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CONTINUOUS MICROCELLULAR FOAMING OF POLYVINYL CHLORIDE AND COMPATIBILIZATION OF POLYVINYL CHLORIDE AND POLYLACTIDE COMPOSITES

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CONTINUOUS MICROCELLULAR FOAMING OF POLYVINYL CHLORIDE AND COMPATIBILIZATION OF POLYVINYL CHLORIDE AND POLYLACTIDE COMPOSITES

By

Bhavesh Shah

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ABSTRACT

CONTINUOUS MICROCELLULAR FOAMING OF POLYVINYL CHLORIDE AND COMPATIBILIZATION OF POLYVINYL CHLORIDE AND POLYLACTIDE COMPOSITES

By

Bhavesh Shah

This dissertation focuses on overcoming existing limitations of WPCs which prevent them from realizing their full market potential. These limitations include: i) lack of a continuous extrusion process for microcellular foaming of polyvinyl chloride (PVC) and its composites using supercritical fluids to reduce the high density of the WPCs, ii) need for an efficient coupling agent for WPCs to overcome the poor compatibility between wood and plastic, and iii) unproven use of wood as a filler for the biopolymer polylactide (PLA) to make "green" composites. These limitations were addressed through experimentation to develop a continuous extrusion process for microcellular foaming, and through surface modification of wood flour using natural coupling agents.

The effects of wood flour, acrylic modifier and plasticizer content on the rheological properties of PVC based WPCs were studied using an extrusion capillary rheometer and a two-level factorial design. Wood flour content and acrylic modifier content were the major factors affecting the die swell ratio. Addition of plasticizer decreased the true viscosity of unfilled and filled PVC, irrespective of the acrylic modifier content. However, the addition of acrylic modifier significantly increased the viscosity of unfilled PVC but decreased the composite viscosity.

Results of the rheological study were used to set baseline conditions for the continuous extrusion foaming of PVC WPCs using supercritical CO₂. Effects of material composition and processing conditions on the morphology of foamed samples were

investigated. Foamed samples were produced using various material compositions and processing conditions, but steady-state conditions could not be obtained for PVC. Thus the relationships could not be determined.

Incompatibility between wood flour and PVC was the focus of another study. The natural polymers chitin and chitosan were used as novel coupling agents to improve interfacial adhesion between the polymer matrix and wood fiber. Results indicated that addition of chitin and chitosan significantly increased the flexural properties and storage modulus of PVC WPCs, compared to composites without coupling agent. Significant improvements were attained with 0.5 wt. % chitosan and with 6.67 wt. % chitin.

Based on the efficiency of chitosan as a coupling agent for PVC based WPCs, a biodegradable composite using polylactide (PLA) and chitosan was developed. Wood flour (0 - 40 wt. %) was evaluated as a filler for PLA composites and its effect on mechanical, thermal and chemical properties was studied with and without chitosan (0 - 10 wt. %). Addition of wood flour significantly increased the flexural and storage moduli of PLA-wood flour composites, but had no effect on glass transition temperature (T_g) . Chitosan had no significant effect on any of the properties of the composites studied.

Development of an efficient and effective coupling agent for PVC wood composite is a significant development which will increase performance while reducing cost. Wood filled PLA composites can further expand WPCs into applications such as packaging and automotive. Results from these studies have broadened the current knowledge base for WPC products and will be useful in the continued expansion of wood composites technology into a variety of industries. Dedicated to my Family and Karana, without them this would not have been

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LIST OF ABBREVIATIONS

ABS	 Acrylonitrile Butadiene Styrene
ANOVA	 Analysis of Variance
CPE	 Chlorinated Polyethylene
DEHP	 Di-2-ethylhexyl phthalate
DMA	 Dynamic Mechanical Analysis
FTIR	 Fourier Transform Infrared Spectroscopy
HDPE	 High Density Polyethylene
HIPS	 High Impact Polystyrene
MFI	 Melt Flow Index
MW	 Molecular Weight
PC	 Polycarbonate
PCL	 Polycaprolactone
PE	 Polyethylene
PLA	 Polylactide
PP	 Polypropylene
PS	 Polystyrene
PVC	 Polyvinyl Chloride
SEM	 Scanning Electron Microscopy
Tg	 Glass Transition Temperature
WPCs	 Wood-Plastic Composites

CHAPTER 1

OVERVIEW

Wood-plastic composites (WPCs) are an emerging class of engineering materials which combine the benefits of both wood and plastic. The market for WPCs in North America was around 1.2 billion pounds in 2004 and is expected to reach 2 billion pounds by the year 2009, at an average annual growth rate of 10%. Major applications of WPCs include decking, railing, fencing, window and door frames and various automotive parts [1]. WPCs use wood flour or fiber as a filler or reinforcing agent in a plastic matrix. Wood has several advantages over conventional mineral fillers (talc, calcium carbonate, clay) such as low density, low cost and it is less abrasive to processing equipment. There are several other natural cellulosic fillers used in manufacturing composites such as flax, hemp, kenaf, newsprint fiber, jute, rice husk, sisal, coir, bamboo, etc. Natural fiber based fillers are abundantly available, recyclable, and biodegradable which makes them the best alternative to mineral fillers. Of all the natural cellulosic fillers, wood flour is the most widely used filler in manufacturing composites in the United States.

WPCs can be made with various different plastics such as polyethylenes (PE), polypropylenes (PP), polyvinyl chloride (PVC), polystyrene (PS) and several others. PVC is the second most widely used polymer for manufacturing WPCs though the market is dominated by PE. PVC as a matrix has several advantages over polyolefins (PE, PP, etc.) such as high stiffness, good weatherability, ease of customizing the final product properties by changes in formulation, and good paintability of the final product. Wood flour is used extensively as a filler and offers several advantages, but it has limited thermal stability and high moisture absorption; further, the addition of wood fiber or flour into the plastic reduces its strength properties (tensile and flexural strength) compared to the unfilled plastic. This is mainly due to the poor dispersion of fiber and lack of strong interaction between the hydrophilic wood fibers and hydrophobic polymer matrix [2]. Coupling or compatibilizing agents can increase the dispersion of fiber in the matrix and form polymer–fiber bonds by modifying the wood surface [3]. The use of coupling agents in manufacturing WPCs has been known for several years. However, there has been limited success with coupling agents for PVC/wood-flour composites. Thus, an effective coupling agent for PVC/wood-flour composites is still needed.

