POLY(3-HYDROXYBUTYRATE-CO-3-HYDROXYVALERATE) – CELLULOSE
NANOWHISKERS COMPOSITES BY SOLUTION CASTING

By

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Long (Edward) Jiang, Ph.D.
To my beloved grandmother Evgenia Kim
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Elena Ten
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Abstract

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In this research, renewable biobased nanocomposites based on poly(3-hydroxybutyrate-co-3-hydroxyvalerate) and cellulose nanowhiskers were prepared by solution casting. Nanocomposite structure and property investigations were characterized to understand the reinforcing mechanism of CNWs in PHBV and establish longstanding goal of predicting structure–property relationships for material design and optimization.

The CNW concentration strongly influenced the extent of nanowhiskers dispersion and level of property enhancement, as determined by structural, mechanical, thermal, dielectric and rheological characterizations. CNW content of 2.3 wt% indicated significant property transitions for all the investigated properties except for rheological ones. The change was believed to be due to the transition from homogeneous CNW dispersion to agglomeration. High CNW content led to CNW agglomerations and reduced nanocomposite moduli, yield strengths and real permittivity. DSC and POM analyses showed that CNWs could alter the nucleation and growth under both non-isothermal and isothermal crystallization conditions. Although the effect of CNW on nucleation ability and degree of crystallinity of PHBV was significant and could contribute to the mechanical properties improvement, the results of this study confirmed that primarily CNW homogeneous distribution and interconnected 3-D structure governed E'
enhancement. Oriented PHBV/CNW composites were fabricated in-situ under electric field. CNW were oriented along the direction of applied filed. Image analysis revealed that degree of order and orientation distribution was mainly influenced by CNW content. TEM, DMA and XRD analysis showed that low CNW concentrations resulted in higher degree of anisotropy. Furthermore, for CNW content above 5 wt% the electric field was not sufficient to align CNW given the increased viscosity of PHBV/CNW solutions, hence, restricted mobility of CNW.

The superior properties observed in both randomly oriented and aligned cellulosic nanocomposites may be explained by conventional ideas of reinforcement as predicted by micromechanics theories like Halpin-Tsai, Voigt-Reuss and Cox “shear lag” models. In latter model, the distribution of orientation angle was taken into account and the predictions were consistent with experimental values. Based on good agreement between experimental nanocomposite moduli and Cox model predictions, especially at low concentrations, it was clear that superior reinforcement arises mainly from the high modulus and aspect ratio of CNWs at these concentrations. Furthermore, the critical concentration corresponding to the formation of percolated CNW structure was modeled based on excluded volume theory. The simulation was in good agreement for randomly oriented nanocomposites. From individual micromechanical properties of the nanofibers and matrix, aspect ratio, orientation and volume fraction of nanofibers, it has been demonstrated that the effective storage moduli can be simulated to obtain properties of random and aligned composite lamina.
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<td>PHAs</td>
<td>Polyhydroxyalkanoates</td>
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<tr>
<td>PHB</td>
<td>Poly(3-hydroxybutyrate)</td>
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<tr>
<td>PHBV</td>
<td>Poly(3-hydroxybutyrateco-3-hydroxyvalerate)</td>
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<tr>
<td>CNW</td>
<td>Cellulose nanowhiskers</td>
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<tr>
<td>DMF</td>
<td>N, N-dimethylformamide</td>
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<tr>
<td>MCC</td>
<td>Microcrystalline cellulose</td>
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<tr>
<td>PEG</td>
<td>Polyethylene glycol</td>
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<td>BN</td>
<td>Boron Nitride</td>
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<td>AFM</td>
<td>Atomic Force Microscopy</td>
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Chapter 1 Introduction

1.1 Background

1.1.1 Biodegradable plastics

Over the past century, increased production of plastics has raised serious concerns about their impact on the environment. Reduced capacities of landfills, environmental persistence, harm to marine mammals, greenhouse gas emission, and fossil fuel depletion are few examples of environmental and economic concerns. As in 2005, in the USA, 28.9 million tons of plastics packaging was generated and only approximately 5.7% of plastic is recycled or reused in some way, 94.3% is sent to landfill and discarded or combusted into the environment (Marsh and Bugusu 2007). Although today the proportion of plastics recycled or reused is gradually increasing, only part of the plastics produced can be recovered. Moreover, not all plastics are suitable for recycling or reuse (e.g., contamination of plastic by other materials and additives, non-reshaped properties of thermosetting materials, and poor compatibility of blends) (Howell 1992, Cao 2002). As a result, the volume of plastics discarded annually creates a substantial plastic waste disposal issue, and the concept of developing sustainable materials systems has gained great attention from scientists and engineers. Global sustainability relies on renewable sources of materials and energy; and use of natural polymers is of current interest.

A number of biodegradable materials have been investigated for use as plastics (Fig. 1). Depending to the evolution of the synthesis process, different classifications of the different biodegradable polymers have been proposed (John and Thomas 2008).
Figure 1.1 Classification of biodegradable polymers.

- **Biodegradable polymers**
  - **Biomass products from agro-resources (argo-polymers)**
    - Polysaccharides
      - Starches: (Maize, potato, wheat)
      - Ligno-cellulosic products (wood, straw)
      - Others: pectin, chitin, chitosan, gums
  - From micro-organisms (obtained by extraction)
    - Protein, lipids
      - Animal: casein, gelatin, collagen, whey
      - Plants: soya, gluten
    - PHA (polyhydroxyalkanoates)
  - From biotechnology (through chemical synthesis from bio-derived monomers)
    - PHB (Polyhydroxybutyrate)
    - PHBV (poly-3-hydroxybutyrate-co-3-hydroxyvalerate)
    - PLA Poly(lactic acid)
  - From petrochemical products (through chemical synthesis from synthetic monomers)
    - PCL poly(ε-caprolactone)
    - Aliphatic co-polyester (e.g. PBSA)
    - Aromatic co-polyesters (e.g. PBAT)
    - PEA poly(ester amide)
Some are naturally occurring polymeric materials like starches, proteins, cellulose, gums; some are produced by polymerizing organic molecules to form polymers, for example, polyurethanes by polyols obtained from vegetable oils, polylactic acid by lactide monomer from 100% renewable resources like corn, sugar, and other starch-rich products and others are manufactured from petrochemicals like poly(e-caprolactone)-PCL, and poly(vinyl alcohol)-PVA). Only three categories (Fig 1.1 a-c) are obtained from renewable resources:

a) polymers from biomass such as the agro-polymers from agro-resources (e.g., starch, cellulose);

b) polymers obtained by microbial production, e.g., the polyhydroxyalkanoates;

c) polymers conventionally and chemically whose monomers are synthesized from agro-resources, e.g., the poly(lactic acid);

d) polymers whose monomers are obtained by chemical synthesis.

When disposed of in compost, these are safely decomposed into CO$_2$, water, and humus through the activity of microorganisms. The CO$_2$ and water could become corn or sugar cane again through plant photosynthesis. Many consumer plastic products may be replaced by the natural biopolymer-based plastics, which may be used for disposal plastic bag, cup, plates, containers and utensils, and others functional plastic products such as pharmaceutical and medical devices. These biodegradable plastics can be treated like food waste, which also gets in the plastics stream, so whatever is used to handle or separate food waste will be effective for biodegradable plastics. By collecting and composting biodegradable plastic wastes, we can generate much-needed carbon-rich compost: humic materials. These valuable soil amendments can go back to the farmland and reinitiate the carbon cycle. Besides, composting is an increasingly key point to maintain the sustainability of the agricultural system by reducing the
consumption of chemical fertilizers. Therefore, biodegradable materials offer a possible alternative to the traditional non biodegradable polymers, especially in short life-time application and when their recycling is difficult and/or not economical. Thus, there is a considerable interest in replacing some or all of the synthetic plastics by biodegradable materials in many applications.

1.1.2 Biodegradable plastics’ drawbacks: Problem statement

As it was mentioned above, by using biomass as feedstock to produce renewable plastics we reduce our dependence on fossil fuels and materials. In addition, these biobased polymers often display enhanced biodegradability and biocompatibility, benefitting diverse applications ranging from packaging to medical devices. The processing parameters and properties of finished products of these different materials vary widely (Sorrentino et al. 2007), however, several commonly occurring factors limiting their industrial application have been reported (Zhao et al. 2008). First, in some instances mechanical properties of biobased polymers are relatively poor compared to many petroleum-based plastics due to the inherent lower stiffness and strength. Second, many are relatively sensitive to water, with some materials dissolving rapidly, which cause substantial decrease in mechanical when these plastics absorb water, especially in humid environments (Debeaufort et al. 1998). Finally, the present limited production and high cost of biobased degradable polymers restrict them from wide range of applications (Rhim et al. 2008). Therefore, in order to reduce the quantity of plastic waste, there is an urgent need to develop biodegradable plastics made from renewable resources with properties comparable to commonly used petroleum-based plastics. Thus, the most important factors to the formation of renewable plastics-based industries include cost reduction of biodegradable polymers, the improvement of mechanical strength and water resistance.
1.1.3 Bio-nanocomposites

An attractive option to tailor and improve properties of biobased plastics is to develop nanocomposite materials where both matrix and nanofiller are of biological origin. These materials are called bio-nanocomposites. Bio-nanocomposites are significant due to their nanoscale constituents with size less than 1,000 nm. They show great promise for potential applications as high-performance biodegradable materials, which are entirely new types of materials based on plant, animal, and other natural materials.

In order for renewable polymer-based bionanocomposites to meet a wide range of applications, bio-nanocomposite formulation must be further researched and modified so that mechanical and other properties can be easily manipulated, depending on the end-users’ requirements. In all, bio-based polymer nanocomposites pave the way to a much broader range of applications and open a new dimension for plastics and composites in the future (Zhao et al. 2008).

1.2 Poly(3-hydroxybutyrateco-3-hydroxyvalerate) (PHBV)

Polyhydroxyalkanoates (PHAs), also known as bacterial polyesters, have shown a lot of promise as novel materials due to their renewability, biodegradability, and biocompatibility (Rhim et al. 2007). In comparison with petroleum-based plastics, PHAs need less energy for production, can reduce the green house gas emissions and generate less landfill waste (Xie et al. 2009). PHAs can replace petroleum-based amorphous and semicrystalline polymers currently in use for packaging, adhesives, and coating applications. Since PHAs are produced from renewable resources and biodegrade to carbon dioxide and water, they are often described as environmentally friendly plastics (Akiyama et al. 2003). PHAs also offer significant advantages in medical applications, particularly in tissue engineering (Asrar et al. 2003, Yasin et al. 1995,
Scherzer 1997). Recent studies have shown that poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHx) tissue scaffolds have better mechanical properties and biocompatibility than other biodegradable polymers, such as polylactic acid (PLA) (Suominen et al. 1997, Beach et al. 1996).

Poly(3-hydroxybutyrate) (PHB) and poly(3-hydroxybutyrateco-3-hydroxyvalerate) (PHBV) (Fig. 1.2) are the main representatives of the polyhydroxyalkanoates (PHAs) family. In the United States both polymers are produced commercially by Monsanto and sold as Biopol®. PHB is a highly crystalline and brittle polymer. It exhibits melting point and mechanical properties comparable to those of isotactic polypropylene (iPP) (Mulhaupt 1996, Marchessault et al. 1981). PHB-based copolymers are being developed to overcome the shortcomings of PHB. Its copolymer PHBV has a lower melting point and higher flexibility than poly-(3-hydroxybutyrate) (PHB) (Barham et al. 1984). The lower melting point of PHBV improves the melt stability and broadens the processing window of this polymer (Holmes 1998). The amount of hydroxyvalerate (HV) content in the PHBV copolymer strongly influences the properties of this polymer such as crystallinity, melting point, and crystallization rate (Billingham et al. 1977). The properties vary with the percentage of HV, the copolymers become less brittle with more HV. As the mol% of HV increase, the Young modulus (stiffness) decreases whereas the impact strength (toughness) increases. The copolymers had only slightly reduced percentage crystallinity, but lower melting points and similar thermal stability. Furthermore, PHBV showed even lower crystallization rates with PHB. In summary, the major drawbacks of PHBV are the development of interlamellar secondary crystallization on storage, reduced stiffness, slow crystallization rate, and high production cost (Kunioka et al. 1989, Biddlestone et al. 1996).
The usage of cellulose nanowhiskers (CNW) as reinforcement can solve major problems associated with limited areas of PHBV application. CNW can improve Young’s modulus maintaining toughness, enhance crystallization rate via induced heterogeneous nucleation and improve thermal stability of PHBV. It also can help in sustaining the biocompatibility and biodegradability of the polymer. The polar nature of the PHBV polymer is also expected to provide better dispersion and interfacial adhesion with polar cellulose nanowhiskers (to be discussed further). Finally, since CNW can be derived from variety of sources (e. g. various plants, sea animals, wood), PHBV/CNW composites fabrication can also utilize agricultural and forest products, reducing the cost of the final product.

1.3. Cellulose nanowhiskers (CNW)

1.3.1 Isolation and morphology of CNWs

Cellulose chains aggregate into the repeated crystalline structure to form microfibrils in the plant cell wall, which also aggregate into larger macroscopic fibers (Fig. 1.3). Due to this hierarchical structure, it is possible to generate cellulose nanowhiskers from plants.
Figure 1.3 Hierarchical structure of cellulose (www.genomicsgtl.energy.gov)

Since the discovery of superior improvements in the properties (mechanical, barrier, thermal, dielectrical, etc) of nanocomposites with cellulose nanowhiskers, substantial research has been directed to cellulose nanowhiskers composites because of the growing interest in fabricating materials from renewable resources. In the 1950s, Rånby reported for the first time a method to obtain colloidal suspensions of cellulose by sulfuric acid treatment of cellulose fibers (Rånby 1949).

Later, Marchessault et al. optimized the acid hydrolysis conditions (Marchessault et al. 1959). The main mechanism for the isolation of CNWs from cellulose fibers is that disordered or paracrystalline regions of cellulose are preferentially hydrolyzed, whereas crystalline regions that have a higher resistance to acid attack remain intact. Thus, following an acid treatment that hydrolyzes the cellulose, cellulose needle-like nanocrystals are produced. Specific hydrolysis and
separation protocols (controlled time, temperature) have been developed that depend on the origin of the cellulosic fibers. The sources of CNWs include cellulose fibers from cotton (Dong et al. 1998, Araki et al. 2000), ramie (Habibi et al. 2008a, Habibi and Dufresne 2008b, Habibi et al. 2007), hemp (Cao et al. 2008a), flax (Cao et al. 2008b, Cao et al. 2007), sisal (Garcia de Rodriguez et al. 2006, Siqueira et al. 2009), wheat straw (Helbert et al. 1996), palm (Bendahou et al. 2009), bleached softwood (Araki et al. 1999) and hardwood (Beck-Candanedo et al. 2005) pulps, cotton linters pulp (Roohani et al. 2008, Cao et al. 2009), microcrystalline cellulose (Bondeson et al. 2006, Pranger and Tannenbaum 2009, Capadona et al. 2009, Jiang et al. 2008, Ten et al. 2010, Ten et al. 2011a, Ten et al. 2011b, Ten et al. 2011c), sugar beet pulp (Azizi Samir et al. 2004), bacterial cellulose (Grunnert and Winter 2002, Araki and Kuga 2001, Hirai et al. 2009), and tunicates (Angles and Dufresne 2000, Angles and Dufresne 2001, de Souza Lima and Borsali 2002). Typically, CNWs from wood are 3-5 nm in width and 100-200 nm in length, while those for Valonia (a sea plant), are reported to be 20 nm in width and 1000-2000 nm in length. Similarly, cotton fibers give CNWs with 5-10 nm in width and 100-300 nm long, and tunicate (a sea animal) gives ca. 10-20 nm in width and 500-2000 nm long. The aspect ratio defined as the length/diameter (L/d) ratio varies between ca. 10 and 30 for cotton and ca. 70 for tunicate.

Due to CNWs’ high aspect ratio, nanoscale size and innate high crystallinity, their reinforcing capabilities are potentially suitable for composite materials. The value of the modulus of crystalline cellulose is quite large compared to other materials, especially if its comparatively lower density is taken into account (Table 1.1). Moreover, the specific modulus (modulus/density) of crystalline cellulose exceeds engineering materials such as steel, concrete, glass and aluminum. It is worth mentioning that cellulose has several obvious disadvantages
compared to traditional engineering materials, for example, moisture absorption and swelling, and enzymatic degradability.

**Table 1.1** Properties of engineering materials compared to crystalline cellulose (Eichhorn *et al.* 2010).

<table>
<thead>
<tr>
<th>Material</th>
<th>Modulus (GPa)</th>
<th>Density (Mg/m$^3$)</th>
<th>Specific modulus (GPa Mg$^{-1}$m$^3$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>69</td>
<td>2.7</td>
<td>26</td>
<td>(Ashby and Jones 1989)</td>
</tr>
<tr>
<td>Steel</td>
<td>200</td>
<td>7.8</td>
<td>26</td>
<td>(Ashby and Jones 1989)</td>
</tr>
<tr>
<td>Glass</td>
<td>69</td>
<td>2.5</td>
<td>28</td>
<td>(Ashby and Jones 1989)</td>
</tr>
<tr>
<td>Crystalline cellulose</td>
<td>138</td>
<td>1.5</td>
<td>92</td>
<td>(Meyer and Lotmar 1936)</td>
</tr>
</tbody>
</table>

1.4 **Research objectives**

The study of CNWs as a reinforcing phase in nanocomposites started over 15 years ago (Favier *et al.* 1995). Favier *et al.* reported the reinforcing effect of CNWs extracted from tunicate for reinforcing poly(styrene-co-butyl acrylate) (poly(Sco-BuA)). They demonstrated a spectacular improvement in the storage modulus, as measured by dynamic mechanical analysis, above the glass transition temperature range of the polymer even at low loading of CNW (6 wt%).

Moreover, it was suggested by Favier *et al.* (Favier *et al.* 1995) that percolation network introduced by hydrogen bonding between neighboring whiskers governs the reinforcing effect of CNWs. The presence of such a network was later confirmed by electrical measurements performed on nanocomposites containing CNW that were coated with conductive polypyrrole (Flandin *et al.* 2000).
Even though there are many research groups studying the properties of CNW reinforced composites, to our knowledge, no information is available in the literature about poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV)/CNW composites. In order to justify CNW isolation process and their nanoreinforcement abilities, one needs to access the effect of CNW on various properties (mechanical, dynamic mechanical, thermal, dielectric, rheological) of PHBV along with microstructure of PHBV/CNW composites. Due to nanoscale dimensions, the addition of nanowhiskers complicates the mechanisms for understanding stress transfer in the composite. Therefore, it is still little known on the mechanisms for improved mechanical properties when CNWs are used as nano-reinforcements. First of all, CNW may alter the nucleation of PHBV crystals, its crystalline morphology and overall crystallization kinetic of the nanocomposites. Moreover, CNW dispersion, size and orientation impact the percolation network and consequently, bulk mechanical properties of PHBV/CNW composites. Thus, this study will investigate into each of the parameters and mechanisms that govern the mechanical performance of the composite. Furthermore, for fundamental understanding of cellulosic nanocomposites, establishing structure-property relation and developing robust models to predict mechanical properties of the nanocomposites will be an important piece in comprehension of CNW reinforcing effect.

The goal of this research is to determine how the addition of cellulose nanowhiskers impacts the morphology and properties of PHBV. This specifically entails understanding of how aspect ratio, dispersion and orientation of CNW influence performance properties of nanocomposites.

Therefore, the specific objectives of this research are:

1. Develop technique for manufacturing nanocomposite films and evaluate the influence of cellulose nanowhiskers on properties of PHBV;
2. Determine mechanical percolation threshold for the nanocomposites;

3. Evaluate effect of cellulose nanowhiskers on crystallization kinetics of PHBV;

4. Develop manufacturing methods for producing oriented nanocellulose composites;

5. Assess the influence of CNW aspect ratio and orientation on the mechanical performance of nanocomposites;

6. Analytically evaluate the anisotropic properties of PHBV/cellulose nanowhiskers composites using micromechanics theory.

1.4.1 Intellectual Merit

The study will develop insightful understanding and establish the knowledge base of reinforcing mechanism of CNW in PHBV. It will focus on effect of CNW on properties of PHBV, mechanical modeling as well as its experimental verification. Based on the differences between observed and predicted behaviors, this project will provide a motivation for development and extension into optimizing matrix/fiber and fiber/fiber interactions. The proposed work will provide new insights into modeling mechanical properties of both randomly dispersed and aligned CNW composites. Additionally, proposed model can easily be modified to determine elastic modulus of composites reinforced with other nanofillers or nanowires such as carbon nanotubes and nanofibers.

1.4.2 Broader Impact

The outcome of the research will provide relevant information for the feasibility and development of randomly oriented and unidirectional reinforced nanocomposites with biocompatible and environmentally benign nature. Moreover, the result will help to design and manufacture nanocomposites from agro- and forest resources improving sustainable development of biomass. This can help meet state goals to reduce petroleum dependency,
improve environmental quality and provide economic development advancing management of residues and wastes.

1.5 Dissertation scope and Organization

Polymer/CNW nanocomposites have been made from a variety of degradable and non-degradable polymers. Cellulose nanowhiskers are unique in the fact that nanocomposites based on these nanoparticles can demonstrate unsurpassed physical and chemical properties. They have been the subject of a wide array of research efforts as reinforcing agents due to their inherent renewability, biodegradability, low cost, abundance and biocompatibility.

Despite the large research effort devoted to cellulosic nanocomposites and their properties, little information is available in the literature as how to tailor mechanical performance of nanocomposites. The aim of this dissertation is to understand what parameters of materials constituents affect the percolated structure. This specifically entails understanding how the morphology, content and orientation of CNW influence the reinforcing mechanism and thus, performance of nanocomposites. Chapter 2 describes the experimental techniques used to produce PHBV/CNW nanocomposites and the effect of CNW on the morphology and properties of nanocomposites.

Chapter 3 deals with the modified fabrication method used to prepare nanocomposites to improve CNW dispersion. Mechanical, rheological, dielectric, thermal and dynamic mechanical properties near mechanical percolation threshold will be also discussed here. Chapter 4 highlights the role of CNW in crystallization kinetics of semicrystalline PHBV. It shows some of the results observed in spherulitic growth and crystallization rates when changing the concentration of CNW in PHBV. Chapter 5 is devoted to the development and characterization of oriented PHBV/CNW composites. Specifically, comparisons are drawn between
nanocomposites tested at different orientation angles and CNW concentrations. Chapter 6
focuses on understanding the relationship between CNW aspect ratio, orientation angle and
mechanical properties of the nanocomposites. Attempts are made to ascertain the origin of
superior reinforcing efficiency observed in PHBV/CNW nanocomposites, and the like, as
compared to conventional composites using composite and excluded volume theories.
Conclusions and recommendations for future work are presented in Chapter 7. Lastly, Appendix
A describes, in detail, the TEM image analysis procedure used to quantify the length and
diameter of individual nanowhisker, orientation angle and angle between adjacent whiskers.

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Chapter 2 Thermal and Mechanical Properties of Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)/cellulose nanowhiskers Composites

Abstract

Bacterial polyester poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) was reinforced with cellulose nanowhiskers (CNW) in 1-5 wt% concentrations using a solvent casting method. The CNW was prepared from microcrystalline cellulose (MCC) using sulfuric acid hydrolysis. The influence of CNW on the PHBV crystallization, thermal, dynamic mechanical and mechanical properties were evaluated using polarized optical microscope (POM), differential scanning calorimeter (DSC), dynamic mechanical analysis (DMA), tensile and bulge tests, respectively. POM test results demonstrated that CNW was an effective PHBV nucleation agent. Tensile strength, Young’s modulus and toughness of PHBV increased with the increasing concentration of CNW. DMA results showed an increased tanδ peak temperature and broadened transition peak, indicating restrained PHBV molecular mobility in the vicinity of the CNW surface. Storage modulus of the PHBV also increased with the addition of CNW, especially at the temperatures higher than the PHBV glass transition temperature. These results indicated that the CNW could substantially increase the mechanical properties of PHBV and this increase could be attributed to the strong interactions between these two phases.
2.1 Introduction

Due to the growing environmental awareness and concerns over reliable availability of petrochemicals in the future, the polymer industry and academia have been pressed to design and produce polymers and composites based on renewable natural resources. In the past decades, several biodegradable polymers such as polylactic acid (PLA) and polyhydroxyalkanoates (PHAs) have been developed from renewable substances. Poly(3-hydroxybuterate) (P3HB) is a representative polymer from PHA family, which includes a series of aliphatic polyesters produced by bacteria as carbon and energy storage through natural biosynthesis (Ballard et al. 1987). PHAs have received a great deal of research interests because their mechanical performance is similar to petroleum-based polymers such as polypropylene (Pirrotta 1993). However, P3HB differs in several unsatisfactory manners such as increased brittleness (Bauer and Owen 1988) and low thermal stability (Gatenholm et al. 1992). The toughness of P3HB is significantly improved by forming the copolymer of hydroxybuterate and hydroxyvalerate (HV) – PHBV, which exhibits lower crystallinity due to the incorporation of HV (Mitomo et al. 1987). Finally, increase in HV content decreases the melting point of PHBV thereby lowering processing temperature and the potential of thermal degradation (Avella et al. 2000).

Reinforcing fibers of various sizes and forms, e.g., natural plant fiber (cellulose fiber), glass fiber, carbon fiber, carbon nanotubes, etc., have been effectively used in polymer composites as reinforcing agents. Nanofillers, however, are found to be preferential in many applications due to their high surface area, lower concentrations needed to achieve reinforcing effect, and the ability to improve toughness along with strength and stiffness. Cellulose nano-whiskers (CNW) is a biologically derived nano-fiber reinforcement for polymer materials. CNW are needle-like elementary crystallites which occur naturally in the cell walls of many plants and some animals...
(e.g. tunicin). CNW exhibit a typical length and diameter of 200-400 nm and <10 nm, respectively (Bondeson et al. 2006). CNW has a high surface area and high Young's modulus (ca. 143 GPa) (Sturcova et al. 2005), which makes it a suitable candidate for polymer reinforcement.

