c. A microwave oven composite d. Preparation of specimen for characterization.

3.3 Characterization Techniques

The methods of characterization were chosen to analyze the thermomechanical properties of the polymer. These included applying increasing force or temperature to the material and measuring its response over a certain range. The various methods were chosen intended to complement each other in revealing the effects of the different processing methods on properties such as glass transition temperature, onset of degradation, extent of polymerization, tensile strength, ultimate stress, storage modulus and damping. These macroscopic properties would then offer a glimpse into the molecular structure of the composites as well as suggest uses to which the various composites could be put. The techniques employed are thermogravimetry, differential scanning calorimetry, dynamic mechanical analysis, and tensile testing.

a. Thermogravimetric Analysis (TGA)/Differential Thermogravimetry (DTG)

Thermogravimetry is a thermal characterization technique in which a sample is heated to increasing temperatures while the percentage change in mass is noted. In so doing, information may be obtained about thermal stability, presence of impurities, phase transitions, absorption and desorption. The graph of the decomposition may appear as percentage change versus temperature (TG) or a differential of the TG (DTG) which a TGA may be Isothermal (temperature is held constant and sample weight is measured with time), Quasistatic thermogravimetry (sample is heated to constant weight at each of series of increasing temperatures) or dynamic thermogravimetry (sample is heated and the change in mass is recorded as a function of temperature).

Figure 19. TA Instruments ® Q50 Thermogravimetric Analyzer.

In this experiment, TG has been used in a dynamic mode. Nitogen was used at a rate of 20 ml/min to create an inert atmosphere. The experimental design consisted of heating the sample at a rate of 10 ℃/mon to 950 ℃. This temperature was chosen to ensure the complete degradation of carbon.

b. Differential Scanning Calorimetry (DSC)

DSC studies the change in heat capacity of a material as a function of temperature by heating or cooling a substance. The sample is held in a pan and an empty reference pan is included to cancel the effects of the pan. DSC enables the study of important parameters such as effects of additives on glass transition temperature, the energy needed to process a material (Cp) as well as curing. By repeated heating and cooling, it is possible to identify reversible and irreversible reactions occurring within the material. Using Nitrogen to provide inert atmosphere, the samples were cooled to -20 ℃, heated to 260 ℃, and then cooled back to -20 and heated once more to 260 ℃.

The two-cycle heating was chosen because preliminary tests showed that the glass transition temperature changed became stable after the second heating.

Figure 20. TA Instruments ® DSC 250 Differential Scanning Calorimeter.

c. Dynamic Mechanical Analysis (DMA)

DMA is a thermomechanical, analytical technique that is of tremendous importance in the study of polymers and polymer composites. It studies the changes in visco-elastic behavior of a polymer under changing temperature or frequency. This gives important information about the strength (storage modulus), glass transition, energy dissipation and crosslinking of materials. During DMA analysis, a sample may be subjected to tensile, compressive or flexural forces at a given frequency. The storage and loss modulus are then calculated for changing temperatures. Samples were subjected to flexure at a frequency of 1Hz while heated from 20 °C to 120 °C.

