CHAPTER II

LITERATURE REVIEW

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A study of previous research relevant to the researcher's area becomes necessary to know where the researcher can make improvement or make new contribution. "The literature in any field forms the foundation upon which all future work will be built" (Aggarwal, 1975)

2.1 POLYMER NANOCOMPOSITE RELATED SURVEY

Lingyu Li et al.,(2007) investigated into," Structure and crystallization behavior of Nylon 6,6/multi-walled carbonnanotube nanocomposites", Nylon 6,6-functionalized MWNTs were used as precursors to prepare polymer/MWNT nanocomposites. Excellent dispersion was revealed by optical and electron microscopes. The crystallite sizes L_{100} and L_{010} of Nylon 6,6, determined by WAXD, decreased with increasing MWNT contents. Noncovalent functionalization of MWNT with Nylon 6,6 single crystals was accomplished via controlled solution crystallization. Morphological study showed that the functionalized MWNT was similar to the classical shish kebab and the hybrid structure was named as nanohybrid shish kebabs. The effect of MWNT on Nylon 6,6 melting and crystallization behaviors was also examined.

Guang-Xin Chen et al.,(2006) investigated into "Multi-walled carbon nanotubes reinforced nylon 6 composites", Multiwalled carbon nanotubes (MWNT) were functionalized with amine groups using a 'grafting to' technique. A fine dispersion of MWNTs throughout nylon 6 matrix was observed by SEM and TEM. Multiwalled carbon nanotubes were functionalized successfully with hexamethylenediamine. The resulting MWNT–NH_2 reinforced nylon 6 composites efficiently through a simple melt compounding to endow them with excellent mechanical properties.

Masuduz Zaman and Felipe Chibante (n.d), University of New Brunswick, Fredericton, NB, Canada, examined "Carbon filled Nylon 6,6 composites prepared by simple melt compounding", This study reported the synthesis and characterization of nylon 6,6 composites reinforced with singe-walled nanotubes (SWNTs) and vapor grown carbon fibers (VGCF). High shear twin-screw extrusion was used to compound the formulations. They had successfully processed and characterized SWNT/nylon 6,6 and VGCF/nylon 6,6 composites by simple melt compounding approach. The performance of SWNT and VGCF in reinforcing nylon matrix had been compared. The twin-screw extrusion of nylon 6,6 and fillers produced a uniform dispersion of fillers in the nylon matrix. Mechanical, thermal, and electrical properties were significantly improved over the neat polymer.

Michael F.L. et al., (2013), examined "Carbon Nanotubes: Present and Future Commercial Applications", Worldwide commercial interest in carbon nanotubes (CNTs) is reflected in a production capacity that presently exceeds several thousand tons per year. Currently, bulk CNT powders are incorporated in diverse commercial products ranging from rechargeable batteries, automobile parts, and sporting goods to boat hulls and water filters. CNT powders mixed with polymers or precursor resins can increase stiffness, strength, and toughness. Adding~1 wt % MWNT to epoxy resin enhances stiffness and fracture toughness by 6 and 23%, respectively, without compromising other mechanical properties. These enhancements depend on CNT diameter, aspect ratio, alignment, dispersion, and interfacial interaction with the matrix.

Kenan Song et al,(n.d) studied "Structural Polymer-Based Carbon Nanotube Composite Fibers: Understanding the Processing–Structure–Performance Relationship", Among the many potential applications of carbon nanotubes (CNT), its usage to strengthen polymers has been paid considerable attention due to the exceptional stiffness, excellent strength, and the low density of CNT. This has provided numerous opportunities for the invention of new material systems for applications requiring high strength and high modulus. Precise control over processing factors, including preserving intact CNT structure, uniform dispersion of CNT within the polymer matrix, effective filler–matrix interfacial interactions, and alignment/orientation of polymer chains/CNT, contribute to the composite fibers' superior properties. The current state-of-the-art polymer/CNT high-performance composite fibers, especially in regard to processing–structure-performance. The conclusions were on the various parameters that affect the strengthening mechanisms in polymer/CNT fiber composite systems as a function of processing. CNT containing polymeric fibers have exhibited improved mechanical and physical properties such as tensile strength, Young's modulus, strain-to-failure, toughness, and resistance to molecule changes from both solvent and heat treatments. Experimental factors influencing composite processing include CNT structure, dispersion, interfacial interaction, and alignment/orientation of polymer chains and CNT. The combination of these factors needs to be well controlled in order to optimize the resultant mechanical properties of the bulk composite fiber. An understanding of these factors is complex and a great challenge in the field of nano-composite processing.

Jerome S. Berg, (n.d), Manager of Technical Service, True Temper Sports, "Composite material advances in the golf industry", stated that the popularity of carbon fiber composites as a primary structure for components in sporting goods appeared to gain momentum in the late 1980s and early 1990s. Particularly in the golf industry, these materials offered lighter weight, a variety of design options not possible with steel, and a high tech image to a rather affluent market. The sporting goods consumer desires equipment which represents the latest technology and is more expensive than his competitor's. Sporting goods companies are searching for the next advanced material that will allow them to gain another niche in the marketplace which will command a higher price and margin. Several product development efforts including metal matrix materials, robust resin systems, and high modulus carbon fibers are discussed. He examines early golf shafts being made of glass/epoxy. Although a good engineering material, glass/epoxy met with disapproval from the market place due to perception that fiberglass is a cheap material. Many designs incorporate alternate materials to enhance the feel, fatigue strength, tip strength, and surface cosmetic qualities. One such enhancement is the use of very lightweight glass scrim materials to improve the transverse strength of the shaft laminate in very lightweight shafts.

H. Kuzmany, et al.,(2004) , examined "Functionalization of carbon nanotubes", The functionalization of single wall carbon nanotubes (SWCNTs) is a very actively discussed topic in contemporary nanotube literature because the planned modification of SWCNT properties is believed to open the road towards real nanotechnology applications. In this contribution, some recent results are reported on the subject. Covalent attachment of functional groups, their influence on tube-tube stacking, detachment of functional groups, selective n- and p-type intercalation as well as special reactions carried out in the interior of SWCNTs are discussed. The reported results demonstrate that various ways exist to functionalize SWCNT. Functional groups covalently attached to the outer surface of the nanotubes are able to modify the stacking and solvatation properties of nanotubes. An interesting feature of SWCNT bundles is that their n- and p-type intercalation proceeds in a diameter dependent way, thus making it in principle possible to selectively modify certain nanotubes while leaving others intact. Functionalization inside the tubes in the form of covalent chemical bonds has not yet been demonstrated but chemical reactions which lead to products not observed outside the tubes occur. Such reactions are the polymerization of charged fullerene cages and the catalyst free growth of SWCNTs with a high degree of perfectness. The fullerenes in the smaller tubes exhibit a higher probability for the transformation process as compared to the fullerenes in the larger tubes.