CNW have been used to reinforce both non-biodegradable and biodegradable polymers. Examples of the nonbiodegradable polymers include poly(oxyethylene) (Azizi Samir et al. 2004), poly(vinyl chloride) (Chazeau et al. 1999), polyvinyl acetate (PVA) (de Rodriguez et al. 2006), polypropylene (Ljungberg et al. 2005, Ljungberg et al. 2006), poly(styrene-co-butyl acrylate) latex (Helbert et al. 1996, Hajji et al. 1996) and waterborne epoxy (Ruiz et al. 2000, Ruiz et al. 2001). In general, the resulting composites exhibit improved mechanical properties with the addition of CNW. Surface modification of CNW is found to play an important role in the properties of the CNW reinforced composites (Ljungberg et al. 2005, Ljungberg et al. 2006). Moreover, the processing methods of the composites, e.g., solution blending vs. melt blending, is also shown to have a strong effect on the properties of the final products (Azizi Samir et al. 2004, Hajji et al. 1996).

The biodegradable polymers used as the matrix for CNW reinforcement included polycaprolactone-based waterborne polyurethane (Cao et al. 2007), polycaprolactone (PCL) (Siqueira et al. 2009), poly(hydroxyalkanoates) (PHA) (Dufresne et al. 1999), starch (Angle`s and Dufresne 2001, Mathew and Dufresne 2002, Kvien et al. 2007, Chen et al. 2009), cellulose (Qi et al. 2009), soy protein isolate (SPI) (Wang et al. 2006), poly(lactic acid) (Mathew et al. 2005, Oksman et al. 2006, Bondeson et al. 2007), cellulose acetate butyrate (CAB) (Petersson et al. 2009, Grunert and Winter 2002, Petersson and Oksman 2005), and poly(ethylene glycol) (Goetz et al. 2009). In these studies, CNW was shown to have varying degree of reinforcing
effect on the different polymer matrixes.

Most recently Braun et al. reported a single-step isolation and surface functionalization method for CNW (Braun and Dorgan 2009). Fischer esterification of hydroxyl groups and the hydrolysis of amorphous cellulose chains occurred simultaneously during the isolation process. FTIR results revealed that about half of the surface hydroxyl groups were esterified using this procedure. Using solvent exchange sol-gel process, Capadona et al. prepared the nanocomposites containing ethylene oxide/epichlorohydrin copolymer and nanowhisker through a template approach (Capadona et al. 2009). These composites exhibited significantly higher shear storage modulus than did the composites produced by solvent casting. For example, at 25 vol% CNW concentration the shear modulus was 18 and 39 MPa for solution-cast and template-made composites, respectively. Moreover, the properties of the template-made nanocomposites followed the prediction of percolation model. Rusli and Eichhorn (Rusli and Eichhorn 2008) were able to determine stiffness and deformation of epoxy/CNW nanocomposites under tension and compression stresses using Raman spectroscopy. By measuring molecular deformation corresponding to a shift in the carbonyl (C-O) stretch of cellulose backbone, it was possible to evaluate stress transfer from the compliant matrix to the reinforcing cellulose whiskers.

The effects of CNW on the properties of PHBV were first reported by us in an article where the PHBV/CNW nanocomposites prepared by solution casting and melt blending were compared (Jiang et al. 2008a). No other studies have been reported on this composite system. In this paper, we further elucidate the morphology, crystallization behavior and mechanical properties of the system in an attempt to develop a more complete understanding of this bio-composite system. Therefore, the objectives for our study were to fabricate PHBV/CNW composites by solution casting method and evaluate their thermal, mechanical and dynamic mechanical properties.
2.2 Experimental Section

2.2.1 Materials

PHBV containing 12 mol-% hydroxyvalerate (HV) monomer was supplied by Metabolix Inc, (Cambridge, MA). Organic solvent N, N-dimethylformamide (DMF) was obtained from Acros Organics (Atlanta, GA). Microcrystalline cellulose (MCC) was provided by Avicel (Type PH-102) and was the raw material for producing the CNW. Sulfuric acid (96% concentration) and polyethylene glycol (PEG) with average molecular weight $M_w$ of 20,000 were purchased from J.T. Baker. Boron nitride was used as a nucleating agent and obtained from Saint-Gobain Ceramics (Louisville, KY).

2.2.2 CNW preparation

Acid hydrolysis of MCC was performed in 64 wt% sulfuric acid at 44 °C with strong mechanical stirring for 2 hours. The produced suspension was diluted 10 times with deionized water and kept in a refrigerator to prevent further reaction. The acid was removed by repeated centrifuge (Sorvall) at 5000 rpm for 5-min for each run until the supernatant was turbid. The supernatant was collected and dialyzed (dialysis tube from Spectrum Laboratories Inc., molecular weight cutoff 12000-14000) against deionized water for 4-5 days to remove remaining acid. The dialysis tube was then placed in aqueous PEG solution to concentrate the CNW suspension through osmotic pressure. The CNW suspension was gel-like after the concentration process and it was finally freeze-dried (Labconco FreeZone 4.5) into CNW powder.

2.2.3 PHBV/CNW nanocomposites preparation

5 wt% PHBV was dissolved in DMF at 80 °C. CNW powder at the concentrations of 1-5 wt% of solid PHBV was added into the PHBV solution and sonicated in an ultrasonic bath (Branson 1510) for 1 hour. Following the sonication, the solution was immediately casted onto a
clean glass substrate and evaporated overnight at 50 °C. The molecular weight $M_w$ determined by GPC (GPC Max VE2001, Viscotek) showed that the reduction of $M_w$ due to sonication was ca. 17%. The thickness of the cast films was measured to be 15-30 microns. All the films appeared transparent. To ensure constant moisture and residual solvent contents, all films were conditioned in a desiccator containing calcium sulfate (Drierite) at room temperature for at least 2 weeks prior to any test. Residual solvent content was determined to be less than 2 wt% after the two-week equilibrium by using a vacuum oven drying method.

2.2.4 Characterization

2.2.4.1 Transmission Electron Microscopy (TEM)

The shape and size of CNW were studied by a TEM (JEOL 1200 EX) operating at 100kV. A drop of CNW water solution was introduced on a formvar and carbon-coated copper grid and the water was evaporated naturally. TEM images of CNW were acquired without any sample staining. To study the morphology of the composite film, a small piece of PHBV/5%CNW film was embedded in acrylic resin (London Resin Company Ltd.) and cured at elevated temperature overnight. Thin sections were cut from the resin with a diamond knife on a Reichert-Jung ultramicrotome. The sections were placed on carbon coated copper grids and then stained with 2% uranyl acetate for 30 minutes.

2.2.4.2 Atomic Force Microscopy (AFM)

Surface morphology of PHBV/CNW nanocomposite film was investigated by an AFM. The tests were conducted in tapping mode using a Veeco Multimode AFM equipped with a NanoScope IIIa controller (Digital Instruments Inc.). Film surfaces were scanned in air using Si tips (Digital Instruments Inc.) with a resonance frequency of ca. 330 kHz. The scan rate was 0.5 Hz. CNW suspension in water was also used for AFM study to have a better view of CNW. To
do this, a drop of each suspension was deposited on freshly cleaved mica surfaces. The solution was completely dried by evaporation at ambient condition before being scanned by AFM.

2.2.4.3 Thermogravimetric analysis (TGA)

TGA was conducted on a Mettler-Toledo TGA/SDTA851e to determine the thermal stability of the prepared samples. Based on the weight loss of each sample component, a sample composition was estimated for CNW powder and PHBV/CNW films. Approximately 5-10 mg of material was placed in an aluminum pan. After equilibrating at 25 ºC for 5 minutes, the sample was heated to 600 ºC at 10ºC/minute under 20 ml/min N₂ flow. Three replicates were tested for each sample.

2.2.4.4 Polarized Optical Microscopy (POM)

Crystallization process of PHBV and PHBV/CNW nanocomposites was studied by Olympus BX51 POM equipped with a Linkam hot stage (THMS600/HFS91). PHBV/CNW films were heated up to 220 ºC between two glass slides and then equilibrated at this temperature for 10-min to eliminate any residual PHBV crystallization seeds (Di Lorenzo et al. 2009). The films were then quenched in liquid nitrogen to obtain complete amorphous samples. PHBV nucleation and spherulites growth at 30 ºC was examined by the POM and recorded by an attached digital camera after 5 and 20 minutes of PHBV crystallization.

2.2.4.5 Differential Scanning Calorimetry (DSC)

Thermal transitions of the nanocomposites were examined by a Mettler Toledo DSC 822e under N₂ flow (80ml/min) and liquid nitrogen controlled cooling. Samples were crimple-sealed in aluminum crucibles and heated from -50 to 200 ºC at a heating rate of 10 ºC/min (first heating scan), equilibrated at 200 ºC for 2 min, cooled rapidly at 30 ºC/min to -50 ºC, equilibrated at -50 ºC for 2 min, and heated up again to 200 ºC at 10 ºC/min (second heating scan). The first and
second heating scans examined the thermal behaviors of the samples with and without previous thermal history, respectively.

2.2.4.6 Dynamic Mechanical Analysis (DMA)

DMA was conducted in tension mode on a Tritec 2000 DMA at 1 Hz to examine thermal dynamic properties of the films. DMA samples (10 x 6.5 mm$^2$) were cut from the cast PHBV/CNW composite film. Dynamic strain sweep was first performed to determine linear viscoelastic range of the samples. Then the samples were tested from -40 °C to +80 °C at 5 °C/min with a displacement of 0.001 mm. Five replicates were tested for each sample.

2.2.4.7 Tensile test

Dumbbell-shaped film specimens were prepared with a Type IV (ASTM D638) sample cutter and tested according to ASTM D 638–91. Ten samples for each formulation were tested using an Instron 4466 (capacity 500N) at a tensile rate of 5 mm/min. Tensile strain were monitored by an EIR laser extensometer (model LE-05).

2.2.4.8 Bulge test

The bulge test is a standard technique to characterize mechanical properties of thin films, such as residual stresses and elastic modulus. In bulge testing the composite films were wax-mounted onto an aluminum substrate with a pre-drilled hole (Fig. 2.1a). A varying gas pressure was applied to the film through the hole using a Meriam pressure/vacuum variator and the resulting film deflection was monitored with a scanning laser vibrometer (Polytec OFV500). The pressure and deflection values were acquired using LabView software. Five replicates were tested for each specimen. By fitting the curve of pressure versus deflection to a cubic polynomial, Young’s modulus of the film could be calculated from the slope of the polynomial using the model of circular membrane behavior under uniform pressure (Small and Nix 1992):
\[ P = \frac{8Et}{3a^4} h^3 + \frac{4t\sigma}{a^2} h; \]  

(2.1)

where \( P \) is gas pressure, \( E \) is sample modulus, \( t \) is sample thickness, \( a \) is bulge radius (4.7625 mm), \( h \) is the deflection and \( \sigma \) is the residual stress in the film determined by \( \frac{Pa^2}{4ht} \). Fig. 1b presented a typical set of pressure vs. deflection data of a PHBV/CNW film and its cubic polynomial fitting. The outstanding fitting demonstrated that the film followed the circular membrane behavior depicted by the model.

**Figure 2.1** (a) Schematic representation of the bulge test set up; (b) a typical pressure vs. deflection curve of the nanocomposite films obtained from bulge test.
2.3 Results and Discussions

2.3.1 Morphology of CNW and the composite film

The morphology and dispersion of CNW in water was observed using TEM (Fig. 2.2). Although the whiskers agglomerated on the copper grid after water evaporation, individual whiskers can still be clearly distinguished. The diameter of the whiskers was estimated to be 20 nm. The length of the whisker was difficult to determine due to the whisker agglomeration. However, the AFM images of CNW showed that the whiskers had a wide distribution in fiber length, ranging from 50 nm to 500 nm (Fig. 2.3). The diameters of CNW obtained from both TEM and AFM were similar. It has been reported that CNW diameter is often overestimated from AFM images due to the tip broadening effect (Kvien et al. 2005). This effect occurs when the size of the scanning tip is comparable to that of the sample and it enlarges the lateral sizes of the sample artificially due to the cone shape of the tip. In this study, AFM height profiles (which were free of this artifact) rather than AFM images were used to determine the CNW diameter (Fig. 2.3c). Therefore the diameter values obtained from both TEM and AFM were similar.

TEM micrographs of the PHBV/CNW composite demonstrated a homogenous dispersion of CNW in the PHBV matrix (Fig. 2.4). AFM examination confirmed this dispersion state (Fig. 2.5).
Figure 2.2 TEM micrograph of CNW. The sample was obtained by evaporating CNW water solution (ca. $2.7 \times 10^{-6}$ wt%) on a formvar-coated copper grid.
Figure 2.3 AFM images of CNW. The sample was obtained by evaporating CNW water solution (ca. $2.7 \times 10^6$ wt%) on a freshly cleaved mica surface. (a) topography, (b) phase image, (c) height profile of the selected line in figure (a).

Figure 2.4 TEM images of the PHBV/5% CNW nanocomposite film at 75k magnification.
2.3.2 Thermal and mechanical characterization

Thermal degradation of the neat PHBV, CNW powder, and the PHBV/CNW composite were studied by TGA (Fig. 2.6). It was found that the CNW powder decomposed through a two stage weight loss process, with the first weight loss peak occurring at ca. 307 °C and the second one at ca. 410 °C. Comparing the trace of CNW powder to that of the neat PEG, the first and the second stage could therefore be attributed to the decomposition of CNW and PEG, respectively. The occurrence of PEG in the CNW powder is likely to have resulted from the penetration of the low molecular weight PEG during dialysis. During CNW powder preparation, PEG solution was used to concentrate CNW solution through osmosis. Although the dialysis tube had a molecular weight cutoff of 12,000-14,000 and the PEG used had a weight average molecular weight (M_w) of 20,000, it was obvious that some low molecular weight PEG still penetrated the tube and mixed with CNW. Based on the weight losses of the two stages, the contents of CNW and PEG
in the CNW powder were calculated to be ca. 61 and 30 wt%, respectively. The remaining ca. 9 wt% residual could be salts and other inorganic compounds produced from the acid hydrolysis reaction. It is worth noting that the hydroxyl groups of PEG can hydrogen bond with the hydroxyl groups of CNW. PEG was also miscible with PHBV in molten and solution states (Avella and Martuscelli 1988). Therefore, the PEG in the CNW powder was expected to increase the compatibility between CNW and the PHBV matrix in the composite film.

![TGA traces](image)

**Figure 2.6** TGA traces of the neat PHBV, neat PEG, CNW powder (dialyzed and non-dialyzed), and the PHBV/CNW composite. The inset shows the first derivative of the weight loss.

Comparing the TGA curves of the neat PHBV and the PHBV/5% CNW composite, the addition of CNW was found to slightly reduce the decomposition (maximum weight loss rate) temperature (from ca. 295 to 290 °C) of the polymer matrix. This phenomenon has been reported
in other cellulose nanocrystal reinforced composites (Lu and Hsieh 2009). The reason was believed to be due to the increased thermal conductivity of the sample after the addition of CNW (Shimazaki et al. 2007).

To evaluate the effects of CNW on the thermal behavior of the composites, DSC traces of the PHBV/CNW composites and the neat PHBV were compared (Fig. 2.7a,b). The second heating scan often reveals more thermal transitions in the material than the first heating scan since most of the thermal and stress histories, which usually cover/weaken thermal transition signals, are erased during the first heating scan. In Fig. 2.7a (second heating scan), the glass transition, cold crystallization, and melting of PHBV can be clearly seen. The glass transition temperature ($T_g$) of PHBV was not noticeably affected by the addition of various contents of CNW powder. Similar results had been reported in several other studies (Azizi Samir et al. 2004, Hajji et al. 1996, Favier et al. 1995, Angle`s and Dufresne 2000). However, the cold crystallization temperature ($T_{cc}$) progressively decreased with the addition of CNW. This behavior resulted because the CNW is an effective PHBV nucleation agent, which reduced the energy barrier to form PHBV nuclei. Higher contents of CNW induced bigger $T_{cc}$ drop due to larger nucleus-promoting surface provided by CNW. Neat PHBV and all the composites exhibited two melting peaks ($T_{m1}$ and $T_{m2}$), demonstrating a melting-recrystallization-melting process. PHBV crystals with low perfection/low lamella thickness melted at low temperature and subsequently recrystallize to higher perfection, which eventually melted at high temperature.
Figure 2.7 DSC thermograms of neat PHBV and PHBV/CNW nanocomposites from the second (a) and first (b) heating scans. 1, neat PHBV; 2, PHBV+1%CNW, 3, PHBV+2%CNW, 4, PHBV+3%CNW, 5, PHBV+4%CNW, 6, PHBV+5%CNW.

In the first heating scan no glass transition and cold crystallization could be observed (Fig. 2.7b) because all the samples were fully crystallized from the long casting process at 50 °C, which is close to PHBV’s cold crystallization temperature. Furthermore, \( T_{m1} \) and \( T_{m2} \) of all the samples measured from the first heating scan were remarkably higher than those measured from the second heating scan. \( T_{m1} \) difference between the first and the second scan was ca. 10°C and the difference for \( T_{m2} \) was ca. 7 °C. This indicated that the casting process facilitated PHBV spherulite growth and led to larger lamellar thickness of the spherulites, which consequently exhibited increased melting points. It should be pointed out that no melting of PEG (ca. 66 °C)
was detected in both scans. This result might be due to its small concentration (maximum < 2 wt%) in the composites and its miscibility with PHBV.

The nucleation effect of CNW on PHBV was also investigated by direct POM observation. PHBV spherulites with characteristic banding and Maltese cross could be clearly seen under POM (Fig. 2.8b). Without CNW powder, the number of PHBV spherulites was small and their size was relatively big because the spherulites had large space to grow before impinging on each other (Fig. 2.8a,b). With the addition of CNW powder, the number of PHBV spherulites increased significantly and consequently their size was dramatically reduced (see Fig. 2.8a, c, e for 5 minute crystallization and Fig. 2.8b, d, f for 20 minute crystallization). Interpretation of the POM results given clearly suggested the strong nucleation effect of CNW, which was in agreement with DSC findings. Since the CNW powder contained approximately 30 wt% PEG, its influence on PHBV crystallization was also examined by POM. Fig. 2.8g and h showed that 2 wt% PEG might slightly promote the crystallization of PHBV because more spherulites are evident in the micrographs compared to the neat PHBV. This might be due to the increased mobility of PHBV molecules in the presence of miscible PEG (You et al. 2003). However, it was quite evident that the density of the spherulites with PEG was significantly lower than that with CNW, indicating CNW exhibited much stronger nucleation effect than did PEG. This also suggested that the decrease in T_{cc} observed in DSC tests was mostly caused by the nucleation effect of CNW rather than PEG. Moreover, the nucleation effect of CNW was also compared to that of boron nitride (BN), a commonly used nucleation agent for various polymers. As shown in Fig. 2.8i and j, PHBV spherulites were nucleated on the BN surface and grew around BN particles (bright spots).
Figure 2.8 POM micrographs of isothermal crystallization of neat PHBV and PHBV composites at 30 °C. (a) and (b) Neat PHBV, (c) and (d) PHBV/1 wt% CNW (e) and (f), PHBV/5 wt% CNW, (g) and (h), PHBV/2 wt% PEG, (i) and (j) PHBV/1 wt% boron nitride. Crystallization time: a,c,e,g,i – 5 min; b,d,f,h,j – 20 min. Scale bar represents 20 μm.

Comparing Fig. 2.8c and d to i and j, it was obvious that CNW induced significantly higher density of PHBV spherulites, indicating that CNW showed stronger nucleation effect compared to the commonly used boron nitride.
2.3.3 Mechanical properties

Mechanical properties of the film samples were examined by both tensile and bulge tests. Young’s moduli determined by these two different methods agreed reasonably well (Fig. 2.9). Indeed, Edwards et al. has shown that tensile and bulge test results complement each other, as bulge test being a perfect tool to measure residual stresses while tensile test for the characterization of linear and nonlinear behavior (Edwards et al. 2004). Compared to neat PHBV, the moduli of the nanocomposite with 5% CNW powder were increased by 77% (tensile test) and 91% (bulge test), respectively. This modulus increase could be attributed to the restrained chain movement during the deformation due to the existence of CNW. In addition, the refined crystalline structure of the PHBV after the addition of CNW could also influence the modulus of the composites (Supaphol et al. 2004, Wang and Qiang 2008, Li and Huneault 2007, Tu et al. 2006). However, the effect varied depending on different polymer systems. Jiang et al. showed that boron nitride refined the crystalline structure of PHBV and decreased the modulus of the PHBV (Jiang et al. 2008). The tensile strength of the PHBV/CNW composites also increased with the CNW content, indicating strong interfacial bonding between nanoparticles and polymer (Fig. 2.9). The tensile strength of PHBV/5%CNW was enhanced by 35.5% compared to that of the neat PHBV. Moreover, the tensile toughness, defined as the area below the stress-strain curves (Fig. 2.10), was also shown to follow the same ascending trend. Toughness increased up to 41% for nanocomposite with the 5 wt% of CNW powder (Fig. 2.11).
Figure 2.9 Young’s modulus and tensile strength of neat PHBV and PHBV/CNW nanocomposites determined by tensile and bulge tests.
Figure 2.10 Stress – strain curves of neat PHBV and PHBV/CNW nanocomposites.
Figure 2.11 Tensile toughness of PHBV/CNW nanocomposite with various CNW contents.

The effects of CNW on the dynamic mechanical properties of the nanocomposites were examined by DMA. Tanδ of the samples was shown in Fig. 2.12 (curves are shifted along y-axis) and it demonstrated α-relaxations of the samples. Tanδ peak (α-relaxation) was shifted to higher temperatures with the increasing content of CNW powder from 23.8 (neat) to 25.1 (1 wt% CNW) and 35.2 °C (5 wt% CNW powder loadings). Moreover, the breadth of the peaks was increased and the intensity of the peaks (damping) was reduced at high CNW contents. Since at temperatures above the Tg, PHBV chains in the amorphous areas of the samples were allowed for long-range cooperative motion, higher transition temperatures indicate that increased energy is required for the chains to perform the motion. This change in energy requirement is likely due to the restraint of CNW and the PHBV spherulites, whose size decreased significantly after the addition of CNW. Peak broadening and reduced damping implied a heterogeneous state of the polymer chains, with the ones in the vicinity of CNW being more restrained and the ones further
away being less restrained (or not restrained at all).

Fig. 2.13 showed that storage modulus of the samples increased with the content of CNW powder. The increase was more significant at the temperatures above the $\alpha$-relaxation temperatures of the samples. This was because above the transition temperature the modulus of the sample significantly decreased due to the cooperative chain motion. CNW, through its interaction with the chains, restrained the motion of the polymer and therefore to large degree recovered the modulus.

**Figure 2.12** Tan $\delta$ peaks for neat PHBV and PHBV/CNW nanocomposites determined by DMA.
Dependence of the storage modulus on temperature for neat PHBV and PHBV/CNW nanocomposites.

2.4 Conclusions

PHBV/CNW nanocomposites were fabricated by solution casting technique. Morphological study using TEM and AFM revealed good dispersion of CNW in the composites. TGA results demonstrated that the CNW powder contained approximately 30% PEG as a compatibilizer for CNW and the PHBV matrix. Nucleation effect of CNW was confirmed by both DSC and POM. Mechanical properties of the cast films were examined by both tensile and bulge tests and the results from the two tests were in reasonable agreement. With 5 wt% of CNW, the film showed 77% (by tensile test) and 91% (by bulge test) improvement in Young’s modulus, and 35.5% increase in tensile strength. DMA test results demonstrated a 41% increase in storage modulus (at room temperature) and a shift of Tanδ peak to higher temperatures due to CNW’s restraint on
molecular mobility. Mechanical and dynamic mechanical results indicated that CNW was an effective reinforcing agent for PHBV.

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Chapter 3 Effects of cellulose nanowhiskers on mechanical, dielectric and rheological properties of Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV)/cellulose nanowhiskers (CNW) composites

Abstract

The thermal, mechanical, dielectric, and dynamic mechanical properties of polymer nanocomposites strongly depend on nanoparticles’ content and aspect ratio. In this study, PHBV/CNW composite films with various CNW concentrations (0 - 4.6 wt%) were prepared by solution casting. Bulge, tensile, and dynamic mechanical tests showed that mechanical properties of the films increased with increasing CNW content until the content reached 2.3 wt%. Real permittivity of the composites also peaked at 2.3 wt% CNW over a wide spectrum of frequencies (0.01 - 10^6 Hz). These property transitions occurring at 2.3% CNW content was due to the transition of CNW dispersion from homogeneous dispersion to agglomeration. Rheological results of the composites, however, indicated a transition point lower than 2.3%. This was attributed to the existence of a polymer-CNW network in the composite melt, which required no physical touching or geometrical overlapping between CNWs.
3.1 Introduction

Over the last few decades, interest in developing lignocellulosic fiber reinforced composites has grown enormously. Due to their abundance, high specific moduli (modulus over density), stiffness of about 100-143 GPa (Sakurada et al. 1962, Matsuo et al. 1990, Stucova et al. 2005) and high aspect ratio, cellulose nanowhiskers (CNW) are found to be a good reinforcement agent for a wide variety of polymeric matrices. CNW are rod-shaped highly crystalline fibrils that naturally occur in many plants (e.g. wood, hemp, sugar beet, sisal, cotton, and ramie), bacteria, and sea animals (e.g. tunicin).