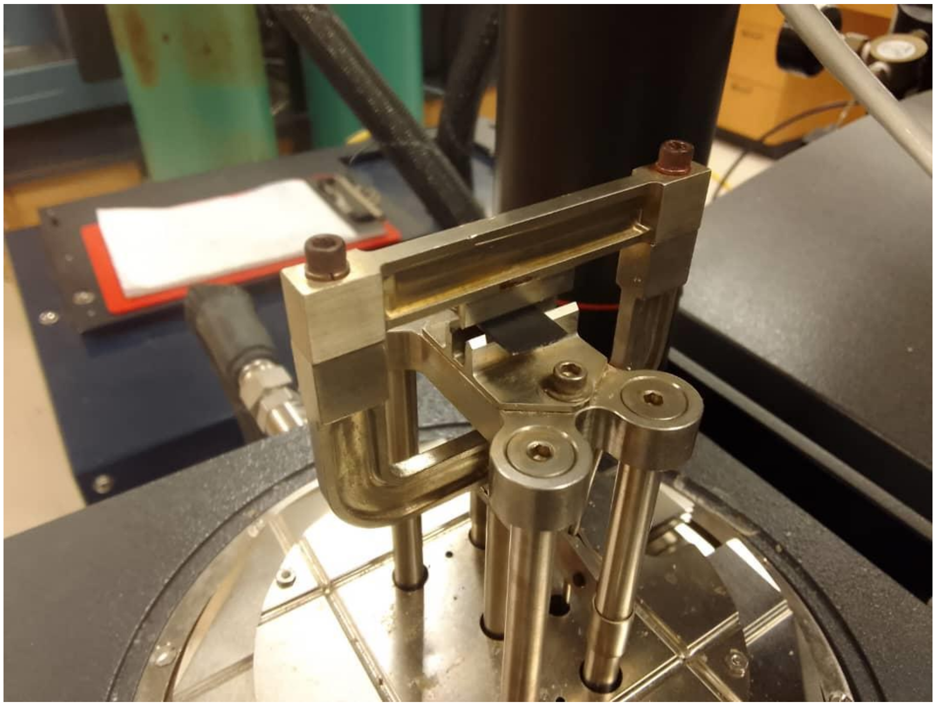


Figure 21. TA Instruments ® DMA Q800 Dynamic Mechanical Analyzer.

d. Tensile Testing

Tensile testing, as the name suggests, subjects the material to a tensile force and measures its response in terms of ultimate stress and Young’s Modulus. Other important information such as ductility, brittleness and toughness can be obtained from the graph of stress versus strain. In this experiment. Samples were subjected to a tensile force at a crosshead speed of 2 mm /s until they broke.

Figure 22. A tensile analyzer from Test Resources ®

CHAPTER 4

CHARACTERIZATION OF NANOCOMPOSITES

4.1 Thermogravimetric Analysis of Nanocomposites.

The TGA of composites shows a mass loss which is more pronounced for polystyrene (figure 24). A good guess is that this is the decomposition of short-chain polystyrene and unpolymerized monomers. This has been confirmed by polymerizing samples at different times and running a TGA. The shorter the polymerization time the larger the bulge, confirming this to be representative of the decomposition of chains not fully polymerized. It is possible to estimate the percentage of unpolymerized materials and, by extension, establish the degree of completion of the polymerization (figure 25 a). Figure 25b shows that the addition of carbon nanotubes increases the extent of polymerization of composites. Given that the rate of polymerization is identical for both microwave and conventional composites, this gives a firm grounding for the assertion that microwave polymerization is faster than conventional (since it achieves identical polymerization in two hours, compared to ten hours for conventional methods).

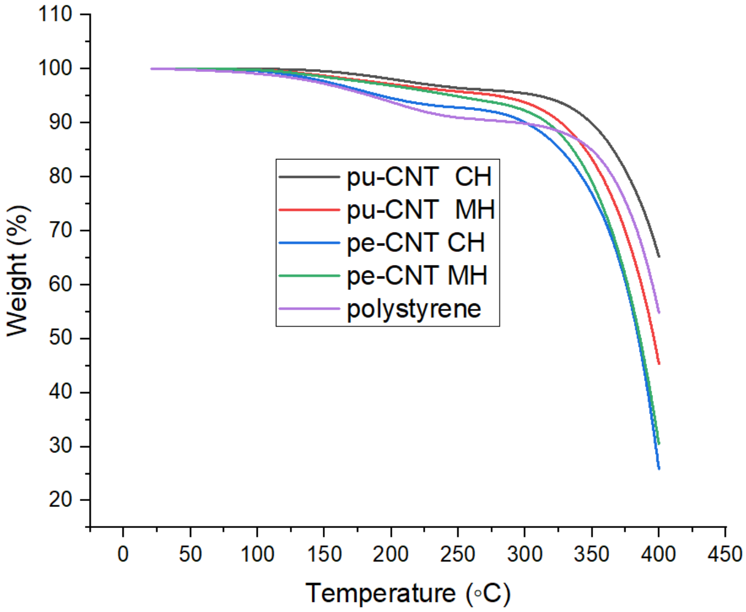


Figure 23. TGA of composites showing mass loss around 200 ℃.