Tianxi Liu, et al., (2004), examined "Morphology and Mechanical Properties of Multiwalled Carbon Nanotubes Reinforced Nylon-6 Composites", Multiwalled carbon nanotubes (MWNTs)/nylon-6 (PA6) nanocomposites with different MWNTs loadings were prepared by the simple melt-compounding approach. A fine and homogeneous dispersion of MWNTs throughout PA6 matrix was observed by transmission electron microscopy. Mechanical testing (by tensile and nanoindentation tests as well as dynamic mechanical analysis) showed that, compared with neat PA6, the elastic modulus and the yield strength of the composite were greatly improved by about 214% and 162%, respectively, with incorporating only 2 wt % MWNTs. In addition, a unique crystallization and melting behavior of MWNTs/PA6 composites were observed and discussed by combining differential scanning calorimetry and X-ray diffraction; that is, only the R-form crystals were observed in MWNTs/PA6 composites, which was quite different from the case observed in PA6/clay nanocomposites. They examined MWNTs-reinforced PA6 nanocomposites with excellent mechanical properties that had successfully prepared by simple melt-compounding method. Systematic studies using different mechanical tests (such as tensile and nanoindentation methods) show that incorporation of a small amount of MWNTs into PA6 matrix can significantly improve the modulus, the strength, and the hardness by about 214%, 162%, and 83%, respectively, with less than 2 wt % CNTs. Microscopy observations indicated that a uniform and fine dispersion of MWNTs throughout PA6 matrix and a strong interfacial adhesion between nanotubes and the matrix had been successfully achieved.

2.2 DESIGN AND ANALYSIS OF TENNIS RACKET RELATED SURVEY

Samuel R. Wilton (n.d) did finite element analysis on a Wilson ncode six-one racket frame. It was a tremendous success .The deflection and stresses under impact force were measured. Overall, the results obtained from the finite element analysis shed abundant light on the subject of stresses and deflection of a tennis racket doing rest and during play.

TOTH-TASCĂU Mirela, et al, (2010), studied the Design Aspects of a Tennis Racket, ie material design using graphite. They attempted to produce a light weight racket. The racket design was performed using CATIA V5R16.They found that carbon fiber helped to achieve high stiffness and low weight.

Yao-dong Gu , Jian-she Li, Faculty of Physical Education, Ningbo University, Ningbo, Zhejiang, P.R .China, International Journal of Sports Science and Engineering (2007),examined " Dynamic Simulation of Tennis Racket and String". The study was based on finite element method, a computer simulation method for the analysis of the dynamic property of tennis racket. They needed graphical assistance for the making of the racket; they claimed to have improved the performance of the racket.

Ti-Yu Chen et al., (n.d) investigated into "The Vibration and Coefficient of Restitution Analysis in Tennis Rackets varied with Material Composition and Fiber Arrangement". They used mixture of carbon and glass fibres. They established that the load in the tennis players arm on centre or off-centre impact could be decreased by increasing the contact of glass fiber in the racket frame. Pure carbon fiber made racket had higher stiffness and its coefficient of restitution was higher than glass fiber made racket.

2.3 TENNIS RACKET MODES AND OTHER RELATED SURVEY

Daniela Naß et al,(1998), examined "Ball impact location on a tennis racket head and its influence on ball speed, arm shock, and vibration'' When a ball hits the racket at its point of maximum restitution (COR),the rebound velocity of the ball will be highest. For ball hits at the node of the racket, vibrations are minimal. Ball contacts at the center of percussion (COP) cause minimal shocks to the arm. The definitions of these points are based on the application of the laws of physics to a simple mechanical body - the tennis racket only. This study investigated the influence of ball impact location on ball velocity, arm shock, and vibration. They experimented using an instrumented tennis racket 570 forehand and 570 backhand strokes by expert players. For ball speed, arm vibration, and arm shock longitudinal and transverse impact locations on the racket head were identified. The results of this study did not confirm the sweet spot racket points hypothesized by Brody (1988) of minimum vibration, minimum shock or maximum ball velocity. Mechanical coupling of the hand with the racket and the contribution of racket rotation during the swing seemed to have a major effect on racket characteristic.

Pei-Xin Kuo et al.,(2010), Taipei Physical Education College Graduate Institute of Exercise and Sport Science, examined "Energy efficiency of different tennis racket stiffness and string tension due to center and off-center impact". This study was to investigate the power of vibration responses and moments of different racket flexibilities and string tensions following center and off-center impacts. Three rackets, classed as stiff, medium, and flexible by their manufacturers, were strung at three string tensions and subjected to 15 trials. They concluded that Racket stiffness and string tension both influenced the level of vibration and twisting. All of the rackets increased the force vibration with increases in string tension under center impacts. However, it was found that the effect of off-center impact for the hand-arm systems was more significant than in center impact. Generally, the stiff racket had smaller power of the force shock and twisting moment for each string tension in off-center impact. This may impair the control of balls struck off-center

Rod Cross,(1999), studied the " Impact of a ball with a bat or racket", A uniform aluminum beam was used as an idealized bat or racket, in order to examine both the rigid body approximation and the assumption that the hand force could be neglected. An aluminum beam was chosen so that its length and stiffness could easily be varied so that the results could be compared with solutions for a flexible beam. It was found that rigid body models of beams, bats, or rackets were of limited use but the hand force could usually be neglected. He concluded that the aluminum beams of different length and thickness were used to simulate the behavior of a ball colliding with a baseball bat or a tennis racket. It was found that the apparent coefficient of restitution, for an impact at any point well removed from either end of the beam, was independent of the impact location or the length of the beam or the method of support at the ends.