Although WPCs have been commercialized, their potential for use in many industrial applications has been limited because of their brittleness, lower impact resistance, and higher density compared to virgin plastics and/or solid wood. The high density of WPCs, which is almost twice that of solid wood, makes them heavier for handling and end use applications which may also hinder their growth in various applications. These drawbacks have been addressed by production of microcellular-foamed structures in WPCs which reduce the density of the composites, thus saving the cost of material while increasing mechanical properties such as impact strength [4-7]. Most of the research on microcellular foaming of PVC and its composites has been done using a batch foaming process. However, the batch foaming process used to generate cellular foamed structures is not likely to be implemented in the industrial production of foams because it is time consuming and not cost-effective. To manufacture microcellular foamed PVC product economically and efficiently a continuous extrusion process using supercritical fluids needs to be developed. This likely has not been done due to the complex processability and intricacies of PVC formulation. Each component in the formulation has a different effect on the behavior of PVC melt which controls the foaming process and these interactions need to be understood before actual foaming process can be successfully implemented.

Increasing use of PVC in manufacturing WPCs has led to a growing concern about its recyclability. Recycling of PVC is a complicated process, due to the presence of several different additives in the product being recycled. Additionally, the type and amount of additives used varies from product to product. It is difficult to obtain desired properties in products made from recycled PVC as it contains an unknown mix of additives. PVC is also prone to thermal degradation during the recycling process, which may cause it to break down and release hydrochloric acid. Due to these recycling issues some manufacturers are replacing PVC in various applications with other commodity polymers.

Consumer awareness about recycling and environmental impact of synthetic polymers in combination with government initiatives has lead to growth of the biodegradable polymer industry in recent years. Polylactide (PLA) is one of the most widely used and produced biobased polymers. The properties of PLA are comparable to most commodity polymers like PP, PE, PVC, and PS. Because of this PLA is a good alternative to synthetic polymers in manufacturing natural fiber composites. Several researchers have shown PLA can be successfully used as a matrix for natural fiber composites [8-10]. However, there is no published literature on using wood as a filler in PLA composites. Even though PLA natural fiber composites are manufactured, poor dispersion and weak interfacial bonding of the hydrophilic fibers with the hydrophobic polymer matrix leads to poorer strength properties than unfilled polymer [9-11]. Maleic anhydride and various maleated compounds have been used to compatibilize the components in PLA composites with limited success. An effective coupling agent for PLA natural fiber composite is still needed to improve the strength properties. A natural material that would function as a coupler would be desirable for biobased composites as it would be completely renewable, resulting in a "green" composite.

WPCs have enormous potential to replace conventional materials in a variety of applications, but there are major limitations that need to be overcome before this possibility can be realized. These limitations include, i) lack of a continuous extrusion process for microcellular foaming of PVC and its composites using supercritical fluids, ii) need for an efficient coupling agent for PVC wood composites that would overcome the poor compatibility between wood and plastic, and iii) unproven use of wood as a filler for biopolymer PLA and need for better interfacial adhesion of PLA natural fiber composites.

This research aims to advance wood composites technology and utilization via experimentation focused on improving WPCs properties and broadening the applications for WPCs. This work has three main areas of focus:

1. To develop a continuous extrusion process for foaming PVC and its wood flour composites using supercritical fluids, which will greatly increase the ease of producing microcellular foamed products in a way that is efficient and

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economical. This will result in improved end-product quality and reduced material consumption compared to unfoamed products.

- 2. To develop a new class of coupling agents for PVC based WPCs. This will improve the interfacial adhesion between polymer and filler and result in stronger performing composite products.
- 3. To demonstrate the use of wood as a filler for PLA, and to improve the properties of these composite with a natural coupling agent. This will result in environmentally friendly, renewable composite products, which are competitive with those made from synthetic polymers, yet can be recycled.

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CHAPTER 2

BACKGROUND, RATIONALE AND SPECIFIC HYPOTHESES

This section will provide background material and justification for the research work conducted in this project. The current state of the knowledge on PVC and PLA wood composites will be discussed, along with the issues that currently limit their use in various applications. Specific hypotheses will be developed to address ways to overcome these limitations.

Foamed PVC/Wood-Flour Composites:

WPCs use wood flour or fiber as a filler or reinforcing agent in a plastic matrix (see Appendix A for information on wood properties). WPCs are increasingly gaining popularity in diverse applications, some of which are replacements for conventional materials. PVC wood composites offer several advantages over polyolefin based wood composites such as good weatherability, high stiffness, ease of customizing the final product properties by changes in formulation, and good paintability of the final product. However, PVC/wood-flour composites have a major disadvantage of high density due to the presence of PVC (see Appendix B for information on PVC properties). The high specific gravity of PVC compared to wood leads to an increase in the density of the final product, making it heavier for handling and end use applications. Addition of wood to PVC also significantly reduces the impact strength of the PVC matrix. These drawbacks have been addressed by production of microcellular-foamed structures in WPCs which reduce the density of the composites, thus saving the cost of material and increasing mechanical properties such as impact strength [1-4]. Foaming also improves the fastening properties of the composites. Matuana et al. [3] showed that introducing a microcellular structure into PVC/wood-flour composites can increase its impact strength while reducing the overall density of the composites. Another approach used to overcome the drawbacks of WPCs is to use impact modifiers in the formulations. However, impact modification of wood/plastic composites does not enhance their ductility or reduce the density of the products [5]. When similar impact modifiers were used in the microcellular foamed formulations, they had a deleterious effect on the cell structure [6]. Addition of impact modifier increases the diffusion coefficient of gas in the samples, resulting in lower density reduction (void fraction) in the foamed sample. The increased gas diffusion coefficient increases the gas loss rate which reduces the amount of gas available for the foaming process. Therefore, the use of impact modifiers in the foam formulations should be avoided.

