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THE RHEOLOGICAL BEHAVIOR OF CARBON NANOFIBER REINFORCED THERMOPLASTIC COMPOSITES

A Thesis

by

QIANG ZENG

Submitted to the Graduate School of the
University of Texas-Pan American
In partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

May 2002

Major Subject: Manufacturing Engineering

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May 2002

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Qiang Zeng, The Rheological Behavior of Carbon NanoFiber Reinforced Thermoplastic Composites. Master of Science (MS), May, 2002, 51PP., 2 tables, 16 figures, references, 49 titles.

ABSTRACT

A rheological study of the thermoplastic HDPE filled with vapor grow carbon nanofiber (VGCNF) has been performed with a RheoStress 150 Tester. VGCNF having average 50 nm diameter were used. These nanofibers were purified to provide for an open network of high purity nanofibers. A rheomixer was used to disperse the nanofibers uniformly in the polyethylene matrix because of shear working conditions. The influence of fiber loading, frequency and temperature on the rheology was investigated. Studies were carried out in the temperature range of 160 to 210 °C and frequency range of 0.062 to 628.3 rad/s. The rheological measurements show that the composites behave as pseudoplastic. Viscosity of the system decreased with increase of temperature. Significant modulus enhancement occurs at low temperature range due to stiffness imparted by the fiber and efficient stress transfer at the interface between nanofiber and matrix. The viscosity difference between composite and pure polyethylene drops steeply when frequency goes higher than 628.3 rad/s which shows that the difficulty of processing advanced electrical products with VGCNFs is not an issue at higher shear rates. In the mean time, it has been realized that the rheological behavior of VGCNF reinforced polymer system cannot be modeled by an existing single mathematical model.

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ACKNOWLEDGEMETS

There are so many people to whom I owe great gratitude for their continuous support and encouragement.

First, I must say thank you to my thesis committee members. To Dr. Karen Lozano, my committee chairperson and great advisor, I express my deepest appreciation and gratitude for your immeasurable support, knowledge, encouragement and guidance. To Dr. Robert. E. Jones and Dr. Rajiv Nambiar, "thank you" for always being there to help me out. Your caring guidance and encouragement helped me complete this thesis.

To the teachers who must remain anonymous, I say "thank you" for all your kindness, from whom I learned the most.

To my family, I wish to express my deepest love, thank you for your support and understanding throughout my life.

To all my friends, thank you for always being there. The memories, words, laughter, tears of sorrow and joy we shared will always be treasured. Your friendship will last forever.

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CHAPTER I

INTRODUCTION

Polymeric materials have been replacing other conventional materials like metals, glass and wood in a number of applications. The use of various types of fillers incorporated into the polymer has become quite common as a means of reducing cost and providing enhancements in mechanical, thermal, electrical and magnetic properties of polymers. Due to the energy crisis and high prices of petrochemicals, there has also been a greater demand to use more and more fillers and/or reinforcements to cheapen the polymeric materials while maintaining and/or improving their properties. This study relies on the rheological analysis of Vapor Grown Carbon Nanofiber (VGCNF) as a filler of a polymer matrix. VGCNF offer great potential as a reinforcement of polymer matrices since significant enhancements can be obtained in thermal conductivity, electrical conductivity, strength, and elastic modulus. The potential applications of thermal conductivity of VGCNF polymer composites make them attractive for purposes such as electronic heat sinks, plasma facing materials, and radiator fins. In terms of electrical conductivity, the growth in the use of plastic housings within this market has generated a need for conductive materials to attenuate ambient Electromagnetic interference (EMI). Given these attractive applications, numerous researchers are starting to conduct important studies in the field.

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Rheology is now recognized as an important field of research since it can provide important data to aid in the process design as well as sensitive measures of the internal structure of the material. Rheology now plays a dominant role in the development of a variety of new polymer composites. This thesis applies rheological analysis onto the subject of Vapor Grown Carbon Nanofiber (VGCNF) reinforced polyethylene composites. The thesis also includes studies on fiber treatment, and sample preparation issues.

The first three chapters have been prepared with the idea of providing readers who may come from different backgrounds, the basics of filled polymer composites, rheology and rheometry.

The first chapter discusses the various types of polymer matrices and fillers for the formation of filled polymer systems. Then composite preparation techniques are presented with discussion of the criteria for good mixing and the various mixing mechanisms by which fillers are compounded with polymers.

The second chapter provides readers a general understanding of the vapor grown carbon nanofibers and their potential applications are also discussed in this chapter.

The third chapter deals with the fundamentals of rheology and rheometry as well as definitions of all the basic rheological parameters. Due to the composite system studied, special emphasis is given to non-newtonian behavior and to the oscillation rheological testing method which is applied in the research.

The fourth, fifth and sixth chapters present the details of how the experiments were conducted as well as the required analysis to understand the effects of the VGCNF on the

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microstructure of the PE matrix and processing issues of the composite. Chapter seven presents the conclusions and provides ideas for future research.

It is hoped that this thesis will provide the necessary background needed to understand the various aspects relating to the rheology of VGCNF reinforced polyethylene systems. For those who have already whetted their appetite with a taste for nanofiber filled composites, it is hoped that this thesis will offer a guide to fill in gaps therefore advancing the state of knowledge in this type of exciting composite materials.

Qiang Zeng

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CHAPTER II

OVERVIEW OF FIBER REINFORCED POLYMER COMPOSITES

Short fiber filled polymer composites form a relatively new family of materials, yet they are already well established in many applications (S. K. De and J. R. White, 1996). There is a vast range of materials in this category, some offering unique properties, some simply competing with other materials because of their relatively low cost. Their potential advantages are far from being fully realized and continued growth is anticipated in their use for many years to come. Research into these materials is crucial to their development and exploitation. Research continues into the design of short fiber reinforced composites and into the fundamental mechanisms that govern their behavior, and also into methods of fabrication that will not only produce the required shape but will result in the achievement of optimal properties. This chapter offers an introduction to short fiber-polymer composites in general. It also meant to inspire materials users to consider new applications for composites. The development of VGCNF reinforced polyethylene was based on following knowledge.

Short Fiber Filled Polymer Composites

The polymer matrix for Short fiber-polymer composites is based on thermoplastics, thermosets or rubbers.

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The most common thermoplastic short fiber reinforced composites are based on polyethylene, polypropylene and nylon (P. K. Sengupta et al, 1994). Thermoplastics are those polymers that can be made to soften and take on new shapes by application of heat and pressure. The changes that occur during this process are physical rather than chemical and hence products formed from such polymers can be remelted and reprocessed.