The most common method to harvest CNW from natural fibers is sulfuric acid hydrolysis followed by centrifugation. The mechanism to isolate CNW is to destroy and remove non-crystalline regions which are present between nanowhiskers through chemical reactions. Hydrolysis conditions such as temperature and time influence the size (Bondeson et al. 2006) and stiffness (Rusli and Eichhorn 2008) of the resulting CNW. The sulfuric acid treatment introduces sulfate groups to the surface of CNW. The negative charges on the CNW surfaces lead to high stability of aqueous CNW suspension (Bondeson et al. 2006). Therefore, water-soluble polymers are readily used to prepare CNW-polymer nanocomposites. For example, polyvinyl alcohol PVOH (Kvien and Oksman 2007; Roohani et al. 2008; Paralikar et al. 2008; Wang et al. 2010), poly(methyl vinyl ether-co-maleic acid) (PMVEMA) with poly(ethylene glycol) (PEG) (Goetz et al. 2009), furfuryl alcohol (Ibnyaich 2010), poly(styrene-co-butyl acrylate) (Favier et al. 1995; Helbert et al. 1996; Hajji et al. 1996; Azizi Samir et al. 2004) and poly(styrene-co-hexyl acrylate) (Elmabrouk et al. 2009) latex, starch (Wang et al. 2010; Angle’s and Dufresne 2001; Mathew and Dufresne 2002; Kvien et al. 2007; Chen et al. 2009; García et al. 2009; Angle’s and Dufresne 2000; de M. Teixeira et al. 2009), PEO (Azizi Samir et al. 2004;
Azizi Samir et al. 2005), natural rubber (Nair and Dufresne 2003a; Nair and Dufresne 2003b; Nair and Dufresne 2003c; Angellier et al. 2005) and soy protein isolate (Wang et al. 2006; Zheng et al. 2009) have been used as the matrix polymers for CNW reinforcement. CNWs have also been successfully incorporated into water insoluble polymers such as polyethylene (Pasquini et al. 2008; Habibi et al. 2008; de Menezes et al. 2009), polypropylene (Ljungberg et al. 2005; Ljungberg et al. 2006), polyvinyl chloride (Chazeau et al. 1999), polyvinyl acetate (de Rodriguez et al. 2006), polycaprolactone (Siqueira et al. 2009), poly(lactic acid) (Mathew et al. 2005; Oksman et al. 2006; Bondeson et al. 2007, Lin et al. 2009; Yu et al. 2008; Pandey et al. 2009; Sanchez-Garcia and Lagaron 2010), poly (L-lactide) (Pei et al. 2010), cellulose acetate (Vargas 2010), PHA (Oksman et al. 2006), cellulose acetate butyrate (CAB) (Petersson et al. 2009; Grunert and Winter 2002; Petersson and Oksman 2005; Ayuk et al. 2009), waterborne polyurethane (Cao et al. 2007; Cao et al. 2008; Chen et al. 2008; Chang et al. 2009) and epoxy (Ruiz et al. 2000; Ruiz et al. 2001; Abdelmouleh et al. 2005). In these studies, the addition of CNW significantly improved mechanical and other physical properties of the polymers, including tensile strength (Roohani et al. 2008; Paralikar et al. 2008; Ibnyaich 2010; Hajji et al. 1996; Angle`s and Dufresne 2001; Chen et al. 2009; García et al. 2009; Zheng et al. 2009; de Menezes et al. 2009; Ljungberg et al. 2006; Pandey et al. 2009; Sanchez-Garcia et al. 2010; Pei et al. 2010; Vargas 2010; Cao et al. 2007), storage modulus (Kvien and Oksman 2007; Roohani et al. 2008; Wang et al. 2010; Ibnyaich 2010; Helbert et al. 1996; Azizi Samir et al. 2004; Ljungberg et al. 2005; Ljungberg et al. 2006; Siqueira et al. 2009; Pandey et al. 2009; Sanchez-Garcia et al. 2010; Pei et al. 2010; Ruiz et al. 2001), water resistance (Goetz et al. 2009; Mathew and Dufresne 2002; Chen et al. 2009; Zheng et al. 2009; Pasquini et al. 2008; Cao et al. 2008), transparency (Chen et al. 2009; Petersson et al. 2009) and barrier properties (García et al. 2009;
Sanchez-Garcia et al. 2010). To the best of our knowledge, only two studies have been reported on poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV)/CNW composites (Jiang et al. 2008; Ten et al. 2010) and they were reported by our group. Our study on this nanocomposite system revealed that the composites prepared by solution casting method showed good CNW dispersion and good mechanical properties. However, melt processed (extrusion followed by injection molding) composites demonstrated reduced mechanical properties due to severe CNW agglomeration (Jiang et al. 2008). Strong nucleating effect of CNW on PHBV led to significant improvement in both mechanical (e.g. Young’s modulus, tensile strength and toughness) and dynamic mechanical properties (e.g. storage modulus) after the addition of 5 wt% of CNW powder (Ten et al. 2010).

Favier et al. were the first to explain the reinforcing effect of CNWs in polymer matrixes (Favier et al. 1995). Formation of mechanical percolation network was reported to be responsible for mechanical properties improvement. They investigated poly(styrene-co-butyl acrylate) latex/cellulose nanocrystals (tunicin) composite films prepared by solution casting. They showed that shear modulus G of the nanocomposites was improved over a wide temperature range above \( T_g \) of the matrix. The reason was ascribed to the whisker percolation network introduced by hydrogen bonding between neighboring whiskers. The presence of such network was later confirmed by electrical measurements performed on nanocomposites containing CNWs that were coated with conductive polypyrrole (Flandin et al. 2000). Later, the percolation behavior of CNWs in polymer matrixes was extensively studied by other research groups (Aziz Samir et al. 2005; Dufresne 2008; Eichhorn et al. 2010; Siqueira et al. 2010; Habibi et al. 2010; Moon et al. 2011).

In this study, a solvent exchange method was used to transfer CNW from water to \( N, N- \)
dimethylformamide (DMF). This method avoided drying and re-dispersion of CNW powder and therefore could reduce the probability of CNW agglomeration. PHBV/CNW nanocomposites were prepared by solution casting. The effects of CNWs on the thermal, dielectric, mechanical and rheological properties of the composites were studied. The dimensions of CNWs and their dispersion in the composites were studied. Based on their aspect ratio, the mechanical percolation threshold of the CNWs was estimated.

3.2 Experimental Section

3.2.1 Materials

PHBV with 12 mol-% hydroxyvalerate (HV) was supplied by Metabolix Inc. N, N-dimethylformamide (DMF) and NaOH were obtained from Acros Organics (Atlanta, GA). Microcrystalline cellulose (MCC), which is derived from wood pulp and has high content of crystalline cellulose, was obtained from Avicel (Type PH-102). Sulfuric acid (96 wt%) was purchased from J.T. Baker. PHBV was dried at 80 °C in a convection oven for 12 hours prior to use.

3.2.2 CNW preparation

Sulfuric acid was diluted to 64 wt% concentration. MCC (1 g per 9.8 ml of acid) was added and vigorously stirred at 44 °C for 2 hours. Then the solution was diluted to about one tenth of its original acid concentration. The acid in the solution was removed by repeated centrifugation (Sorvall, 5000 rpm for 5-min) until the supernatant was turbid. The supernatant was collected and dialyzed against deionized water for 4-5 days to remove remaining acid (dialysis tube from Spectrum Laboratories Inc., cutoff molecular weight 12000-14000). After the CNW suspension reached a constant pH value (pH = 6), it was removed from the dialysis tubes and neutralized with 1 wt% NaOH solution. The neutralized suspension was condensed at 80 °C using a Büchi
Rotavapor (R-200) until the CNW concentration reached 2 wt%.

3.2.3 PHBV/CNW nanocomposites preparation

Various amounts of condensed CNW suspension was added drop-wise into 40 ml of DMF under continuous stirring. Water was evaporated from the mixture at 80 °C for an hour (DMF boiling temperature 153 °C) to obtain CNW/DMF suspension. Different amounts of PHBV were then dissolved in the suspension. Sonication treatment was applied to the solution for 5 min to facilitate CNW dispersion. The solution was casted on a clean glass substrate and evaporated overnight at 50 °C, resulting in PHBV/CNW transparent films with thickness ranging from 15 to 30 microns (measured by digital micrometer). DMF content of the films was measured to be less than 2 wt% through vacuum drying. CNW content of the films was determined to be 0.5, 1.2, 2.0, 2.9, 3.3, 3.6, 4.2 and 4.6 wt% using thermogravimetric analysis (TGA).

3.2.4 Characterization

3.2.4.1 Transmission Electron Microscopy (TEM)

Morphology of CNWs was studied by a TEM (JEOL 1200 EX) operating at 100 kV. A drop of CNW suspension was introduced on a formvar and carbon coated copper grid and the water was naturally evaporated at ambient temperature. TEM images of CNWs were acquired without any sample staining. To study the morphology of the composite film, PHBV/CNW films were embedded in acrylic resin (London Resin Company Ltd.) and cured at elevated temperature overnight. Thin sections of ~50 nm were cut from the cured block with a diamond knife using a Reichert-Jung ultramicrotome. The sections were placed on carbon coated copper grids and were subsequently stained with 2 wt% uranyl acetate for 90 minutes.

3.2.4.2 Atomic Force Microscopy (AFM)

Morphology of CNWs and PHBV/CNW films were also studied by AFM. A drop of CNW
suspension was deposited on freshly cleaved mica surfaces and AFM scan was performed after water was completely evaporated. The AFM tests were carried out in tapping mode using a Veeco Multimode AFM equipped with a NanoScope IIIa controller (Digital Instruments Inc.). Silicon tips (Digital Instruments Inc.) with a resonance frequency of ca. 330 kHz were used. The scan rate was 0.5 Hz.

3.2.4.3 Thermogravimetric analysis (TGA)

TGA was performed on a TA Instruments Q600 to determine the thermal stability of the PHBV/CNW films. Based on the percentage weight loss, CNW contents in the films were deduced. Approximately 5-10 mg of the composite was placed in an aluminum pan. After equilibrating at 25 ºC for 5 minutes, the sample was heated to 600 ºC at 20 ºC/minute under 100 ml/min N₂ flow. Three replicates were tested for each sample.

3.2.4.4 Polarized Optical Microscopy (POM)

Crystallization behavior of neat PHBV and PHBV/CNW nanocomposites was studied by an Olympus BX51 POM equipped with a Linkam hot stage (THMS600/HFS91). PHBV/CNW films were heated up to 220 ºC between two glass slides and then equilibrated at this temperature for 10 min to eliminate any residual PHBV crystallization seeds (Di Lorenzo et al. 2009). The films were then quenched in liquid nitrogen to obtain complete amorphous samples. Isothermal crystallization of PHBV at 30 ºC was examined by the POM and the micrographs of the crystals were taken by an attached digital camera after 5 and 20 minutes of crystallization time, respectively.

3.2.4.5 Differential Scanning Calorimetry (DSC)

Thermal transitions of the nanocomposites were examined by a Mettler Toledo DSC 822e under N₂ flow (80ml/min) and liquid nitrogen controlled cooling. Samples were crimple-sealed
in aluminum crucibles and heated from -50 to 200 °C at a heating rate of 10 °C/min (first heating scan), equilibrated at 200 °C for 2 min, cooled rapidly at 30 °C/min to -50 °C, equilibrated at -50 °C for 2 min, and then heated up again to 200 °C at 10 °C/min (second heating scan). The first heating scan was performed to eliminate the sample’s thermal history.

3.2.4.6 Dynamic Mechanical Analysis (DMA)

DMA was conducted in tension mode on a Tritec 2000 DMA at 1 Hz to examine thermal dynamic properties of the films. DMA samples (10 x 6.5 mm²) were cut from the PHBV/CNW composite film. Dynamic strain sweep was first performed to determine linear viscoelastic range of the samples. Then the samples were tested from -40 °C to +80 °C at 5 °C/min heating rate with a strain of 0.02%. Ten replicates were tested for each composite formulation.

3.2.4.7 Tensile test

Dumbbell-shaped film specimens were prepared with a Type IV (ASTM D638) sample cutter and tested according to ASTM D 638–91. Ten samples for each formulation were tested using an Instron 4466 (capacity 500N) at a deformation rate of 5.08 mm/min. Tensile strain was recorded by an EIR laser extensometer (model LE-05).

3.2.4.8 Bulge test

Bulge testing is commonly used to test mechanical performance of thin films. In this test, PHBV/CNW films were loaded by pressurized dry air and the deflection of the films was measured (Fig. 1). Air pressure was applied and varied by a Meriam pressure/vacuum variator. Film deflection was measured with a scanning laser vibrometer (Polytec OFV500). The pressure and deflection values were acquired using LabView software. Five replicates were tested for each specimen.

By fitting the curve of pressure versus deflection to a cubic polynomial, Young’s modulus of
the film could be calculated from the slope of the polynomial using the model of circular membrane behavior under uniform pressure (Small and Nix 1992):

\[ P = \frac{8Et}{3a^4}h^3 + \frac{4t\sigma}{a^2}h \]  

(3.1)

where \( P \) is the differential pressure, \( E \) is modulus, \( t \) is the thickness of the film, \( a \) is the radius of the membrane (4.76 mm), \( h \) is the center deflection and \( \sigma \) is the residual stress in the film determined by the deflection relationship at zero differential pressure:

\[ \sigma = \frac{Pa^2}{4ht} \]  

(3.2)

The experimental set-up is depicted in Fig. 3.1.

**Figure 3.1** Schematic representation of the bulge test.

### 3.2.4.9 Dielectric properties measurement

Real (\( \varepsilon' \)) and imaginary (\( \varepsilon'' \)) part of dielectric constant and dielectric loss (tan \( \delta \)) of the films were measured by an Alpha-N high resolution dielectric analyzer (Novocontrol Inc) over 0.01 - \( 10^6 \) Hz frequency range at room temperature. Five replicates were tested for each composite formulation. Before measurements, samples were cleaned with acetone and dried at ambient temperature.

### 3.2.4.10 Rheology test

A strain-controlled rheometer (RDA III, Rheometric Scientific) was used to measure dynamic rheological properties of PHBV/CNW composites. The measurements were performed
at 175 °C using parallel plate geometry (25 mm diameter). The gap between the two plates was 0.5 mm. Samples were equilibrated at 175 °C for 5 min before tests. A strain sweep test was first performed to determine the linear viscoelastic region of the composites and a shear strain of 0.6% was chosen for all subsequent frequency sweep tests. The frequency was varied from 1 to 500 rad/s.

3.3 Results and Discussions

3.3.1 Morphology of CNWs and PHBV/CNW films

To confirm that CNW formed stable dispersion in DMF after solvent exchange, CNW/water and CNW/DMF suspensions were first observed between two crossed polarizers. If stable and homogeneous CNW suspensions were formed, flow birefringence can be observed due to the anisotropy of CNW. Fig. 3.2 shows that both suspensions exhibited strong flow birefringence, indicating that CNW dispersion remained stable and homogeneous in DMF after solvent exchange.

![CNW suspensions showing flow birefringence between two crossed polarizers. CNW concentration is 0.9 wt% (a) in water; (b) in DMF.](image)

AFM images (topographic and phase) and a TEM micrograph of CNWs were shown in Fig.
3.3. A wide distribution in CNW dimension was evident from both graphs. The dispersion of CNWs in the PHBV matrix was demonstrated by the TEM images shown in Fig. 3.4.

![AFM topographic and phase image](image1.png) ![TEM micrograph](image2.png)

**Figure 3.3** AFM topographic and phase image (a and b, respectively) and TEM micrograph (c) of CNWs. CNW samples were obtained by evaporating water from the aqueous suspension of CNWs.
Figure 3.4 TEM images of PHBV/CNW composite films. (a) 2.3 wt% CNW; (b) 3.3 wt% CNW; (c) 4.6 wt% CNW. The circles indicate CNW agglomerations.
It was clear that CNWs were homogeneously dispersed in the PHBV matrix at low CNW concentration (Fig. 3.4a). At higher concentrations (Fig. 3.4b and c), agglomeration of CNWs became evident as indicated by the circles. Due to the tip broadening effect in AFM micrographs, the dimensions (length and diameter) of CNWs were measured from their TEM micrographs. The TEM image in Fig. 3.3c could not be used for the measurement because it was difficult to identify the ends of a single fiber. Therefore all the measurements were performed on the CNWs in the PHBV/CNW composites (Fig. 3.4) CNW aspect ratio (length/diameter) of the fiber was determined based on the measurements of 300 individual whiskers using ImageJ software (National Institute of Health). The average length and diameter were determined to be 221 ± 48 nm and 12.3 ± 4.0 nm, respectively. And the average aspect ratio was calculated to be 18.01±7.5.

An aspect ratio distribution histogram of CNWs is also shown in Fig. 3.5. A log-normal distribution that is commonly used to describe particle size-distribution was used to fit the histogram:

\[
f(x) = \frac{\exp\left(-\frac{1}{2}\left(\frac{\ln(x) - \mu}{\sigma}\right)^2\right)}{x\sigma\sqrt{2\pi}};
\]

(3.3)

where \( x \) is a random variable (in this case aspect ratio) with normal distribution, \( \mu \) and \( \sigma \) are location and scale parameters, respectively. \( \mu = 2.7 \) and \( \sigma = 0.58 \) were obtained for the best fitting. Therefore, the aspect ratio distribution can be described as:

\[
f(x) = \frac{\exp\left(-\frac{1}{2}\left(\frac{\ln(x) - 2.7}{0.58}\right)^2\right)}{0.58\sqrt{2\pi x}};
\]

(3.4)
Figure 3.5 CNW aspect ratio distribution histograms and log-normal function fit.

An average aspect ratio can be determined as:

$$\frac{L}{d} = e^{\mu + \frac{\sigma^2}{2}} = 18.02$$

(3.5)

This value is very close to the measured average aspect ratio. It should be recognized that this aspect ratio is most likely smaller than the actual value because CNWs were randomly oriented in the film. The measured fiber length in this situation was actually projected fiber length, which was often smaller than the real fiber length. The measurements taken on unidirectionally aligned CNW composites should give CNW aspect ratios close to the actual values. This part of work has been done and will be reported in our next paper.

3.3.2 Thermal properties

Thermal behavior of PHBV with respect to the CNW concentration was studied by DSC. The thermograms for the 1st cooling and the 2nd heating scan are presented in Fig. 3.6(a) and (b), respectively. In Fig. 3.6a, no PHBV crystallization peak is evident for the composites comprising
less than 2.3 wt% of CNW. The crystallization peak appeared and became more pronounced with increasing CNW content when the content is > 2.3 wt%. This result shows that there seemed to be a transition in PHBV crystallization behavior at 2.3 wt% CNW content. In Fig. 3.6b, similar transitions in glass transition temperature, cold crystallization temperature, and melting temperatures could also be found. Neat PHBV had the lowest glass transition temperature (T_g: -5.7 °C). The addition of CNW (content ≤ 2.3 wt%) increased T_g by ca. 4 °C. At higher CNW contents (≥ 2.9 wt%), T_g decreased and was only ca. 1.5 °C higher than that of the neat PHBV. Cold crystallization temperature decreased with CNW content up to 2.3 wt%. Higher than that concentration, cold crystallization temperature remained largely unchanged. In terms of melting temperatures, the samples comprising ≤2.3 wt% CNW exhibited higher melting temperatures than those containing ≥3.3 wt% CNW. All these thermal transitions indicated that the microstructures of the nanocomposites experienced a rapid change at about 2.3 wt% CNW concentration.

Isothermal crystallization behaviors of PHBV and PHBV/CNW composites were studied by POM (Fig. 3.7). PHBV spherulites in the neat PHBV showed the typical Maltese cross related to crystalline structures (Fig. 3.7a and b). The number of the spherulites was small and their diameter was large. By adding 0.5 wt% of CNWs, spherulite number dramatically increased and the radius of the spherulites decreased (Fig. 3.7c and d). Adding 2.3 wt% of CNW further reduced spherulite size and increased nucleation density of PHBV crystals (Fig. 3.7e and f). However, 4.6 wt% of CNW did not seem to cause further reduction in spherulite size (Fig. 3.7g and h). This effect was previously described as a “saturation” of nucleation effect (Xu and Wang 2008). More detailed study on the effects of CNW on the crystallization of PHBV is underway.
Figure 3.6 DSC thermograms of the 1\textsuperscript{st} cooling scan (a) and the 2\textsuperscript{nd} heating scan (b) of the neat PHBV and the PHBV/CNW composites.
3.3.3 Mechanical properties

Mechanical properties of the neat PHBV and the PHBV/CNW composite films were studied by tensile and bulge tests. Young’s moduli $E$ obtained from both methods are shown in Fig. 3.8 and the two results are in reasonable agreement. The results from both tests indicated that the properties of the nanocomposites experienced a transition at 2.3 wt% CNW. For the bulge test, 2.3 wt% CNW was the concentration dividing high modulus group (0.5, 1.2, and 2.0 wt%) and low modulus group (2.9, 3.3, 3.6, 4.2, and 4.6 wt%). For the tensile test, 2.3 wt% CNW was the concentration where the modulus of the composites started leveling off. Tensile strength and effective toughness (area below stress-strain curve) were also improved by the addition of CNW (content $\leq$ 2.3 wt%) (Fig. 3.9). The increase in tensile strength was an indication of strong interfacial bonding between the PHBV matrix and CNWs. The improvement in toughness was due to the increase in tensile strength and elongation. Both of them started to decrease after CNW content reached 2.3 wt%.
Figure 3.7 POM images of isothermal crystallization of neat PHBV (a,b); PHBV/0.54%CNW (c,d); PHBV/2.3% (e,f); PHBV/4.6% (g,h). Elapsed time was 5 min (a,c,e,g) and 20 min (b,d,f,h). Scale bar represents 20 um.
Figure 3.8  Young’s moduli E for the neat PHBV and the PHBV/CNW composites obtained from tensile and bulge tests.

Figure 3.9  Tensile strength and toughness of the neat PHBV and the PHBV/CNW composites.
Storage modulus $E'$ of the neat polymer and the nanocomposites were measured by DMA over the temperature range of -40 – 85 °C and their representative curves were shown in Fig. 3.10. Modulus drop between 10 and 30 °C was due to the $\alpha$-relaxation of PHBV. Ten replicates were tested and their average moduli at -10 and 60 °C, respectively, were plotted against CNW content in Fig. 3.11. Again, a modulus transition was evident at the CNW content of 2.3 - 2.9 wt%.

![Figure 3.10](image)  
**Figure 3.10** Storage modulus $E'$ as a function of temperature for the PHBV/CNW composites with different CNW contents.
3.3.4 Dielectric properties

Dielectric permittivity is an indicator of a material's ability to transmit an electric field. It is determined by the ability of a material to polarize in response to the applied field. Due to its frequency dependence, dielectric permittivity of a material is often represented by complex permittivity $\varepsilon^*$:

$$\varepsilon^* = \varepsilon' - i\varepsilon'';$$  \hspace{1cm} (3.6)

where $\varepsilon'$ is the real part or dielectric constant and $\varepsilon''$ is the imaginary part of dielectric permittivity. The specific conductivity is related to the dielectric constant by:

$$\sigma^* = i \ 2 \pi \ f \ \varepsilon_0 (\varepsilon^* - 1) = \sigma' - i\sigma'';$$  \hspace{1cm} (3.7)
where \( f \) is frequency (Hz), \( \varepsilon_0 \) is vacuum permittivity (8.85*10^{-12} F/m), and \( \sigma' \) and \( \sigma'' \) are real and imaginary parts of electric conductivity, respectively. The dielectric constant for a polymer depends on the polarizability of its molecules. High molecular polarizability leads to high \( \varepsilon^* \). As a heterogeneous system, a composite also has its dielectric properties influenced by interfacial polarization, i.e. charge build-up at the interfaces.

Fig. 3.12 compares the real permittivity \( \varepsilon' \) of the neat PHBV and the PHBV/CNW composites in the electric field with frequency ranging from \( 10^{-2} \) to \( 10^6 \) Hz. \( \varepsilon' \) increased with CNW concentration and peaked at 2.3 wt%. It decreased when the concentration increased further. This trend is better shown in Fig. 3.13a, where \( \varepsilon' \) at 1 Hz of all the samples are compared. On the other hand, specific conductivity of the composites increased monotonously with increasing CNW content (Fig. 3.13b). Fig. 3.12 also shows that \( \varepsilon' \) of all the samples decreased with increasing frequency. This could be attributed to the relatively slow rotation and motion of the dipoles in the material, which was not able to follow the applied electric field at high frequencies.
Figure 3.12 Real permittivity of neat PHBV and PHBV/CNW composites at room temperature in the electric fields of different frequencies.
Figure 3.13 Real permittivity (a) and real conductivity (b) for the neat PHBV and the PHBV/CNW composites. $\varepsilon'$ and $\sigma^*$ were sampled at 1 Hz.
3.3.5 Rheological properties

Neat PHBV showed typical polymer melt behavior in the terminal region: G' and G'' increased with shear frequency \( \omega \) and G'' was larger than G' (Fig. 3.14 a and b). The larger G'' indicated the fact that the PHBV melt was highly viscous rather than elastic at the test temperature. The addition of CNWs increased G' and G'' of the composites, especially within the terminal region. G' and G'' also appeared to be more independent of shear frequency with increasing CNW content, a sign of transition from “liquid” like rheological behavior to “solid” like one. The most rapid change seemed to occur when the CNW content was between 0.5 and 2 wt%. The relative magnitude of G' and G'' also changed with increasing CNW content because G' increased faster than did G''. Fig. 3.14c shows that 1.2 wt% was the transitional CNW content where G' and G'' had similar values (for clarity, only the values of three formulations were shown). Below this content G' was larger than G'', whereas above this content G' was smaller than G''. This relative magnitude change indicated that the composites were dominantly elastic when the CNW content was higher than 1.2 wt%. This transition was also demonstrated by the dissipation factor tan\( \delta \) (Fig. 3.14d). The factor was significantly reduced at 1.2 wt% CNW content, implying that the material became substantially more elastic and dissipated much less energy during shear deformation compared to the samples with lower CNW contents.
Figure 3.14 Storage modulus (a), loss modulus (b), storage/loss modulus (c) and dissipation factor (d) of neat PHBV and PHBV/CNW composites.
3.4 Discussion

The morphology, thermal and crystallization, and mechanical and dielectric properties of the PHBV/CNWs composites showed transitions at the CNW content of 2.3 wt%. Strength, modulus, and real permittivity of the composites all increased with increasing CNW content before they peaked at 2.3 wt%. Abrupt property increases of composites are often explained using the percolation theory, i.e. the formation of a long range network structure. A percolation threshold \( v_{RC} \) of nanoparticles can be calculated by:

\[
v_{RC} = \frac{0.7}{L/D};
\]

where \( v_{RC} \) is the minimum volume ratio for the nanoparticles to form a continuous network within a polymer matrix and \( L \) and \( D \) are particle length and diameter, respectively (Aziz Samir et al. 2005; Dufresne 2008; Eichhorn et al. 2010; Siqueira et al. 2010; Habibi et al. 2010; Moon et al. 2011; Paul and Thomas 1997). Based on this equation, the percolation threshold of CNWs was calculated to be 3.8 vol% using the CNW aspect ratio of 18. Given the density of PHBV (1.2 g/cm\(^3\)) and CNWs (1.5 g/cm\(^3\)) (Holmes 1987; Gindl and Keckes 2004), the percolation threshold in weight ratio was 4.7 wt%. This result shows that the increases in the composite properties were not caused by CNW percolation. Rather, the continuous increases are the results of homogeneous dispersion of the CNWs and the strong interactions between PHBV and the CNWs. The decreases in the properties above the 2.3 wt% concentration was believed to be induced by CNW agglomeration as revealed in Fig. 3.14.