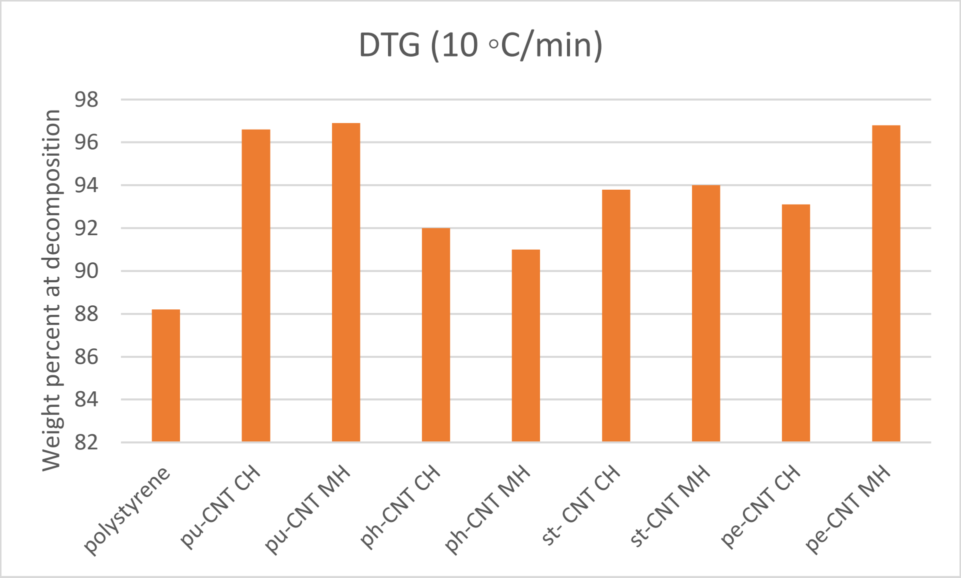


Figure 24. The percentage weight of composites at degradation.

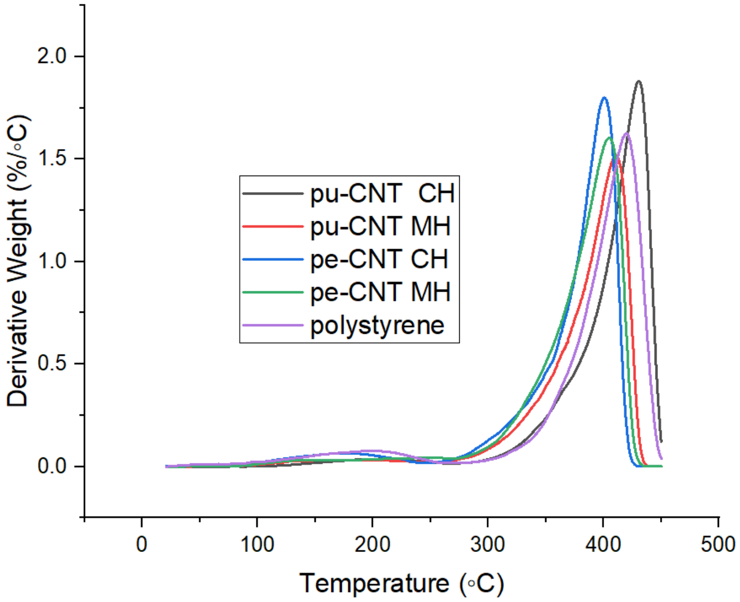


Figure 25. DTG of composites. Composites comtining functionalized CNTs appear to have loer thermal stability.

From figure 26, it can be observed that the onset of degradation of composites containing CNTs is lower than that of pure polystyrene, suggesting that the addition of carbon nanotubes generally decreases the thermal stability of polymers. While this makes CNT composites undesirable for high heat applications, it may prove useful in microwave recycling of composites [40]. The lower thermal degradation implies a potentially lower energy cost during such recycling process.

4.2 Dynamic Mechanical Analysis

The graph storage modulus of five specimens is shown in the graph of fig (27). The first part for the graphs consists of a plateau region which gives the value of storage modulus at room temperature. Composites generally showed higher storage modulus than pure polystyrene. This is attributable to the immobilization of the polymer chains by carbon nanotubes [64]. Pure carbon nanotubes in microwave and conventional oven show marginally higher storage modulus of about 2500, suggesting that the addition of functionalized carbon nanotubes probably lowered the storage modulus of the polymer. The only clear case for comparison (where error bars do not overlap, figure 28), however, is that of pe- CNT composites in microwave and conventional oven. Here, microwave composites show higher storage modulus than conventional counterparts. This reinforces the idea that the initiation by functional groups in the microwave oven led to more covalently linked polymers in comparison to conventional heating, leading to better storage modulus.