Microcellular Foamed Polymer:

Microcellular polymers are foamed plastics characterized by average cell size less than 10 μ m and cell-population density greater than 10⁹ cells/cm³. Manufacturing microcellular foam involves three basic steps viz., i) saturation ii) nucleation and iii) cell growth and stabilization. These basic steps are illustrated in Figure 2.1. Microcellular foam can be produced by batch, semi-continuous and continuous processes. Irrespective of the process, a blowing agent is required to generate the foamed structure in the polymer. Two major classes of blowing agents are used in the foaming process, chemical and physical blowing agents. Chemical blowing agents work by breaking down the compound into a gas at a specific temperature during processing. In contrast, physical blowing agents are typically inert gases injected into the polymer at a certain stage of processing. Since they are generally more eco-friendly, physical blowing agents are usually preferred over chemical blowing agents which may generate environmentally undesirable products. CO_2 and N_2 are the most common physical blowing agents being used in manufacturing microcellular foaming, but the most favored one is CO_2 . This is due to higher diffusivity and solubility of CO_2 in most polymers compared to N_2 .

Most of the early research on microcellular foaming involved a batch process. A typical setup of a batch process is shown in Figure 2.2. In the typical batch foaming process, a pre-prepared solid sample is saturated with a physical blowing agent under specific conditions of temperature and pressure in a sealed chamber (Figure 2.2a). The saturation process can last up to several days depending on the saturation temperature, pressure, sample geometry and polymer system. Once the sample is saturated with the gas it is transferred to a heated oil bath, the temperature of which is maintained above the glass transition temperature (T_g) of the polymer being foamed (Figure 2.2b). The increase in the temperature drives the nucleation of bubbles in the sample, and the time the sample is kept at that temperature determines the growth of the bubbles. Several amorphous, semi-crystalline and crystalline polymers such as HDPE [7], PP [8], PVC [9], PS [10], PC [11], etc. have been foamed using this technique.



Figure 2.1 Microcellular Foaming Process



Figure 2.2 Schematic of a Batch Foaming Process [12]

In spite of the ease and simplicity of batch foaming, it cannot be used for industrial applications due to the time consuming process of sample saturation, which makes the whole process uneconomical. To overcome these drawbacks, a continuous process of manufacturing microcellular foam using an extrusion technique was proposed by several researchers [13-16]. The continuous extrusion process has been successfully used for several polymers, but to date there has been no available literature on using this process for PVC and its wood flour composites with online injection of supercritical fluid as the blowing agent. The research carried out on continuous extrusion process of microcellular foaming of PVC and its composites has been mainly focused on chemical blowing agents, although the use of moisture as a foaming agent has also been reported in the literature [17]. Chemical blowing agents require extra care during dry blending to avoid migration, which results in density variations in the final product. Apart from this, chemical blowing agents have several other disadvantages including difficulties in adjusting foam densities during processing [18]. Physical blowing agents such as carbon dioxide (CO₂₎, nitrogen (N₂) and argon (Ar) are economical and eco-friendly, which makes them a better alternative to chemical blowing agents. One of the goals of this research is to manufacture microcellular foamed PVC and its composites in a continuous extrusion process using supercritical fluids.

Before continuous microcellular foaming can be implemented for PVC and its composites, the effects of material compositions and extrusion processing conditions on the melt viscosity of the polymer must be investigated. The melt viscosity of the polymer matrix has a major effect on the processability of the polymer and the end product quality. Rheological data can be a vital part of process design and setting correct processing conditions for the polymer. On the basis of rheological data, process variables can be modified to avoid processing problems such as melt fracture, sharkskin, and die swell. The viscosity of the polymer melt also plays a vital role in cell nucleation and growth during the foaming process. Therefore, it is of great importance to study the effect of different additives and processing conditions on the rheology of the polymer.

The rheological properties of PVC have been continuously studied for several decades and are still of interest to researchers [19-23]. Collins and Krier [19] have found two different activation energies for PVC. A low activation energy for viscosity was observed for a low temperature region characterized by particulate flow, while a high activation energy was found for the high temperature region characterized by molecular flow. The temperature at which the transition from the low to the high temperature region occurred was a function of shear stress. The effect of low molecular weight polymers like acrylate, polypropylene terephthalate and PVC polymer on the viscosity of PVC has also been studied [20]. The decrease in viscosity of the PVC matrix by addition of low molecular weight polymers depends on their compatibility and binding force with PVC. A different approach has been used to understand the melt behavior of PVC by considering PVC as a fluid which contains filler (PVC primary particles) [22]. It has been shown that fully fused PVC has lower viscosity than PVC powder (partially fused). This phenomenon was explained as analogous to the behavior of fluid which contains filler, and reduction in viscosity at fusion was attributed to the reduction in filler level as the PVC primary particles melt out at higher temperatures.

Hayes [24] studied the effect of two lubricants, a process aid, and an impact modifier on rheological properties of PVC using a central composite design. All studied factors had a significant effect on the rheological properties of PVC. PVC in its melted state is a non-Newtonian fluid with shear thinning behavior, also known as psuedoplastic in nature. As a result, an increase in shear rate will decrease the viscosity of the PVC melt. It was found that the increase in impact modifier and process aid content resulted in increased non-Newtonian behavior of the PVC melt. Opposite effects were observed between the two different lubricants studied (wax and oxidized polyethylene). Wax decreased the non-Newtonian behavior while oxidized polyethylene increased the behavior. This was attributed to the effect of these lubricants on the fusion behavior of PVC. Oxidized polyethylene promotes a higher degree of fusion compared to wax, which results in more entanglements of polymer chains, consequently increasing the non-Newtonian behavior of the melt.

The incorporation of filler into polymer matrices complicates rheological measurements of the system. The effect of filler on different rheological properties of a polymer melt is a complex phenomenon and depends on several factors such as content, shape and size of filler, interaction between filler and polymer, etc. Several researchers have investigated the rheological properties of natural fiber filled polymer [25-28]. Maiti and Hassan [28] studied the rheological properties of PP/wood-flour composites in a capillary rheometer. They found that increasing the wood flour content increases the viscosity and shear thinning behavior of the PP melt, whereas it reduces the melt elasticity of the matrix. It was also observed that the viscosity of filled polymer is less sensitive to temperature changes than that of unfilled polymer. Similar results were observed by Xiao and Tzoganakis [26] for an HDPE/wood-flour composite system

except for melt elasticity, where the opposite trend was observed (increased melt elasticity with increased wood content).