H. Brody,(1997), investigated "The physics of tennis. III. The ball racket interaction". A simple, one-dimensional, rigid-body model of a tennis racket interacting with a tennis ball agreed well with data taken when balls were fired at a stationary, free racket. The results were then transformed into the tennis court frame of reference, where the racket was moving. Data obtained conducted on the rotational aspects of a tennis swing were then included in the model. He concluded that this rigid-racket frame model and the experimental data for the ball speed ratio, e, agreed quite well for impacts near the center of the head. Impacts near the throat of the racket produced a slightly lower value of e than the model predicted, possibly because the model used a constant value of the ball– string COR ~0.85%, and it was known that this value fell off as the impact point moved toward the periphery of the frame. For impacts very close to the tip of the racket, the experimental value of e was significantly lower than the model predicts. This was probably due to the reduction in ball–string COR, mentioned above, and the fact that the racket frame was more flexible near the tip, where the rigid-body model might be most suspects. When a racket flexes, most of the energy that goes into racket frame deformation is not returned to the ball since most players tend to hit the ball at or near the center of the head on their ground strokes.

S Miller,(2006), examined "Modern tennis rackets, balls, and surfaces", Modern rackets have facilitated a change in playing style from one of technique to one characterized by power and spin. The combination of the increased stiffness of modern rackets and the tendency for tennis balls to have become harder has led to an increased shock transmission from the racket to the player, which is probably a major contributor to tennis elbow. He examined the changes in racket construction to make it easy to overlook the contribution of strings to racket performance. The ball normally does not even touch the frame of the racket; all of the contact is with the strings. There are several variables that influence the performance of strings, the key ones being material, tension, gauge, and roughness. For example, it is generally accepted that lower string tension generates more power, whereas higher tension gives more control. This is because the majority of energy loss during racket/ball contact is in the ball, which returns up to about 50% of its pre-impact energy, whereas the strings are much more efficient, being 90–95% energy efficient. When they collide, both the ball and strings deform. If more energy can be stored in the strings, then the collision will be more efficient and more energy will be returned. By reducing string tension, the string bed deforms more and the ball deforms less, so returning more energy. The reason for higher string tension generating more control is not as well established.

Hiroshi Maeda, et al, (2010), studied the `"Properties of friction during the impact between tennis racket surface and ball", The 'feel' of hitting a ball with a tennis racket has been quantified by vibrations to the hand and by the coefficient of restitution. As play styles are shifting toward hitting with topspin to the ball, the friction between the ball and racket surface; in other words tangential forces in the racket surface, is becoming another index to quantify the feel. In this work, they detected friction by attaching two strain gauges close to the center of right and left frames supporting the cross strings at the middle, and aimed to understand the mechanism behind friction from the viewpoint of difference in the angle of incidence of the ball when impacting the racket surface. They designed a method to measure vertical and horizontal forces in the surface of a racket in contact with a ball. Balls were launched from four different angles (15, 30, 45 and 60 degrees) toward a racket. They compared the impulse obtained by integration over time of the tension in the strings, the impulse derived from the change in angular momentum of the ball, and the impulse calculated from the velocities of the ball before and after impact. As a result, they predicted the existence of a critical angle of incidence between 30 and 45 degrees where the properties of friction changed.

Linlin Li et al., (2009) examined "Effects of string tension and impact location on tennis playing", Studies using the finite element method [FEM] revealed that decreasing the string tension lowered the coefficient of restitution. The ratio of speed to angle change increased with a decrease in string tension. Moreover, the resultant force on the player's hand was stronger if the tennis ball hit the dead spot than when it hit the sweet spot. For instance, as a tennis ball hits the dead spot with a speed of 10.05m/s, an angle of 15°, and a string tension of 222N, the player's hand feels a maximum resultant force of almost 424N, which is 1.61 times higher than if the ball hits the sweet spot, at t=0.081 and t=0.0149. Moreover, the force exerted on the player's hand if the ball hits either the best-bounce spot or the off-center spot is 1.4 times higher than if the ball hits the sweet spot. A finite element simulation of the impact of a tennis ball on a tennis racket revealed that the string tension affected both the ball rebound speed and the accuracy. Within the recommended tension range, a lower tension provided more power and less impact on the arm, while a higher tension offered more control. Therefore, selecting the right string tension and impact point control are the most important elements in playing tennis.

Xin Wang et al., (2011) examined "Mechanical and electrical property improvement in CNT/nylon composites through drawing and stretching". The excellent mechanical properties of carbon nanotubes (CNTs) made them the ideal reinforcements for high performance composites. The misalignment and waviness of CNTs within composites were two major issues that limited the reinforcing efficiency. An effective method was suggested to increase the strength and stiffness of high volume fraction, aligned CNT composites by reducing CNT waviness using a drawing and stretching approach. Stretching the composites after fabrication improved the ultimate strength by 50, 150, and 200% corresponding to stretch ratios of 2, 4 and 7%, respectively. Improvement of the electrical conductivities exhibited a similar trend. These results demonstrated the importance of straightening and aligning CNTs in improving the composite strength and electrical conductivity. A novel drawing and stretching approach was developed for fabricating CNT/nylon6,6 composites with good CNT alignment, high CNT volume fraction and straight nanotubes. The winding method created aligned CNT composites, while the local heating and stretching strategy led to further reduction of CNT waviness. Both mechanical and electrical properties showed substantial increases (191%, 294% and 207% for tensile strength, Young's Modulus and electrical conductivity, respectively) as the stretch ratio was increased to 7%. Macroscopically aligned CNTs and microscopically reduced waviness are critical to improving mechanical properties of CNT composites. These new insights might lead to further development of other types of CNT-based high performance materials.

Miles A. Buechler, (n.d), examined "Vibration modeling and suppression in tennis rackets". The size of the "sweet spot" is one measure of tennis racquet performance. In terms of vibration, the sweet spot is determined by the placement of nodal lines across the racquet head. In this study, the vibration characteristics of a tennis racket were explored to discover the size and location of the sweet spot. A numerical model of the racket was developed using finite element analysis and the model was verified using the results from an experimental modal analysis. The effects of string tension on the racquet's sweet spot and mode shapes were then quantified. An investigation was also carried out to determine how add-on vibration dampers affected the sweet spot.

Using the nodal lines definition of the sweet spot, the location of the sweet spot was located at the anti-node of the first string percussion mode. This anti-node was also very close to the node of the first frame bending mode. Consequently, most of the energy went into the strings and was then returned to the ball. In addition, because the frame was not excited, the player felt few vibrations at the handle. The commercial vibration dampers were seen to have a varied influence on vibrations at the handle. Although they damped out vibrations near 500 Hz, they caused more vibrations to be transmitted between 180 Hz and 330 Hz. This result holds true for the experimental racquet as well as the FE model of higher string tension.