In Fig. 3.6b cold crystallization temperature decreased until the CNW content reached 2.3 wt%. Higher than that, the temperature remained largely unchanged. CNWs facilitated PHBV cold crystallization by acting as nucleation agents. Below the CNW agglomeration content, higher CNW concentration meant larger interfacial area and more nucleation sites, which could
improve PHBV cold crystallization. Above the content, the number of the nucleation sites might not increase further due to the agglomeration. The nucleation effect of CNWs might also saturate at high CNW contents. Therefore, the cold crystallization temperature did not decrease further. Moreover, it was also believed that above the CNW agglomeration content, excessive CNWs in the composites could retard PHBV crystal growth (non-crystallizable barriers) (Homminga et al. 2005) and hinder the diffusion of PHBV chains to the growing crystallites (Fornes and Paul 2003). In either case the perfection of PHBV crystallites was reduced and the melting point of PHBV was lowered (Fig. 3.6b).

Tensile strength, storage modulus, and toughness of the composites all achieved their maximum values at 2.3 wt% CNW content (Fig. 3.4). The CNW agglomerates which occurred at higher contents introduced stress concentration and material defects into the samples, which in turn led to lower mechanical properties.

Real permittivity of the composites peaked at 2.3 wt% CNWs (Fig. 3.12a). Conductivity of the composites, on the other hand, increased monotonously (Fig. 3.12b). PHBV molecules possessed low polarity and therefore the neat polymer showed lower permittivity compared to the composites due to the presence of the polar groups such as hydroxyls and sulfates on CNWs. The increase in permittivity could also be partially ascribed to the interfacial polarization occurred at the interface between PHBV and CNWs. Interfacial polarization occurs between materials of different dielectric constants and conductivities (Paul and Thomas 1997). The interfacial area between PHBV and CNWs increased with CNW concentration. This resulted in increased $\varepsilon'$ when the concentration varied from 0 to 2.3 wt%. However, above 2.3 wt% $\varepsilon'$ started to decrease because of reduced number of interfaces due to poor dispersion of CNW (Fig. 3.5). The variation of the real permittivity was believed to be due to the change in interfacial
polarization. When CNW content increased from 0 to 2.3%, Interconnections between CNWs and interfacial area between PHBV and CNWs increased. This increase led to higher interfacial polarization and consequently higher real permittivity. However, when the content was higher than 2.3 wt%, CNW agglomeration could reduce the interconnections and the interfacial area and therefore decrease the real permittivity. In addition, high conductivity of the composites at high CNW contents (> 2.3 wt%) could also reduce the permittivity.

Rheological results are often used to indicate the formation of an interconnected network structure in polymer melts. The results in this study show that 1.2 wt% should be the transition content, which is lower than the value determined by other methods. Potschke et al. (Potschke et al. 2003) found similar results in polycarbonate/MWCNT composites – rheology determined gelation point (determined at 280 °C melt temperature) was smaller than dielectric property determined one. The reason was attributed to the polymer-nanotube network structure in the rheological tests which was formed without physical touching or geometrically overlapping between nanotubes. When two nanotubes were close enough, e.g. their gap distance lower than twice of the radius of gyration of the polymer chains, such polymer-nanotube network could be formed. The required nanotube concentration for the formation of this network was substantially lower than that required by geometrical percolation as determined by dielectric, mechanical, and thermal tests.

3.5 Conclusion

PHBV/CNW nanocomposites were prepared by solvent exchange and solution casting techniques. CNW content in the composites was varied and its effects on morphological, mechanical, thermal, electrical, and rheological properties of the composites were investigated. Property transitions were noticed at the CNW content 2.3 wt% for all the investigated properties
except the rheological property. These property transitions were believed to be due to the transition of CNW dispersion state, i.e. from homogeneous dispersion to agglomeration. Rheological results indicated a lower transition point (1.2 wt%) for the composites because a polymer-CNW network could be formed without physical touching and geometrical overlapping. The calculation for percolation threshold revealed that CNW agglomeration occurred before a percolation network was formed. This could be due to the strong interactions (e.g. hydrogen bonding) between the CNWs and their low aspect ratio.

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Chapter 4 Crystallization kinetics of Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)/cellulose nanowhiskers Composites

Abstract

In this study, biodegradable PHBV films with 1.2 - 4.6 wt% of cellulose nanowhiskers (CNWs) were manufactured by solution casting method using N,N-dimethylformide (DMF) as a solvent. An aqueous suspension of CNW was prepared by sulfuric acid hydrolysis and the CNW was re-dispersed in DMF using solvent exchange. Crystallization behaviors of PHBV/CNW composites under isothermal conditions were studied using differential scanning calorimetry (DSC) and polarized optical microscopy (POM). The changes in crystalline structure of PHBV with CNW were studied by XRD. Avrami analysis showed that overall crystallization rate of PHBV increased at low CNW concentrations corresponding to homogeneous dispersion of CNWs and then decreased at higher concentrations. This result was ascribed to increasing nucleation sites at low CNW concentrations. Higher CNW contents than this critical concentration resulted in decreasing nucleation sites due to CNW agglomeration. Crystallization temperature was also found to be an important factor. High temperature increased the chain diffusion rate and the spherulite growth rate but decreased the nucleation effect of CNWs. The changes in nucleation ability and crystalline structure of PHBV with CNW might contribute to mechanical properties improvement (Ten et al. 2010). However, the results of this study show that the main reasons for $E'$ enhancement were homogeneous distribution and interconnected 3-D structure of CNWs.
4.1 Introduction

Poly(3-hydroxybutyrate-c-o-3-hydroxyvalerate) (PHBV) is a semicrystalline copolymer naturally synthesized by bacteria. Due to its biodegradability and biocompatibility, PHBV has been studied extensively as a biodegradable plastic for many applications. However, wide-spread applications of PHBV are still hindered by several material drawbacks such as poor thermal stability, brittleness and low crystallization rate. Numerous efforts have been made to overcome these drawbacks. Adding nucleating agents to PHBV is one route to increase crystallization rate of the polymer. Nucleating agents improve crystallization rates via heterogeneous nucleation by decreasing the surface free energy barrier. Various chemicals have been studied and are currently used as nucleating agents, including boron nitride (BN) (Weihua et al. 2005; Jiang et al. 2008; Qian et al. 2007; Withey and Hay 1999; Liu et al. 2002), talc (Weihua et al. 2005, Liu et al. 2002), lanthanum oxide (La$_2$O$_3$) (Liu et al. 2002), terbium oxide (Tb$_2$O$_3$) (Liu et al. 2002), saccharin (Withey and Hay 1999; El-Hadi 2002), terephthalic acid (Zhou 2006), phthalimide (Withey and Hay 1999), thymine and melamine (Qian et al. 2007), α-cyclodextrin (He and Inoue 2003), ammonium chloride (Organ and Barham 1994, Figuly 2004), etc.

It was reported that one of the most effective nucleating agents for PHBV is boron nitride (Withey and Hay 1999; Liu et al. 2002). BN reduces the degree of supercooling and accelerates crystallization rate of the polymer. Jiang et al. reported that the addition of 1 wt% of BN increased spherulite density and refined crystalline structure of PHBV. Tensile/flexural strength, tensile/flexural elongation/deflection, and impact strength of the polymer increased after the addition of BN, while tensile/flexural modulus of the polymer was slightly reduced (Jiang et al. 2008).

The use of nanoparticles as nucleating agents has become attractive because the nanoparticles
are not only useful in nucleating the polymer but are also beneficial to mechanical and thermal properties of the composites (Pei et al. 2010; Lai et al. 2004; Xie et al. 2009; Ma et al. 2008; Chen et al. 2004; Ublekov et al. 2009; Dagnon et al. 2009; Jiang et al. 2008; Ten et al. 2010; Ten et al. 2011). For example, inorganic nano-fillers such as multi-walled carbon nanotubes (Lai et al. 2004), silica (Xie et al. 2009; Ma 2008), clay (Chen et al. 2004; Ublekov et al. 2009), and layered double hydroxides (LDH) (Dagnon et al. 2009), have been shown to improve the nucleation ability and increase the crystallization rate of PHBV.

Moreover, due to the addition of the nanoparticles PHBV composites showed higher stiffness (Xie et al. 2009; Chen et al. 2004; Dagnon et al. 2009) and higher thermal stability (Lai et al. 2004; Xie et al. 2009; Ma et al. 2008) compared to the unfilled polymer. In particular, the effects of fumed silica and clay on the crystallization kinetics of PHBV were studied by Ma et al. and Chen et al., respectively (Ma et al. 2008, Chen et al. 2004). It was shown that the overall crystallization rate and crystallinity increased at low silica concentrations (≤ 2 wt%) and decreased at high concentration (5 wt%) (Ma et al. 2008). The authors suggested that when the content of silica was too high, it acted as large impurities and blocked crystallite growth. Isothermal crystallization kinetics revealed that the crystallization process was controlled by the silica-promoted heterogeneous nucleation. The overall crystallization rate of PHBV/2%SiO₂ (measured by DSC) was substantially higher than that of the neat PHBV, whereas the spherulite radial growth rates (measured by POM) of both materials were similar. These results indicated that the crystallization mechanism was governed by nucleation and the overall crystallization rate was controlled by the nucleation rate and nucleation density at a given crystallization temperature (Ma et al. 2008). Similarly, for PHBV/clay nanocomposites fabricated by solution casting, isothermal DSC study showed that at low nanoparticle concentrations (≤ 3wt%), the free
energy of PHBV crystals decreased after adding the organophilic clay, indicating that a small amount of clay accelerated PHBV crystallization (Chen et al. 2004). In contrary, at high clay concentration (10 wt%), the transportation of polymer segments was hindered by the clay particles, resulting in delayed crystallization (Chen et al. 2004).

Several studies on the production and properties of PHBV/cellulose nanowhiskers (CNWs) composites have been reported by our group (Jiang et al. 2008; Ten et al. 2010; Ten et al. 2011). CNWs are needle-like elementary crystals that occur naturally in cell walls of plants. It can be isolated using an acid hydrolysis process (H$_2$SO$_4$ or HCl). We have shown that solution cast PHBV/CNW composites had higher mechanical performance and better CNW dispersion compared to the melt processed composites (Jiang et al. 2008). Further, PHBV film with 5 wt% CNWs showed significant improvement in Young’s moduli (77% by tensile test and 91% by bulge test) and tensile strength (35.5% by tensile test). DMA test results demonstrated a 41% increase in storage modulus (at room temperature) and a shift of tanδ peak to higher temperatures, indicating restrained PHBV molecular mobility due to its interactions with CNWs. Our recent report on the content effects of CNWs showed that the maximum reinforcing effect was achieved when CNW content was 2-3 wt%. Moreover, DSC and POM data showed that CNWs were effective nucleating agents for PHBV (Jiang et al. 2008; Ten et al. 2010; Ten et al. 2011).

Since nanoparticles play important roles in both crystallization and mechanical performance of PHBV, the objective of this research was to conduct an in-depth study on the influence of CNWs on the crystallization kinetics of PHBV. The effects of CNWs on the isothermal crystallization kinetics of PHBV were evaluated using Avrami analysis. PHBV spherulite growth rate and nucleation density were calculated based on POM observations.
4.2 Experimental Section

4.2.1 Materials

PHBV containing 12 mol-% hydroxyvalerate (HV) was provided by Metabolix Inc. (Cambridge, MA). \( N, N \)-dimethylformamide (DMF) was obtained from Acros Organics (Atlanta, GA). Microcrystalline cellulose (MCC) was supplied by Avicel (Type PH-102). Sulfuric acid (96 wt%) was purchased from J.T. Baker.

4.2.2 CNW preparation

MCC (1 g per 9.8 ml of acid) was mixed with 64 wt% sulfuric acid and the resultant suspension was stirred at 44 °C for 2 hours. The suspension was diluted 10 times with deionized water and kept in a refrigerator to prevent further reaction. Sulfuric acid in the suspension was removed by repeated centrifuge (Sorvall, 5000 rpm for 5-min) until the supernatant was turbid. The supernatant (CNW suspension) was collected and dialyzed (Spectrum Laboratories Inc., molecular weight cutoff 12,000-14,000) against deionized water for 4-5 days to remove the remaining acid. When the suspension reached a constant pH value, it was removed from the dialysis tubes and neutralized with 1 wt% NaOH solution. The neutralized suspension was finally condensed at 80 °C using a Büchi Rotavapor (R-200) until the CNW concentration reached 2 wt%.

4.2.3 PHBV/CNW nanocomposites preparation

Various amount of condensed CNW suspension was added drop-wise into 40 ml of DMF under continuous stirring. Water was evaporated from the mixture at 80 °C for an hour (DMF boiling temperature 153 °C) to obtain CNW/DMF suspension. 5 wt% of PHBV (based on the total weight of the CNW/DMF suspension) was added and the suspension was stirred at 80 °C until complete PHBV solution. The solution was sonicated for 5 min and then cast on a clean
glass substrate. PHBV/CNW transparent films (thickness 15-30 microns) were obtained after overnight evaporation at 50°C.

4.2.4 Characterization

4.2.4.1 Atomic force microscopy (AFM)

Morphology of cellulose nanowhiskers was investigated by an AFM. The tests were performed in tapping mode using a Veeco Multimode AFM equipped with a NanoScope IIIa controller (Digital Instruments Inc.). Prior to the tests, a drop of CNW suspension (in water) was deposited on freshly cleaved mica surfaces. The suspension was completely dried by evaporation at ambient temperature before being scanned by the AFM. The samples were scanned in air using Si tips (Digital Instruments Inc.) with a resonance frequency of ca. 330 kHz. The scan rate was 0.5 Hz.

4.2.4.2 Transmission electron microscopy (TEM)

The shape and size of CNWs were also studied by a TEM (JEOL 1200 EX) operating at 100 kV. Similar to the sample preparation method used for AFM, a drop of CNW water suspension was introduced on a formvar- and carbon-coated copper grid and the water was evaporated naturally. TEM images of CNWs were acquired without any sample staining.

To study the morphology of the PHBV/CNW composite films, small pieces of films were embedded in acrylic resin (London Resin Company Ltd.) and cured at elevated temperature overnight. Thin sections (50 nm thick) were cut from the resin with a glass knife using a Reichert-Jung ultramicrotome. The sections were placed on formvar coated copper grids and then stained with 2% uranyl acetate for 90 minutes.

4.2.4.3 X-ray diffraction (XRD)

Powder X-ray diffraction (XRD) was performed in reflection mode on a Phillips X’Pert
diffractometer with an X’celerator detector using Ni-filtered CuKα radiation ($\lambda = 1.5418$ Å). The PHBV/CNW films were examined in the range of $2\theta = 10^\circ$-35° at 45 kV tension and 40 mA current at ambient temperature. XRD data was collected with a step size of 0.02° and count time of 50 sec per point. A polycarbonate sample holder was used to avoid any peak overlap associated with the holder material.

4.2.4.4 Differential Scanning Calorimetry (DSC)

Isothermal crystallization of the neat PHBV and its nanocomposites was analyzed using a Mettler Toledo DSC 822e under N₂ flow (80ml/min) with liquid nitrogen cooling. 5-10 mg samples were crimple-sealed in 40-ul aluminum crucibles and heated from room temperature to 200 °C at a heating rate of 200 °C/min and equilibrated at 200 °C for 2 min to remove any prior thermal history. The samples were subsequently cooled rapidly at 100 °C/min to pre-determined crystallization temperatures ($T_c = 50, 60$ and $70$ °C) and then kept isothermal for 15 min. Heat flow was measured during the isothermal crystallization. 3 replicates were performed for each formulation.

4.2.4.5 Polarized Optical Microscopy (POM)

Isothermal crystallization behavior of the samples was studied by an Olympus BX51 POM equipped with a Linkam hot stage (THMS600/HFS91). Sample films were sandwiched between two glass slides and heated up to 220 °C. The films were equilibrated for 10-min to eliminate any residual PHBV crystallization seeds and then quenched in liquid nitrogen to obtain complete amorphous samples. The amorphous films were studied for PHBV nucleation and spherulite growth at 50, 60 and 70 °C using the POM. Sequential images of PHBV spherulites were taken by an attached digital camera every 3 seconds. Spherulite radii $R$ were measured using SPOT Advanced software (Diagnostic Instruments Inc.).
4.3 Results and discussion

4.3.1 Morphology of CNWs and PHBV/CNWs composites

The shape and size of CNWs were shown in AFM and TEM micrographs (Fig. 4.1). The aspect ratio of the nanowhiskers was determined based on the measurements of 300 individual whiskers from the TEM micrographs using ImageJ software (National Institute of Health). The average aspect ratio was found to be 18.01±7.5 (Ten et al. 2011).

![Morphology of CNWs.](image)

**Figure 4.1** Morphology of CNWs. a: AFM topography; b: AFM phase image; c: TEM micrograph.
Figure 4.2 TEM images of PHBV/CNW composites comprising 2.3% (a), 3.3% (b), and 4.6% (c) of CNWs.
Fig. 4.2 shows TEM images of PHBV/CNW composites comprising different concentrations of CNWs. It can be seen that CNWs were dispersed evenly in the PHBV matrix at 2.3 wt% concentration (Fig. 4.2a). CNW agglomeration occurred and intensified with increasing CNW concentration (Fig. 4.2b and c).

4.3.2 XRD analysis of PHBV/CNW composites

X-ray diffraction 1-D patterns of the neat PHBV and PHBV/CNW composite films are shown in Fig. 4.3. All the diffractograms correspond to the crystal structure of PHB homopolymer (Bloembergen et al. 1986; Owen et al. 1992). Typical diffraction peaks at 2θ = ca. 13.4°, 16.8°, 30.5° are attributed to (020); (110) and (200) crystal planes, respectively (Owen et al. 1992). It can be seen from Fig. 4.3 that peak 13.4° become sharper and more intense with CNWs suggesting that nanowhiskers induced ordering of PHBV molecular chains. Moreover, this increase in the peak intensity of (020) crystal plane with CNW shows that nanowhiskers provoke the increase in the degree of crystallinity.

Using Bragg’s law is it possible to establish a relationship between the angle of the diffracted beam θ and the interplanar distance d:

\[ n\lambda = 2d \sin \theta; \]  

(4.1)

where \( n \) is the reflection number (integer) and \( \lambda \) is the wavelength of the Cu (1.5418 Å). The magnitude of a distance between two adjacent parallel crystal planes is a function of Miller indexes (hkl) and the lattice parameters (a,b,c). In this work, PHBV has 12 wt% HV content, therefore PHBV has the same crystal structure as that of PHB demonstrating the orthorhombic unit cell (Owen et al. 1992; Miao et al. 2008). The relationship between \( d \) and lattice parameters is given by:
The crystalline lattice parameters of neat PHBV were calculated from the (020), (110) and (021) diffraction peaks corresponding to 13.4° (d = 6.6 Å); 16.8° (d = 5.3 Å) and 20° (d = 4.4 Å), respectively. The parameters a = 5.748 Å; b = 13.20 Å; and c = 5.904 Å were in good agreement with results reported previously for PHBV12 (Hirota et al. 2005).

Comparison of diffractograms (Fig. 4.3) also verified that there is no formation of new diffraction peaks with the CNWs, which indicates that nanowhiskers do not cause the appearance of new crystalline symmetries.

According to monoclinic indexation by Sugiyama et al. (Sugiyama et al. 1991), cellulose nanowhiskers typically reveal distinct diffraction peaks at ca. 14.5°, 16.4° and 22.5° attributed to (1̅11), (110) and (200), respectively (Sugiyama et al. 1991; Tokoh et al. 1998; Martínez-Sanz et al. 2011). The strongest cellulose peak, characteristic of cellulose I, is located at 22.5° and can recognized even at low CNW concentrations (Fig. 4.4). Furthermore, it can be seen from Fig. 4.4 that the position of the peaks representing (101) and (111) PHBV crystal planes at 21.5° and 22.3°, respectively, shifts to toward the higher diffraction angle, which showed that there were changes in the crystalline structure of the PHBV with regard to the content of CNWs. These changes occurred because PHBV crystallized in a defect ridden crystalline form. The unstable growth of crystallites of PHBV in the presence of CNW particles was due to the percolated structure form between CNWs. Changes in the diffraction angle imply changes in the interplanar distances. They indicate changes in parameters of the reinforced samples lattice and the crystalline structure of PHBV (Zhou et al. 2011).
Figure 4.3 X-ray diffraction pattern of neat PHBV and randomly oriented PHBV/CNW composites.
Figure 4.4 X-ray diffraction patterns of PHBV and PHBV/CNW composites over $2\theta = 20.5-24^\circ$.

* indicates (101) and (111) PHBV crystal planes and ◊ - (200) CNW crystal plane. Data were smoothed over 25 adjacent points.

The dimensions of the crystal perpendicular to the diffracting planes $D_{hkl}$ can be determined using Scherrer’s equation (Klug and Alexander 1954):

$$D_{hkl} = \frac{0.9 \lambda}{\beta_{1/2} \cos \theta};$$  \hspace{1cm} (4.3)

where ($\theta$) is the diffraction angle, ($\lambda$) wavelength of Cu (1.5418 Å) and ($\beta_{1/2}$) is the peak width of half intensity (in radians) prior to smoothing. For this calculation diffraction peak $2\theta = ca. 30.5^\circ$ corresponding to the plane (200) of PHBV was utilized. The results are shown in Table 4.1. It can be seen that apparent crystal size of PHBV $D_{hkl}$ in composite films is lower than that in
pure PHBV. This result implies that the introduction of CNWs to PHBV is deleterious for the packing of PHBV molecular chains (Zhou et al. 2011; Zhang et al. 2010). Moreover, PHBV/1.5CNW and PHBV/2CNW have the smallest $D_{hkl}$ indicating that compatibility of PHBV and CNW was improved due to better dispersion of CNW at lower contents. This conclusion is in agreement with TEM observations (Fig. 4.2) and mechanical properties assessment (Ten et al. 2010). Similar results were observed for polyethylene oxide/cellulose nanocrystals composites comprised of electrospun fibers at higher shear rates (Zhang et al. 2010).

This change in $D_{hkl}$ can also be justified by means of a nucleation. The great crystallites with bigger $D_{hkl}$ were not allowed to form by percolated CNW structure, followed by appearance of small and innumerable crystallites. However, if the nucleation is predominant phenomenon, new crystalline symmetries would be observed in XRD diffractograms, which did not occur (Fig. 4.3).

**Table 4.1** Apparent crystal size ($D_{hkl}$) of PHBV and PHBV/CNW composites.

<table>
<thead>
<tr>
<th>CNW (wt%)</th>
<th>$D_{hkl}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>32.1</td>
</tr>
<tr>
<td>1.5</td>
<td>12.85</td>
</tr>
<tr>
<td>2</td>
<td>12.86</td>
</tr>
<tr>
<td>3</td>
<td>16.1</td>
</tr>
<tr>
<td>4</td>
<td>18.4</td>
</tr>
<tr>
<td>5</td>
<td>16.1</td>
</tr>
</tbody>
</table>

**4.3.3 Isothermal crystallization kinetics of neat PHBV and PHBV/CNW composites**

The crystallization kinetics combining nucleation and growth effect can be analyzed using the Avrami equation (Avrami 1939):
\[ 1 - X_t = \exp(-kt^n); \]  
(4.4)

Or

\[
\log[-\ln(1 - X_t)] = n \log(t) + \log(k); \tag{4.5}
\]

where \( X_t \) is the relative degree of crystallinity at time \( t \), \( n \) – Avrami exponent which depends on nucleation and growth mechanisms, \( k \) – overall crystallization rate constant. Nucleation rate and spherulite linear growth rate are assumed to be constant in the equation (Lorenzo et al. 2007). Nucleation and spherulite growth are separate phenomena, but are both influenced by the same processing parameters such as temperature. Avrami exponent \( n \) is determined as the dimensionality of the growing crystals. \( X_t \) is given as:

\[
X_t = \frac{\int_0^t (dH / dt) dt}{\int_0^\infty (dH / dt) dt}; \tag{4.6}
\]

The numerator is the heat flow after time \( t \) and the denominator is the total heat flow during crystallization. Induction time \((t=0)\) was determined by a flat baseline after the initial spike on a DSC curve (Lorenzo et al. 2007).

Fig. 4.5 shows \( X_t \) as a function of the crystallization time \( t \) at different crystallization temperatures. DSC measurements at 30, 40, and 80 °C did not show any crystallization peak within the measurement periods and therefore their curves are not shown in the figure. This is most likely because that these three temperatures are out of the cold crystallization range of PHBV. It can be seen from Fig. 4.5 that CNW content had different effects on PHBV crystallization at different temperatures. For instance, at 50 °C, the sigmoidal isotherms were shifted to the left after the addition of different concentrations of CNWs, indicating faster crystallization process (Fig. 4.5a). In particular, PHBV/2.3% CNW composite crystallized 7
times faster compared to the neat PHBV (crystallization time decreased from 12 min to 1.7 min).

At $T_c = 60 \, ^\circ C$ PHBV/CNW composites (at all CNW concentrations) still crystallized faster than unfilled polymer, but their rate difference was much smaller compared to $T_c = 50 \, ^\circ C$ (Fig 4.5b).

At $T_c = 70 \, ^\circ C$, the composites containing 2.3 and 3.3% CNWs crystallized slower than did the neat PHBV. The composites containing 1.2 and 4.6 wt% CNWs still crystallized faster than did the neat polymer. It is unclear why the crystallization rate was reduced when 2.3 and 3.3% CNWs were added.

Neat PHBV had a cold crystallization temperature ($T_{cc}$) of 55 $^\circ C$ (Ten et al. 2010; Ten et al. 2011). The crystallization rate of PHBV diminished at temperatures lower or higher than this temperature. A lower-than-$T_{cc}$ temperature makes chain diffusion and folding difficult and a higher-than-$T_{cc}$ temperature reduces polymer nucleation (discussed more with POM results).