Recently, Guffey and Sabbagh [29] used chlorinated polyethylene (CPE) as a compatibilizer for PVC/wood-flour composites and showed that addition of CPE to PVC/wood-flour composites reduced the viscosity of the composites, resulting in increased processability of the composites and higher outputs. The melt viscosity of plasticized PVC is significantly increased when wood flour is added [30]. Increased viscosity hinders bubble formation and growth during foaming and generally results in poor foam quality in terms of average cell size and cell-population density. In contrast, the blowing gas reduces the viscosity of the molten polymer due to the plasticization effect on the polymer. The viscosity of the polymer matrix is a critical parameter for bubble formation and growth during the foaming process; therefore it needs to be studied in depth in order to understand how the wood flour, plasticizer, foam modifier and gas content will affect the rheology and thus the foamability of the PVC composites.

Foaming of PVC WPCs addresses some of the drawbacks of these materials by reducing the density and improving the end product properties. Unfortunately, this does not solve another major issue related to incompatibility between hydrophilic wood and hydrophobic PVC.

Coupling Agents for PVC/Wood-Flour Composites:

To achieve maximum reinforcement benefits from a filler used in a polymer, the filler, which is strong and stiff, should bear most of the load or stress applied to the composite system. Conversely, the polymer, which is of low strength, fairly tough and flexible, should effectively transmit the load to the filler. To effectively transfer the load from matrix to filler, the matrix must have strong interfacial adhesion with the filler. Weak interfacial bonding will result in fiber pullout from the polymer matrix on application of load, and will reduce the overall strength of the composite. Thus, it is the interface which controls the final strength properties of the composite.

Although WPCs are superior to neat polymers in terms of material cost and stiffness, their strength performance (tensile, flexural, and impact) is generally lower than the unfilled polymers. A general trend of increasing modulus and decreasing strength properties is observed as more wood is added to the polymer. Increased modulus by addition of wood is a result of the high stiffness of the filler compared to the polymer, while decreased strength is likely a result of the natural incompatibility of phases during the mixing of the hydrophilic wood fibers with the hydrophobic polymer matrix [31-33]. Phase incompatibility yields very weak interactions and thus a weak interface between the fiber and the matrix.

One approach to designing WPCs is to modify the wood fiber surface with coupling agents to improve the strength. Coupling agents convert the hydrophilic surface of wood fibers to a more hydrophobic state. Thus, the surface tension of wood fibers is reduced and approaches that of the molten polymer. As a result, wetting and adhesion are improved via mechanisms such as diffusion and mechanical interlocking between treated fibers and the polymer matrix [33].

Due to its strong effect in altering the hydrophilic surface of wood fibers to a more hydrophobic one, maleic anhydride functionalized polyolefin is commonly used as a coupling agent for polyolefin/wood-fiber composites [34, 35]. Similarly, to enhance the interfacial adhesion between wood fibers and a PVC matrix, several investigators have assessed the effects of various fiber treatments, including different types of isocyanates, maleic anhydride, linoliec acid, silanes, etc. as coupling agents [29, 36-38].

Kokta et al. [38] used linoleic acid, abietic acid and maleic anhydride as coupling agents for composites of PVC with chemi-thermomechanical pulp of aspen. All of the coupling agents showed increased tensile strength of the composites, compared to composites without coupling agent. However, the strength properties of coupled composites were still much lower than unfilled polymer. Linoleic acid treated composites showed the highest tensile strength of the three coupling agents studied. Interestingly, when aspen sawdust was used instead of chemi-thermomechanical pulp as a filler for PVC with maleic anhydride as a coupling agent, the treated composite showed reduced strength properties compared to untreated composites.

Most mechanical properties of the composites were improved by these chemical treatments compared to those of composites with non-treated fibers. However, the properties of the composites were inferior to those of the unfilled PVC, suggesting that, unlike polyolefin/wood-fiber composites, the well-known method of converting the hydrophilic surface of wood fiber to a hydrophobic one is not effective for enhancing the adhesion of PVC to wood fibers.

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Matuana et al. [39] demonstrated that when PVC is used as a matrix in WPCs, acid-base interactions, in which one phase acts as an electron donor (base) and the other acts as an electron acceptor (acid), are a significant factor in enhancing interfacial adhesion. Therefore, surface modification of wood fibers to be used with PVC should be designed to modify the acid-base interactions at the matrix/fiber interface in order to improve the performance of these composites. For example, by changing the acidic characteristics of wood fibers through surface modification with γ -amino propyltriethoxy silane, PVC/wood-fiber composite with equal tensile strength and greater modulus than unfilled PVC was developed. The aminosilane successfully modified the wood surface, and facilitated the interaction between the wood and PVC according to Lewis acid-base theory [39].

In spite of these benefits, γ -amino propyltriethoxy silane has not been extensively used as a coupling agent for PVC/wood-fiber composites, mainly due to its high cost but also due to the difficulty in evenly coating the surface of wood fibers, owing to its tendency to hydrolyze and self-condense. Consequently, aminosilane is not a desirable coupling agent in this application. Thus, one of the objectives of this study is to explore the use of amine-containing natural polymers such as chitin and chitosan as cost-effective and novel coupling agents for PVC/wood-fiber composites. The acetylamine functionality of chitin, and the amine functionality of the chitosan, should permit these polymers to interact with wood and PVC in a manner similar to the aminosilane, and so enhance the interfacial adhesion between PVC and wood fibers. Chitin and chitosan are natural, biodegradable and biocompatible materials which are desirable for a variety of applications. Chitin is the second most abundant polysaccharide in nature, following cellulose. Chitosan is produced by deacetylating chitin under alkaline conditions, usually with sodium hydroxide. The structural difference between chitin and chitosan has many consequences. For example, chitin is not water soluble, while chitosan is soluble at acidic pH. Chitosan is also much more reactive than chitin, due to the primary amine in the structure.

Several investigators have reported the use of chitin and chitosan with different polymers for various applications [40-46]. In one study, the interfacial adhesion between chitin fibers and polycaprolactone (PCL) was increased by an irradiation treatment of the composites. The treatment showed an overall increase in mechanical properties of the composite compared to composite prepared from untreated chitin fiber. This increase in interfacial bonding was attributed to a free-radical grafting reaction [40]. Chitosan has also been reported to have been crosslinked to a polymer matrix [41]. That process used formaldehyde, which is a known carcinogen and hazardous to the environment, as a cross linking agent.