Using the FE model for higher string tension, the string mode shapes do not change. The frequencies they occur at increase by almost 90%, but the shapes themselves stay the same.

Andre Roux, (2007) studied "Coefficient of Restitution of a Tennis Ball". The coefficient of restitution (COR) of a tennis ball was investigated over a range of impact velocities. It was found that the COR of the ball was lower than ATP regulations specify, and that the COR decreased with increasing impact velocity.

The governing bodies of all modern sports carefully define the specifications of the equipment which may be used in the sport. This is to ensure that all tournaments are played under standard conditions and that all players compete with standard equipment. The ATP has defined the specifications for tennis balls which may be used in official tournament play. An important characteristic of tennis ball is its “bounciness”. According to ATP regulations, a tennis ball must bounce to a height of between 135 cm and 147 cm when dropped from 254 cm on to a hard surface. In physics, the “bounciness” of a ball is referred to as the coefficient of restitution. The coefficient of restitution (COR) for a ball bouncing off a fixed surface is defined as the ratio of the velocity of a ball after it bounces to the velocity of the ball before it bounces.

$$\mathrm{COR} = V'/V_0 \qquad (1)$$

V_O = initial velocity, V'= velocity after the bounce

An object with a coefficient of restitution of 1.0 will have no loss of speed after it bounces. If it is released from a certain height, that object will fall and bounce back up to the exact same height. An object with a COR of 0.0 will hit the ground and not bounce at all. The COR for regulation tennis balls can be calculated from the ATP regulations. Ignoring the effects of air resistance, a ball dropped from a height of 254 cm will have a velocity of 7.06 m/s just before it hits the ground. According to the regulations, the tennis ball must then bounce to a height of between 135 cm and 147 cm, meaning the ball must have a velocity of between 5.14 m/s and 5.36 m/s as it leaves the ground. This means that, ignoring the effects of air resistance, a regulation tennis ball would have a COR of between 0.728 and 0.759. Taking into account the effects of air resistance, the actual COR of a tennis ball would be larger than this. When a tennis ball strikes a surface, the rubber and fabric shell of the ball is deformed.

Some of the kinetic energy of the ball is converted to thermal energy during this process. Since a higher initial velocity will cause a greater ball deformation, it can be predicted that higher initial velocity will lead to a higher proportion of energy being lost, and thus a lower COR. Since a lower initial velocity will lead to less ball deformation, it is predicted that the COR will approach one as the initial velocity approaches zero. It is predicted that the relationship between the COR and the initial velocity (vi) is:

$$\mathrm{COR} = 1 - A vi^{B} \tag{2}$$

Where A and B are positive constants. Not enough is known about the characteristics of tennis ball deformation during a bounce to predict the values of A and B with any confidence.

He obtained a relationship between coefficient of rescission and initial velocity of the tennis racket ball has been shown to be

$$\mathrm{COR}=1-(0.18 \pm 0.070\ (v_i)^{(0.5}\pm 0.1) \tag{3}$$

The uncertainty in the constants of the derived equation was as much as 40% for the coefficient, and 20% for exponent, leaving very little confidence in our conclusion. At 7ms m/s the COR was only 0.5. It was only when the ball's initial velocity was as low as 2.m/s that the COR increased to the regulation 0.75. This could have been due to the fact that a "fresh out of the can" ball was not used, and tennis balls are known to lose "bounciness" after they have been taken out of the can.

Seongyeong Yang et al., (2011), conducted an "Analytic study on structural behavior of the string bed in a tennis racket". The structural behavior of string bed of tennis rackets was investigated subjected to transverse force perpendicular to the string bed. The mathematical model developed for the string bed was implemented into a computer programming code. This code was used to conduct extensive parametric studies on the structural behavior of the string bed for various parameters, including string tension, axial rigidity of the string, string spacing and head size. The analysis results showed that while the transverse stiffness of the string bed was proportional to the string tension, the transverse stiffness of the string bed was inversely proportional to string spacing and head size. In addition, the axial rigidity of the string significantly amplified the transverse stiffness of the string bed for relatively large transverse deflection of the string bed. The string bed of a tennis racket was investigated on the structural behavior of the string bed subjected to transverse force. A mathematical formulation of the structural behavior of the string bed was developed and implemented into a computer programming code. Extensive parametric studies were conducted by using the computer programming code to investigate the effects of the string and string bed configuration. The parameters of the string bed considered in the studies included string tension, axial rigidity of the string, string spacing, and head size. The following conclusions were reached:

- The transverse stiffness of the string bed is proportional to the string tension in the string bed.
- Although the axial rigidity of the string does not affect the initial transverse stiffness of the string bed, the axial rigidity of the string significantly amplifies the transverse stiffness of the string bed for relatively large transverse deflection of the string bed.
- Smaller string spacing leads to larger transverse stiffness of the string bed.

- Although the initial transverse stiffness of the string bed is almost the same for different head sizes, the transverse stiffness of the string bed is inversely proportional to the head size of the string bed otherwise.

Morphological and mechanical properties of carbon nanotube/polymer composites via melt compounding were studied by William E. Dondero a thesis submitted for masters in textile engineering from North Carolina State University in the year of 2005.

The mechanical properties and morphology of multi-wall carbonnanotube (MWNT)/polypropylene (PP) nanocomposites were studied as a function of nanotube orientation and concentration. Through melt mixing followed by melt drawing, using a twin screw mini-extruder with a specially designed winding apparatus, the dispersion and orientation of multi-wall carbon nanotubes was optimized in polypropylene Tensile tests showed a 32% increase in toughness for a 0.25 wt % MWNT in PP (over pure PP).Moreover, modulus increased by 138% with 0.25 wt % MWNTs. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) all demonstrated qualitative nanotube dispersion and orientation. Wide angle X-ray diffraction was used to study crystal morphology and orientation by calculating the Herman's Orientation Factor for the composites as function of nanotube loading and orientation. The addition of nanotubes to oriented samples caused the crystalline morphology to shift from a and mesophase to only a phase. In addition, differential scanning caloriometry (DSC) qualitatively revealed little change in overall crystalline. In conclusion this work showed that melt mixing coupled with melt drawing yielded MWNT/PP composites with a unique combination of strength and toughness suitable for advanced fiber applications, such as smart fibers and high performance fabrics.