CNWs increase overall crystallization rate of PHBV by acting as a nucleation agent to increase polymer nucleation rate (Ten et al. 2010; Ten et al. 2011). Therefore at the temperatures higher than $T_{cc}$ (e.g. 60 and 70 $^\circ C$ in this study), the nucleation effect of CNWs was reduced and the overall crystallization rate at these two temperatures was less affected by CNWs than at 50$^\circ C$. 
Figure 4.5 Relative crystallinity $X_t$ versus isothermal crystallization time of PHBV and PHBV/CNW composites at crystallization temperatures: (a) 50 °C; (b) 60 °C; (c) 70 °C.

The overall crystallization rate can be calculated using the following equation:

$$G = \frac{1}{t_{0.5}};$$  \hspace{1cm} (4.7)

where the half time crystallization $t_{0.5}$ is the time when $X_t$ reaches 50%. It can be directly determined from $X_t$ data (Fig. 4.5). Fig. 4.6 shows the variation of $G$ as a function of CNW concentration. At 50 °C, $G$ increased with increasing CNW content, peaked at 2.3 wt% concentration, and started to decline afterwards. At low concentrations, CNWs provided heterogeneous nucleation sites for PHBV crystallization and therefore increased its overall crystallization rate. However, CNW agglomeration started to occur when its concentration increases reached a percolation threshold, which was determined to be 2.3% from one of our previous studies (Ten et al. 2011). This agglomeration can also be noticed from the TEM
micrographs shown in Fig. 4.2. The agglomeration essentially reduced the total surface area of CNWs and therefore reduced their nucleation ability. As a result, $G$ decreased when CNW concentration was higher than 2.3%. The reduced nucleation effect at high CNW concentration was also confirmed by POM micrographs discussed later.

It is also worth noting that the variations of $G$ at 60 and 70 °C are less dramatic compared to that at 50 °C (Fig. 4.6). Furthermore, the variation at 70 °C is even less that at 60 °C. As explained earlier, this is due to the diminishing nucleation effect of CNWs at increasing temperatures. At the same CNW concentration, $G$ is smaller at 70 °C than at 60 °C due to the same reason.

![Figure 4.6 Overall crystallization rate G of PHBV and PHBV/CNW composites at different crystallization temperatures.](image)

High crystallization rate does not necessarily mean high degree of crystallinity. The absolute degree of crystallinity of PHBV/CNWs samples can be derived from the overall heat flow of the complete crystallization process:
\[ X_c = \frac{\Delta H_c}{(1 - \phi)\Delta H_m}; \]  

(4.8)

where \( \Delta H_m \) is heat of fusion of the PHBV with 100% crystallinity (146 J/g) (Barham et al. 1984), \( \phi \) – CNW mass fraction in PHBV/CNW composites, \( \Delta H_c \) – heat of fusion of the sample. Fig. 4.7 displays the dependence of \( X_c \) on CNW concentration for the neat PHBV and PHBV/CNW composites at different crystallization temperatures. Overall, the crystallinity increases with increasing crystallization temperature, which is opposite to the trend of the crystallization rate shown in Fig. 4.6. The high crystallization rate at 50 °C was the result of the strong nucleation effect of CNWs. However, this temperature is not ideal for spherulite growth. The spherulites produced at this low temperature could be defect-ridden with low laminar thickness due to slow PHBV chain diffusion. This type of spherulites exhibited low heat of fusion and hence the samples showed low \( X_c \). On the contrary, although higher temperatures (i.e. 60 and 70 °C) resulted in decreased CNW nucleation effect and lower crystallization rate, large spherulites with more perfect structures could be obtained (within a longer period of time compared to at 50 °C) due to higher level of chain mobility. These spherulites had high heat of fusion and therefore a high sample \( X_c \) was resulted.

At 50 °C, \( X_c \) is the lowest whereas \( G \) is the highest at 2.3 wt% CNWs. CNWs can restrict PHBV chain mobility through its interfacial interactions with the polymer. This confinement effect has been demonstrated by low frequency solid-like behavior in rheological tests and broadened relaxation peaks and increased moduli at high temperatures in DMA tests (Ten et al. 2011). Especially, the confinement effect peaks at CNW 2.3% and decreases at higher concentrations due to CNW agglomeration. The confinement can hinder the diffusion of polymer chains into crystalline lattice and hence slowdown the growth of PHBV spherulites. Therefore, the nucleation and confinement effects of CNWs are two competing factors contributing to
PHBV crystallization. Crystallization rate is more controlled by the nucleation effect whereas crystallinity is more affected by the confinement effect. When the CNW concentration was lower than 2.3%, the increasing concentration resulted in declining sample crystallinity because of the increasing confinement effect. Above 2.3%, the confinement effect was reduced due to CNW agglomeration. Therefore the sample’s crystallinity increased again. The confinement effect on spherulite growth was further discussed together with POM observations.

Avrami plots for the PHBV/CNWs samples at different crystallization temperatures are shown in Fig. 4.8. Avrami exponent \( n \) and overall crystallization rate constant \( k \) can be deduced from the slope and the intercept of the lines, respectively. The obtained values are listed in Table 4.2.
Figure 4.8 Avrami plots of PHBV and PHBV/CNW composites crystallized at 50 (a), 60 (b), and 70 (c) °C.

Avrami exponent $n$ varied from 2.24 to 2.89 depending upon CNW concentration and crystallization temperature (Table 4.2). For predetermined (i.e. nucleation agent added) three dimensional crystallization a theoretical value of 3 should be obtained for $n$. The lower-than-3 $n$ values in the table could be due to mixed sporadic and predetermined crystallization and/or mixed 3-D and 2-D crystallization (because the samples were confined between two glass slides).

The crystallization rate parameter $k$ increased with decreasing crystallization temperature for all formulations studied (Table 4.2). This trend is in agreement with the overall crystallization trend shown in Fig. 4.6. At the same crystallization temperature, $k$ first increased with CNW concentration until it reached 2.3 wt% and then decreased due to CNW agglomeration at higher concentrations (reduced nucleation sites). The same result was reported for multi-walled carbon nanotubes (MWNT)/Nylon 66 composites by Li et al. (Li et al. 2007).
4.3.4 Spherulitic growth rate and nucleation density

Isothermal crystallization behaviors of PHBV and PHBV/CNW composites at 50, 60 and 70 °C were also studied by direct polarized optical microscopy (POM) observation. PHBV spherulites with characteristic Maltese cross could be clearly seen under POM (Fig. 4.9). For neat PHBV, the number of spherulites was small and their size was relatively large because there was ample space for them to grow before impinging onto each other (Fig. 4.9a). However, with the addition of just 1.2% CNWs, the number of PHBV spherulites increased significantly and consequently their size was dramatically reduced (Fig. 4.9b). The micrograph for 2.3% CNWs shows the highest spherulite density and the smallest spherulite size among all the concentrations. These POM observations clearly suggested the strong nucleation effect of CNWs. Moreover, at 3.3% and 4.6% CNW concentrations, the spherulite density decreased and the spherulite size increased (Fig. 4.9d and e), an indication of CNW agglomeration which caused reduced nucleation sites and increased chain diffusion. The POM micrographs taken at 60 and 70 °C (picture not shown) exhibited larger spherulites compared to at 50 °C over the same crystallization time, indicating larger spherulite growth rate at higher temperatures.

Nucleation effect of CNWs can be evaluated based on spherulitic growth rate analysis and nucleation density estimation. The spherulite growth rate $G_s$ can be determined from time-resolved optical micrographs. The radius of spherulites grew linearly with time for all the formulations under three isothermal temperatures. This linearity of spherulite radius $R$ suggested that cellulose nanowhiskers did not accumulate at crystal growth fronts but were trapped in the interlamellar regions of the PHBV spherulites (Chiu 2002).
The spherulite growth rate $G_s$ can be determined from the slopes of these spherulite radii vs. time lines. $G_s$ for all the samples are compared in Fig. 4.10. The growth rate showed the same trend at all crystallization temperatures, i.e. $G_s$ first decreased with increasing CNW concentration and then increased with the concentration. Similar results were reported for multi-wall carbon nanotubes/isotactic polypropylene composites (Xu and Wang 2008).

## Table 4.2 Kinetic parameters for isothermal crystallization of PHBV and PHBV/CNW composites crystalized at 50, 60, and 70°C.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>CNW (wt%)</th>
<th>$n$</th>
<th>$k \times 10^4$ (min$^{-n}$)</th>
<th>$t_{0.5}$ (min)</th>
<th>$X_c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0</td>
<td>2.24 ± 0.1</td>
<td>8.13</td>
<td>4.12</td>
<td>36.89</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>2.40 ± 0.1</td>
<td>13.29</td>
<td>1.97</td>
<td>28.39</td>
</tr>
<tr>
<td></td>
<td>2.3</td>
<td>2.59 ± 0.09</td>
<td>97.94</td>
<td>0.89</td>
<td>22.46</td>
</tr>
<tr>
<td></td>
<td>3.3</td>
<td>2.42 ± 0.01</td>
<td>59.44</td>
<td>1.07</td>
<td>26.58</td>
</tr>
<tr>
<td></td>
<td>4.6</td>
<td>2.29 ± 0.05</td>
<td>125.01</td>
<td>1.27</td>
<td>33.23</td>
</tr>
<tr>
<td>60</td>
<td>0</td>
<td>2.74 ± 0.04</td>
<td>10.53</td>
<td>3.72</td>
<td>40.24</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>2.67 ± 0.07</td>
<td>24.91</td>
<td>1.85</td>
<td>34.58</td>
</tr>
<tr>
<td></td>
<td>2.3</td>
<td>2.85 ± 0.13</td>
<td>8.51</td>
<td>1.49</td>
<td>33.58</td>
</tr>
<tr>
<td></td>
<td>3.3</td>
<td>2.67 ± 0.18</td>
<td>11.14</td>
<td>1.62</td>
<td>36.44</td>
</tr>
<tr>
<td></td>
<td>4.6</td>
<td>2.62 ± 0.06</td>
<td>16.42</td>
<td>1.84</td>
<td>37.60</td>
</tr>
<tr>
<td>70</td>
<td>0</td>
<td>2.73 ± 0.46</td>
<td>2.26</td>
<td>2.0</td>
<td>51.18</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>2.62 ± 0.13</td>
<td>1.78</td>
<td>1.44</td>
<td>41.77</td>
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<tr>
<td></td>
<td>2.3</td>
<td>2.89 ± 0.05</td>
<td>0.99</td>
<td>2.12</td>
<td>43.94</td>
</tr>
<tr>
<td></td>
<td>3.3</td>
<td>2.50 ± 0.14</td>
<td>1.44</td>
<td>2.04</td>
<td>49.30</td>
</tr>
<tr>
<td></td>
<td>4.6</td>
<td>2.42 ± 0.15</td>
<td>4.22</td>
<td>1.73</td>
<td>47.11</td>
</tr>
</tbody>
</table>
Figure 4.9 POM images of isothermal crystallization of neat PHBV (a); PHBV/1.2%CNW (b); PHBV/2.3%CNW (c); PHBV3.3%CNW (d); PHBV/4.6%CNW (e) at 50 °C. Elapsed time is 2 min. Scale bar is 20 um.
Figure 4.10 Spherulitic growth rate of PHBV and PHBV/CNW composites at 50, 60 and 70 °C isothermal crystallization temperatures.

As it was explained before, the decrease was due to the confinement effect of CNWs, which hindered chain diffusion and folding into crystalline lattice. CNW agglomeration at high concentrations essentially reduced the total surface area of CNWs and allowed larger degree of mobility of PHBV chains. This resulted in the increase in $G_s$.

Fig. 4.10 also shows that $G_s$ increases with temperature. This was because PHBV chains diffused faster at high temperatures. More polymer chains were able to configure themselves into the crystalline lattice of the spherulite growth front per unit time, leading to higher spherulite growth rate.

The nucleation effect of CNWs was further confirmed by calculating nucleation density from the POM micrographs. The number of heterogeneous nuclei or the primary nucleation density $N$
can be roughly estimated based on maximum radius of the spherulites before impingement $R_m$ (Maiti et al. 2002; Nam et al. 2003):

$$N = \frac{3}{4} \pi R_m^{-3};$$  \hspace{1cm} (4.9)

Fig. 4.11 shows the variation of $N$ under different conditions. It is evident that the nucleation effect of CNWs is most prominent at 50 °C and $N$ peaks at 2.3% CNW. The nucleation density for PHBV/2.3wt%CNWs is 2800 times higher compared to that of the neat PHBV. The nucleation density rebounded at 4.6% for all three temperatures. This was probably due to the wide size distribution of the spherulites as shown in Fig. 4.9e, which in turn was attributed to highly uneven distribution of CNWs at high concentrations.

The change in nucleation density has a potential influence on mechanical performance improvement at CNW content $\geq$ 2.3wt% due to refined structure of PHBV (Ten et al. 2010). On the other hand, the reduction of degree of crystallinity will typically reduce mechanical properties of composites, but for PHBV/CNW composites, $E'$, in fact, increased indicating that change in nucleation ability and crystalline structure of PHBV was not the main reason for $E'$ improvement. Therefore, it is reasonable to believe that CNW homogeneous distribution and interconnected 3-D structure governed $E'$ enhancement.
Figure 4.11 Nucleation density of PHBV and PHBV/CNW composites at 50, 60, 70 °C isothermal crystallization temperatures.

4.4 Conclusions

This study investigated the effects of CNWs on the crystallization of PHBV under different crystallization temperatures and CNW concentrations. Crystallization kinetics was studied using DSC and POM. The changes in crystalline structure of PHBV with CNWs were investigated by XRD. Avrami theory was used to analyze isothermal crystallization of PHBV. The results suggested that CNW content and isothermal crystallization temperature could significantly alter crystallization kinetics of PHBV. CNWs influenced PHBV crystallization through two aspects: nucleation and spherulite growth. CNWs increased PHBV crystallization rate by promoting heterogeneous nucleation when CNWs were homogeneously dispersed in the PHBV matrix (CNW content < 2.3%). The crystallization rate started to decrease when CNW agglomeration occurred. High crystallization rate did not always lead to high degree of crystallinity. The calculation of crystallization rate was based on the first half (t₀.5) of the whole crystallization
process, where nucleation played a major role. The results derived from DSC tests were confirmed by the spherulite growth rate and nucleation density calculated based on POM studies. Although the effect of CNW on nucleation ability and degree of crystallinity of PHBV is significant and can contribute to the mechanical properties improvement, the results of this study confirmed that mainly CNW homogeneous distribution and interconnected 3-D structure governed E' enhancement.

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Weihua K, Yong H, Yoshio I. “Fast Crystallization of Poly(3-hydroxybutyrate) and Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) with Talc and Boron Nitride as Nucleating


Chapter 5 Fabrication and mechanical properties of aligned Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)/Cellulose Nanowhiskers composites

Abstract

In this study, biodegradable unidirectional reinforced nanocomposites were developed. The objectives of this study were to align cellulose nanowhiskers (CNW) in Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) matrix under external electric field and evaluate the mechanical performance of these anisotropic reinforced composites. PHBV films with 1.5-7 wt% of cellulose nanowhiskers were manufactured by solution casting method using N,N-dimethylformide (DMF) as a solvent. To align CNW in PHBV/DMF solution a DC electric field of 56.25 kV/m was applied. The solvent was evaporated for simultaneous formation of aligned composites. Both microstructural and mechanical analyses confirmed that the electric field was effective to align CNW up to 4 wt%. Samples were tested at 0, 15, 30, 45 and 90° with respect to electric field direction by a dynamic mechanical analyzer (DMA). DMA results showed that CNW concentration has a main influence on efficiency of CNW alignment by the external electric field. E’ in longitudinal vs. transverse direction increased by 49 % and 39 % for 1.5 and 3 wt% of CNW, respectively. Samples with 5-7 wt% CNW revealed isotropic behavior, due to significantly improved viscosity of PHBV/CNW suspensions that confined CNW mobility. Rheological study confirmed this conclusion.
5.1 Introduction

Polyhydroxyalkanoates (PHAs) are a family of biodegradable polyesters produced by bacteria as carbon and energy storage through natural biosynthesis (Ballard 1987). PHAs show mechanical performance and glass transition temperature comparable to some petroleum-based commodity polymers such as isotactic polypropylene (Pirrotta 1993). Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) is a copolymer of hydroxybuterate and hydroxyvalerate (HV) and is a representative polymer from PHA family. The incorporation of HV increases the toughness of pure PHB by reducing its crystallization.

Nanofillers are found to be preferential for PHBV reinforcement due to their high surface area, low concentration requirement, and the ability to improve toughness along with strength and stiffness. Cellulose nanowhiskers (CNWs) have received much attention for their abundance, biodegradability, biocompatibility and excellent reinforcement ability. CNWs are needle-like elementary crystallites which occur naturally in the cell walls of many plants and some sea animals (e.g. tunicin). Depending upon sources and isolation methods, CNWs exhibit a high Young’s modulus of 57-143 GPa (Rusli and Eichhorn 2008; Sakurada et al. 1962; Matsuo et al. 1990; Stucova et al. 2005; Bondeson et al. 2006) and a typical length and diameter of 200-400 nm and <10 nm, respectively (Bondeson et al. 2006). Such properties enable CNWs, when homogeneously dispersed in a polymer matrix, to carry a significant percentage of the applied load. Due to the environmental benign nature and biocompatibility of both PHBV and CNWs, PHBV/CNW composites have the potential to be used for, packaging materials and medical and pharmaceutical devices.

We have systematically studied the preparation and properties of PHBV/CNW composites (Jiang et al. 2008; Ten et al. 2010; Ten et al. 2011a; Ten et al. 2011b). Our results showed that
PHBV samples reinforced with homogeneously distributed CNWs could be prepared by solution casting (Jiang et al. 2008). Significant improvements in tensile strength, Young’s modulus, toughness, dynamic modulus were observed. (Ten et al. 2010). Thermal, and electrical properties exhibited sudden transitions at 2.3-2.9 wt% CNW concentrations due to the change in CNW dispersion state. (Ten et al. 2011a). We have also shown that CNWs play an important role in PHBV crystallization (Ten et al. 2010; Ten et al. 2011a). Depending on its concentration, CNWs could either improve heterogeneous nucleation of PHBV (at low CNW concentrations) or hinder its spherulite growth rate (at high CNW concentrations) (Ten et al. 2011b).

Fiber composites often show better properties in the direction of fiber orientation. Developing unidirectional fiber composites/plies is useful to the production of fiber composites/laminates for performance demanding applications. Ultimately, highly reinforced composites can be manufactured by constructing several layers of unidirectional reinforced films alternating orientations. Based on reported literatures, there is an ever-increasing interest to consolidate CNW use in “smart” packaging, drug delivery, biosensors, tissue engineering, inks for security paper, and structural composite platforms. For most of the potential applications the ability to orient nanowhiskers and further development of relevant fabrication method of unidirectional composites are of fundamental importance.

Attempts have been made to produce oriented CNW fiber composites. Three methods have been noted from the literature to align CNW fibers, including applying mechanical forces (shearing and spin coating) (Cranston and Gray 2008; Edgar and Gray 2003; Nishiyama et al. 1997), magnetic force (Sugiyama et al. 1992; Cranston and Gray 2006; Kvien and Oksman 2007; Kimura et al. 2005; Li et al. 2010) and electric force (Bordel et al. 2006; Habibi et al. 2008). CNWs were oriented radially in layer-by-layer (LbL) self-assembled polyelectrolyte multilayer
films prepared by spin-coating (Cranston and Gray 2008). Linearly oriented films were also obtained by shearing a drop of concentrated aqueous nanocrystal suspension along mica or polystyrene surfaces (Edgar and Gray 2003). In another study (Nishiyama et al. 1997), a vial containing aqueous CNW suspension was kept in a horizontal position. The vial was rotated around its axis at 500 rpm at room temperature. The resulting film was found to be highly anisotropic and brittle in the direction perpendicular to the fiber orientation.

Magnetic fields have been reported to produce good CNW orientations. Sugiyama et al. aligned CNWs using rather moderate magnetic field of 7 T (Sugiyama et al. 1992). Later, preliminary experiments relevant to layer-by-layer self-assembly of oriented cellulose nanocrystals were performed also in a 7 T magnetic field (Cranston and Gray 2006). First attempt to orient CNWs in polymeric matrix was reported by Kvien et al. (Kvien and Oksman 2007). CNWs (2 wt%) were incorporated in a polyvinyl alcohol matrix using solution casting with water as the solvent. The water evaporated while a ~7 T homogeneous magnetic field was applied. Dynamic mechanical thermal analysis (DMTA) showed that the dynamic modulus of the nanocomposite was ~47% higher in the transverse direction than in the field direction, an indication of CNW orientation in the transverse direction (Kvien and Oksman 2007). Previously, it was explained that the diamagnetic susceptibility of the nanowhiskers in the direction of the whisker axis was smaller than in the direction perpendicular to the whisker axis and the helical axis of nematic phase of CNW aqueous suspension aligned along the applied field. Since the helical axis coincided with the direction normal to the CNW axis and the helical axis aligned parallel to the applied field, therefore, the whiskers would align perpendicular to the magnetic field (Kimura et al. 2005).

Applying electric field is another alternative to align CNWs. Most studies on the orientation
of suspended particles in an electric field have dealt with aqueous suspensions, which exhibit limitations arising mainly from the high conductivity of water. Bordel et al. successfully demonstrated for the first time the ability to align ramie cellulose fibers at macroscopic and colloidal levels when they are dispersed in apolar organic solvents (Bordel et al. 2006). However, this pioneer study did not investigate the effects of the electric field (frequency and amplitude) on the fiber orientation. Recently, Habibi et al. reported a highly reproducible, efficient and quick method to create anisotropic films from aqueous suspensions of tunicate and ramie CNW. A high percentage of fiber orientation was observed under the electric field of 2 kV/cm and higher (Habibi et al. 2008).

Literature study has shown that the development of oriented CNW composites is still in its early stage. Producing polymer/CNWs nanocomposites with desirable polymer matrix material and CNW orientations remains a technical and scientific challenge. In this study, we developed a method to prepare PHBV/CNWs nanocomposite with unidirectional CNW orientation. The effects of CNW content and orientation angle on the dynamic mechanical properties of the composites were evaluated. This study provided a new anisotropic CNW-reinforced biodegradable composite and it may find useful applications in many areas.

5.2 Experimental Section

5.2.1 Materials

PHBV with 12 mol-% content of hydroxyvalerate (HV) was supplied by Metabolix Inc. N, N-dimethylformamide (DMF) and NaOH were purchased from Acros Organics (Atlanta, GA). Microcrystalline cellulose (MCC) was obtained from Avicel (Type PH-102). Sulfuric acid (96 wt%) was purchased from J.T. Baker. PHBV was dried at 80°C in a convection oven overnight prior to use.
5.2.2 CNW preparation

Sulfuric acid was diluted to 64 wt% concentration. MCC (1 g per 9.8 ml of the acid) was added and vigorously stirred at 44 °C for 2 hours. Then the suspension was diluted to about one tenth of its original acid concentration. The acid in the solution was removed by repeated centrifugation (Sorvall, 5000 rpm for 5-min) until the supernatant was turbid. The supernatant (CNW suspension) was collected and dialyzed against deionized water for 4-5 days to remove remaining acid (dialysis tube from Spectrum Laboratories Inc., cutoff molecular weight 12000-14000). After the CNW suspension reached a constant PH value, it was removed from the dialysis tubes and neutralized with 1 wt% NaOH solution. The neutralized suspension was condensed at 80 °C using a Büchi Rotavapor (R-200) until the CNW concentration reached 2 wt%.

5.2.3 Preparation of aligned PHBV/CNW nanocomposites

Various amount of condensed CNW suspension was added drop-wise into 40 ml of DMF under continuous stirring. Water was evaporated from the mixture at 80 °C for an hour (DMF boiling temperature 153 °C) to obtain CNW/DMF suspension. Depending on the desired CNW content in the final PHBV/CNWs composites, different amount of PHBV were dissolved in the suspension under continuous stirring. The dispersion of CNWs in the suspension was improved by sonication for 5 minutes. The solution was cast on a clean glass substrate (9x9 cm²) which was placed between two electrodes separated by a distance of 10 cm (Fig. 5.1). A 9 kV voltage was applied on the electrodes, which resulted in a maximum electric field of 56.25 kV/m (9 kV/0.16 m) between the electrodes. It is worth noting that the dielectric constant of DMF is high (ε = 36.7 at 25 °C). Therefore, the actual magnitude of the electric field was lower within the volume of DMF. The suspension on the glass substrate was heated with a lamp to accelerate
DMF evaporation. The temperature under the light was 80 °C. Both the electric field and the light were applied continuously until the film was completely dry. The final PHBV/CNW films were transparent (Fig. 5.2) with a thickness of 15-30 microns. DMF content of the obtained films was measured to be less than 2 wt% through vacuum drying.

**Figure 5.1** Experimental set-up used to prepare unidirectional PHBV/CNW composite film using electric field.

**Figure 5.2** Photographs of PHBV/CNW composite films: a – neat PHBV; b – PHBV/3%CNW; c – PHBV/7%CNW.
5.2.4 Characterization

5.2.4.1 Atomic force microscopy (AFM)

Morphology of CNWs was investigated using AFM. The tests were performed in tapping mode using a Veeco Multimode AFM equipped with a NanoScope IIIa controller (Digital Instruments Inc.). Prior to the test, a drop of CNW suspension in water was deposited on freshly cleaved mica surfaces. The solution was completely dried by natural evaporation. The dried sample was scanned in air using Si tips (Digital Instruments Inc.) with a resonance frequency of ca. 330 kHz. The scan rate was 0.5 Hz.

5.2.4.2 Transmission electron microscopy (TEM)

The shape and size of CNWs were also studied using a Philips CM-200 TEM operating at 200 kV. Similar to the sample preparation method used for AFM, a drop of CNW water suspension was introduced on a formvar-coated nickel grid (300 mesh), rinsed with double-deionized water and dried naturally. TEM images of CNWs were acquired without any sample staining.

To study the morphology of the composite films, small pieces of PHBV/CNW films were embedded in acrylic resin (London Resin Company Ltd.) and cured at elevated temperature overnight. Thin sections (~ 50 nm) of the films were cut in the direction parallel to the film surface using a Reichert-Jung ultramicrotome. The sections were placed on formvar-coated nickel grids and then stained with 2% uranyl acetate for 90 minutes.