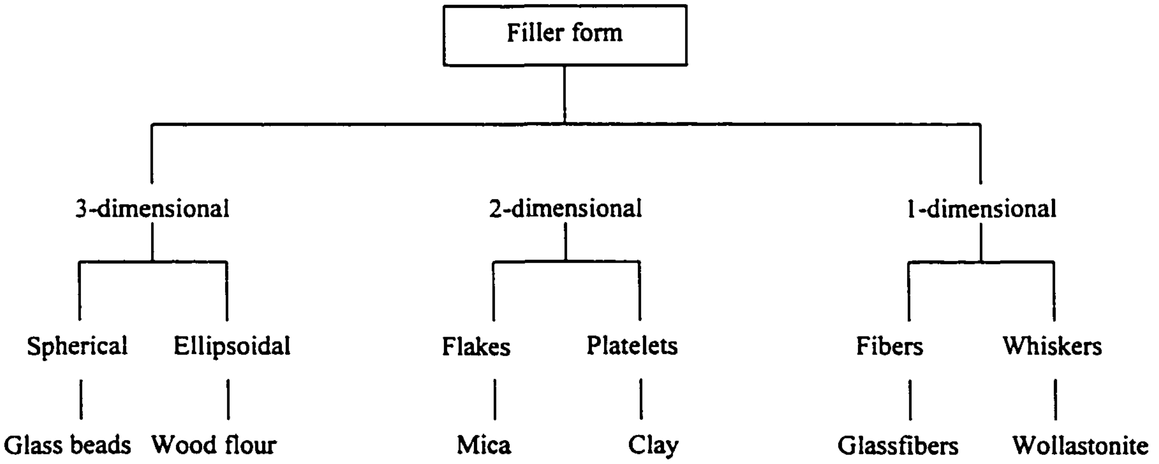
Thermoset matrices include polyesters, epoxies and phenolics. Thermosets are generally less suitable than thermoplastics for composites mass production.

Both natural and synthetic rubbers are candidates for short fiber reinforcement.

Considerable attention is paid to thermoplastic short fiber reinforced composites in this paper because thermoplastics have unique properties that are applied widely in industries.

The term "filler" is used for describing those inert, solid materials that are physically dispersed in the polymer matrix to enhance matrices properties. It usually does not exceed a few inches in length. Filler can be categorized by physical forms shown in Table 2.1.

Table 2.1 Filler classification by physical form



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Fillers may be used at concentrations of 5% to 50%, targeted at some desired physical or chemical properties (S. K. De and J.R. White, 1996 etc.), but also frequently useful as cheapeners. In this paper, special attention is given to the 1-dimensional filler VGCNF reinforcement. Fillers available as fibers are glass, nylon, polyester, carbon and other ceramics.

Vapor grown carbon nanofibers applied in this research are a new class of carbon fiber with fascinating thermal conductivity, electrical conductivity, strength and elastic modulus (Jyh-Ming Ting, 1995, G.G. Tibbells, 1986.)

The addition of fibers (usually long fibers) to thermoplastics can produce significant improvements in mechanical properties. As with most long fiber composites both the stiffness and strength are much higher than in the corresponding unfilled polymer and the toughness is often improved as well. The resistance to creep is much higher in fiber reinforced grades and the dimensional stability is generally better, though moldings made from fiber reinforced polymers are sometimes more prone to warping than molding made from unfilled polymers. The inclusion of fibers can often provide a useful increase in the maximum service temperature. Short fiber reinforced polymer can also lead to the reinforced enhancements in mechanical properties with the addition of ease of processing. They can be used in conventional injection molding machines with tools designed for unfilled thermoplastics. Nanofibers have been shown to provide enhancements mostly in the physico-chemical properties of a polymer; this is in the thermal stability and electrical conductivity as explained by Lozano et al. (2001). Extensive research is being conducted to prove structural enhancements (Pulickel M Ajayan, 2000).

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Preparation of Filled Polymer System

In this thesis, mixing is applied to the polymer composite preparation to achieve a homogeneous mixture. Mixing refers to operations that have a tendency to reduce nonuniformities or gradients in concentration, temperature, size of a dispersed phase, or other materials. Mixing is considered to be one of the most widespread industrial unit operations and it is found in the core of many areas in the general industry (Vicholasp. Cheremisinoff, 1993).

Mixing is accomplished by movement of material from various parts by the flow field. This movement occurs by a combination of the following mechanisms, the first is convective transport. It is present in both laminar and turbulent regimes, and it can also be called bulk diffusion. The second mechanism is eddy diffusion, which is produced by local turbulent mixing. In almost all cases both good distribution and good dispersion are required (Aroon V. Shenoy, 1999).

There are a number of types of compounding equipment that can potentially carry out the compounding of fillers with polymers. Compounding has traditionally been carried out on two-roll mills, internal mixers and nowadays single and twin-screw extruders. The extruders are being increasingly adopted as a means of giving a consistent product in a readily usable form, i.e. pellet or sheet. Those techniques available to produce filled polymer materials vary greatly in their methods and results. Internal batch mixers, such as the Banbury type mixer, are the oldest mixing devices in polymer processing but are slowly being replaced by continuous ones for certain applications.

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Each material formulation presents a distinct problem. It is important to know how sensitive the compound is to temperature. The need to control or change the temperature and pressure during compounding should be considered (Sangcheol Kim, 1998).

To achieve optimum material quality, the equipment for compounding fillers into a polymer must be capable of performing some of the following tasks:

1. Incorporation and homogenization of fillers without exceeding degradation temperatures;
2. Generation of sufficiently high internal shear stresses to facilitate good dispersion of reinforcing fillers;
3. Provision of uniform shear stress to each filler particle at any heat history;
4. Provision of short and uniform residence time distribution to minimize heat history;
5. Provision of precise temperature control over the process to ensure narrow temperature distribution throughout the process and at discharge, again to regulate and minimize heat history.

Every processor has its merits and its limitations. A batch system may be considered more flexible since it need not be tied in with other in-line equipment. There are still some filiers, that can not be processed effectively with a continuous system such as the nanofibers where high shear rates are required to break up the agglomerates and evenly dispersed them within the matrix. Therefore for this particular study, an internal batch mixer was utilized for compounding.

The internal mixer is among the oldest members of the mixer family. It has adopted the open mill mixing principle but has a complete enclosed mixing chamber in which two

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rotors are mounted. The rotors are sealed at each end to avoid leakage of material from the chamber. Internal batch polymer mixers (torque rheometers) are design to create as much turbulent flow and complex shear action as possible to provide an optimal mixing of all the heterogeneous components of i.e. polymer melts or rubber compounds under process conditions which provide nonlinear visco-elastic responses of the highly sheared materials (Je Kynn Lee and Chang Dae Han, 1999). The resistance of the test sample against being mixed is proportional to its viscosity and it is measured in a torque rheometer as the reactionary torque on the rotors. This torque is normally recorded as a function of time. The graphs of torque versus time are called rheograms.