2.4 CARBON NANOTUBES RELATED SURVEY

In 1991, Japanese microscopist, Sumio Iijima observed graphitic carbon needles, ranging from 4 to 30 nm in diameter and up to 1 mm in length, as byproducts of the arc-discharge evaporation of carbon in an argon environment. Carbon nanotubes have unique physical and chemical properties which chemists are trying to better understand through laboratory research. One of the physical properties of carbon nanotubes is that it is possible to make them as only a single atomic layer thick. This means that they can be about 1/50,000th the thickness of a human hair. Because of the bonding characteristics of carbon atoms, the physical appearance of carbon nanotubes can often resemble rolled up chicken wire with diameters ranging from 0.7 nm to 1.6 nm. As demonstrated by Iijima, One of the interesting physical properties about carbon nanotubes is that when you have two of them which have slightly different physical structures and they are joined together, the junction (gap or small space) between them can function as an electronic device. Since carbon nanotube science is relatively new, scientists from the fields of chemistry, physics and the material sciences are just beginning to unlock its mysteries and hypothesize about its potential applications.

Based on the very high aspect ratio of these nanotubes, scientists expected the material to be stronger than the current materials. Therefore, a group of scientists used the vibration of the nanotubes as a function of temperature to calculate the Young's modulus of 1 TPa. Such high strength nanotubes have as compared to other materials, Nanotubes are synthesized in two structural forms, single-wall and multi-wall as shown in Figure 15,15(a) &15(b).

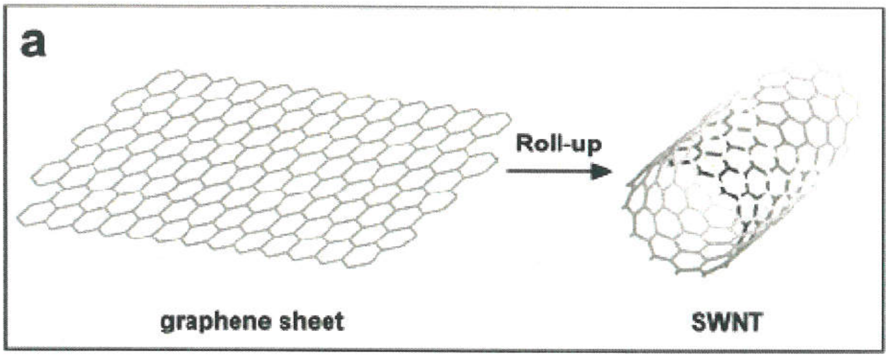


Figure 15. Rolling of graphite sheet

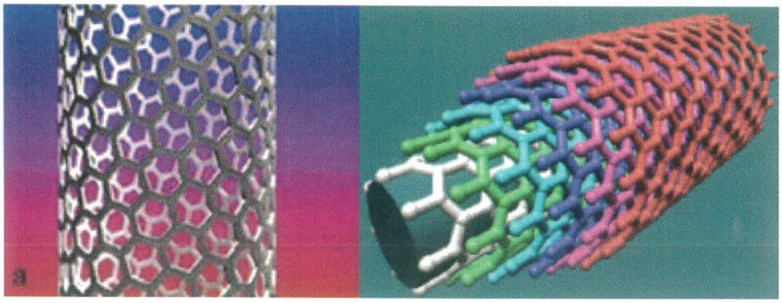
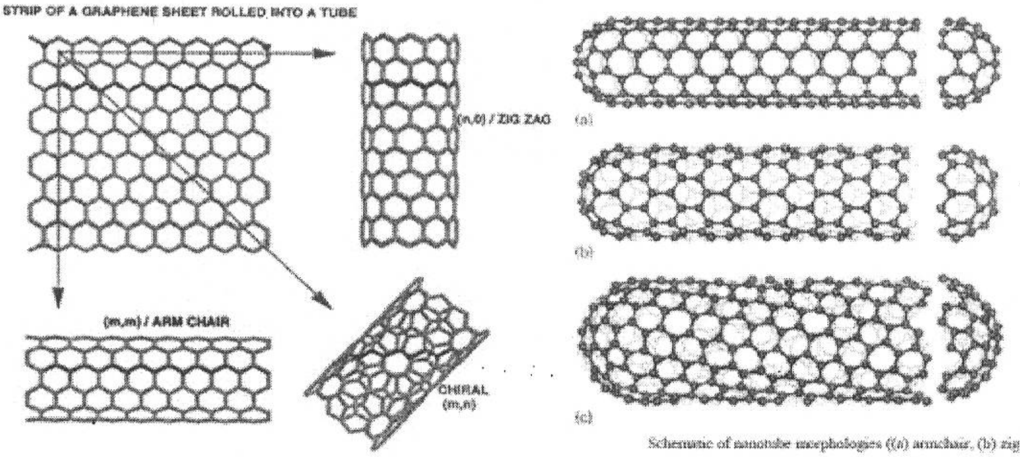


Figure 15a. SWNT and MWNT

The first tubules Iijima discovered exhibited the multi-wall structure of concentric nanotubes forming one tube defining a multi-wall nanotube (MWNT).After further work, he observed a single-shell structure believed to be the precursor to the MWNTs. The single graphitic sheet rolled into a tube with a cap at either end or diameter around 1 nm was defined as a single-wall nanotube (SWNT). Additionally, nanotubes are described using one of three morphologies: armchair, zigzag, and chiral as shown in Figure 15b.



Schematic of nanotube morphologies ((*a*) armchair, (b) zig-zag, (c) chiral).

Figure 15b. Various formations of carbon nanotubes

The packing of the carbon hexagons in the graphitic sheets define a chiral vector and angle. The indices of the vector determine the morphology of the nanotube. Variations in the nanotube morphology can lead to changes in the properties of the nanotube. The electronic properties of an armchair nanotube are metallic; however, the electronic properties of zigzag and chiral nanotubes can be either metallic or semi-conducting. The behavior is determined based on a mathematical model developed using the chiral vector indices.