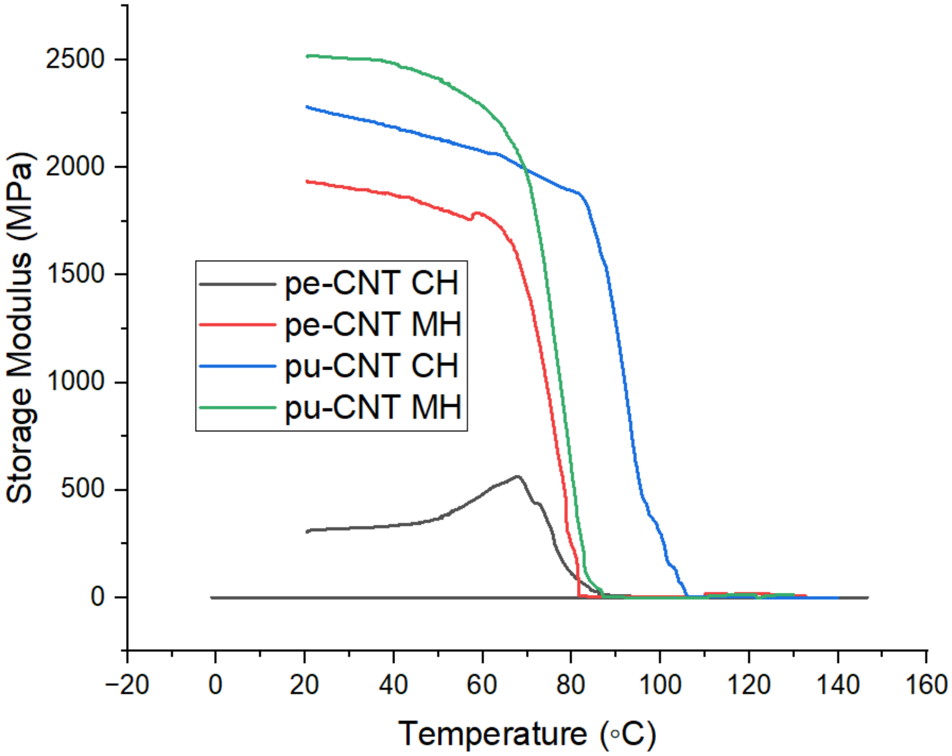


Figure 26. Storage modulus of selected composites as a function of temperature.

Pure-CNT composites have larger glass transition temperatures (evidenced by the declining portion of the graph) may also be indicative of higher molecular weight, implying that the incorporation of CNTs lowered the molecular weight of the polymer. This may be explained in terms of CNTs getting in the way of growing polymer chains and causing premature terminations. The graph of pe-CNT composites (MH) shows a bulge just before glass transition. This is caused by accumulation of stress during the microwave polymerization and also manifests in the DSC values for glass transition temperature. The absence of the rubbery plateau regions emphasizes the absence of crosslinking in the composites [66]. The Storage modulus is well over 1500 for 0.2% loading, compared to 1494 MPa for 0.5% loading in one research [69].