The most commonly used internal batch mixer is the Banbury type as mentioned earlier. The mixer consists of a temperature controlled chamber and two rotors aligned parallel and at some distance to each other. Three different mixing actions take place in the internal mixer; intensive or dispersive mixing around the tips of the rotor blade, extensive mixing due to simple shear flow and extensional flow between the chamber walls and the cylindrical portions of the rotors and in the entrance region to the narrow gaps between rotor tip; and distributive mixing due to random plug convection, as a result of the interaction between the two rotor tips (Nicholas P. Cheremisinoff, 1993).

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CHAPTER III

INTRODUCTION TO VGCNF AND ITS APPLICATIONS

VGCNF are a novel class of carbon fiber manufactured by Applied Sciences, Inc. VGCNF is produced by a combination of catalytic and chemical vapor deposition (CVD) processes which allow independent control of filament length and diameter. Fibers can be produced in a broader variety range from 1mm to tens of centimeters, and diameters from under 40nm to over 100 microns.

VGCNFs are distinctively different from other types of carbon fiber in its methods of production, its unique physical characteristics, the prospect of low-cost fabrication and fascinating properties. VGCNFs are similar to fullerene tubes in the nanoscale domain of initial formation and the highly graphitic structure of the initial fibril. VGCNFs are dissimilar to fullerenes in that a catalyst is used to form the initial filament, and typically, the catalyst particle remains buried in the growth tip of the filament after production, at a relative concentration of a few parts per million. Depending on the size to which the fiber is allowed to grow. As would be expected, the formation of the core fibril by diffusion through a catalyst particle and subsequent chemical vapor deposition of carbon on the surface of the fibril favors carbon deposition of relatively high purity, so that the diameter of the fiber may be thicker and the outer layers less graphitic than the core fibril. VGCF may be highly graphitized with a heat-treatment of about 280°C. Consequences of the circumferential orientation of high purity graphene planes is a lack of cross-linking

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between the graphene layers, and a relative lack of active sites on the fiber surface, making it more resistant to oxidation, and relatively unreactive to matrix materials (R. Alig, 1996).

Potential applications for VGCF would exploit the noteworthy properties of thermal conductivity, electrical conductivity, strength, and elastic modulus (Jyh-Ming Ting et al, 1995). A significant portion of the development and work conducted on VGCF composites has been motivated by the potential of these types of composites for thermal management in high performance applications and for conductive plastics with structural enhancements. The thermal conductivity of VGCF composites make them attractive for purposes such as electronic heat sinks, plasma facing materials, and radiator fins. Composites fabricated with VGCF can be designed with fibers oriented in preferred directions to produce desired combinations of thermal conductivity and coefficient of thermal expansion. While such composites are not likely to be cost-competitive to metals in the near future, the ability to design for premium values of thermal conductivity in preferred directions, combined with lower density and lower coefficient of thermal expansion, could warrant the use of such VGCF composites in less price sensitive applications, such as improvement of reliability in electronics for aerospace vehicles (R. Haggenmueller et al, 2000). Composites fabricated with the smaller floating-catalyst fiber are most likely to be used for applications where near-isotropic orientation is favored. Such isotropic properties would be acceptable in carbon/carbon composites for pistons, brake pads, and heat sink applications, and the low cost of fiber synthesis could permit these price-sensitive applications to be developed economically. A random orientation of

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CHAPTER IV

RHEOLOGICAL BACKGROUND

In this thesis, the introduction to the subject of rheological science will be separated into two parts: the fundamental rheological concepts and rheometry. Followed by some experiments that will be utilized to explain important factors related to the rheology of VGCNF filled polymer systems.

Rheological Behavior and Concepts

The subject of polymer rheology has received the unabated attention of a number of research workers and various books (Carreau, et al, 1997) have been written each giving a different perspective of this rather complex subject. Rheology is a relatively young branch of natural science that deals with the relationships between forces (stresses) and deformations of material bodies. Hence, it is also connected to the flow properties of polymers both in solution and the melt as well as the reaction of materials in the solid state to mechanical stresses. Most polymeric materials exhibit the combined reactions of both liquid and solid states, called viscoelasticity, that is, their response to external load lies in varying extent between that of a viscous liquid and an elastic solid. In an ideal viscous liquid, the energy of deformation is dissipated in the form of heat and cannot be recovered just by releasing the external forces; whereas, in ideal elastic solid, the deformation is fully recovered when the stresses are released.

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A softened or molten polymer represents a cluster of entangled, flexible strings of varying lengths. The sensitivity of rheological tests is mainly due to chain entanglements resulting in large differences in flow behavior even for small differences in chain length or branching. Rheological measurements are used as an effective tool for:

(a) Quality control of raw materials, manufacturing process/final product.
(b) Predicting material performance
(c) Understanding of the microstructure of materials.

A typical viscosity vs. shear rate curve for softened or molten unfilled polymer would be like the one shown in Figure 4.1.

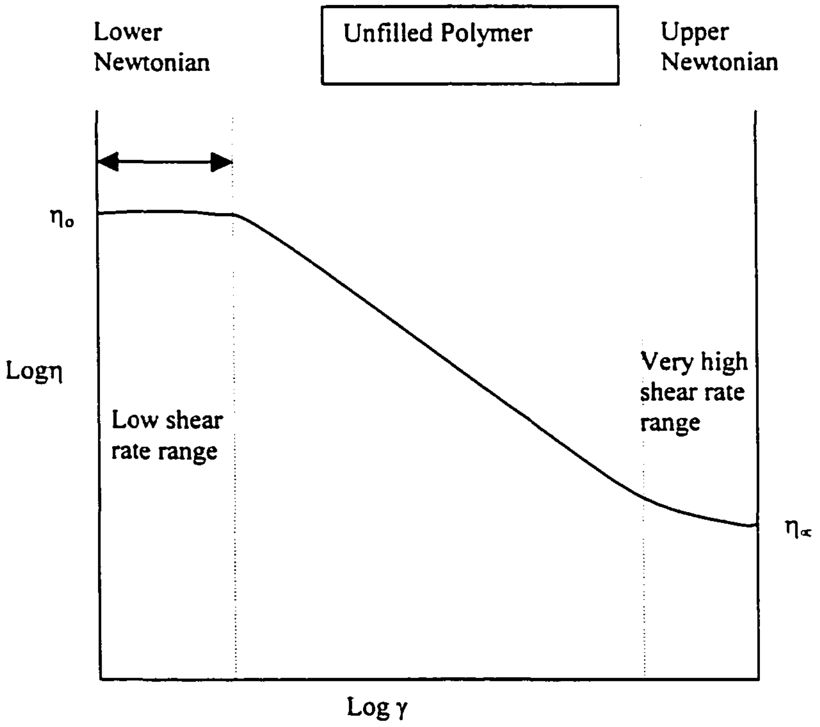

Figure 4.1 A typical viscosity vs. shear rate curve for a softened or molten unfilled polymer, showing the effect of physical structural changes during flow