2. 4.1 PRODUCTION METHODS

Since the discovery of the carbon nanotube, research devoted to nanotube related materials has increased dramatically. The increase began with the investigation of production methods for both MWNTs and SWNTs. The current methods of manufacturing nanotubes include direct-current arc discharge, laser ablation, thermal and plasma enhanced chemical vapor growth depositions (CVD), and self-assembly of single crystals of SWNTs. Each method has advantages and disadvantages. Direct-arc discharge and laser ablation require addition of a small amount of metal catalyst and very high temperature. The products of such methods are normally tangled and poorly oriented. However, laser ablation has become the common method for producing SWNTs. CVD produces nanotubes from the decomposition of a continuously supplied carbon containing gas onto a substrate. Owing to the continuous supply of the gas and the fact that a catalyst is not needed, high-purity nanotubes can be produced on a large volume scale. Producing the nanotubes in an ordered array with controlled length and diameter can be achieved through CVD methods as well. Furthermore, plasma enhanced chemical vapor deposition (PECVD) results in further nanotube uniformity within the array. More recently a team led by Schlittler (2001) has developed a self-assembly method for making an ordered array of nanotubes with identical geometry and high purity.

2.4.2 NANOSCALE TO MACROSCALE

After quantifying the remarkable properties of carbon nanotubes, it has become a challenge to translate these properties from nanoscale to macroscale. Currently many methods of producing macroscale nanotube materials are being investigated. Some methods attempt to form fibers from nanotubes alone; whereas, other procedures use a matrix to support the nanotubes. Without a support medium, research teams expect to achieve property values closer to the values of the individual nanotubes. However, the use of a matrix or binder often makes production of macroscale materials more feasible. Forming fibers directly from nanotube production methods, such as arc discharge and chemical vapor deposition has been investigated. Furthermore, research has shown the feasibility to create nanotube yarns by twisting them together as they are pulled out of a nanotube forest. Other studies have proposed using super-acid solutions as a medium to support the fiber through a conventional spinning process followed by the removal of the medium. However, the most common method has been to incorporate them in a polymer matrix as a reinforcing material. The combined polymer/nanotube structure is often referred to as a nanocomposite. Research has proposed that the nanotubes will provide load transfer in the same way chopped glass fibers do in conventional composite systems. The property response of polymer/nanotube composites have varied from no change to moderate increases in mechanical properties (25%-50% modulus increase; 80%-150% toughness increase), electrical properties (with aperculation threshold of 0.0025 wt-%; conductivity 2 S/m), and thermal properties (125%increase at room temperature). However, optimal property improvements have not been achieved due to deficiencies in nanotube dispersion and alignment.

2.5 EXTRUSION PRINCIPLES

Extrusion of thermoplastics is a process in which the material is melted by external heat / frictional heat and conveyed forward by a screw to the opening of the die, which gives the shape of the required product. Extrusion process is a continuous process by which many products like Films, Raffia tapes, Pipes, Sheets, Mono filaments, Fibre and Filaments can be manufactured.

The common explanation of the extrusion is a process which plastic resins or pellets are used in a heated barrel or chamber, and carried along by a screw to the die which gives final shape of the products. Extrusion is one of the most efficient, most significant technologies of polymer processing. Almost 40% of polymer products are produced with extrusion. Extrusion has some advantages over other plastic processing techniques such as continuity, low cost, efficiency, broad raw material range, high production volume, and efficient mixing. The first extruders were used in the food industry by bakers for noodle production. H. Bewley and R. A. Brooman made the first light industrial application in 1845, but the first extruder was patented by M. Grey. These extruders were mainly used in the rubber industry.

Today, modern extruders are not very different from the old ones, but there have been a lot of changes at the geometry of the screws. Mainly, there are five considerations in an extrusion process for high quality products:

- Appropriate polymer melt temperature
- Uniform/stable melt temperature
- Accurate melt pressure in the die
- Uniform/stable melt pressure in the die
- Well-mixed product

2.5.1 EXTRUDERS

Extruders comprise of Hopper, Barrel/Screw and Dies. Figures shows 16&17 show the components of a modern extruder.

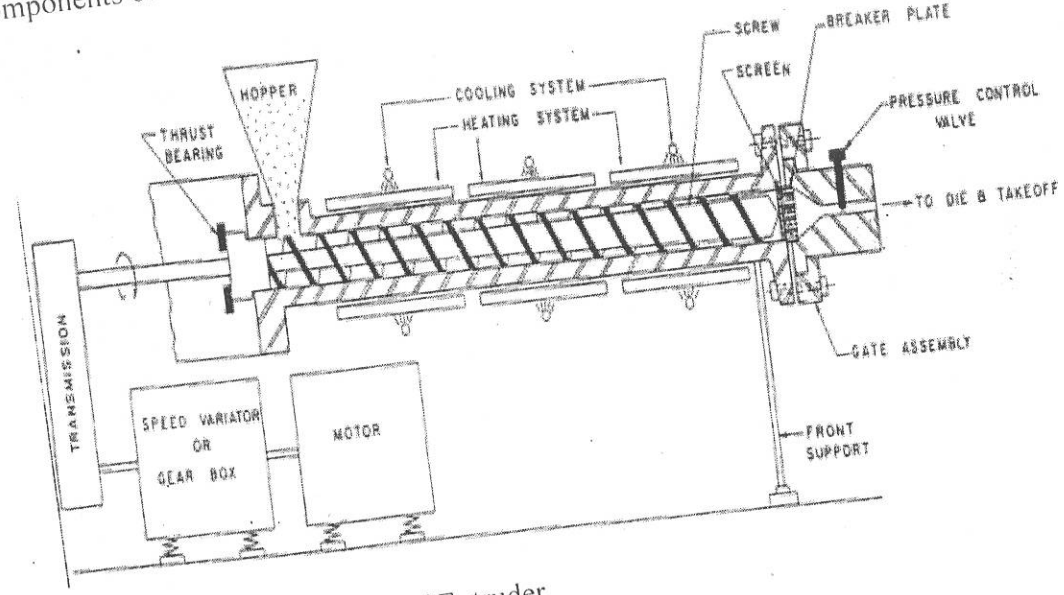


Figure 16. components of Extruder

Screw: This is the heart of the extruder. The screw conveys the molten polymer to the opening of the die after properly homogenizing the molten polymer. Figure 2 illustrates a typical screw configuration. There is considerable variation in the design of the screw for various materials, the most important variable being the depth of the channels. Despite much desire for universal screw, it is advisable to use a different design for each material to achieve the best results. So for optimum process of PVC, PP/PE following screw designs is advice.