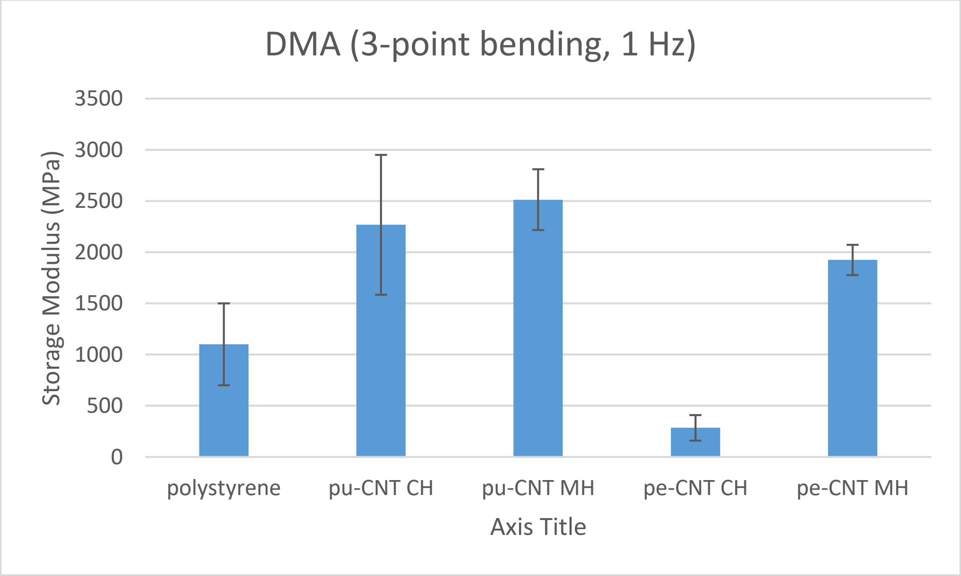


Figure 27. Storage modulus of selected composites. measured from DMA

4.3 Differential Scanning Calorimetry

DSC was run in two cycles and showed two glass transition temperatures, the latter being settled on as the glass transition temperature of the material. The existence of multiple glass transition temperatures could be explained in terms of stress relaxation. The first glass transition corresponded to the material's stressed state. This stress is confirmed by the hump on the DMA right before glass transition. These stresses are trapped within the polymer until it is heated and attains mobility beyond glass transition temperature. At this point, polymer chains realign themselves in positions of lower energy. The glass transition temperature, thus, increases with heating and cooling of the sample until the actual glass transition is reached. Overall, the addition of CNTs had no effect on the glass transition temperature of polystyrene [64].

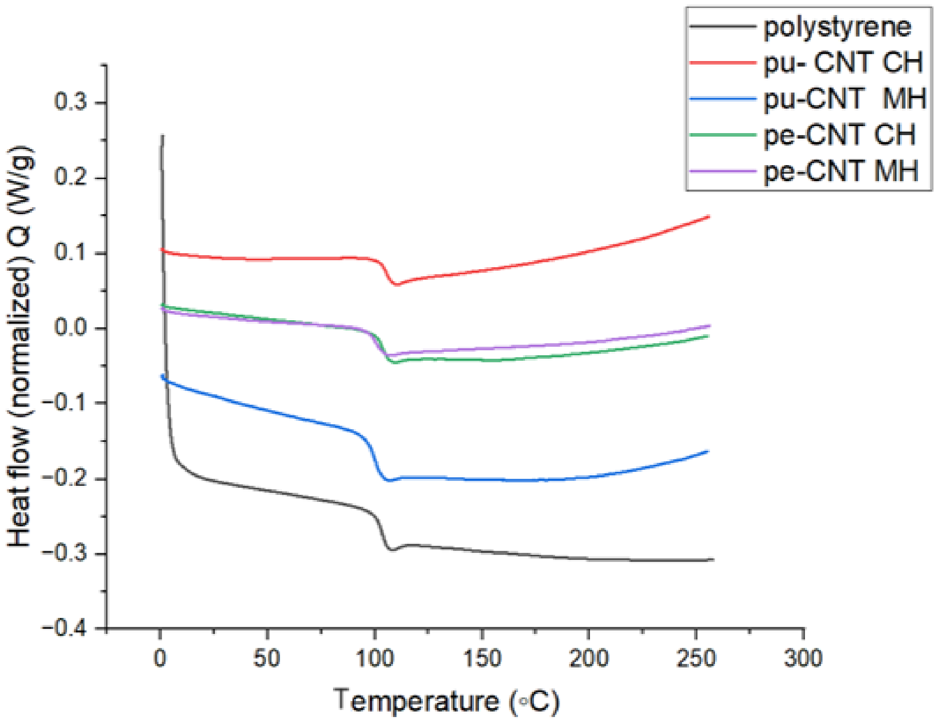


Figure 28. DSC curves of selected composites (second heating).

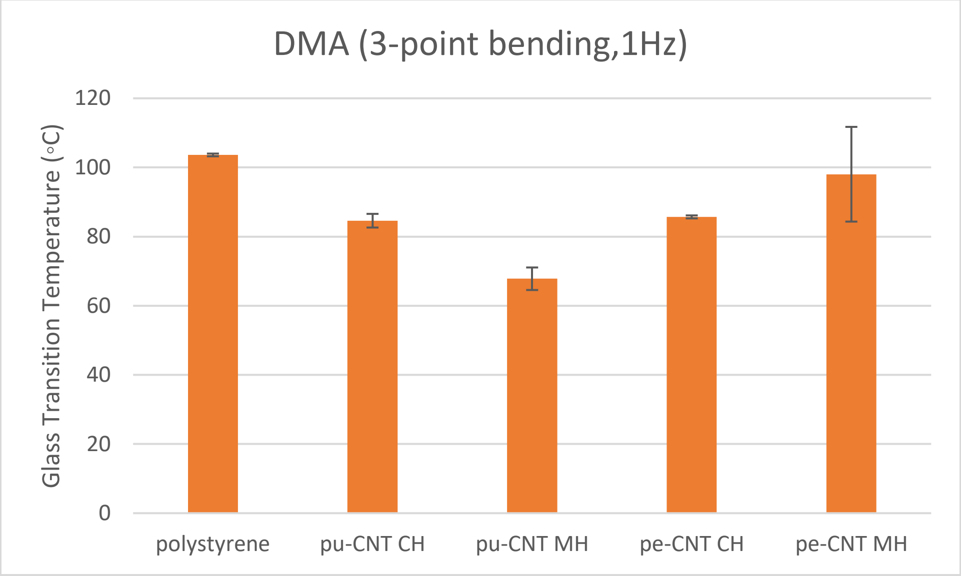


Figure 29. Glass transition temperatures of selected composites, measured from DMA (DMA).