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There is a Newtonian region in the low shear and very high shear where the viscosity does not change with shear rate. However, the Newtonian plateau at the very high shear rates is rarely observed as it is often beyond the measuring range. The curve in Figure 4.1 should thus be considered as the "ideal" flow curve. In the low to medium shear rate range, at some critical shear rate there is a continuous drop-off of viscosity with shear rate. The drop-off of viscosity with shear rate would occur sooner if the molecular weight distribution is widened. This is because the shorter molecular chains are of lower viscosity and cause the viscosity to decrease sooner from the Newtonian region. However, at higher shear rates, the viscosity of the polymer having wide molecular weight distribution would be higher. The molecular chains that are very long tend to act tenaciously and elastically at higher shear rates, giving higher viscosity. Therefore, the slope of the viscosity vs. shear rate curve can be used as a tool to describe the molecular weight distribution. The height of the low shear (Newtonian) viscosity can relate to the average molecular weight. However, these relationships are considerably affected by influences such as branching, crosslinking and molecular entanglement.

The advantages that filled polymer systems have to offer are normally offset to some extent by the increased complexity in the rheological behavior that is introduced by the inclusion of the fillers. Usually when the use of fillers is considered, a compromise has to be made between the improved mechanical properties in the solid state and the increased difficulty in melt processing. There is extensive literature on the rheology of filled polymer systems (Michael Foltes, 1997) including comprehensive chapters in a number of books (Aroon V. Shenoy, 1999), the bulk of the literature deals with the

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rheology of systems in the range of 5 to 40% filler loading by weight. Aspects relating to this loading level have been effectively reviewed by Utracki and Fisa (1982).

Typical viscosity vs. shear rate curves for a softened or molten filled polymer would appear similar to the one shown in Figure 4.1. However, the low shear rate ranges viscosity could be constant Newtonian, slightly variable or unbounded depending upon the characteristics of the filled polymer system due to the effect of filler agglomerates. Beside this, there are a number of other factors that could be responsible for changing the curve from Figure 4.1 for the unfilled polymer to the filled polymer curve. When it is filled, similar changes would be observed in all other flow parameters that respond to deformation.

The rheological properties are not only determined by the type of filler, but also by its size, shape, size distribution and concentration. A key factor in the use of fillers without adversely affecting the material properties is the stress transfer at the filler-polymer interface. The interfacial adhesion can be substantially enhanced via a coupling agent that adheres well to both the polymer and the fillers. The type and amount of the surface treatment on the filler are thus additional parameters affecting the rheological properties of filled polymeric systems.

Through the general introduction of the usage of rheological testing method, the readers might have the clear answer to the purpose of rheological testing. In the following sections, the author will introduce some basic concepts which are necessary for reader to understand the rheological properties.

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Most polymeric materials exhibit the combined properties between the extremes of the conceptual views of the Newtonian fluid and the Hookean solid, called viscoelasticity.

When a small stress is suddenly exerted on a solid, a deformation begins, the material will continue to deform until molecular (internal) stresses are established, which balance the external stresses. The term “deformation” refers to the equilibrium deformation that is established when the internal and external stresses are in balance.

Not all materials reach an equilibrium deformation. In a fluid, if an external stress is exerted, deformation occurs, and continues to occur indefinitely until the stress is removed. A fluid response is one in which no resistance to deformation occurs. Internal frictional forces retard the rate of deformation (Arie Ram, 1997).

It is therefore appropriate to state Newton’s law, in which the coefficient of viscosity, η, appears. Newton’s law in flow is expressed as:

$$\tau = \eta \dot{\gamma}$$

where, τ represents the shear stress that acts on the fluid, and ŕ represents the rate of shear that expresses the rate of deformation. Only in the case of simple liquids, a constant viscosity coefficient (η) may occur, dependent only on temperature.

In the case of polymers, it has been found that the viscosity is not a constant, but varies with the flow conditions. Therefore, these liquids are termed non-Newtonian. In Figure 4.2 the relationship between shear stress and shear rate (the so-called “flow curve”) is shown, the Newtonian liquid is represented by a straight line from the origin while there may be several curves representing non-Newtonian liquids. Most polymeric

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melts and solution show pseudoplastic behavior, which means with the shear rate increase, viscosity shows drop-off behavior.

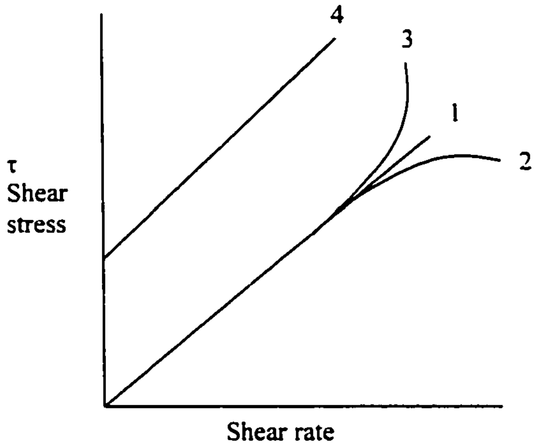

Figure 4.2 Flow curves of various liquids
1. Newtonian liquid. 2. Shear-thinning (pseudoplastic) liquid.
3. Shear thickening (dilatant) case. 4. Bingham liquid

A convenient physical interpretation may be illustrated by simulating mechanical models. In which a spring represents an elastic or Hookean solid (modulus), while a piston moving in an infinite cylinder filled with a viscous liquid (a dash-pot) represents the Newtonian liquid (viscosity). Recall that properties of polymers or its composites are the combination of both liquid and solid behavior. Thus, the deformation of the solid (spring) is completely recoverable, while that of the liquid (dash-pot) is non-recoverable and is converted to heat. Some models were developed though combinations of those spring and dash-pots. The most common ones are the Maxwell visco-elastic liquid (a series combination) or the Voigt (Kelvin) viscoelastic solid (a parallel combination).

Normally, the flow of polymer is a very complex process. Therefore, more parameters models were needed to be developed to match the flow behavior. There have

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been a number of rheological models proposed that represent the flow behavior of softened or molten polymer and these are readily available in a number of books (Carreau, 1997). The constitutive equations, which relate shear stress or apparent viscosity with shear rate, involve the use of two to five parameters. Here, several useful models will be described.