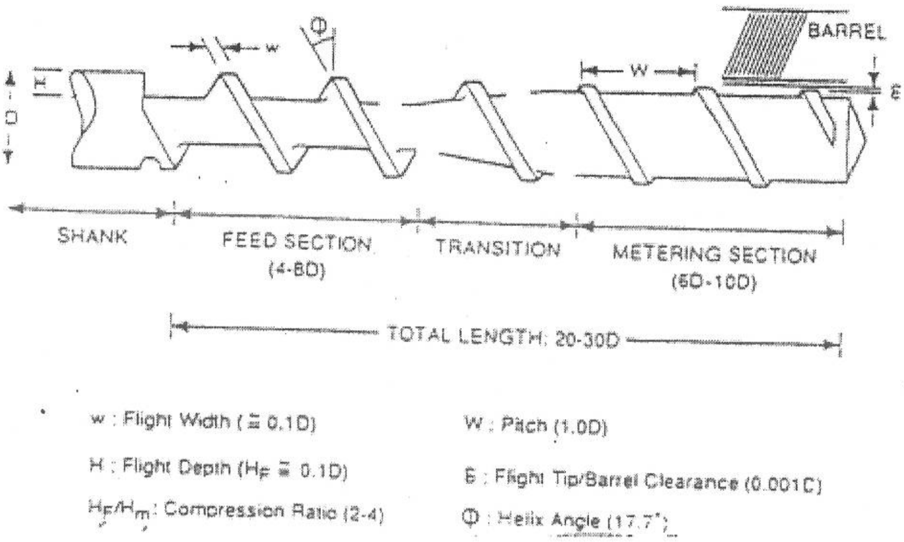


Figure 17. Screw configuration

2.6 PROPERTIES

Owing to the size scale of nanotubes, directly measuring the properties of interest (such as mechanical properties and thermal/electrical conductivity, is difficult when conventional experimental methods are used. Therefore, mathematical modeling primarily has been used to obtain property values. These models are often derived based on models used for similar structures, such as graphite, with modifications to account for the tubular shape. For example, molecular dynamics, empirical potentials and first-principles total-energy, continuum shell, and empirical lattice model were used to describe the elastic properties of nanotubes. The empirical lattice models, previously used to calculate the elastic properties of graphite, led to tensile modulus values in the range of 1 TPa for multi- and single-wall nanotubes. These values compared well with diamond and out-performed conventional carbon fibers.

These exceptionally high theoretical values led to increased interest in nanotubes as both structural and conductive materials and have therefore led to the development of techniques to measure nanotube properties experimentally. Common methods to measure the elastic properties of individual nanotubes include micro-Raman spectroscopy, thermal oscillations by transmission electron microscopy, and application of a force to a nanotube rope suspened across a pit using an atomic force microscope cantilever. Other groups measured the properties of a rope and obtained an average value for each tube based on the number of nanotubes in the rope. The experimental values measured ranged from significantly below theoretical values to values in agreement with the models. These methods have produced tensile modulus and strength values for single- and multi-wall nanotubes ranging from 270 GPa to 1 TPa and 11 GPa to 200 GPa respectively.

In addition to the mechanical properties, research has been performed to determine the electrical and thermal conductivity of nanotubes. In a similar fashion, modeling has been used to determine the conductivity via the structure of the nanotubes as compared with graphite. Much of the theoretical work found that conductivity depends on the small structural variations in the nanotubes. For example Berberet al., (2000) ,found unusually high thermal conductance of 6600 W/m K at room temperature for a particular nanotube structure using nonequilibrium and equilibrium molecular dynamics. However, Hone et al.,(1999) , reported slightly lower values in the range of 1750-5800 W/m K for the room temperature of a single nanotube rope by comparing the temperature drop across a constantan rod of known thermal conductance to a nanotube mat sample in series with the rod. In a similar fashion, the static electrical conductive and superconductive nature of nanotubes was modeled based on the conductivity of the graphite sheet structure. The scale of the individual nanotubes eliminated many of the conventional methods used to measure conductivity. As with the mechanical properties, the variation in the conductivities lies in the procedures used and the differences in the nanotube structure.

2.7 POLYMER NANOCOMPOSITES

Polymer/carbon nanotube composites have the potential to offer a vast improvement over current materials available today. Research scientists believe that the excellent physical, thermal and electrical properties of the nanotubes can be realized at the macroscale by incorporating them into polymer matrices. The amount of research devoted to carbon nanotubes has grown significantly since Iijima's discovery of them in 1991. Theoretical calculations and preliminary experimentation have shown that carbon nanotubes have excellent mechanical properties, electrical conductivity and thermal conductivity (1750-5800 W/m^3 K) found the Young's modulus of individual nanotubes to be in the range of 1 TPa using intrinsic thermal vibrations. Although, carbon nanotubes show exceptional properties on the nanoscale, the difficulty lies in creating a material that exhibits carbon nanotube properties on the macroscale. Incorporating the nanotubes as filler into polymer matrices is the most common method currently being explored.

Similar to other composites made from chopped fiber in a polymer matrix, filler dispersion and orientation are essential to achieve optimal property improvements. Gelation/Crystallization, nanotube surface modification, and melt compounding have demonstrated improved nanotube dispersion in a polymer matrix.

Carbon nanotubes, in the single- and multi-wall form, agglomerate due to strong Van der Waals forces and a high relative surface area. Owing to this agglomeration, achieving homogenous nanotube dispersion throughout the polymer matrix is one of the biggest challenges to date. Furthermore, achieving nanotube orientation (to further enhance strength and toughness) is challenging due to the size scale of the particles. Finally, the addition of nanotubes could lead to pronounced viscosity increases during melt processing.

A polymer nanocomposite (PNC) is a two-phase material where one of the phases has at least one dimension in the nanometer range. PNCs can have enhanced mechanical and electrical properties in terms of their strength, weight, flame retardancy and electrical conductivity due to the very high surface/volume ratio of its reinforcements. The interfacial properties and the interfacial area have a crucial role to obtain good final properties in composites due to the nanosize of the fillers which provide them those above mentioned advance properties.