The T_g measured from DSC differs slightly from that measured from the peak of the tan delta curve in DMA. The latter suggests increased glass transition for composites, compared to pure polystyrene. The verdict of DMA is more plausible, given that DMA is a more reliable method for measuring glass transition temperature [66].

4.4 Tensile Testing

The Young's modulus was determined in the 10% load range since this was a more reliable portion of the graph [70]. The tensile testing is inconclusive in differentiating between the stiffness of the various composites. This is because the error bars overlap in all cases. This is probably due to the fact that 0.2% loading is not enough to distinguish between the behavior of the composites, given that literature is usually above 1% [48,64,68].

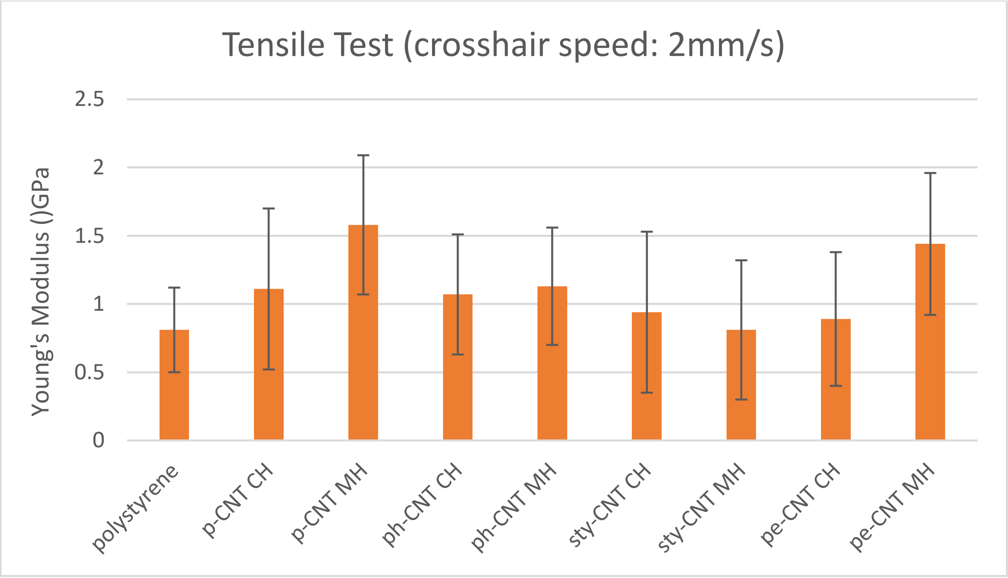


Figure 30. Young's modulus of selected composites. No statistically significant differences in Young's modulus for oven and microwave composites.

The graph of ultimate tensile strength, however, indicates that pure carbon nanotube composites made in the oven are superior to their functionalized counterparts in the microwave. Also, they are better than composites made with n-pentenyl functionalized CNTs in CH and MH. This behavior could be attributed to destruction of mechanical properties of the CNTs due to the covalent functionalization [18, 46]. Another explanation is the de-functionalization of CNTs owing to intense microwave heating [38]. The high heating rates in microwave synthesis have also been reported to have detrimental effect on mechanical properties [76]. However, it is worth noting that ph-CNT composites have storage modulus comparable to that of pure CNT composites. Hence, pu-CNT composites cannot be said to be better than functionalized CNT composites in general.