5.2.4.3 X-ray diffraction (XRD)

Powder X-ray diffraction (XRD) was performed in reflection mode on a Phillips X’Pert diffractometer with an X’celerator detector using Ni-filtered CuKα radiation (λ = 1.5418 Å). The PHBV/CNW films were examined in the range of 2θ = 10°-35° at 45 kV tension and 40 mA
current at ambient temperature. XRD data was collected with a step size of 0.02° and count time of 50 sec per point. A polycarbonate sample holder was used to avoid any peak overlap associated with the holder material. The samples were installed so that the incident beam was aligned parallel and normal to the CNW orientation.

5.2.4.4 Dynamic Mechanical Analysis (DMA)

DMA was conducted in tension mode on a Tritec 2000 DMA at 1 Hz to examine thermal dynamic properties of the films. DMA samples (10 x 6.5 mm²) were cut from the PHBV/CNW composite film. Dynamic strain sweep was first performed to determine linear viscoelastic range of the samples. Then the samples were tested from -40 °C to +80 °C at 5 °C/min heating rate with a strain of 0.02%. To study the effect of fiber orientation angle θ (Fig. 5.3) on the storage modulus of the composites, the samples were cut at 0, 15, 30, 45 90 ° with respect to the direction of the applied electric field. Ten replicates were tested for each orientation angle θ. The storage moduli E’ of the samples were compared at temperatures below (-20 °C) and above (60 °C) the glass transition temperature T_g of PHBV (ca. 25 °C).

![Figure 5.3](image)

Figure 5.3 Explanation of material coordinates as compared to composite coordinates. E – electric field (kV/m); θ – orientation angle (°).

5.2.4.5 Rheology test

A strain-controlled rheometer (RDA III, Rheometric Scientific) was used to measure dynamic rheological properties and viscosity of PHBV/CNW composites. The measurements
were performed at 175 °C using a parallel plate geometry (25 mm diameter). The gap between the two plates was 0.5 mm. PHBV/CNW films were stacked and melted at 175 °C in the geometry. Care was taken to make sure there were no air bubbles in the sample melt. A strain sweep test was first performed to determine the linear viscoelastic region of the composites and a shear strain of 0.6% was chosen for all subsequent frequency sweep tests. The frequency was varied from 1 to 500 rad/s.

5.3 Results and Discussions

5.3.1 Morphology of CNWs

The morphology of CNWs is shown in TEM and AFM micrographs (Fig. 5.4). Individual nanowhiskers can be seen from TEM image (Fig. 5.4a). The concentration of the CNWs in the AFM micrographs appears much higher than in the TEM because of their different sample preparation methods. In TEM the nickel grid was rinsed by trickling deionized water over the grid after an initial drop of CNW suspension was deposited. This operation reduced CNW concentration significantly and allowed the imaging of individual CNWs. Thus, CNW dimensions were calculated based on TEM micrographs. The aspect ratio of the nanowhiskers was determined based on the measurement of 300 individual whiskers using ImageJ software (National Institute of Health). An average diameter d of CNW determined from micrographs of isolated CNW after water evaporation (described in section 5.2.4.2) was 12.32±4.0 nm which is close to d determined from composites 12.34±3.7 nm. This result implies that nanowhiskers were homogeneously dispersed and existed as individual nanofibers in PHBV. The aspect ratio (L/d) of CNWs was fitted to a probability density function (pdf) of the two-parameter Weibull distribution (Fig. 5.5). The Weibull distribution is a probabilistic model that allows describing the size distribution of particles (Rosin and Rammler 1933).
Figure 5.4 Morphology of CNWs: (a) TEM micrograph; (b) AFM topography; (c) AFM phase image.

The probability density function (pdf) can be described as:

\[
f(x) = \frac{\beta}{\alpha} \left( \frac{x}{\alpha} \right)^{\beta-1} e^{-\left( \frac{x}{\alpha} \right)^{\beta}};
\]  

(5.1)
where $\alpha$ and $\beta$ are scale and shape parameters, respectively. Both $\alpha$ and $\beta$ are positive numbers. The closed form solution to the pdf is shown in Equation 2 as the cumulative distribution function (cdf) (Law and Kelton 1982).

$$
cdf = 1 - e^{-\left(\frac{x}{\alpha}\right)^\beta}; \text{ if } x > 0;$$

Weibull distribution was plotted to fit experimental CNW aspect ratio distribution. $\alpha = 20.26$ and $\beta = 2.04$ were obtained under the condition of $R^2 = 0.947$. Therefore, the CNW aspect ratio distribution can be described as:

$$
f(x) = \frac{2.04}{20.26} \left(\frac{x}{20.26}\right)^{1.04} e^{-\left(\frac{x}{20.26}\right)^{2.04}};$$

The average $\left(\frac{L}{d}\right)$ value can be determined as:

$$
E(x) = \alpha \Gamma \left(1 + \frac{1}{\beta}\right) = 17.95;$$

**Figure 5.5** CNW aspect ratio distribution fitted with the Weibull probability density function.
The experimental average aspect ratio, taken as the mean value of measured CNW, is 18.01±7.5, which is close to the predicted value of 17.95. Thus, it can be concluded that the aspect ratio distribution of CNWs can be described by a two-parameter Weibull distribution.

5.3.2 Microstructure of aligned PHBV/CNW composites by TEM

The alignment of CNWs in the PHBV matrix was studied using TEM (Fig. 5.6). It can be seen that for the samples with low CNW concentrations, i.e. 1.5% and 2% (Fig. 5.6 a,b), CNWs were aligned along the direction of the applied electric field. Because of the structural anisotropy of CNWs, the dipole moment of the CNWs in the axial direction is stronger than that in the transverse direction. Therefore, cellulose nanowhiskers could be aligned along the direction of the electric field if the alignment is not hindered by its surrounding environment. At high CNW concentrations, the micrographs do not show preferential fiber orientation (Fig. 5.6 c-g). Although in these situations there were still similar levels of field-induced dipolar interactions in the CNWs, the orientation of the fibers was restrained presumably due to strong fiber-fiber and fiber-matrix interactions at high fiber concentrations. The presumption was confirmed by rheological and dynamic mechanical tests on the samples containing 0-7wt% CNWs.
Figure 5.6 TEM images of PHBV/CNW composites: a – PHBV/1.5CNW; b – PHBV/2CNW; c – PHBV/3CNW; d – PHBV/4CNW; e – PHBV/5CNW; f – PHBV/6CNW; g – PHBV/7CNW. Scale bars represent 200 nm. Arrows show the direction of applied electric field.
5.3.3 XRD analysis of PHBV/CNW composites

X-ray diffraction 1-D patterns of the neat PHBV and PHBV/CNW composite films with random CNW orientation were introduced and analyzed in Chapter 4. The effect of CNW on crystalline structure of PHBV was evaluated as well.

Effect of CNW orientation was also evaluated by XRD. PHBV films with aligned CNW were scanned parallel and perpendicular to the incident beam. The intensity for the (200) reflection was used to assess the effect of applied electric field to orient CNWs (Sugiyama et al. 1991). A sharp peak with high intensity indicates high degree of alignment, while a broad distribution represents the opposite. The full width at half-maximum (FWHM or $\beta^{1/2}$) which is an inverse relation with alignment was measured for each formulation (Urena-Benavides and Kitchens 2011). The results are shown in Fig. 5.7. A distinct anisotropic behavior demonstrated by higher degree of order of CNW in the direction of applied electric field.

The observed behavior is most prominent for nanocomposites with CNWs content < 4wt%. The highest degree of orientation showed composites with 2 and 3wt% of CNWs. With increased CNW load, nanocomposites revealed reduced degree of orientation of CNW. This result confirmed our hypothesis that CNW alignment in PHBV/CNW composites at high CNW concentration becomes restrained due to fiber-fiber and fiber-matrix interactions.

5.3.4 Melt viscosity of PHBV/CNW composites

Fig. 5.8 shows the complex viscosity ($\eta^*$) of the samples plotted as a function of frequency. $\eta^*$ increased with the increasing CNW content within the whole frequency range (1-500 rad/s). The increase was especially significant in the terminal zone (low frequency zone) (Fig. 5.10). In this region, the neat PHBV showed a Newtonian plateau – a constant viscosity regardless of the frequency.
Figure 5.7 Effect of CNW content on the inverse of the full width at half-maximum (FWHM).

The plateau disappeared even when a minimum content of CNWs (1.5 wt%) was added. All the PHBV/CNW samples displayed a significant shear-thinning behavior in the terminal zone. In this region, the neat PHBV showed a Newtonian plateau – a constant viscosity regardless of the frequency. The plateau disappeared even when the smallest content of CNWs (1.5 wt%) were added. Fiber-fiber and fiber-matrix interactions played influential roles in PHBV chain mobility. Chain movements were refrained under these interactions and chain relaxation was hindered. Physical network structure could be formed under the influence of these interactions and the progressive destruction of the structure with increasing shear rate led to the shear thinning behavior in the terminal zone.

Within the terminal (low frequency) zone, polymer melts should be fully relaxed and follow the characteristic power laws for frequency dependence of the shear storage, loss moduli and complex viscosity: \( G' \sim \omega^2; \; G'' \sim \omega^1 \) and \( \eta^* \sim 1/\omega \sim \omega^{-1} \). The PHBV/CNW melts with high
concentration of CNW demonstrated a typical liquid-like behavior that logarithmic complex viscosity ($\eta^*$) versus logarithmic angular frequency ($\omega$) showed a smooth linear relationship with slopes of -0.877 (PHBV/5CNW); -0.876 (PHBV/4CNW); -0.737 (PHBV/3CNW); -0.728 (PHBV/2CNW); -0.507 (PHBV/1.5CNW), -0.201 (pure PHBV) (Fig. 5.8).

**Figure 5.8** Complex viscosity $\eta^*$ vs. angular frequency of PHBV/CNW composites.

Fig. 5.8 also shows that the addition of 5 wt% of cellulose crystals was sufficient to increase the low-frequency viscosity to a value about ca. 42 times higher than that of the neat polymer. This is a clear indication of the non-Newtonian behavior introduced by the presence of the nanowhiskers. These observations are consistent with a system of percolating cellulose nanowhiskers for various polymers. The increase in melt viscosity appears to be commonly observed in both thermoplastics and thermosets based cellulosic nanocomposites (Dubief *et al.* 1998; Habibi and Dufresne 1998; Marcovich *et al.* 2006; Mabrouk *et al.* 2011). On the other
hand, Marcovich et al. mentioned that the shear thinning behavior observed at high frequencies or covering the entire range of frequencies for the cellulosic nanocomposites might be the result of the alignment of the crystals under flow (Marcovich et al. 2006). This observation was first described for cellulose aqueous suspensions (Ebeling et al. 1999; Azizi Samir et al. 2004).

Furthermore, complex viscosity $\eta^*$ determined at 1.5 rad/s for PHBV composites showed non-linear dependence with CNW concentrations (Fig. 5.9). It is evident that the sample viscosities increased with increasing CNW concentration. This effect indicates the correlation with TEM microstructural study; specifically, composites with CNW content higher than 3 wt% showed significantly improved complex viscosity indicating CNW percolation. The complex viscosity $\eta^*$ of PHBV/4CNW was more than 1.67-fold larger than that for PHBV/3CNW composites (Fig. 5.9).

**Figure 5.9** The effect of CNW concentration on complex viscosity $\eta^*$ of PHBV/CNW composites at $\omega = 1.5$ rad/s.
5.3.5 Dynamic mechanical properties of aligned PHBV/CNW composites

The dynamical mechanical properties of the nanocomposites were measured at $\theta = 0$, 15, 30, 45 and 90° with respect to the direction of the applied electric field. Representative curves of the storage modulus $E'$ as a function of temperature for the oriented PHBV/1.5%CNW samples tested at longitudinal ($\theta = 0$°) and transverse directions ($\theta = 90$°) and a non-oriented control sample (random CNW orientation) are compared in Fig. 5.10. The control sample was prepared under the same condition as the oriented samples except that no electric field was applied. The decrease of $E'$ between 5 to 60 °C corresponded to the glass transition of PHBV. The large difference of $E'$ in the longitudinal and transverse directions indicated high anisotropy of the aligned films. For instance, $E'$ in the longitudinal direction was 58% higher than that in the transverse direction at -10 °C and 49% higher at 60 °C. $E'$ in the transverse direction was almost identical to that of the randomly oriented sample (RO), suggesting no reinforcement in the transverse direction.

To understand the effects of CNW concentration and orientation angle on the dynamic mechanical properties of the films, $E'$ of all the samples were compared in Fig. 5.11 at -20 and 60 °C, the temperature blow and above the glass transition temperature of PHBV, respectively. The degree of anisotropy was calculated as difference between storage moduli in longitudinal ($\theta = 0^\circ$) and transverse directions ($\theta = 90^\circ$) using equation (8):

$$Degree\ of\ anisotropy = \frac{E'_{\theta=0} - E'_{\theta=90}}{E'_{\theta=90}} \times 100\%;$$

(5.5)
Figure 5.10 Storage modulus as a function of temperature of neat PHBV, randomly oriented (RO) PHBV/CNW, and aligned PHBV/CNW. CNW content: 1.5%.

Table 5.1 Effect of CNW concentration and orientation angle θ on storage moduli E' of PHBV/CNW composites determined at 60 °C.

<table>
<thead>
<tr>
<th>CNW (wt%)</th>
<th>Degree of anisotropy (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-20 °C</td>
</tr>
<tr>
<td>1.5</td>
<td>32.6</td>
</tr>
<tr>
<td>2</td>
<td>33.2</td>
</tr>
<tr>
<td>3</td>
<td>23.5</td>
</tr>
<tr>
<td>4</td>
<td>18.0</td>
</tr>
<tr>
<td>5</td>
<td>1.5</td>
</tr>
<tr>
<td>6</td>
<td>5.9</td>
</tr>
<tr>
<td>7</td>
<td>12.0</td>
</tr>
</tbody>
</table>
As shown in Table 5.1, electric field was effective to align nanowhiskers for CNW concentrations below 4 wt%. In addition, with increasing amount of CNW, the degree of anisotropy reduces which is consistent with the increased complex viscosity confining CNW movement at CNW > 3wt% (discussed above). For composite films with 5, 6 and 7 wt% CNW dynamic mechanical properties have not changed significantly with orientation angle indicating virtually isotropic behavior (Table 5.1).

In order to assess efficiency of improving mechanical properties by CNW alignment, the reinforcing effect of aligned composites was compared to that of randomly oriented samples (RO). The overall trend of E' dependence on CNW concentrations for composites prepared without applying electric field is present in Fig. 5.12. The CNW content ranges from 0 to 7 wt%.
Figure 5.11 Effects of the CNW orientation and concentration on the storage moduli $E'$ at (a) -20 °C and (b) 60 °C.

As it was stated previously (Ten et al. 2011a), the main mechanism responsible for reinforcing effect of CNW in PHBV is based on percolation theory (Stauffer and Aharony 1992). In particular, percolation is a statistical geometrical model that can be applied to any random multiphase material involving components that are able to commingle (Stauffer and Aharony 1992). By variation of the number of connections, this approach allows for a transition from a disconnected set of objects to an infinite connected state. The percolation threshold $\upsilon_{RC}$ is defined as the critical volume fraction separating these two states. It is a critical volume fraction required to achieve the geometrical percolation. The percolation threshold depends upon a
number of variables, primarily the geometry of the nanoparticles and their orientation. Based on the concept of excluded volume $<V_{EX}>$ theory, one can predict the critical concentration knowing shape of the particles and their orientation with respect to each other (Onsager 1949; Balberg et al. 1984a; Grujicic and Cao 2004). The excluded volume is the volume around an object into which the center of another similar object is not allowed to enter if overlapping of the two objects is to be avoided (Onsager 1949). Balberg et al. derived excluded volume of capped cylinders in the three-dimensional space by simply moving one cylinder around the other and registering the center of the moving cylinder (Balberg et al. 1984a):

$$<V_{EX}>=\left(\frac{4\pi}{3}\right)W^3 + 2\pi W^2 L + 2WL^2 <\sin(\gamma)>;$$ (5.6)

where $W$, $L$ is average diameter (which is equal to width of the CNWs) and length of CNW, respectively, $<\sin(\gamma)>$ - the average value of $\sin(\gamma)$ describing the degree of alignment of CNW with respect to each other, $\gamma$ – angle between two CNWs. Hence, we propose to measure $\gamma$ by TEM for each CNW concentration and orientation angle $\theta$.

For random distribution of CNW orientations (low limit) (Balberg et al. 1984a):

$$<\sin(\gamma)> = \int_0^\pi f(\gamma) \sin(\gamma) d\gamma = \int_0^\pi 0.5 \sin^2 \gamma d\gamma = 0.25\pi;$$ (5.7)

where $f(\gamma) = 0.5\sin(\gamma)$ – the probability density distribution function for $\gamma$. Detailed calculation can be found elsewhere (Balberg et al. 1984a; Grujicic and Cao 2004). In contrary, for oriented CNW, when CNW are parallel to each other (upper limit) $\gamma = 0$, thus $\sin(\gamma) = 0$. The total excluded volume is the average excluded volume multiplied by $N_c$ – critical number density of CNW in the composite, in other words, the critical aggregate concentration for percolation:

$$V_{EX} = <V_{EX}> N_c \sim const;$$ (5.8)
Based on various numerical experiments (Balberg et al. 1984b) $V_{\text{EX}} \sim 1.4$ for cylindrical particles. Therefore, once the $\sin(\gamma)$ is identified, the percolation threshold can be computed:

$$
\nu_{\text{RC}} = 1 - \exp \left( - \frac{V_{\text{EX}} V}{<V_{\text{EX}}>} \right); \tag{5.9}
$$

where $V$ – volume of CNW (capped cylinder):

$$
V = \left( \frac{4\pi}{3} \right) \pi r^3 + \pi r^2 L; \tag{5.10}
$$

Estimated percolation threshold for two cases:

1) randomly oriented PHBV/CNW:

$$
\nu_{\text{RC}} = 1 - \exp \left( - \frac{V_{\text{EX}} V}{<V_{\text{EX}}>} \right) = 1 - \exp \left\{ - \frac{1.4((\frac{4}{3})\pi r^3 + \pi r^2 L)}{\frac{4}{3} \pi (2r)^3 + 2\pi (2r)^2 L + \pi r^2 L^2} \right\} = 3.22\% ; \tag{5.11}
$$

for $r = d/2 = 12.3/2 = 6.15$ nm and $L = 221.4$ nm (estimated from TEM) $\nu_{\text{RC}} = 3.22$ v/v %.

2) aligned CNWs:

$$
\nu_{\text{RC}} = 1 - \exp \left( - \frac{V_{\text{EX}} V}{<V_{\text{EX}}>} \right) = 1 - \exp \left\{ - \frac{1.4((\frac{4}{3})\pi r^3 + \pi r^2 L)}{\frac{4}{3} \pi (2r)^3 + 2\pi (2r)^2 L + 0} \right\} = 16.05\% . \tag{5.11}
$$

Knowing the densities of PHBV and cellulose nanowhiskers being 1.2 g/cm$^3$ (Holmes 1987) and 1.5 g/cm$^3$ (Gindl and Keckes 2004), respectively, the calculated CNW percolation threshold in weight ratio is 3.99 wt% and 19.3 wt% for randomly oriented and aligned CNWs, respectively. The films with CNW concentration of 19.3 wt% was not technically viable to prepare, because even at 7wt% films were hard to handle due to increased brittleness.

Based on evaluation of dynamic mechanical properties of the PHBV/CNW composites, percolation threshold was not reached when storage modulus was measured below glass
transition temperature (Fig. 5.12a). Although, it is evident from Fig. 12a that the range of CNW between 2 and 3 wt% indicate significant improvement of E' suggesting good reinforcing ability of CNWs, samples with higher than 3wt% of CNWs exhibited reduced E'. This result is consistent with our previous characterizations of thermal, mechanical, rheological and dielectrical properties of PHBV/CNW composites (Ten et al. 2011a) and isothermal crystallization study (Ten et al. 2011b). Decreased mechanical properties (Fig. 5.14) might be a result of CNW agglomerations (evidence of strong hydrogen bonding between CNW) that act like stress concentrations. TEM images confirmed this conclusion (Ten et al. 2011a; Ten et al. 2011b).

At 60 °C however, storage modulus increases beyond 3 wt% and levels off until CNW content reaches 5 wt%. The range of CNWs between 3 and 5 wt% is a critical concentration required to for percolated CNW structure. The experimental results are in good agreement with predicted value of 4 wt%. The constant E’ with increasing load of CNWs indicates “saturation point” of CNW reinforcement This term is typically used to describe mechanical or electrical properties saturation for carbon nanotubes-filled composites (Allaoui et al. 2002; Larijani et al. 2011; Blond et al. 2006; Osorio et al. 2011). For example, the “saturation effect” was previously described by Allaoui et al. (Allaoui et al. 2002). The group studied mechanical and electrical properties of multi-walled carbon nanotubes (MWCT)/epoxy composites.
Figure 5.12 Storage moduli E' of neat PHBV and randomly oriented PHBV/CNW composites determined at (a) -20 °C and (b) 60 °C. Insets indicate dispersion of CNW in PHBV.
The reinforcement coefficient was determined as stress of composites of different CNTs wt% divided by the stress of the pure matrix at the same strain level. The ratio was about 2 for 1 wt% CNTs composite and 2.5 for 4 wt% composite. It was concluded that the reinforcement role was much reduced in the case of 4 wt% composite. The same phenomenon was observed for Young’s modulus and electrical conductivity. By adding 4wt% CNTs, the conductivity was only improved by one order of magnitude compared to 1 wt% whereas for epoxy/1wt%CNT it was enhanced by 7 orders of magnitude compared to unfilled epoxy (Allaoui et al. 2002). Theoretically, strength reduces due to a lack of matrix continuity when the matrix is interrupted by the high quantity of reinforcement present in the microstructure (Osorio et al. 2011). This reinforcement plays now a different role in the material and the previous reinforce effect may not exist anymore. This phenomenon can be seen as a saturation of dispersed phase in the matrix with consequent precipitation of a second phase that will be controlled by the reinforcement material. This second phase may act as a stress concentrator and as a result, mechanical properties drop down (Osorio et al. 2011). Similarly, in our study, this highest reinforcing effect is achieved due to uniform dispersion of CNW within PHBV which was shown in microstructural study by TEM (Ten et al. 2011a). Finally, composites with CNW > 3 wt% at -20 °C and 5wt% at 60 °C had reduced storage moduli due to CNW agglomerations introducing stress concentrations to the composites. According to this, the insets in Fig. 5.14 depict the assumed dispersion of CNW at different loadings of nanoparticles. It can be established that amount of CNW higher than 5 wt% is not viable from reinforcing and manufacturing standpoints. Hence, in further results explanation only composite with 0-5 wt% of cellulose nanowhiskers will be discussed.
Figure 5.13 Effect of orientation angle \( \theta \) on storage moduli \( E' \) of neat PHBV and aligned (A) and randomly oriented (RO) PHBV/CNW composites determined at 60 °C.

The effect of orientation angle on \( E' \) for aligned PHBV/CNW composites was compared to control samples (RO) (Fig. 5.12-15, Table 5.1). As shown in Fig. 5.13, storage modulus for PHBV/1.5CNW and PHBV/2CNW determined under \( \theta = 0, 15, 30 \) and 45° were higher than \( E' \) of randomly oriented sample (RO) demonstrating high degree of CNW alignment under electric field. For \( \theta = 90° \), on the other hand, \( E' \) is the lowest, because there is smaller statistical probability of contacts among the aligned nanowhiskers, which is consistent with the predictions of excluded volume theory (Balberg et al. 1984a; Balberg et al. 1984b, Balberg and Bozowski 1982; Balberg et al. 1983a; Balberg et al. 1983b). Based on XRD results, the highest degree of order was also obtained for PHBV1.5CNW and PHBV/2CNW compositions.

At concentrations corresponding to percolation threshold of CNW in PHBV, only \( E' \) in longitudinal direction (\( \theta = 0° \)) exceeded \( E' \) of control or isotropic samples (Fig. 5.14). This result
can be explained by two separate reasons or their combination. First, the increased viscosity due to the addition of nanowhiskers restricted their mobility under electric field. Second reason is that the strong mechanical coupling between nanowhiskers governed by hydrogen bonds was stronger than field-induced dipolar interactions among CNW in a liquid matrix.

**Figure 5.14** Effect of orientation angle $\theta$ on storage moduli $E'$ of neat PHBV and aligned (A) and randomly oriented (RO) PHBV/CNW composites determined at 60 °C.
Figure 5.15 Effect of orientation angle $\theta$ on storage moduli $E'$ of neat PHBV and aligned (A) and randomly oriented (RO) PHBV/CNW composites determined at 60 °C.

Finally, aligned PHBV/5CNW films showed ca. 35% improvement in $E'$ compared with control samples (Fig. 5.15). Although the orientation angle did not affect dynamic mechanical properties at this CNW content, but the overall enhancement over the entire range of angles can be an indication of improved CNW dispersion. The improved dispersion of CNW for PHBV/5CNW was verified by TEM (Fig. 5.16). Fig 5.16a corresponding to TEM image of isotropic PHBV/5CNW composite revealed clusters of nanowhiskers, whereas aligned sample showed uniform CNW dispersion (Fig 5.16b). It is, possibly, due to the fact that CNW dispersion and distribution in PHBV is influenced by two competing forces: hydrogen interactions and applied external electric field. Based on mechanical properties reduction, at high CNW contents (>5 wt%), hydrogen bonding become dominant, therefore, electric field was not sufficient enough to align CNW, therefore, composites showed isotropic behavior. Nonetheless, it is possible that applied current was strong enough to prevent severe agglomerations.
Figure 5.16 TEM images of PHBV/5CNW (a) random orientation (b) aligned. Scale bar is 1 µm.