Power-Law Model

This is a two-parameter model for engineering applications. It is given by

$$\eta = m\left|\gamma\right|^{n-1}$$

with the parameters m and n, this equation results in a linear relation between η and γ̇. The parameter n is less than one for shear-thinning or pseudoplastic materials. When n=1, the model reduces to the one-parameter Newtonian case.

Ellis Model

In this model, the apparent viscosity vs. shear rate relationship is given in the following form:

$$\eta = \frac{\eta_o}{1 + (\tau / \tau_{1/2})^{\alpha' - 1}}$$

where $\tau_{1/2}$ is the shear stress at the viscosity of η_o /2.

This is a three parameters model. α'-1 is related to the slope of the viscosity vs. shear rate curve and describes the shear-thinning behavior. The model is able to fit data in the low to medium shear rate ranges.

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Carreau model

This model has basically four parameters, which are η_o, η_∞, λ, and N. the relaxation time λ is considered to be the characteristic time available as the inverse of the shear rate at which the shear-thinning behavior begins. N is a measure of the shear-thinning characteristics. Both λ and N, are considered to be adjustable parameters and the model is written as follows:

$$\eta - \eta_\infty = (\eta_o - \eta_\infty)(1 + \lambda^2 \dot{\gamma}^2)^{-N}$$

This carreau model can be fitted to the entire viscosity vs. shear rate curve. However, the data up to η_∞ is rarely determinable. Hence, sometimes the form of the carreau model is used as a truncated three-parameter model after neglecting η_∞.

Herschel-Bulkley model

This model was developed by Herschel and Bulkley specifically for describing pseudoplastic fluids with yield stress and is useful for filled polymer systems. The model form is given by

$$\tau = \tau_y + k\dot{\gamma}^2$$

This model can predict the power-law flow behavior at all shear rates.

The rest of many constitutive equations are quite cumbersome to use in engineering analyses. The interested reader may find them in a number of literatures cited in references (Carreau, et al, 1997).

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Introduction to Rheometry

Rheometry is defined as the measuring method of rheology and its basic function is to quantify the rheological material parameters of practical importance. A rheometer is an instrument used to measure the rheological properties. This research has been conducted with a rotational viscometer using a parallel-disc configuration. Therefore special attention will be given to this type of rheometers.

The chief advantage of the parallel disc configuration is that it can be used for filled polymer systems of extremely high viscosity and elasticity. The basic limitation in rotational viscometers is that they are restricted in their use only to low shear rates for unidirectional shear and low frequency oscillations during oscillatory shear. At high shear rates as well as at high frequencies, a flow instability normally sets in the polymer sample which then begins to emerge out of the gap between the cone and plate or parallel-disc, thereby giving erroneous results. As a consequence of the above, the measured material functions do not actually conform to the higher deformation rates which are normally prevalent in processing operations.

The parallel-disc rheometer is a widely used instrument for shear flow rheological properties of polymer system. The sample whose rheological properties are to be measured is trapped between the two parallel circular horizontal plates. It is made use of serrated discs placed in a pressurized cavity to prevent polymer slippage. The principal features of this viscometer are shown schematically in Figure4.3.

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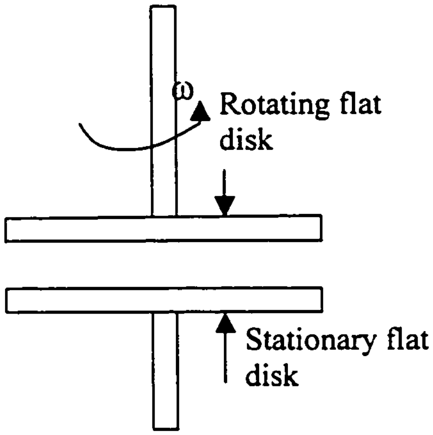

Figure 4.3 Schematic diagram showing the principal features of a cone and plate rotational viscometer

The following applies for the shear rate:

$$\gamma = \varpi R / H$$

where ω is the angular velocity (rad/sec), R is the radius of the disc (m) and H is the gap between the two parallel discs (m).

The following relationship is for the shear stress τ:

$$\tau=2M/\pi R^3 = GM$$

where G is measuring system constant.

Oscillation Testing method was used for the present study. Compared with the creep or the strain and relaxation test, Oscillation tests provide more detailed information about the elasticity of a sample. The creep and relaxation tests are made with a given constant load (shear stress or shear rate) and permit the determination of the ratio between the viscous and the elastic portions (as a relative value), the retardation or creep time or the relaxation time respectively, the shear modulus G and the compliance J. All

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these statements depend on the size of the constant presetting and only under these constant conditions they yield a result.

In contrast, the oscillation test can be made under varying loads (frequency and amplitude sweep) with controlled shear stress or controlled strain. The results are the dynamic quantities for the shear moduli (complex dynamic shear modulus G*, storage modulus G', loss modulus G"), their ratio (by means of the loss angle δ) and the dynamic complex viscosity η^* respectively. Therefore, the measuring points at different load levels provide more information than a measuring curve at only one constant load level.

The sample to be examined is between the two plates; the upper plate is oscillating under a given torque, which was measured automatically. The oscillating movement must not be too strong in order not to destroy the structure of the examined sample. Too high stresses prevent the sample from remembering its initial state after relief and thus from re-forming at all. Under the oscillating stress form, the volume element undergoes the strain γ. This is named controlled shear stress test.

The other testing method is controlled strain test which means that when the certain strain γ is applied the force or stress applied on sample was recorded.

During those processes, the linear-viscoelastic range must not be exceeded.

Since it is the oscillatory testing, we would like to applied sinusoid curve on three group substances to express the various phase between strain and stress as follows for ideally elastic, ideally viscous and viscoelastic substances.

(1) For ideally elastic substances (according to Hooke) the following applies:

$\tau(t) = G\gamma(t)$ when strain was controlled or

$\gamma(t) = \tau(t)/G$ when stress was controlled.

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Under this condition, the $\tau(t)$ curve is in phase with the $\gamma(t)$ curve (here both as sinusoid) shown in the Figure 4.4, because G=const.