Souza Rosa and Andrade prepared biodegradable composites by incorporating chitin flakes ranging from 0-30 wt% into a plasticized starch matrix using an injection molding process. Chitin flakes increased the elastic modulus, tensile stress and water resistance of the composites when compared to the unfilled starch [42]. Biodegradation of synthetic polymers was shown to increase by incorporating a natural biodegradable polymer such as chitosan [43]. Thwe and Liao showed that the treatment of glass and

bamboo fiber with chitosan solution can improve the adhesion and properties of the polypropylene hybrid composites [44].

Chitosan is also used in the wood industry. For example, chitosan forms a Schiff base when reacted with aldehyde compounds. This property of chitosan can be very useful in reacting with the formaldehyde released from the glue line of plywood, thus reducing the overall emission of formaldehyde to the environment. Hence, the chitosan can be used as a functional coating reagent for wood [45]. The use of chitosan as an environmentally friendly adhesive for wood has also been reported in the literature. Glue made from chitosan showed excellent water resistance and was proposed as a replacement for synthetic adhesives [46]. The use of chitin and chitosan as coupling agents for wood composites has not been reported in the literature.

Development of an efficient, cost effective method of introducing foamed structure into PVC via a continuous microcellular foaming process using supercritical fluids will reduce the weight and material cost of the composite while increasing various properties. Similarly, improvements in strength properties can be achieved with a coupling agent. Both of these developments would broaden the application base for PVC wood composites. However, certain segments of the composites market are beginning to look for alternatives to synthetic polymers. As biopolymers have emerged as a viable, environmentally friendly alternative to synthetic polymers, natural polymers such as PLA are finding use in several applications.
Polylactide:

Polylactide (PLA) is a renewable and biodegradable linear polyester formed from lactic acid (see Appendix D for additional information). PLA offers high stiffness, easy processability and excellent clarity and gloss. This makes PLA a better alternative to replace synthetic commodity polymers in many applications. Products such as packaging and some automotive parts have relatively short life spans compared to materials used in the building and construction industry and would be ideal markets for PLA.

Natural fiber provides a low cost, biodegradable, stiff and lightweight reinforcement for PLA, which has a disadvantage of higher density than most commodity polymers such as PE, PP and PS. The melting point of PLA is around 165°C, which also makes it suitable to use with natural cellulosic fibers. Oksman and coworkers [47] have shown that PLA/flax fiber composites have superior mechanical properties compared to PP/flax fiber composites, and therefore have the potential to replace PP/natural fiber composites in many industrial applications. PLA composites have also been demonstrated with cellulose [48], newsprint [49] and bamboo fibers [50]. These results imply that wood, which is comparable in composition to other natural fibers, could also be used in making PLA composites. Wood flour is abundantly available in the US as a waste product of other manufacturing processes such as lumber production and furniture manufacture, which makes the use of wood flour economical and easy to implement. Thus, another goal of this study is to evaluate the use of wood flour as a filler for PLA.

Oksman et al. have reported the need for better interfacial adhesion between the PLA matrix and natural fibers to improve overall mechanical properties of the composites. Huda et al. [51] found that addition of 30 wt. % cellulose fibers reduces the

flexural strength of the composite while increasing the modulus by two folds over unfilled PLA polymer. Similar results were obtained by other researchers when bamboo [50] and recycled newsprint fibers [49] were used. These results show there is weak interfacial bonding between the reinforcing fibers and polymer matrix. The strength of natural fiber composites depends on the fiber dispersion and the interfacial bonding between the fibers and the polymer matrix. Poor dispersion is inherent to cellulosic materials due to hydrogen bonding between the fibers [31, 52, 53]. Different approaches have been used to overcome this problem. In one case, bamboo fiber itself was esterified with maleic anhydride and successfully used as a compatibilizer for PLA/bamboo fiber composites [50]. Addition of 5% esterified bamboo fiber resulted in around 21% improvement in the tensile strength and 10% increase in tensile modulus, while further addition of compatibilizer had no significant effect on the properties. This increase in the properties is an indication of increased interaction between the PLA matrix and bamboo Even though bamboo fiber esterified with maleic anhydride increased the fiber. properties of the PLA composite, this approach has several drawbacks, including the additional step of manufacturing reactive fibers before processing of the composites, and the use of a solvent process to produce reactive fibers, which is less desirable in the industry as well as uneconomical. Another approach is to use maleated PLA as a coupling agent. Initial results suggest that this would be an effective coupling agent for PLA/natural fiber composites [54]. However, this coupling agent is not available commercially and would be expensive and time consuming to produce as a part of a composite manufacturing process. A commercially available natural product is desirable as a coupling agent for PLA cellulosic fiber composites. Chitosan is natural,

biodegradable and readily available as a consumer product, and has been shown to have compatibility with wood. An additional goal of this work is to investigate the use of chitosan as a coupling agent for PLA wood flour composites that could improve the interfacial adhesion between hydrophilic wood and the hydrophobic PLA matrix.

Summary

WPCs have gained tremendous attention in recent years, and the market continues to grow. However, several drawbacks need to be addressed before they can reach their maximum potential. Microcellular foaming of PVC wood composites addresses some of the drawbacks by not only reducing the weight and material cost of the composite but also increasing numerous composite properties. Although microcellular foaming of PVC and its composites has been successfully demonstrated by the batch process, a continuous process is needed to make it commercially viable. Continuous extrusion using supercritical fluids would be a cost effective, efficient way to produce these foams. In order to control the morphology and tailor the end product properties of microcellular foamed PVC composites, various factors that control the rheology of the polymer must be investigated. Specifically, the complex interactions between wood flour and other additives must be understood.

Incompatibility between hydrophilic wood and hydrophobic polymer matrix leads to poor strength properties of the composites. Coupling agents are routinely used to overcome this issue. However, there has been only limited success with coupling agents for PVC wood composites. An effective, low cost coupling agent is still needed for PVC wood composites.

Biopolymers such as PLA represent a growing alternative to synthetic polymers. PLA natural fiber composites could be developed for use in many applications. Biopolymers like PLA which offer comparable properties to synthetic polymers while being renewable, sustainable and biodegradable would be preferred for use in products with relatively short life spans. Results of other studies suggest that wood can be used as

a filler for PLA composites, but this must be investigated to determine whether PLA WPCs would have sufficient properties for use in various applications. Regardless of the cellulosic based filler used, a natural and cost effective coupling agent is needed to improve the interfacial adhesion between the filler and PLA.