Today in sports equipments/automotive, aeronautics industry most, most common applied polymer nanocomposites are carbonnanotubes and nanoclay incorporated polymers. They are preferred due to their enhanced physical properties example. Light weight ratio, noise dampening, high impact strength, high strength to weight ratio, dimensional stability, long term durability, directional strength and etc., CNT enhanced PNC parts can be manufactured via injection moulding, extrusion, melt compounding, resin transfer moulding, sheet moulding compound etc., Processing of PNC parts using CNT enhanced propregs is promising. In the injection moulding process the polymer melt is forced to flow through the gate, runner and mould cavity system. The geometry of the flow channel can significantly affect the end property of the injection moulded products, especially when the materials being processed show anisotropic properties when oriented differently. For example, polymer nanocomposites reinforced with CNTs may show different properties at different directions as the CNTs with high aspect ratios may orient differently at different direction, drastic improvement in conductivity can be achieved, while in the transverse directions, no obvious improvement is observed. For this reason, controlled alignment of CNTs is important to get most out of PNCs when CNTs are used as fillers.

2.7.1. FUNCTIONALIZATIONS OF CARBONNANOTUBE

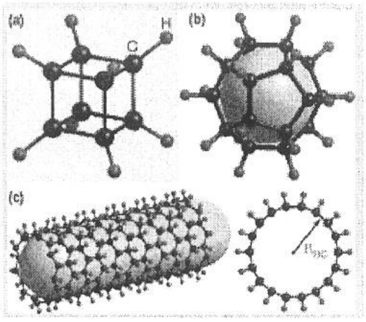


Figure 18 Functionalization of CNT

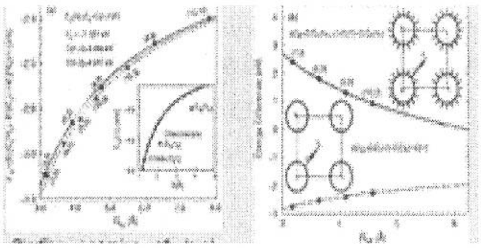


Figure 19 Atomic Energy breaking of CNT

Three different polyhedra ofcarbon and hydrogen: (a) cubane, (b) dodecahedrane, and c) a side and top view of a single wall exo-hydrogenatedcarbon nanotube.

Energy to break (circle) and to attach (square) asingle H to acarbonnanotube as depicted inC_nH_n nanotubes are stable. Binding energies of (n,n)(square) and (n,0) (circle)nanotubes as a function of a Weak but stable CH bonding in nanotubes may be important consideration for possible hydrogen storage. Hybridization of zigzag nanotubes is more likely than armchair nanotubes with the same radius, suggesting a possible selective chemical functionalization of nanotubes as shown in figures 18 & 19.

2.8 CARBON NANOTUBE PROCESSING WITH POLYMER

Two essential components for optimal reinforcement in particle-reinforced composite systems are filler dispersion and orientation. Dispersion of single-wall carbon nanotubes (SWNTs) and higher concentrations of multi-wall carbon nanotubes (MWNTs) into a polymer matrix has been one of the largest challenges, due to the aggregation of the nanotubes as a result of the Van der Waals interactions between individual tubes. Consistent dispersion of reinforcing material throughout the matrix leads to consistent load transfer from matrix to particle. Moreover, it can assist with the realization of a network for conductivity of electrical and thermal energy. Many composite researchers believe that SWNTs will be the ultimate reinforcements for the next generation high performance structural and multifunctional composite materials.

The SWNTs agglomerate more easily than MWNTs due to their size difference (i.e., greater surface area) and can form ropes or aligned bundles of SWNTs. The SWNTs often require more specialization to produce than MWNTs. Therefore, the cost of purified SWNTs tends to be greater than that for MWNTs. The MWNTs, on the other hand, have been found to demonstrate lower mechanical, electrical, and thermal properties due to the ability of the concentric nanotubes to slide past each other. Owing to the inherent tube within a tube structure, the MWNTs tend to have a larger diameter (10 nm) as compared with SWNTs (1 nm). However, improvements in nanotube fabrication have led to

MWNTs with more precise, smaller diameters. This may lead the nanotubes with improved properties over larger diameter MWNTs with less agglomeration than SWNTs. Similarly, orientation in the direction of applied forces allows for greater load transfer. If the particle is oriented in a direction other than the direction of the applied force, the full potential of the particle cannot be realized. In addition, having all the particles oriented in the same direction allows for easier transfer of energy (electrical or thermal). Achieving consistent dispersion and orientation will allow optimal property improvements.

Researchers have used many different techniques in an attempt to disperse nanotubes in polymer matrices including solution chemistry to functionalize the nanotube surface the use of polymers to coat the nanotube surface in situ polymerization of the nanocomposite ultrasonic dispersion in solution melt processing the use of surfactants electro spinning electrode chemistry and gelation/crystallization. In gelation/crystallization experiments, the nanotubes were dissolved in a solvent, polymer solution was added, a gel was formed, the gel was formed into a film, and finally the solvent was evaporated. Nanotube surface modifications used plasma treatment or chemical oxidation to attach the functional groups. These groups allowed the nanotubes to bond better to the matrix and overcome the Van der Waals interactions between nanotubes. Melt compounding involves creating a pre blend by dry mixing polymer powder .The pre blend is fed into an extruder allowing for control of shear, temperature, and residence time. After the residence time, the material is extruded in the film or fiber form. Good dispersion alone has shown moderate property improvements, but nanotube alignment, or orientation, has led to further improvements. Using melt compounding followed by melt drawing, has shown a significant increase in mechanical properties

.Transmission and scanning electron microscopy have shown good dispersion and orientation using such methodology. These improvements have been shown to increase until an optimal loading level and then decrease above this concentration. In addition to mechanical drawing, the inherent conductive nature of carbon nanotubes has been utilized to induce alignment. The scholar concludes carbon nanotubes and polymer/nanotube composites are a fast growing area of materials research and development. The theoretical and experimental mechanical, electrical, and thermal properties of individual nanotubes are exceptionally high. Therefore, tremendous opportunity to transfer the nanoscale properties to macroscale materials exists. To create such macroscale materials, many issues surrounding the incorporation of nanotubes into polymer matrices, strategies for property improvements, and the mechanisms responsible for those property improvements still remain. Since only moderate success has been made over the last ten to fifteen years, researchers continue to investigate materials such as polymer/nanotube composites to achieve properties of nanotubes on the macroscale.

The insight gained from a study of above researches, by various scholars, prompted the researcher to contribute his mite to the sports field by taking the making of the tennis racket using polymer carbon nanotube composites of different ratios for his study which included the structural and modal analysis of the tennis racket model with various conditions and parameters.

CHAPTER III

RESEARCH METHODOLOGY