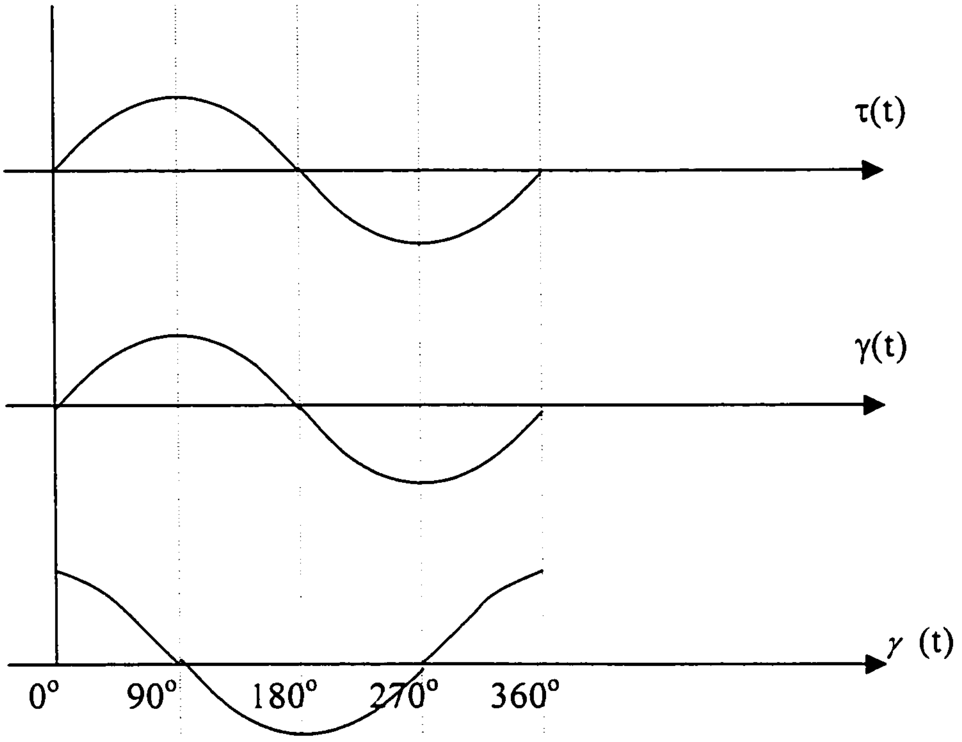

Figure 4.4 Stress, strain and shear rate phase diagram for ideally elastic substances

The γ (t) curves are always displaced against the γ curve by 90 °, which means that when the strain goes through zero (γ=0 in the positions 0° and 180°), there is the maximum strain rate. In the two points of maximum strain (90° and 270°), the strain rate is zero because the strain movement is reversed. In other words, the time derivative of the sinusoid $\gamma(t) = \gamma_0 \sin \omega t$ is the cosinusoid $\gamma = \gamma_0 \omega \cos \omega t$.

The phase displacement between the $\tau(t)$ curve and the $\gamma(t)$ is $\delta=0$.

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(2) For ideally viscous substances (according to Newton law), the following relationships were applied:

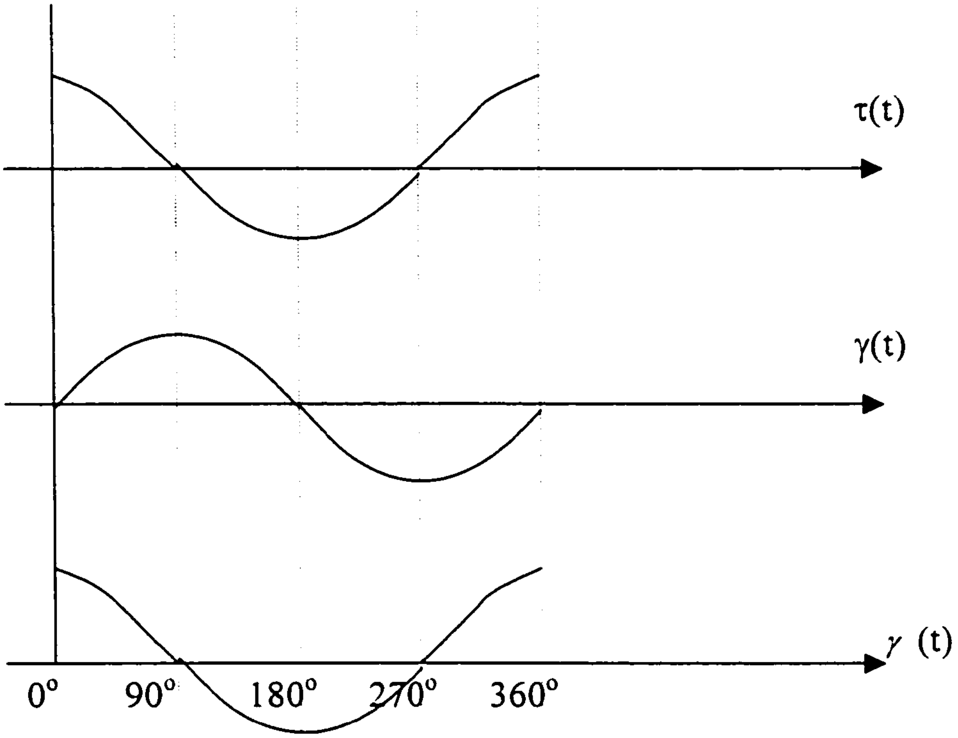

Figure 4.5 Stress, strain and shear rate phase diagram for ideally viscous substances

$\tau(t) = \eta\ \gamma(t)$ when strain or shear rate was controlled or

$\gamma(t) = \tau(t)/\ \eta$ when stress was controlled.

For those ideally viscous substances, the $\tau(t)$ curve is in phase with the $\gamma(t)$ curve because the viscosity η is constant. However, the delay of the $\tau(t)$ curve against the $\gamma(t)$ curve has the phase displacement angle of $\delta = -90^\circ$ shown in Figure 4.5.

(3) For viscoelastic substances, the following relationships can be applied;

a. with controlled strain:

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strain curve $\gamma(t) = \gamma_0 \sin\omega t$ was shown in Figure 4.6. The shear rate curve is

$\dot{\gamma}(t) = \gamma_0\omega\cos\omega t = \dot{\gamma}_0 \cos\omega t$

b. with controlled stress:

stress curve $\tau(t) = \tau_0 \sin \omega t$

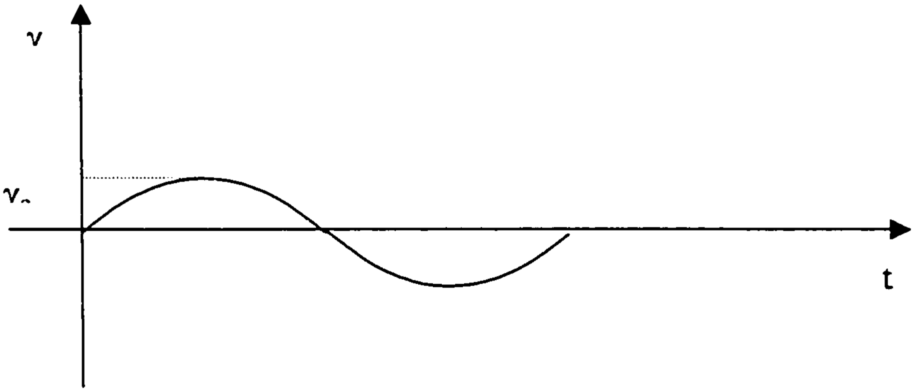

Figure 4.6 Strain phase diagram for viscoelastic substances

The same we use curve to express the measuring result:

When the strain was controlled, for these viscoelastic substances, the shear stress curve will have a displacement angle ($0° < \delta < 90°$) shown in Figure 4.7.