Circled areas indicate CNW agglomerations.
5.4 Conclusions

This study has demonstrated the intrinsic potential of CNW alignment in PHBV by external electric field. Unidirectional reinforced PHBV/CNW nanocomposites were developed by DC electric field of 56.25 kV/m. Composites were manufactured by solution casting method using N,N-dimethylformide (DMF) as a solvent. Prior casting, CNW were transferred from H₂O to DMF by solvent exchange method. The effects of CNW concentrations and orientation angle θ on storage moduli E’ were evaluated by DMA. CNW content was varied from 0 to 7 wt% while θ was at 0, 15, 30, 45 and 90° with respect to applied electric field. TEM, XRD and DMA results confirmed that the electric field was effective to align CNW up to 4 wt%. TEM images showed that CNW were aligned along the direction of applied electric field. Based on DMA study, concentration of CNW has a main influence on efficiency of CNW alignment by electric field. Due to significantly improved viscosity of PHBV solution with addition of CNW, the degree of anisotropy reduced with increasing CNW content indicating restricted CNW movement. That is why films with 5-7 wt% CNW did not show significant change in E’ over entire range of angle θ demonstrating isotropic behavior. The results of this study suggest that it would not be sufficient to reinforce PHBV with CNW at concentrations higher than 5 wt% for CNW with random orientation. The electric field is sufficient to align CNW for concentrations up to 4 wt% which makes CNW to enable special functionalities and precise control over properties of the resulting composites.

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Ten, E.; Jiang, L.; Wolcott, M. P. Crystallization kinetics of Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)/cellulose nanowhiskers Composites – under review (2011b)


Chapter 6 Modeling properties and mechanical percolation threshold of PHBV/cellulose nanowhiskers (CNW) composites

Abstract

This study explores the possibility of developing robust model to predict storage modulus of PHBV/CNW composites with randomly dispersed and unidirectionally aligned cellulose nanowhiskers. Anisotropic properties of PHBV/CNW composites were analytically evaluated using micro-mechanics model. Based on orientation angle of CNW to applied load, storage modulus was predicted by Cox “shear lag” model. Additionally, critical volume fraction corresponding to the formation of interconnected 3-D CNW network (percolation threshold) was predicted from the angle between CNWs. With this information, one is able to infer effect of cellulose nanowhiskers’ aspect ratio, volume fraction and orientation on mechanical properties of PHBV/CNW composites.
6.1 Introduction

Modeling the mechanical properties of fiber-reinforced composites is a way to evaluate the individual effect of how matrix, fiber modulus, matrix/fiber interaction, fiber geometry, orientation and dispersion affect composite stiffness. Micromechanical modeling has been demonstrated to be a powerful tool to predict macroscopic constitutive response especially for those materials having periodic microstructure. Experimental morphological and mechanical properties’ analysis can help to establish and justify assumptions for prediction model. Alternatively, model predictions compared with experimental results will elucidate composite behavior within proposed assumptions. Therefore, the objective of the research was to comprehend the origin of superior reinforcing efficiency of CNW in PHBV matrix and establish mechanical model to predict elastic modulus of PHBV/CNW composites.

The “shear lag” model originally developed by Cox (Cox 1952) for paper is most widely used to describe the effect of loading on elastic modulus of aligned discontinuous fiber composites. “Shear lag” model was the first micro-mechanics model for fiber-reinforced composites. Under applied load, the tensile stress is zero at the fiber ends, and a maximum at the center. At the same time, the interfacial shear stress is zero at the center and a maximum at the fiber ends. At this point it is important to note that there is a minimum aspect ratio $s_t$ beyond which the fiber strain at the center is approaches the strain of the matrix. $s_t$ depends upon stiffness of the fibers and matrix, and fiber/matrix interactions (Chakraborty et al. 2006). Fiber ends act as stress concentrations in the matrix; therefore, increasing the aspect ratio of the fibers reduces this effect by increasing the amount of stress being transferred to the fibers. Orientation of the filler relative to applied load will influence the stress transfer mechanism. In extreme case of misalignment, when fibers are perpendicular to applied load, the stress at the interface
transforms from a shear mode into the tensile that generates higher concentrations of stress in the matrix and less tension in the fibers, which is similar to what happens at the end of a fiber (Fornes 2003). Since Cox model typically gives reasonable $E$ predictions for aligned fiber reinforced composites, it is viable to expect good agreement between experimental results and Cox estimations for PHBV/CNW nanocomposites. In order to show feasibility of Cox model, the predictions by Halpin-Tsai and Voigt-Reuss models were compared to those of Cox model. One of the assumption common in many composite theories is the filler is completely aligned in one direction. Given the large aspect ratios and nanoscopic dimensions of dispersed CNWs, small deviations from unidirectional alignment are expected to cause significant changes in nanocomposite strength and stiffness, among other properties. The unique geometry of these fillers will also increase the likelihood of particle-particle interactions. Such interactions, often not considered in composite theory, therefore, the distribution of the orientation angle and its effect on $E'$ was investigated in this study.

According to the results discussed previously in Chapter 5, significant improvement of PHBV/CNW mechanical properties is governed by interactions between nanofibers. This phenomenon is classically explained by percolation model. In particular, percolation is a statistical geometrical model that can be applied to any random multiphase material involving components that are able to commingle (Stauffer and Aharony 1992). By variation of the number of connections, this approach allows for a transition from a disconnected set of objects to an infinite connected state. The percolation threshold is defined as the critical volume fraction separating these two states. The percolation threshold depends upon a number of variables, primarily the geometry of the nanoparticles and their orientation (Balberg, I. and Bozowski 1982; Balberg et al.1983; Balberg and Binenbaum 1983). Upon reaching this critical CNW
concentration, stiffness of PHBV/CNW composites increases significantly, as shown in Chapter 5. Thus, to assess the reinforcing effect of CNW in PHBV, a prediction model must also involve the filler percolating network, and the non-percolating filler. For that reason, specific objectives for this study are:

1. Analytical evaluation of anisotropic properties of PHBV/CNW composites using Cox model to predict bulk mechanical properties.

2. Model the mechanical percolation threshold based on the angle between CNWs.

3. Experimental verification of predicted parameters by dynamic mechanical analysis;

6.2 Experimental section

6.2.1 Materials

PHBV with 12 mol-% content of hydroxyvalerate (HV) was supplied by Metabolix Inc. N, N-dimethylformamide (DMF) and NaOH were purchased from Acros Organics (Atlanta, GA). Microcrystalline cellulose (MCC) – refined wood pulp, was obtained from Avicel (Type PH-102). Sulfuric acid (96 wt%) was purchased from J.T. Baker. PHBV was dried at 80°C in a convection oven overnight prior to use.

6.2.2 CNW preparation

Sulfuric acid H₂SO₄ was diluted with water to 64 wt% concentration. MCC (1 g per 9.8 ml of the acid) was added and vigorously stirred at 44 °C for 2 hours. Then the suspension was diluted to about one tenth of its original acid concentration. The acid in the solution was removed by repeated centrifugation (Sorvall, 5000 rpm for 5-min) until the supernatant was turbid. The supernatant (CNW suspension) was collected and dialyzed against deionized water for 4-5 days to remove remaining acid (dialysis tube from Spectrum Laboratories Inc., cutoff molecular weight 12000-14000). After the CNW suspension reached a constant PH value, it was removed.
from the dialysis tubes and neutralized with 1 wt% NaOH solution. The neutralized suspension was condensed at 80 °C using a Büchi Rotavapor (R-200) until the CNW concentration reached 2 wt%.

6.2.3 In-situ preparation of aligned PHBV/CNW nanocomposites

Various amount of condensed CNW suspension was added drop-wise into 40 ml of DMF under continuous stirring. Water was evaporated from the mixture at 80 °C for an hour (DMF boiling temperature 153 °C) to obtain CNW/DMF suspension. Depending on the desired CNW content in the final PHBV/CNWs composites, different amount of PHBV were dissolved in the suspension under continuous stirring. The dispersion of CNWs in the suspension was improved by sonication for 5 minutes. The solution was cast on a clean glass substrate (9x9 cm²) which was placed between two electrodes separated by a distance of 10 cm (Chapter 5). A 9 kV voltage was applied on the electrodes, which resulted in a maximum electric field of 56.25 kV/m (9 kV/0.16 m) between the electrodes. It is worth noting that the dielectric constant of DMF is high (ɛ = 36.7 at 25 °C). Therefore, the actual magnitude of the electric field was lower within the volume of DMF. The suspension on the glass substrate was heated with a lamp to accelerate DMF evaporation. The temperature under the light was 80 °C. Both the electric field and the light were applied continuously until the film was complete dry. The final PHBV/CNW films were transparent with a thickness of 15-30 microns. DMF content of the obtained films was measured to be less than 2 wt% through vacuum drying.

6.2.4 Characterization

6.2.4.1 Transmission electron microscopy (TEM)

The morphology of PHBV/CNW composites was studied by a Philips CM-200 TEM operating at 200 kV. Small pieces of PHBV/CNW films were embedded in acrylic resin (London
Resin Company Ltd.) and cured at elevated temperature overnight. Thin sections (~ 50 nm) of the films were cut in the direction parallel to the film surface using a Reichert-Jung ultramicrotome. The sections were placed on formvar-coated nickel grids and then negatively stained with 2% uranyl acetate for 90 minutes.

6.2.4.2 Dynamic Mechanical Analysis (DMA)

DMA was conducted in tension mode on a Tritec 2000 DMA at 1 Hz to examine thermal dynamic properties of the films. DMA samples (10 x 6.5 mm²) were cut from the PHBV/CNW composite film. Dynamic strain sweep was first performed to determine linear viscoelastic range of the samples. Then the samples were tested from -40 °C to +80 °C at 5 °C/min heating rate with a strain of 0.02%. To study the effect of fiber orientation angle θ (Fig. 6.1) on the storage modulus of the composites, the samples were cut at 0, 15, 30, 45 90 ° with respect to the direction of the applied electric field. Ten replicates were tested for each orientation angle θ. The storage moduli E’ for PHBV/CNW composites were compared above glass transition temperature Tg (ca. 25 °C) of PHBV +60 °C.

Figure 6.1 Explanation of material coordinates as compared to composite coordinates. E – electric field (kV/m); θ – orientation angle (°).

6.3 Results and Discussions

6.3.1. Morphology of aligned PHBV/CNW composites

The orientation of CNWs in PHBV under electric field was studied by TEM. Due to the fact
that electric field between two electrodes is stronger in the middle of the electrodes than on the edges (this can be characterized with an electric flux concept), there is a distribution of CNW orientation throughout the composite (Fig. 6.2). For data consistency, samples for TEM were cut close to the electrodes corresponding to the position shown in Fig. 6.2c. However, even for composites with low content of CNWs, there is still an orientation angle distribution (Fig 6.2c, d). To account for multiple fiber orientations, the image analysis was performed with ImageJ software based on 300 measurements (National Institute of Health). The distributions were fitted using 3-parameter Weibull distribution. Knowing that CNW volume fraction \( \frac{V_\theta}{V} \) for each angle of orientation \( \theta \), may be reduced to the probability of this angle \( P(\theta) \) by assuming CNW are of equal volume:

\[
E_c = \sum \frac{V_\theta E_\theta}{V} = \sum P(\theta)E_\theta;
\]

(6.1)

Fig. 6.3 shows the alignment of CNWs in the PHBV matrix. It can be seen that for PHBV/1.5CNW and PHBV/2CNW (Fig. 6.3 a,b), nanowhiskers were aligned along the direction of the applied electric field. Owing to the structural anisotropy of CNWs, the dipole moment in the direction of the nanowhisker long axis is much stronger than that in the transverse direction. Therefore, cellulose nanowhiskers could be aligned along the direction of the electric field if the viscosity of the solutions is low enough so that CNW movement is not restricted. At high CNW concentrations, the micrographs do not show preferential fiber orientation (Fig. 6.3 c-g).

Although under applied electric field, there were still similar levels of field-induced dipolar interactions within CNWs, the orientation of the fibers was restrained presumably due to fiber-fiber and fiber-matrix interactions which became influential at high fiber concentrations (> 4wt%).
Figure 6.2 Schematic representation of top view of the PHBV/CNW films during CNW alignment: a) Assumed CNW orientation; b) real CNW orientation (top view); c) and d) TEM images of PHBV/1.5%CNW oriented film, arrow indicates the direction of applied electric field.
Figure 6.3 TEM images of PHBV/CNW composites: a – neat PHBV; b – PHBV/1.5CNW; c – PHBV/2CNW; d – PHBV/3CNW; e – PHBV/4CNW; f – PHBV/5CNW; g – PHBV/6CNW; f – PHBV/7CNW. Scale bars represent 200 nm. Arrows show the direction of applied electric field.

The presumption was confirmed by the rheological study reported in Chapter 5 for the samples containing 0-7wt% CNWs. Even though no obvious orientation was observed from
TEM micrographs at high CNW content, image analysis to determine distribution of orientation angle $\theta$ and angle between two adjacent CNWs $\gamma$ was performed for composites containing 0-5wt% CNWs.

### 6.3.2 TEM images analysis for $\theta$ and $\gamma$ determination

The bin width, $\Delta \theta$ (in degrees) was evaluated through a sensitivity analysis at constant volume fraction and $\theta = 5^\circ$ (Fig. 6.4). Value for $\Delta \theta = 0^\circ$ was computed from actual experimental data. Smaller width will increase accuracy at decreasing rates, while also increase computational difficulty. Therefore, an optimum bin width between accuracy and ease in calculations has to be found. According to Sturges (Sturges 1926) the bin width can be estimated as:

$$m = 1 + 3.3 \log n; \ldots$$

where $m$ is the bin width, $n$ is the number of data values. For $n = 300$, $m$ is 9.2. From sensitivity analysis and estimation the smaller widths $\Delta \theta \leq 10^\circ$ is an optimum value. Thus, for modeling and data representation bin width was chosen to be $\Delta \theta = 5^\circ$ (Fig. 6.4).

![Figure 6.4 Sensitivity analysis of bin width.](image-url)
Supporting results from TEM observations, the probability distributions for PHBV/4CNW and PHBV/5CNW had broad distributions indicating less ordered structure of such composites (Fig. 6.5 d,e). This result also suggests that for composites with high CNW content (4 and 5 wt%), applied electric was not effective to align nanofibers along the direction of applied electric field due to strong hydrogen interaction between adjacent CNWs. On the other hand, it can be seen in Fig. 6.3 that composites containing CNWs <4wt% exhibited preferential orientation along the direction of electric field (Fig. 6.5 a-c).

Knowing the orientation angle of CNW with respect to applied electric field ($\theta = 0^\circ$), it is possible to evaluate the distribution of angle between two CNWs $\gamma$. Using statistical independence concept, if

$$P(\theta_1|\theta_2) = P(\theta_1); \quad (6.3)$$

than $\theta_1$ is statistically independent of $\theta_2$: whether $\theta_2$ happens makes no difference to how often $\theta_1$ happens. Since

$$P(\theta_1 \cap \theta_2) = P(\theta_1|\theta_2) * P(\theta_2); \quad (6.4)$$

if $\theta_1$ is independent of $\theta_2$, then the probability of two CNWs with $\theta_1$ and $\theta_2$ to form an angle $\gamma_{12}$ is:

$$P(\gamma_{12}) = P(\theta_1 \cap \theta_2) = P(\theta_1) * P(\theta_2); \quad (6.5)$$

Based on this principal the probability of two nanofibers overlapping at $\gamma$ angle was calculated based on distribution of $\theta$. The results are shown in Fig. 6.5 and example of calculation is given in Appendix A. Supporting our TEM and DMA results, for composites with 1.5-3 wt% CNW the highest probability was obtained for $\gamma = 0^\circ$ indicating that most of the CNWs were parallel to each other and the composites were highly oriented. For PHBV/4CNW and PHBV/5CNW, however, the distribution is merely the same for all $\gamma$ suggesting isotropic
microstructure. $\gamma$ distribution was used to model percolation threshold (6.3.4). This information elucidated concentrations for maximum reinforcement at a given CNW orientation.

![Figure 6.5](image)

**Figure 6.5** Orientation angle $\theta$ distributions and cumulative distribution function (cdf): a – PHBV/1.5CNW; b – PHBV/2CNW; c – PHBV/3CNW; d – PHBV/4CNW; e – PHBV/5CNW.
Figure 6.6 Distribution of the angle between two CNWs $\gamma$: a – PHBV/1.5CNW; b – PHBV/2CNW; c – PHBV/3CNW; d – PHBV/4CNW; e – PHBV/5CNW.
6.3.3 Modeling E' of PHBV/CNW composites using micromechanics models

Based on different microstructure, there are three different types of PHBV/CNW composites (Fig. 6.7):

1) Aligned discontinuous fibers (a);

2) Off-axis aligned discontinuous fibers (b);

3) Randomly oriented discontinuous fibers (control) (c);

![Figure 6.7 Types of PHBV/CNW composites based on CNW alignment: (a) Aligned discontinuous fibers; (b) Off-axis aligned discontinuous fibers; (c) Randomly oriented discontinuous fibers (control).](image)

For the aligned discontinuous fiber composite longitudinal modulus of elasticity was determined by Cox “shear lag” model. The specific assumptions of the model are present in Table 6.1. Assuming periodic structure and square packing array, the representative volume element (RVE) is shown in Fig. 6.8.
Table 6.1 Fundamental assumptions for Cox “shear lag” model

<table>
<thead>
<tr>
<th>Assumptions</th>
<th>Matrix</th>
<th>Fibers</th>
<th>Composite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix is isotropic</td>
<td>CNW are isotropic (E_f, G_f,</td>
<td>CNW is elastic;</td>
<td>Load is applied at the end of CNW;</td>
</tr>
<tr>
<td></td>
<td>v_f);</td>
<td>Aspect ratio distribution is described by</td>
<td>Flexural stiffness of single fiber is negligible;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Weibull distribution;</td>
<td>Fiber can transmit load only in tension;</td>
</tr>
<tr>
<td></td>
<td>Homogeneous dispersion</td>
<td>Orientation angle distribution is described</td>
<td>Load is equal for every fiber;</td>
</tr>
<tr>
<td></td>
<td>within matrix;</td>
<td>by Weibull distribution;</td>
<td>Interfacial shear stress $\tau$ is equal everywhere to the matrix yield</td>
</tr>
<tr>
<td></td>
<td>orientation angle distribution is described by Weibull distribution;</td>
<td></td>
<td>stress in shear $\tau_y$;</td>
</tr>
<tr>
<td></td>
<td>Fibers are straight</td>
<td>Fibers are straight</td>
<td>Composite doesn’t have transverse stiffness, only axial</td>
</tr>
<tr>
<td></td>
<td>Fibers lie in plane of the film (2D).</td>
<td>Fibers are isolated with contiguous matrix;</td>
<td>Fibers are isolated with contiguous matrix;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Composite materials have periodic microstructure;</td>
<td>Square packing array;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Elastic modulus is taken as storage modulus</td>
<td>Composite materials have periodic microstructure;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(E=E’).</td>
<td>Elastic modulus is taken as storage modulus (E=E’).</td>
</tr>
</tbody>
</table>

Figure 6.8 Representative volume element (RVE) for aligned PHBV/CNW composites.

Considering static equilibrium and solving associated differential equation, elastic modulus of composite $E_{c1}$ based on assumptions listed above is:

$$
E_{c1} = E_f \left[ 1 - \frac{\tanh(\beta L/2)}{\beta L/2} \right] + E_m v_m;
$$

(6.6)
where \( \beta^2 = \frac{2\pi G_m}{A_f E_f \ln(D/d)} \);

Knowing the definition of volume fraction: \( \nu_f = \frac{\pi d^2}{4 D^2} \Rightarrow \frac{D}{d} = \sqrt[4]{\frac{\pi}{4 \nu_f}} \);

L – CNW length, d – diameter, D – mean separation of the fibers normal to their length,

\( A_f = \frac{\pi d^2}{4} \) - cross sectional area of CNWs, where \( E_f, E_m, \nu_f, \nu_m \) – elastic moduli and volume fractions of fibers (CNW) and matrix (PHBV), respectively.

Assuming both constituents to be isotropic, properties of matrix and fibers taken for modeling, are present in Table 6.2.

**Table 6.2 Independent constants required for modeling.**

<table>
<thead>
<tr>
<th>Nomenclature</th>
<th>Description</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_f (E_{f1}=E_{f2}) )</td>
<td>Modulus of elasticity of nanowhisker</td>
<td>57 GPa</td>
<td>Rusli, Eichhorn 2008</td>
</tr>
<tr>
<td>( E_m (E_{m1}=E_{m2}) )</td>
<td>Modulus of elasticity of PHBV</td>
<td>0.63 GPa</td>
<td>by DMA</td>
</tr>
<tr>
<td>( \nu_f )</td>
<td>Inplane Poisson’s ratio of nanowhisker</td>
<td>0.3</td>
<td>Dalmas* et al. 2007</td>
</tr>
<tr>
<td>( \nu_m )</td>
<td>Inplane Poisson’s ratio of PHBV</td>
<td>0.4</td>
<td>Owen and Koller 1996</td>
</tr>
<tr>
<td>( L/d )</td>
<td>Aspect ratio (length over diameter)</td>
<td>( \frac{L}{d} = 18 )</td>
<td>by TEM</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( L = 221.4 \text{ nm}, ) ( d = 12.3 \text{ nm} )</td>
<td></td>
</tr>
<tr>
<td>( G_f (G_{12}=G_{23}) )</td>
<td>Inplane shear modulus of nanowhiskers</td>
<td>21.92 GPa</td>
<td></td>
</tr>
<tr>
<td>( G_m (G_{12}=G_{23}) )</td>
<td>Inplane shear modulus of PHBV</td>
<td>0.23 GPa</td>
<td></td>
</tr>
</tbody>
</table>
Experimental data of randomly oriented CNW composites (determined by DMA at 60 °C) and results of predicted by Cox, Halpin-Tsai and Voigt-Reuss models are compared in Fig. 6.9. Since we don’t have CNW orientation distribution, elastic modulus was calculated by:

\[
E = E_f \eta_0 \left[ 1 - \frac{\tanh(\beta L / 2)}{\beta L / 2} \right] \nu_f + E_m \nu_m;
\]

(6.8)

with coefficient \( \eta_0 = 0.375 \) for randomly oriented fibers in 2D (Krenchel 1964).

For the predictions by Cox model, probability of CNW orientation \( P(\theta) \) was taken equal for 0<\( \theta \)<180.

**Figure 6.9** Experimental data and Cox, Voigt-Reuss and Halpin-Tsai predictions of \( E' \) of PHBV/CNW composites vs. CNW concentrations (wt %).

Both Voigt-Reuss and Halpin-Tsai models estimate Young’s modulus for a lamina of short
random fibers applying simplified equation of Akasaka (Akasaka 1974):

\[ E = \frac{3}{8} E_1 + \frac{5}{8} E_2; \]  

(6.9)

where \( E_1 \) and \( E_2 \) are the expressions for the longitudinal and transverse moduli, respectively.

For Voigt-Reuss model:

\[ E_1 = E_f \nu_f + (1 - \nu_f)E_m; \]  

(6.10)

\[ E_2 = \frac{E_f E_m}{E_f (1-\nu_f) + E_m \nu_f}; \]  

(6.11)

For Halpin-Tsai model:

\[ E_1 = \frac{E_m(1 + \xi \frac{L_f}{d_f} \nu_f)}{1 - \eta \nu_f}; \]  

(6.12)

where \( \eta = \frac{E_f}{E_m} - 1 \) and \( \xi = \frac{E_f}{E_m} + \frac{L_f d_f}{E_m} \).

\[ E_2 = \frac{E_m(1 + \xi \nu_f)}{1 - \eta \nu_f}; \]  

(6.13)

with \( \eta_1 = \frac{E_f}{E_m} - 1 \) and \( \xi = \frac{E_f}{E_m} \).

Here \( \xi \) is a measure of the degree of fiber reinforcement determined by curve fitting. Excellent fit was found for value \( \xi = 2 \) (Adams and Doner 1947; Adams and Doner 1967).

Due to the fact that Voigt-Reuss model does not take into account geometry of the fibers and Halpin-Tsai is a semiempirical model, even though good theoretical-experimental correlation is obtained, we conclude that Cox prediction gives reasonably good estimation for \( E' \) of PHBV/CNW composites within proposed assumptions (Table 6.1). Therefore, Cox model was used to model \( E' \) of nanocomposites with aligned CNWs.

Since CNW are not aligned in one preferred direction (Fig. 6.2, 6.3), there is a need to define compliance matrix \( S \) and the transformation matrix \( T \) for orthotropic material. Based on the
plain-stress assumptions we first reduce compliance matrix to 3x3. Two of the major pitfalls associated with using the plane-stress assumption are:

1) The stress components equated to zero are often forgotten and no attempt is made to estimate their magnitude;

2) It is erroneously assumed that because the stress component $\sigma_3$ is zero and therefore ignorable, the associated strain $\varepsilon_3$ is also zero and ignorable.

Next step is to transform the stress-strain relationship from the 1-2-3 coordinate system to the global coordinate system (Fig. 6.1). It was done for the state of plane stress using the standard transformation relationships:

$$
S = \begin{bmatrix}
\frac{1}{E_1} & \frac{\nu_{12}}{E_1} & 0 \\
-\frac{\nu_{12}}{E_1} & \frac{1}{E_2} & 0 \\
0 & 0 & \frac{1}{G_{12}}
\end{bmatrix} \begin{bmatrix}
S_{11} & S_{12} & 0 \\
S_{12} & S_{22} & 0 \\
0 & 0 & S_{66}
\end{bmatrix} = [S]; \quad (6.14)
$$

$$
T = \begin{bmatrix}
c^2 & s^2 & 2sc \\
2sc & c^2 & -2sc \\
-sc & sc & c^2 - s^2
\end{bmatrix}; \quad (6.15)
$$

where $E_1$ and $E_2$ – elastic moduli in the principal material directions, $\nu_{12}$ – Poisson’s ratio, $G_{12}$ – shear modulus, $s$ and $c$ are sine and cosine of the orientation angle $\theta$, respectively.