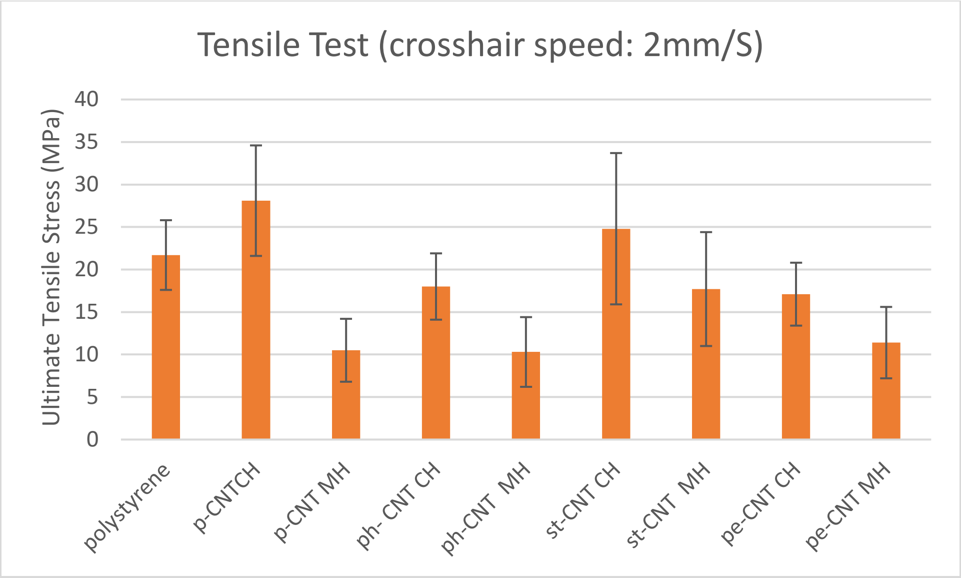


Figure 31. Ultimate tensile stress of composites.

A comparison of DMA and Tensile test results shows the storage modulus to be generally higher than the tensile modulus. This can be explained in terms of the different forces applied during these two tests. Tensile testing exerts a tensile force on specimen while DMA exerts flexural force. The force needed to delaminate polymers in tensile testing is less than that required to bend the composites in DMA.

A comparison of the tensile characteristics of pure polystyrene and pe-CNT MH composites reveals a substantially improved Young's modulus up to about 1.5 MPa. Beyond this point, the characteristics of the composite deteriorate in comparison with polystyrene. The beginning of the plateau-region of pe-CNT represents the onset of delamination. The pulling out of CNTs at this point resulted in the weaking of the composites. Carbon nanotubes therefore increase the tensile strength of polystyrene while degrading the ultimate stress and toughness.

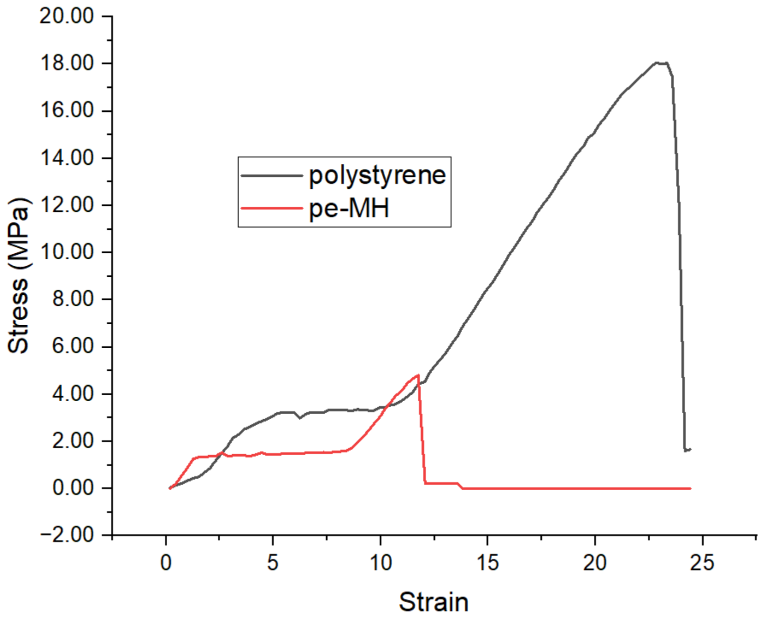


Figure 32. Delamination in composites. CNTs pull out in the elastic region (around 2MPa), resulting in degradation of characteristics.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Carbon Nanotube Reinforcement

Carbon nanotubes were successfully used to reinforce polymer composites. Storage modulus and Young's modulus increased with the addition of carbon nanotubes. However, the use of CNTs to reinforce polymers could also result in undesired characteristics such as increase in brittleness [82]. Hence, balance must be struck between enhancing upon selected properties of the polymer matrix without compromising other properties.

5.2 Functionalization

The settling tests have been corroborated by TGA, showing that functionalization was successful. More reactive functional groups such as pentenyl showed better dispersion, compared to aromatic groups. The good dispersion for pentenyl could also be attributed to the absence of pi-pi stacking as pentenyl is aliphatic. Further research should look at the use of aliphatic functional groups for functionalization.