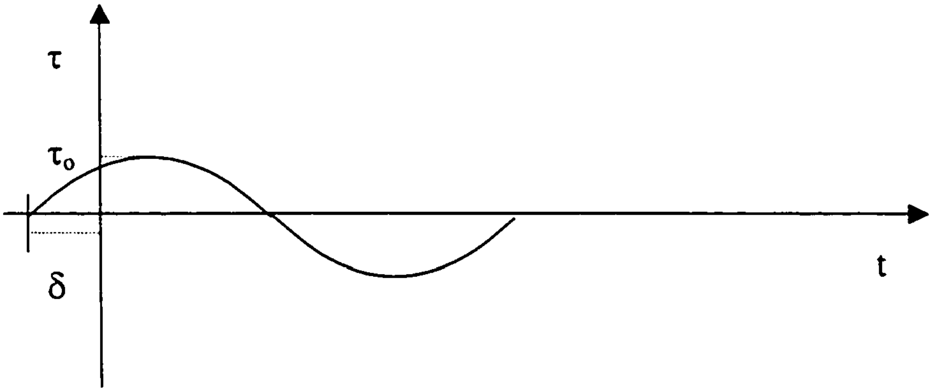

Figure 4.7 Stress phase diagram for viscoelastic substances

From the displacement angle we can derive out some important factors in unsteady shear viscoelastic properties.

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Storage modulus: $G' = \frac{\tau_o}{\gamma_o} \cos\delta$

Its value represents a dimension for the quantity of strain energy reversibly shored in the substance and recoverable. Thus it characterizes the elastic behavior of the sample.

Loss modulus: $G'' = \frac{\tau_o}{\gamma_o} \sin\delta$

Its value represents a dimension for the quantity of the energy irreversibly given off by the substance to its environment and thus lost. So it characterizes the viscous behavior of the sample.

Loss factor: $\tan\delta = \frac{G''}{G'}$

It indicates the ratio between the amount of the dissipated and the stored energy and hence also between the viscous and the elastic portion of the sample.

Other quantities can be determined from the oscillation testing were list in the following relationships:

Real part of the viscosity that stands for the viscous behavior:

$$\eta' = \frac{G''}{\varpi} = \frac{\varsigma}{\varpi * \gamma_o} \sin\delta$$

Imaginary part of viscosity which stands for the elastic behavior:

$$\eta'' = \frac{G'}{\varpi} = \frac{\tau}{\varpi * \gamma_o}$$

Therefore, for the loss factor also the following relationship applies:

$$\tan\delta = \frac{\eta'}{\eta''}$$

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Oscillation Testing Procedures

The two basic test steps are the strain/stress sweep and the frequency sweep.

The Strain/Stress Sweep is first of all needed to determine the linear viscoelastic range. It might be also used to provide a clue about product strength and stability.

Strain Sweep The stability of the structures of viscoelastic substances is measured with increasing strain. This is of interest for instance of the quality control of polymer melt, gels and highly concentrated dispersions.

The test is mostly chosen to determine the limit of the linear-viscoelastic strain range. The value of $G'(\gamma)$ drops steeply at the critical limit amplitude γ. For amplitudes below the value γ_l, remains at a constantly high plateau value, the structure of the examined substance remains undestroyed and stable. For amplitudes above γ_l, the linear-viscoelastic range is exceeded. The substance structure is now destroyed.

Stress Sweep To investigate the stability of viscoelastic substances, the dependence of the moduli G' and G'' on the stress amplitude can also be determined. In the same way, the following applies: the linear-viscoelastic range is exceeded as soon as at a critical shear stress the values of $G'(\tau)$ or $G''(\tau)$ respective drop deeply.

Frequency Sweep The Frequency Sweep is used to characterize test materials. The sample is not supposed to change its properties throughout the test time. The certain strain or stress value should already been set through the Stress/Strain Sweep test.

From the frequency sweep test information about the structural conditions of the sample was obtained and will be explained in detail in chapter 6.

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CHAPTER V

SAMPLE PREPARATION

Materials

VGCNFs (Pyrogreaph III Carbon Fiber, PS and HT grade) were supplied by Applied Science, Inc, these fibers were produced by a catalytic process of hydrocarbons in the vapor-state (for detail information please reference to chapter III). These VGCNF have circular cross sections (with average diameter 50 nm) and central hollow cores commonly called filaments. The as-received VGCNF were observed by scanning electron microscopy to be highly entangled having dispersed amorphous carbon and metal catalysts. The physical data was listed in table 5.1.

Table 5.1 Physical data for VGCNF

BOILING POINT:	SPECIFY GRAVITY $(H_2O=1)$	APPARENT DENSITY LBS/FT
N/A	2.0	2 to 20
VAPOR PRESSURE @__F__C	PERCENT VOLATILE BY VOLUME (%)	PERCENT SOLID BY WEIGHT (%)
N/A	N/A	>99%
VAPOR DENSITY (AIR=1)	EVAPORATION RATE	PARTICLE DIAMETER (microns)
N/A	N/A	Average: 0.05
SOLUBILITY IN WATER	PH	APPEARANCE AND ODOR
No	N/A	Fluffy agglomerates with no odor

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High-density polyethylene, the chosen polymer matrix was a HXM50100 from Phillips Chemical Company. It is a very well known thermoplastic and is commercially available in different grades with different types. It is a nonpolar semicrystalline polymer.

Fibers Purification

To utilize the VGCNF, purification process was needed to remove those unwanted impurities, providing opening of the highly tangled nests of nanofibers without shortening the fibers. In this research, a purification process developed by Lozano et al (1999) was conducted. It consists on the refluxing of the fibers in dichlormethane for 5 days at a temperature of 35 °C, followed by several deionized water washings and refluxing for 24 hours at 90 °C and dried in air at 120 °C for 48 hrs. The experiment device set was shown in Figure 5.1.