The transformation compliance matrix can be expressed as:

$$
\tilde{S} = T^T S T; \quad (6.16)
$$

Transformed reduced compliances are defined by:

$$
\tilde{S}_{11} = S_{11} c^4 + (2S_{12} + S_{66}) s^2 c^2 + S_{22} s^4; \quad (6.17)
$$

$$
\tilde{S}_{12} = (S_{11} + S_{22} - S_{66}) s^2 c^2 + S_{12} (s^4 + c^4); \quad (6.18)
$$
Knowing the relationships between the compliances $S_{ij}$ and engineering constants, we can write

$$
\begin{align*}
\tilde{S}_{16} &= (2S_{11} - 2S_{12} - S_{66})sc^3 - (2S_{22} - 2S_{12} - S_{66})s^3c; \\
\tilde{S}_{22} &= S_{11}s^4 + (2S_{12} + S_{66})s^2c^2 + S_{22}c^4; \\
\tilde{S}_{26} &= (2S_{11} + 2S_{22} - S_{66})s^3c - (2S_{22} - 2S_{12} - S_{66})sc^3; \\
\tilde{S}_{66} &= 2(S_{11} + 2S_{22} - 4S_{12} - S_{66})s^2c^2 + S_{66}(s^2 + c^2);
\end{align*}
$$

(6.19)

(6.20)

(6.21)

(6.22)

However, to compute transformed lamina stiffness matrix, we need to know transverse $E_2$, shear moduli $G_{12}$ and Poisson’s ratio $\nu_{12}$. By solving the geometric compatibility relationships in 1 and 2 directions, $\nu_{12}$ can be predicted from rule of mixture: $\nu_{12} = \nu_f \nu_f + (1-\nu_f)\nu_m$ (Gibson 2007); In terms of transverse and shear moduli, Halpin concluded that $E_2$ and $G_{12}$ are not significantly affected by the fiber length (Halpin 1969). Thus $E_2$ and $G_{12}$ in the continuous fiber case can be used for the discontinuous fiber composites (Gibson 2007). Using Halpin-Tsai semiempirical model:

Similarly to equation 6.12 and 6.13: $G_{12} = \frac{G_m(1 + \xi \eta \nu_f)}{1 - \eta \nu_f}$;

where $\eta = \frac{G_f}{G_m} - 1$;

(6.24)

(6.25)

$\xi = 2$ and $\zeta = 1$ for the transverse and shear moduli of a square array of circular fibers respectively (Adams and Doner 1947; Adams and Doner 1967). It is worth mentioning that curve-fitting parameter $\xi$ has theoretical basis: when $\xi = 0$, the Halpin-Tsai equation reduces to
the inverse rule of mixture, whereas $\xi = \infty$ yields to the rule of mixture. Finally, knowing $E_1$, $E_2$, $G_{12}$, and $\nu_{12}$ we can determine $E_{x\theta}$ and $E_{y\theta}$ using transformation matrix. The overall transformed $E_{c\theta}$ can be calculated by integrating $E(\theta)$ over the angle distribution determined in 6.3.2.

$$E_{c\theta} = \sum_{n=1}^{180/\Delta\theta} \left[ \int_{(n-1)\Delta\theta}^{n\Delta\theta} P(\theta) \cdot [E_\theta]_{(n\Delta\theta-\Delta\theta/2)} \right]; \quad (6.26)$$

Here $\Delta\theta$ is a bin width which was taken as $5^\circ$.

A comparative study of the proposed simulation based on modified Cox “shear lag” model is shown in Fig. 6.10. Two separate approaches were used to predict $E'$ of aligned PHBV/CNW composites by Cox model: first approach was assuming one preferential orientation of CNWs, whereas, second approach involved orientation angle distribution $f(\theta)$. From the figure it is observed that Cox approximation is well above the experimental results for all formulations at $\theta < 30^\circ$. This is because Cox gives results for the unidirectionally aligned fiber reinforced composites which, in fact, is not the case for aligned PHBV/CNW composites. Specifically, the TEM images analysis indicated sharp distribution of orientation angles for composites with 1.5-3wt% CNW, while PHBV/4CNW and PHBV/5CNW films exhibited wide $\theta$ distribution suggesting reduced degree of alignment (Fig. 6.5). Owing to the distribution of $\theta$, predictions from Cox model for unidirectional orientation is too high for $\theta \leq 30^\circ$ and too low for $\theta > 30^\circ$ (Fig. 6.9).
Figure 6.10 Comparison of $E'$ determined from Cox “shear lag” model assuming unidirectional orientation $\theta$; from Cox model considering orientation angle $\theta$ distribution and experimental data for (a) PHBV/1.5CNW; (b) PHBV/2CNW; (c) PHBV/3CNW; (d) PHBV/4CNW; (e) PHBV/5CNW.
Figure 6.11 Schematic representation of CNWs orientation within PHBV: (a) CNW aligned off-axis reduce E' for $\theta = 0^\circ$; (b) aligned CNW reinforce PHBV for $\theta = 30^\circ$.

The results obtained from Cox model considering distribution, are in better agreement with those obtained from experimental results. Especially for PHBV/1.5CNW, the predictions give good approximation. Although distribution $\theta$ was taken into account in modeling, Cox theory does not consider fiber-fiber interaction which is main mechanism responsible for CNWs reinforcing abilities. Hence, the approximations are underestimated for composites with 2-4wt% CNW at $\theta > 30^\circ$. Composite PHBV/5CNW, however, showed merely constant E' with orientation angle demonstrating isotropic behavior.

Based on analytical predictions, storage modulus was supposed to exhibit downward-upward trend, because when CNWs are aligned under $\theta > 30^\circ$ to applied load, certain percentage of CNWs reinforce PHBV in $0^\circ$ direction (Fig. 6.11). Nonetheless, PHBV/5CNW showed high storage modulus for all $\theta$. This effect was due to the percolated structure formed at this concentration. The critical concentration indicating development of interconnected 3-D structure of CNWs can be calculated based on excluded volume concept.
6.3.4 Prediction of percolation threshold for randomly oriented and aligned PHBV/CNW composites

It has been shown in Chapter 5 that when the percolation threshold is reached a significant increase of the elastic properties is associated with strong mechanical coupling between nanowhiskers governed by hydrogen bonds. This behavior is highly noticeable above $T_g$ where amorphous regions of polymer chains exhibit long-range cooperative motion. The main mechanism responsible for reinforcing effect of CNW in PHBV is based on percolation theory (Onsager 1949). The percolation threshold $\nu_{RC}$ is a critical volume fraction required to achieve the geometrical percolation. In our case the percolation threshold is related to excluded volume $<V_{EX}>$ of the CNW, the volume around an object into which the center of another similar object is not allowed to enter if overlapping of the two objects is to be avoided (Onsager 1949).

Balberg et al. derived excluded volume of capped cylinders in the three-dimensional space by simply moving one cylinder around the other and registering the center of the moving cylinder (Balberg et al. 1984a):

$$<V_{EX}> = \left(\frac{4\pi}{3}\right)W^3 + 2\pi W^2 L + 2WL^2 <\sin(\gamma)> ; \quad (6.27)$$

where W, L is average diameter (which is equal to width of the CNWs) and length of CNW, respectively, $<\sin(\gamma)>$ - the average value of $\sin(\gamma)$ describing the degree of alignment of CNW with respect to each other, $\gamma$ – angle between two CNWs, as determined in 6.3.2.

For random distribution of CNW orientations (low limit) (Balberg et al. 1984a):

$$<\sin(\gamma)> = \int_0^{\pi} f(\gamma) \sin(\gamma) d\gamma = \int_0^{\pi} 0.5 \sin^2 \gamma d\gamma = 0.25\pi ; \quad (6.28)$$

where $f(\gamma) = 0.5\sin(\gamma)$ – the probability density distribution function for $\gamma$. Detailed calculation can be found elsewhere (Balberg et al. 1984a; Grujicic and Cao 2004). In contrary, for oriented
CNW, when CNW are parallel to each other (upper limit) $\gamma = 0$, thus $\sin(\gamma) = 0$. The total excluded volume is the average excluded volume multiplied by $N_c$ – critical number density of CNW in the composite, in other words, the critical aggregate concentration for percolation:

$$V_{EX} = <V_{EX} > N_c \sim \text{const} ;$$  \hspace{1cm} (6.29)

Based on various numerical experiments (Balberg et al. 1984b) $V_{EX} \sim 1.4$ for cylindrical particles. Therefore, once the $\sin(\gamma)$ is identified, the percolation threshold can be computed:

$$\nu_{RC} = 1 - \exp \left( - \frac{V_{EX}}{<V_{EX}>} \right) ;$$  \hspace{1cm} (6.30)

where $V$ – volume of CNW (capped cylinder):

$$V = \left( \frac{4\pi}{3} \right) r^3 + \pi r^2 L ;$$  \hspace{1cm} (6.31)

Estimated percolation threshold for two cases:

1) randomly oriented PHBV/CNW:

$$\nu_{RC} = 1 - \exp \left( - \frac{V_{EX}}{<V_{EX}>} \right) = 1 - \exp \left( - \frac{1.4(\frac{4}{3}\pi r^3 + \pi r^2 L)}{\frac{4}{3} \pi (2r)^3 + 2\pi (2r)^2 L + \pi r L^2} \right) = 3.22 \% ;$$  \hspace{1cm} (6.32)

for $r = d/2 = 12.3/2 = 6.15$ nm and $L = 221.4$ nm (estimated from TEM) $\nu_{RC} = 3.22$ v/v %.

2) aligned CNWs:

$$\nu_{RC} = 1 - \exp \left( - \frac{V_{EX}}{<V_{EX}>} \right) = 1 - \exp \left( - \frac{1.4(\frac{4}{3}\pi r^3 + \pi r^2 L)}{\frac{4}{3} \pi (2r)^3 + 2\pi (2r)^2 L + 0} \right) = 16.05 \% .$$  \hspace{1cm} (6.33)

Similarly, for real CNW orientation was considered and percolation threshold $\nu_{RC}$ based on average $\gamma$ was calculated. Knowing the densities of PHBV and cellulose nanowhiskers being 1.2 g/cm$^3$ (Holmes 1987) and 1.5 g/cm$^3$ (Gindl and Keckes 2004), respectively, the percolation
threshold can be obtained in wt%. Fig. 6.12 presents dependence of percolation threshold on the angle between two CNWs determined by excluded volume theory. For randomly oriented composites percolation threshold is 3.99 wt% for $\gamma = 90^\circ$, whereas for aligned samples it is 19.3 wt% CNW for $\gamma = 0^\circ$ (Fig. 6.12).

**Figure 6.12** Effect of the angle between two CNWs $\gamma$ on percolation threshold $\nu_{RC}$.

CNW concentration of 4wt% corresponding to percolation threshold for randomly oriented composites was within experimental determination. The films with CNW concentration of 19.3 wt% was not technically viable to prepare, because even at 7wt% films were hard to handle due to increased brittleness.
Section 6.3 Effect of CNW concentration on storage moduli $E'$ of neat PHBV and randomly oriented PHBV/CNW composites determined 60 °C. Insets indicate dispersion of CNW in PHBV.

Based on evaluation of dynamic mechanical properties of the randomly oriented PHBV/CNW composites, percolation threshold was reached in the range of CNW between 3 and 5 wt%. This was supported by significant improvement of $E'$ suggesting good reinforcing ability of CNWs. Given the fact that distribution of orientation angles give increased $\nu_{RC}$ for low $\gamma$ and vice versa, the experimental data of 3-5wt% is in good agreement with the prediction of 4wt% for percolation threshold. Decrease in mechanical properties (Fig. 6.13) is a result of CNW agglomerations (evidence of strong hydrogen bonding between CNW) that act as stress concentrations.

Moreover, due to the fact that nanowhiskers exhibit distribution of $\theta$ and $\gamma$, PHBV/CNW composites simultaneously fabricated under electric field can still form percolated structure.
Based on γ distribution determined in 6.3.2, for each γ, percolation threshold $v_{RC\gamma}$ (wt%) was obtained and similarly to $E'_c$, overall $v_{RC}$ was calculated as:

$$v_{RC} = \sum \frac{V_{\gamma} v_{RC\gamma}}{V} = \sum P(\gamma) v_{RC\gamma} ;$$

(6.34)

Table 6.3 indicates percolation threshold predictions for a given γ distribution. It can be concluded that for high CNW content where induced eclectic field was not effective to align CNW, percolation threshold decreases verifying importance of γ on $v_{RC}$.

**Table 6.3** Percolation threshold predictions for PHBV/CNW composites based on γ distribution.

<table>
<thead>
<tr>
<th>CNW (wt%)</th>
<th>$v_{RC}$ (wt%)</th>
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<tr>
<td>1.5</td>
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<tr>
<td>2</td>
<td>8.4</td>
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<tr>
<td>3</td>
<td>7.1</td>
</tr>
<tr>
<td>4</td>
<td>6.4</td>
</tr>
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<td>5</td>
<td>6.4</td>
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</table>

**6.4 Conclusions**

From individual micromechanical properties of the fibers (CNWs) and matrix (PHBV), aspect ratio, orientation and volume fraction of nanofibers, it has been demonstrated that the effective storage moduli can be simulated to obtain properties of random and aligned composite lamina. It has been observed that CNW exhibit orientation angle distribution for all CNW loading levels (1.5-5wt%). The distribution was analytically evaluated and fitted to exponential distribution. For the contents of < 4wt% CNW revealed preferred orientation along the direction of applied electric field. PHBV/4CNW and PHBV/5CNW samples, however, showed uniform distribution indicating isotropic behavior. This result is consistent with our mechanical evaluation. Although the orientation angle distribution was taken into account in modeling the $E'$
by Cox “shear lag” model, Cox approximations were relatively consistent with experimental data only for PHBV/1.5CNW, PHBV/2CNW, and PHBV/3CNW at $\theta = 15, 30^\circ$. High orientation angle gives underestimated $E'$, because Cox model does not consider positive impact of bigger $\theta$ on $E'$ due to CNW-CNW interaction. Similarly to $\theta$, the distribution of angle between CNW $\gamma$ was determined using statistical probability calculation. Owing to the distribution, even in aligned composites CNW are able to form percolated structure and reduce percolation threshold. Theoretical predictions of percolation threshold based on $\gamma$ for randomly oriented composites were in good agreement with experimental results. The results of current Chapter elucidate mechanisms of mechanical property enhancement in PHBV/CNW composites. Understanding how aspect ratio, concentration and orientation angle influence $E'$ is a crucial factor in longstanding goal of predicting nanoparticles–nanocomposites–property relationships in material design and optimization.

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Chapter 7 Summary and Conclusions

Cellulosic nanocomposites are gaining growing interest for packaging, biomedical and common plastics applications. For these applications, solution casting is one of the preferred methods of uniform dispersed nanocomposites production. The understanding of how CNW morphology, concentration and orientation influence thermal, mechanical, rheological and dielectric properties and establishing structure-property relationship are of great scientific and engineering importance.

A fundamental study of PHBV/CNW nanocomposites formed by solvent casting has provided valuable insights about why cellulose nanowhiskers are capable of producing well-dispersed morphologies and superior nanocomposite properties. The rationale behind this behavior may be described by the relationships between constituents structure affecting nanocomposite morphology and property performance. Effects of three major factors, such as CNW aspect ratio, CNW concentration and degree of CNW orientation were thoroughly investigated. For that, randomly oriented and aligned PHBV/CNW composites were fabricated by solution casting and solution casting combined with the application of the external electric field, respectively.

CNW structure and morphology plays an essential role in the development of well-dispersed nanocomposites. Hydroxyl groups present on the surface of CNWs form strong hydrogen bonding with PHBV allowing CNW to homogeneously disperse in the polymer. Morphological comparison between nanocomposites with different CNW contents under comparable microstructural conditions suggest that the level of dispersion is better for low level of CNWs; increasing the filer content results in nanofibers agglomerations which reduces reinforcing efficiency. Natural variation in the length of CNWs that can be tuned by controlled hydrolysis
conditions, e.g. time, temperature, H$_2$SO$_4$ concentration, may cause noticeable differences in final filler particle size, extent of CNW dispersion, and level of reinforcing efficiency observed in the nanocomposite. Therefore, the distribution of CNW aspect ratio was examined based on TEM images of pure CNWs and PHBV/CNW composites. The L/d ratio was determined to be ca. 18 for both as-hydrolyzed pure CNWs and CNWs from nanocomposites indicating that nanowhiskers were not agglomerated and were present as single nanofibers in PHBV. This result suggests good interfacial bonding between nanofibers and matrix.

Addition of CNWs to the PHBV does result in a number of noteworthy polymer matrix related effects. Isothermal crystallization studies on PHBV/CNW nanocomposites show that nanowhiskers serve as nucleation sites for crystallization at very low CNW contents; however, high CNW contents retard polymer crystal growth. In contrary, radial spherulite growth rate determined from direct POM observations decreased at low CNW concentrations and then increased at high concentrations. The spherulite growth rate was determined by chain diffusion rate at the growth fronts. Below the uniform CNW dispersion, the confinement effect caused by CNWs decreased PHBV chain diffusion rate and consequently reduced its spherulite growth rate. Above this CNW loading level, the confinement effect was reduced due to CNW agglomeration and therefore the growth rate increased again. Although the effect of CNW on nucleation ability and degree of crystallinity of PHBV is significant and can contribute to the mechanical properties improvement, the results of this study confirmed that mainly CNW homogeneous distribution and interconnected 3-D structure governed E' enhancement.

The concentration of the CNW is also essential in the development of well-dispersed and highly reinforced cellulosic nanocomposites. Changes in the amount of CNWs have pronounced effects on the level of CNW dispersion and the extent of property improvements observed. The
homogeneous dispersion and distribution of CNWs, however, limits to 2.3-5 wt% due to high surface area of CNWs. Moreover, the even dispersion is achieved at different CNW loading levels for two different types of nanocomposites. In particular, for randomly oriented PHBV/CNW films the content of CNWs corresponding to their even dispersion limit is 3 wt%, whereas for aligned nanocomposites it is 5 wt%. It is believed that this effect arises from the two competing forces that influence the dispersion: hydrogen interactions and applied external electric field. Based on mechanical properties reduction, for aligned nanocomposites at high CNW contents (>5 wt%), hydrogen bonding become dominant, therefore, electric field was not sufficient enough to align CNW (Chapter 5). Moreover, due to significantly improved viscosity of PHBV solution with addition of CNW, the degree of anisotropy reduced with increasing CNW content indicating restricted CNW movement. That is why composites with CNW concentrations beyond 4wt% showed isotropic behavior. Nonetheless, it is possible that applied current was strong enough to prevent severe agglomerations. Due to high functionality of CNWs owing to hydroxyl and/or carboxyl acid groups, the esterification and etherification are the possible routes to overcome the cohesive forces between neighboring CNWs so that homogeneous dispersion and strong f-m interaction can occur during solvent casting. The results of study on mechanical properties of aligned PHBV/CNW composites suggest that it would not be sufficient to reinforce PHBV with CNW at concentrations higher than 5wt% for CNW with random orientation. The electric field is sufficient to align CNW for concentrations up to 4 wt% which makes CNW to enable special functionalities and precise control over properties of the resulting composites.

Mechanical property responses observed in PHBV nanocomposites may be explained in terms of percolated structure formed by hydrogen bonding between CNWs. The percolation
threshold was modeled based on L/d and CNW orientation angle. The storage moduli, in turn, were modeled by micro-mechanical Cox theory of composites, which assumes that each phase has the same properties as if the other phase were not there. The effect of distributions of the orientation angle and the angle between two CNWs on the storage modulus E' were considered as well. For the contents of < 4wt% CNW revealed preferred orientation along the direction of applied electric field. PHBV/4CNW and PHBV/5CNW samples, however, showed uniform distribution indicating isotropic behavior. This result is consistent with our mechanical evaluation. Although the orientation angle distribution was taken into account in modeling the E' by Cox “shear lag” model, Cox approximations were relatively consistent with experimental data only for PHBV/1.5CNW, PHBV/2CNW, and PHBV/3CNW at θ = 15, 30°. These results indicate that the superior reinforcement seen in these nanocomposites arises primarily from the combination of high modulus and aspect ratio of CNWs. High orientation angle gives underestimated E’, because Cox model does not consider positive impact of bigger θ on E’ due to CNW-CNW interaction. Similarly to θ, the distribution of angle between CNW γ was determined using statistical probability calculation. Owing to the distribution, even in aligned composites CNW are able to form percolated structure and reduce percolation threshold. Theoretical predictions of percolation threshold based on γ for randomly oriented composites were in good agreement with experimental results. The results of current study elucidate mechanisms of mechanical property enhancement in PHBV/CNW composites. Understanding how aspect ratio, concentration and orientation angle influence E' is a crucial factor in longstanding goal of predicting nanoparticles–nanocomposites–property relationships in material design and optimization.
Appendix A: Statistical analysis of the angle between two CNWs

Based on orientation angle \( \theta \)

Knowing the orientation angle distribution from TEM images, the distribution of \( \gamma \) can be computed according to assumption that \( \theta_1 \) is statistically independent of \( \theta_2 \). Therefore, the probability two CNWs with \( \theta_1 \) and \( \theta_2 \) to form an angle \( \gamma_{12} \) is defined as:

\[
P(\gamma_{12}) = P(\theta_1 \cap \theta_2) = P(\theta_1) \ast P(\theta_2);
\]

(6.6)

An example of calculation for PHBV/1.5CNW composite using Equation 6.6 is shown in Table A.1.

Knowing the distribution of \( \gamma \), the percolation threshold can be calculated using excluded volume theory (6.3.4)
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Table A.1 Spreadsheet for calculation of $\gamma$ distribution for PHBV/1.5CNW composite.
| \(\gamma\) | \(P(\gamma=0)\) | \(P(\gamma=5)\) | \(P(\gamma=10)\) | \(P(\gamma=15)\) | \(P(\gamma=20)\) | \(P(\gamma=25)\) | \(P(\gamma=30)\) | \(P(\gamma=35)\) | \(P(\gamma=40)\) | \(P(\gamma=45)\) | \(P(\gamma=50)\) | \(P(\gamma=55)\) | \(P(\gamma=60)\) | \(P(\gamma=65)\) | \(P(\gamma=70)\) | \(P(\gamma=75)\) | \(P(\gamma=80)\) | \(P(\gamma=85)\) | \(P(\gamma=90)\) | \(SUM\) |
| 50 | 0.016667 | 0.0E+00 | 5.6E-05 | 1.1E-04 | 5.6E-05 | 1.1E-04 | 0.0E+00 | 5.6E-05 | 1.7E-04 | 0.0E+00 | 5.6E-05 | 1.7E-04 | 0.0E+00 | 5.6E-05 | 1.7E-04 | 0.0E+00 | 5.6E-05 | 1.7E-04 | 0.0E+00 | 5.6E-05 | 1.7E-04 | 0.0E+00 | 5.6E-05 | 1.7E-04 |
| 55 | 0.01 | 0.0E+00 | 3.3E-05 | 6.7E-05 | 3.3E-05 | 6.7E-05 | 0.0E+00 | 3.3E-05 | 2.2E-05 | 0.0E+00 | 3.3E-05 | 2.2E-05 | 0.0E+00 | 3.3E-05 | 2.2E-05 | 0.0E+00 | 3.3E-05 | 2.2E-05 | 0.0E+00 | 3.3E-05 | 2.2E-05 | 0.0E+00 | 3.3E-05 | 2.2E-05 |
| 60 | 0.003333 | 0.0E+00 | 1.1E-04 | 2.2E-05 | 1.1E-04 | 2.2E-05 | 1.1E-04 | 2.2E-05 | 1.1E-04 | 2.2E-05 | 1.1E-04 | 2.2E-05 | 1.1E-04 | 2.2E-05 | 1.1E-04 | 2.2E-05 | 1.1E-04 | 2.2E-05 | 1.1E-04 | 2.2E-05 | 1.1E-04 | 2.2E-05 | 1.1E-04 | 2.2E-05 |
| 65 | 0 | 0.0E+00 | 1.7E-04 | 4.4E-05 | 2.2E-05 | 1.7E-04 | 4.4E-05 | 2.2E-05 | 1.7E-04 | 4.4E-05 | 2.2E-05 | 1.7E-04 | 4.4E-05 | 2.2E-05 | 1.7E-04 | 4.4E-05 | 2.2E-05 | 1.7E-04 | 4.4E-05 | 2.2E-05 | 1.7E-04 | 4.4E-05 | 2.2E-05 | 1.7E-04 |
| 70 | 0.006667 | 0.0E+00 | 2.2E-05 | 4.4E-05 | 2.2E-05 | 4.4E-05 | 2.2E-05 | 4.4E-05 | 2.2E-05 | 4.4E-05 | 2.2E-05 | 4.4E-05 | 2.2E-05 | 4.4E-05 | 2.2E-05 | 4.4E-05 | 2.2E-05 | 4.4E-05 | 2.2E-05 | 4.4E-05 | 2.2E-05 | 4.4E-05 | 2.2E-05 | 4.4E-05 |
| 75 | 0.003333 | 0.0E+00 | 1.7E-04 | 4.4E-05 | 2.2E-05 | 1.7E-04 | 4.4E-05 | 2.2E-05 | 1.7E-04 | 4.4E-05 | 2.2E-05 | 1.7E-04 | 4.4E-05 | 2.2E-05 | 1.7E-04 | 4.4E-05 | 2.2E-05 | 1.7E-04 | 4.4E-05 | 2.2E-05 | 1.7E-04 | 4.4E-05 | 2.2E-05 | 1.7E-04 |
| 80 | 0.006667 | 0.0E+00 | 2.2E-05 | 4.4E-05 | 2.2E-05 | 4.4E-05 | 2.2E-05 | 4.4E-05 | 2.2E-05 | 4.4E-05 | 2.2E-05 | 4.4E-05 | 2.2E-05 | 4.4E-05 | 2.2E-05 | 4.4E-05 | 2.2E-05 | 4.4E-05 | 2.2E-05 | 4.4E-05 | 2.2E-05 | 4.4E-05 | 2.2E-05 | 4.4E-05 |
| 85 | 0.003333 | 0.0E+00 | 1.7E-04 | 4.4E-05 | 2.2E-05 | 1.7E-04 | 4.4E-05 | 2.2E-05 | 1.7E-04 | 4.4E-05 | 2.2E-05 | 1.7E-04 | 4.4E-05 | 2.2E-05 | 1.7E-04 | 4.4E-05 | 2.2E-05 | 1.7E-04 | 4.4E-05 | 2.2E-05 | 1.7E-04 | 4.4E-05 | 2.2E-05 | 1.7E-04 |
| 90 | 0 | 1.9E-01 | 8.3E-02 | 6.7E-02 | 4.1E-02 | 3.0E-02 | 2.5E-02 | 2.2E-02 | 1.8E-02 | 2.2E-02 | 2.5E-02 | 3.0E-02 | 4.1E-02 | 6.7E-02 | 8.6E-02 | 8.3E-02 | 1 |

**SUM**