HYPOTHESES

This research is focused on improving WPCs properties and broadening their use for a variety of applications. End results of this project are expected to advance wood composite technology by providing both fundamental and applied knowledge that can be used to improve WPCs performance. The following hypotheses comprise the main focus of this project.

- Material composition (wood flour, plasticizer and foam modifier contents) will have a significant effect on the rheological properties of the PVC matrix, which will affect both the processability of the PVC/wood-flour composites and the cell nucleation and growth process during foaming.
- 2. Extrusion processing conditions (gas content, die temperature and extrusion speed) and material composition variables (wood flour and foam modifier content) will significantly affect the cell morphology of foamed PVC samples, thus these factors must be investigated to understand the dynamics of bubble nucleation, growth and stabilization during a continuous extrusion process.
- Chitin and chitosan can effectively increase the interfacial adhesion between PVC and wood flour and thus can be used as effective coupling agents for PVC/woodflour composites.
- 4. Wood flour will be a suitable filler for PLA in natural, biodegradable composites. Further, chitosan can be used as a natural coupling agent to overcome the natural incompatibility between hydrophilic natural fibers and the hydrophobic PLA matrix.

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CHAPTER 3

ONLINE MEASUREMENT OF RHEOLOGICAL PROPERTIES OF PVC/WOOD-FLOUR COMPOSITES*

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ABSTRACT

Using a factorial design approach, this study examined the effect of the component materials on the viscoelastic properties of PVC/wood-flour composites. Statistical analysis was performed to determine the effects of wood flour content, acrylic modifier content and plasticizer content on the die swell ratio and viscosity of the composites measured online on a conical twin-screw extrusion capillary rheometer. The visco-elastic properties of the samples were also measured using dynamic mechanical analysis (DMA). Wood flour content and acrylic modifier content were the two important variables affecting the die swell ratio, whereas the addition of a low level of plasticizer did not affect the die swell ratio. The die swell increased with the increased acrylic modifier content but it was considerably reduced by adding wood flour into the PVC matrix. The true viscosity of neat PVC and PVC/wood-flour composites decreased with the plasticizer content, irrespective of the acrylic modifier content. However, the addition of acrylic modifier significantly increased the viscosity of unfilled PVC while an opposite trend was observed for the composites due to the differing effect of acrylic modifier on the melt elasticity and viscosity of these materials.

Keywords: PVC/wood-flour composites, die swell ratio, viscosity, extrusion capillary rheometer, plasticizer, acrylic modifier.

INTRODUCTION

The United States of America has the largest market for both unfoamed and foamed wood-plastic composites (WPCs) in the world, with an expected annual growth rate of 12 % [1]. The enormous advantages of unfoamed and foamed WPCs over solid wood like the low maintenance, high strength to weight ratio, no splintering, chemical resistance, water resistance and good weatherability make them more suitable for stringent applications ranging from decking to automotive parts [1-5].

Polyvinyl chloride (PVC), being the second largest plastic used in manufacturing WPCs, preceded by polyethylene, has limitations due to its complex processability, which worsens in combination with wood flour. The high melt viscosity of PVC/wood-flour composites, due to the incorporation of wood flour into the PVC matrix, may lead to poor quality products or restrain the bubble formation and growth during the foaming process. This can prevent the formation of low density foamed composite products with uniform and homogeneous cell structures [6].

Selecting a proper processing aid to get a better quality product with enhanced processability is a key factor in manufacturing [8]. With appropriate addition level, the incorporation of acrylic processing aid is known to promote fusion of the PVC matrix with an increase in melt strength and melt elasticity. However, excessive addition of acrylic processing aid may change the rheology of the resin resulting in melt fracture [7]. Acrylic processing aid (foam modifier) has been used for several years to modify the PVC matrix to ease the foaming process. Matuana and Mengeloglu [2] have reported that the addition of acrylic modifiers, even at a low level, can significantly affect the melt

viscosity of the filled PVC matrix, thus enhancing the foamability of PVC/wood-flour composites. Processing of both unfoamed and foamed PVC/wood-flour composites can also be enhanced by the addition of plasticizer into the formulation due to the softening effect of plasticizer [9].

Several researchers have characterized the rheological properties of neat PVC [10-14]. Collins and Krier [10] have found two different activation energies for PVC. A low activation energy for a low temperature region characterized by particulate flow and a high activation energy for the high temperature region characterized by molecular flow was observed. The temperature at which the transition from the high to the low temperature region occurred was a function of shear stress. The effects of low molecular weight polymers like acrylate and polypropylene terephthalate on the viscosity of PVC have also been studied [11]. The decrease in viscosity of the PVC matrix by addition of low molecular weight polymers depends on their compatibility and binding force with PVC. A different approach has even been used to understand the melt behavior of PVC by considering PVC as a fluid which contains filler (PVC primary particles) [13]. It has been shown that fully fused PVC has lower viscosity compared to PVC powder (partially fused). This phenomenon was explained as analogous to the behavior of fluid which contains filler, and reduction in viscosity at fusion was attributed to the reduction in filler level as the PVC primary particles melt out at higher temperatures.

It is of immense importance to know the rheological behavior of polymer at processing conditions during extrusion to predict or tailor the extrudability of the polymer and the surface quality of the extrudate. Compared to a traditional capillary rheometer, an extrusion capillary rheometer generates the test results at the processing conditions,

which gives it a wide applicability. Glomsaker *et al.* [12] have analyzed and compared the in-line (extrusion capillary rheometer) versus off-line (capillary rheometer) rheological data of PVC for better simulation of flow in extrusion dies. Different formulations showed different comparisons of in-line data with off-line. Rheological data measured in the capillary rheometer are useful in predicting the thermal stability and the processability of PVC [15,16].