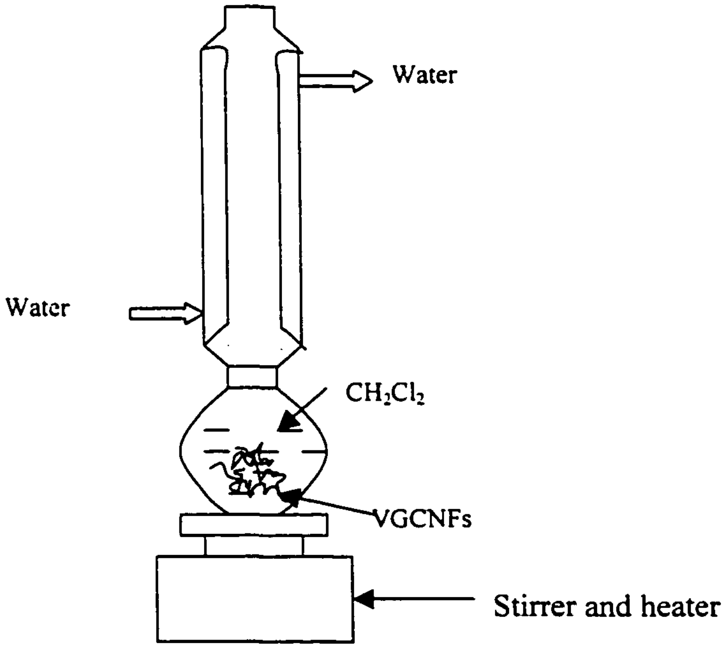

Figure 5.1 Schematic diagram showing the principal device of the purification process

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After the purification, a considerable amount of soot has been removed and a better dispersion of the individual fibers can be observed.

Mixing

A Haake Rheomex mixer from Haake was used. The operation was monitored by the polylab software system.

The mixing process was also conducted following Lozano's process (2001). Small batch of polyethylene was melted in the mixer for one minute; this was followed by the addition of small amount of purified VGCNF. Then these two steps were repeated until all the components were in the chamber. The materials were mixed with a speed of 60 rpm for about 8 minutes followed by 90 rpm for last one minute and the mixer chamber temperature kept at 190 °C. This mixing process led to a homogeneous dispersion of nanofibers with no agglomerates present due to the high shear processing conditions.

Pressing

After mixing, a batch of composites was delivered into a pair of plates, and pressed by compression molding at 200 °C, and at the pressure 7 tons. When the composites were completely melted, the ultimate pressure was maintained for 2 min, and then cooled by water until the temperature fell down to room temperature. The sheets were then cut into the designed shape for rheology testing, composites of 2cm diameter and 1mm thickness were used.

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CHAPTER VI

RHEOLOGICAL PROPERTIES TESTING

Instrument Description

The Haake Rheometer applied in this study was the RheoStress® RS 150 with the high temperature measuring system TC501, ceramic rotors and the electric heating system.

Experiment Procedures

The linear viscoelastic range was determined by a strain sweep test. The frequency sweep measurements were then made in the linear viscoelastic region, where the viscoelastic properties are independent of strain.

This test was conducted with controlled strain. The stability of the structures of viscoelastic substances is measured with increasing strain. This is of interest for instance for the quality control of polymer melts, gels and highly concentrated dispersions. The value of $G'(\gamma)$ drops steeply at the critical limit amplitude γ. For amplitudes below the value γ_l, $G'(\gamma)$ remains at a constantly high plateau value, the structure of the examined substance remains undestroyed and stable. For amplitudes above γ_l, the linear-viscoelastic range is exceeded. The substance structure is now destroyed.

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The constant strain value of 0.001 was selected because this fell below the critical strain above which there was a detectable change in viscoelastic behavior (Fig. 6.1).

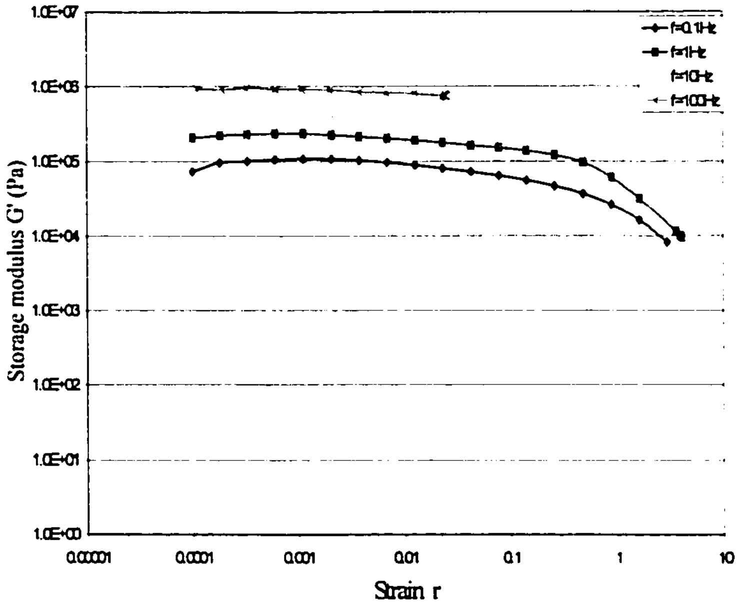

Fig 6.1 Linear viscoelastic range

The rotational measurements were performed using a parallel-plate sensor PP20 (0=20mm) and initial gap of 1mm. The samples were set between parallel plates

PJL USTATUS DEVICE=ON to 100 °C and after temperature equilibrium was obtained (about 10min)
@PJL USTATUS TIMED = 30

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CHAPTER VII

CONCLUSIONS

In this research, a banbury type mixer was used to mix the purified VGCNF in the thermoplastic polyethylene. Melt rheological properties of vapor grown carbon nano-fiber reinforced high density polyethylene composites have been studied as a function of fiber loading, shear rate and temperature. In general the viscosity of the system increased with fiber loading due to an increased hindrance to the melt flow which was proved by DSC testing. However, The composites show stronger pseudoplastic behavior with increase fiber loading, especially at high frequency region that the rheological properties of the composites were dominated by PE matrix at high frequency so that addition of VGCNF to the polyethylene does not bring a significant change in processing behavior. The influence of surface treatment on the melt flow properties was studied. It is found that addition of bonding increases the viscosity of composite due to increased fiber-matrix interaction. The melt flow studies were carried out in the temperature 160,190, 210 °C. It was found that viscosity of the melt decreases with increase of temperature. This is associated with the molecular motion due to the availability of greater free volume and weaker intermolecular interactions. However, the effect is less significant at high frequency due to the breakage of the bonding between matrix/fibers and matrix. A comparison is made between theoretical and experimental viscosity values and it is found that experimental viscosity fit theoretical one very well, however, a significant deviation

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from theoretical value was observed at high frequency due to weaker bonding and unexpected flow of filled melt composites. It is suggested that a multiple parameters rheological model is required to predict the melt composites flow behavior.

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