5.3 Microwave Heating versus Conventional Heating

Microwave polymerization also proved to be five times faster than conventional heating. This represents huge savings in cost and time for any industry [74]. It is recommended that more research be done to scale up microwave polymerization for industrial purposes. One issue to consider here is the selective heating in a scaled-up reactor. The absorption of microwave depends on the penetration depth of the substance in relation to its dimensions [28]. If the dimensions are small (as in the case of styrene in a vial), the material is practically transparent and selective heating may be exploited. However, if it is in a bigger container as is the case with industrial processing, the penetration depth may be smaller than the dimensions, making the material absorbing of microwaves and altering the selectivity of heating between CNTs and the matrix.

Moreover, the DMA results who that MH composites showed higher storage modulus than CH ones. This could be attributed to the initiation of polymerization by functional in the microwave oven, leading to more covalent linkages being formed with polymers and, hence, better reinforcement.

5.4 Composites of Pristine and Functionalized Carbon Nanotubes

Pure CNTs had marginally better storage modulus, compared to functionalized CNT composites. Intense heating in the microwave could have defunctionalized the nanotubes considerably. Further research should focus on the effects of heating rate on the functionalization of carbon nanotubes as well as the properties of resulting composites.

5.5 Microwave recycling

The idea of microwave recycling could also be explored with carbon nanotube composites. The intense heating of carbon nanotubes and the lower thermal stability of composites means that microwave energy could be used to depolymerize nanocomposites in a way that results in the recovery of pristine monomers [40]. This would represent a reduction in the cost of recycling and ensure reusability of monomers.

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APPENDICES

A CALCULATIONS FOR FUNCTIONALIZATION

Magnesium

2 % of CNTs to be functionalized (by moles), 5 times more reagent to be prepared

mass of magnesium required

1g (CNTs) x $\left(\frac{1\text{ mol}}{12\text{ g}}\right)$ x 0.02 x $\left(\frac{24.35\text{ g}}{1\text{ mol}}\right)$ x 5 = 20 mg

Bromostyrene

volume of bromostyrene: $1\text{ g}(\text{CNTS})\,.\left(\frac{1\text{ mol}}{12\text{ g}}\right)$ x 0.02 x $\left(\frac{183\text{ g}}{1\text{ mol}}\right)$ x $1.41\frac{\text{g}}{\text{ml}}$ x 5 = 2.2 ml

mass of styrenyl added (theoretical) = 1 g (CNTs) x $\left(\frac{1\text{ mol}}{12\text{ g}}\right)0.02$ x $\left(\frac{104.3\text{ g}}{1\text{ mol}}\right)\left(\frac{1000\text{ mg}}{1\text{ g}}\right)$ = 170 mg

2% functionalization equals a mass change of about 17%. The actual mass change form TGA TGA was 3.6%

Actual percentage of functionalization: $=\frac{2\ x\ 3.6}{17}$ = 0.4% (predicted = 2%) Actual = 0.4%

Bromobenzene

10% of CNTs to be functionalized by mole.

volume of bromophenyl: = $1\ g\ (CNTs)\left(\frac{1\text{ mol}}{12\text{ g}}\right)$ x 0.1 x x $\left(\frac{1L}{3\ mol}\right)$ x $\left(\frac{1000\ ml}{1L}\right)$ = 2.7 ml

mass of phenyl added (theoretical): 1 g CNT $\left(\frac{1\text{ mol}}{12\text{ g}}\right)$ x 0.1 x $\left(\frac{77.1\text{ g}}{1\text{ mol}}\right)$ = 0.64 g.

10% functionalized CNTs were predicted to show a change in mass of about 64 %. The change in mass from TGA, however, was 2.4%.

Actual functionalization: $\frac{2.4x\ 10}{64}\ x\ 10 = 0.38\%$

Bromopentene

c. pe-CNTS (6% functionalization)

volume of bomopentene: $= \frac{1\text{g}}{12\ \text{g/mol}}\ 0.06$ x x $\frac{149.03\ \text{g/mol}}{1.26\ g/mol}$ x $\frac{1000\ ml}{1L} = 0.59$ ml

mass of n-pentenyl added (theoretical): 1 g (CNT)s $x\ \left(\frac{1\ \text{mol}}{12\ \text{g}}\right)$ x 0.06 x $(\frac{70\ \text{g}}{1\ \text{mol}}) = 0.35$ g

6% functionalization equals a mass change of 35% .Actual mass change on TGA was 1.9%.

Actual functionalization = $\frac{1.9\ x\ 6}{35}\ x\ 10 = 0.33\%$