The rheological properties of natural fiber filled polyolefins have been investigated and reported by a number of researchers [17-20]. Incorporation of natural fibers in polyolefins increases the melt viscosity of the matrix and decreases the die swell ratio of the compound [17,20]. However, much less attention has been paid to evaluating the rheological properties of PVC/wood-flour composites; in particular the effect of various additives on the rheology of PVC/wood-flour composites has not been studied thoroughly. The addition of cellulose fibers into the plasticized PVC matrix increases the viscosity of the composite compared to neat PVC [21]. Recently, Guffey and Sabbagh [22] used chlorinated polyethylene (CPE) as a compatibilizer for PVC/wood-flour composites and showed that addition of CPE to PVC/wood-flour composites reduced the viscosity, resulting in increased processability of the composites and higher outputs.

The rheological characteristics of the melt are the most vital aspects in determining not only the surface quality of unfoamed products but also the bubble formation and growth during the foaming process, and need to be studied in detail. The main objective of this study was to investigate the effect of different formulation variables on the rheological properties (die swell and true viscosity) of PVC/wood-flour composites using a factorial design approach. A two-level factorial design was selected

in this study because it is a valuable approach for examining the effect of several variables in the system at one time, in addition to revealing the effects of interactions between variables that cannot be obtained from the traditional method of changing one variable at a time [23].

EXPERIMENTAL

Materials

PVC (K value-66) resin was supplied by Oxyvinyls. Tin stabilizer (PlastiStab 2808) used was from OMG Americas. Calcium stearate (Synpro, Ferro Corp.) and paraffin wax (Gulf Wax) were used as lubricants. Di-2-ethylhexyl phthalate (DEHP) plasticizer (Aristech Chemical Corp.) and acrylic processing aid (foam modifier) (Paraloid K-400, Rohm and Haas Co.) were also used in the formulations. Wood flour from hardwood maple species (40-mesh size – 425 μ m) supplied by American Wood Fibers (Schofield, Wisconsin) was used as a filler. Table 3.1 summarizes the typical formulations used in the experimental design.

Ingredients	Concentration (phr)			
PVC K-66	100			
Tin stabilizer	2			
Calcium stearate	1.5			
Paraffin wax	2			
Acrylic modifier (K-400)	0 – 8			
Wood flour	0 – 50			
Di-2-ethylhexyl phthalate (DEHP)	0 – 4			

Table 3.1. Formulations Used in Neat PVC and PVC/Wood-Flour Composites.

Experimental Design and Compounding

A two-level factorial design with center point was developed to study the rheological properties of PVC/wood-flour composites using Design Expert[®] software v.6.0 (Stat-Ease Corp., Minnesota). Wood flour content, acrylic modifier content and plasticizer content were the three key variables studied, whereas the die swell ratio and true viscosity were the variable responses obtained in this study. The generated experimental design is summarized in Table 3.2.

The Design Expert[®] software provides two different methods of displaying the factor levels in the experimental design: (i) the actual levels of the factors (i.e., the actual values in the experiment) and (ii) the coded factor levels (i.e., -1 for low levels, +1 for high levels and 0 for center point). The coded factor levels are defined as [6,19]:

$$Coded factor levels = \frac{actual value - factor mean}{(range of the factorial value/2)}$$
(1)

Coding reduces the range of each factor to a common scale, -1 to +1, regardless of its relative magnitude. It is also easier to think in terms of changes from low to high for the factors than to think about their actual values. The experimental design matrix in terms of both actual and coded factor levels is shown in Table 3.2. Six replicates were used for each experiment to determine the statistical significance of the results. Relationships between the wood flour content, acrylic modifier content and plasticizer content and the responses (die swell ratio and true viscosity) were statistically modeled to better understand the significant factors and interactions in the system.

	True viscosity at different shear rates (Pa-s)	2000 (s ⁻¹)	135.6	192.6	209.5	153.5	81.3	163.1	96.6	133.1	131.0
Responses		1200 (s ⁻¹)	159.3	233.5	263.1	188.2	92.5	195.8	122.6	164.9	168.2
		500 (s ^{.1})	199.9	303.7	355.1	247.8	111.7	251.8	167.1	219.4	231.8
	Die swell ratio		1.18	1.07	1.81	1.33	1.27	1.08	1.71	1.31	1.28
	Plasticizer content	(phr)	0 (-1)	0 (-1)	0 (-1)	0 (-1)	4 (+1)	4 (+1)	4 (+1)	4 (+1)	2 (0)
Factors ^a	Acrylic modifier content	(phr)	0 (-1)	0 (-1)	8 (+1)	8 (+1)	0 (-1)	0 (-1)	8 (+1)	8 (+1)	4 (0)
	Wood flour content	(phr)	0 (-1)	<u>5</u> 0 (+1)	0 (-1)	50 (+1)	0 (-1)	50 (+1)	0 (-1)	50 (+1)	25 (0)
	Type -		Fact	Fact	Fact	Fact	Fact	Fact	Fact	Fact	Center
	Experiment Number		1	C1	Ś	च	Ś	6	7	8	6

Table 3.2. Experimental Design Matrix in Terms of Actual and Coded Factor Levels Generated by Design-Expert® Software.

^aValues in parentheses are coded values

Before compounding, wood flour was dried in an oven for 48 hrs at 105°C to remove the moisture. The ingredients were weighed at the addition levels described in the experimental design (Table 3.2) and mixed in a high intensity batch mixer (Papenmeier, TGAHK20) for 10 min. It should be mentioned that a low level of plasticizer was used throughout the experiments to remain in the antiplasticization region where both neat PVC and PVC/wood-flour composite samples exhibit greater stiffness and strength compared to unplasticized counterparts [9]. The compounded batch was then used for rheological tests.

Rheology Experiments

The rheology of the compounded batch was measured online on an Intelli-Torque Plasticorder® Torque Rheometer (C. W. Brabender Instruments Inc.) equipped with a 32 mm conical counter-rotating twin-screw extruder (L/D ratio 13:1). Different L/D ratios (10:1 and 15:1) of capillary inserts were used. The extruder's barrel temperature profile and die temperature were kept constant at 190°C to maintain a constant melt temperature for accurate viscosity measurements. However, the speed of the screws was varied from 5 rpm to 30 rpm to generate different shear rates. The collected extrudates were used to measure the die swell ratio, which was calculated as the ratio of the solid extrudate diameter to the diameter of the die.

The apparent shear stress (τ_a) in a capillary die is given by [24,25]:

$$\tau_{a} = \frac{\Delta P}{4(L/D)}$$
(2)

where ΔP is the pressure drop across the capillary die and L/D is the length to diameter ratio of the die.

The apparent shear rate ($\dot{\gamma}_a$) was calculated using the following equation [24,25]:

$$\dot{\gamma}_{a} = \frac{4Q}{\pi R^{3}} \tag{3}$$

where Q is the volumetric flow rate of the polymer melt and R is the radius of the capillary.

The Bagley correction was applied to the apparent shear stress to account for the excess pressure drop at the capillary entry. This correction converts apparent shear stress to true wall shear stress. Measurements of viscosity at the same shear rate, with at least two different capillaries are needed to apply the Bagley correction. Data of total pressure drop versus flow rate are collected for each capillary die. The pressure drop versus L/D data are plotted at each flow rate and lines are extrapolated to L/D equals to zero. The resulting pressure drop (ΔP_e) is the pressure loss due to entrance effect at the particular flow rate and die diameter. The Bagley corrected shear stress was calculated by [24, 25]:

$$\tau_{\rm w} = \frac{\Delta P - \Delta P_{\rm e}}{4(L/D)} \tag{4}$$

where ΔP_c is the pressure drop at the capillary entrance.

As the apparent shear rate gives only Newtonian behavior (constant viscosity), a correction is necessary for shear thinning fluids (pseudoplastic fluids). The Rabinowitsch correction was done to calculate shear rate at the wall ($\dot{\gamma}_w$) of the capillary die by using the following equation [24, 25]:

$$\dot{\gamma}_{w} = \left[\frac{3n+1}{4n}\right] \dot{\gamma}_{a} \tag{5}$$

where n is the flow behavior index obtained as the slope of the linear plot of log $\dot{\gamma}_a$ vs. log τ_w .

The true melt viscosity was then calculated from the corrected shear stress and corrected shear rate by using the following equation:

$$\eta = \frac{\tau_{\rm W}}{\dot{\gamma}_{\rm W}} \tag{6}$$

This calculated true viscosity was used for further analysis.

Dynamic mechanical analysis was carried out on a Perkin Elmer (DMA 7e) instrument in the three-point bending mode to determine the storage modulus (elastic modulus) and loss modulus (viscous modulus) of neat PVC and composites. The test was performed under a helium atmosphere at a frequency of 1 Hz and a heating rate of 5°C/min in a temperature range from 25 to 150°C. The samples were cut from a panel made by compression molding the extrudates at 190°C for 5 min. Sample dimensions were 15 mm x 3 mm x 1.5mm thick. The average of three replicates was reported.

RESULTS AND DISCUSSION

Statistical Analysis of the Die Swell Ratio

Die swell is a phenomenon that occurs due to the elastic recovery of polymer after shear deformation. This can be attributed to the memory effect of polymer chains, which try to regain their original shape and size on stress removal.

A two-level factorial design was employed to evaluate the statistical effects of wood flour content, acrylic modifier content and plasticizer content on the die swell ratio of neat PVC and PVC/wood-flour composites. The analysis of the data was done to identify the key factors affecting the die swell ratio and also to understand interactions between different variables.

The die swell ratio data were entered into the design matrix (Table 3.2) generated by Design-Expert[®] software and a regression analysis was carried out to obtain the bestfit model to the experimental data. A standard analysis of variance (ANOVA) showed that the die swell data were best fitted with a linear model (values of "Prob > F" less than 0.05). When the values of "Prob > F" less are than 0.05, this indicates that the terms in the model have a significant effect on the response. In other words, the probability of the factors having no effect on the response is less than 5%. The ANOVA also showed that curvature in the model was insignificant, i.e. the relationship was linear (see Appendix B). The test for curvature compares the experimental data at the center point conditions to the predicted values for that same point. Significant curvature can indicate quadratic effects are present in the system, which are not accurately represented by the linear equation. As the model contained both significant and non-significant terms, it was simplified by dropping the insignificant term (plasticizer, term C). This modification did not affect the adequacy of the model, which can be seen in Table 3.3 by reasonably good R^2 and adjusted R^2 values as well as the adequate precision value of 19.6. R^2 represents the variation around the mean, adjusted R^2 shows the variation around the mean adjusted by the number of terms, and adequate precision is the signal to noise ratio for the model. As a result, the derived linear regression equation describing the relationship between the die swell ratio and different variables (in terms of coded factors) was reduced to:

Die swell ratio =
$$+1.34 - 0.15A + 0.20B - 0.073AB$$
 (8)

where A is the coded variable that represents wood flour content and B is the coded variable that represents acrylic modifier content.

Equation 8 indicates that wood flour content (factor A) and acrylic modifier content (factor B) are the main effect factors, while wood flour content/acrylic modifier content (interaction AB) is the only significant two-factor interaction term that affects the die swell ratio. The effect of plasticizer (factor C) on die swell ratio was not significant at the low addition level used in this study and was eliminated from the model. Comparison of the coefficient and algebraic sign of each factor in Eq. 8 gives an estimation of its relative influence on the die swell ratio of the sample.

As expected, wood flour content (factor A) had a negative effect on the die swell, i.e., the die swell decreased as the concentration of wood flour increased in the composites because of two main reasons: (i) reduction in normal stresses owing to low shear strain in the capillary [24] and (ii) the addition of wood flour to plastics greatly

Responses	F- Value	Prob > F ^a	R ²	Adjusted R ²	Adequate Precision ^b
Die swell ratio	79.2	0.0005	0.9834	0.9710	19.6
True viscosity at 500 s ⁻¹	651.7	0.0015	0.9994	0.9979	79.7
True viscosity at 1200 s ⁻¹	1675.2	0.0016	0.9998	0.9992	122.6
True viscosity at 2000 s ⁻¹	3473.2	0.0003	0.9999	0.9982	166.8

Table 3.3. Probability and Summary Statistics for Two-Level Factorial Model

^aValues of "Prob>F" less than 0.05 indicates the model terms are significant.

^bAdequate precision measures the signal to noise ratio. A ratio greater than 4 is desirable for the model.

reduces the coefficient of thermal expansion of the matrix, which reduces the amount that the polymer expands with applied heat [26]. By contrast, the die swell increased with the acrylic modifier content (factor B) due to the increased melt elasticity [7].

The perturbation plot of die swell ratio against all three investigated variables (Figure 3.1) provides supporting evidence of the relative importance of wood flour content (factor A) and acrylic modifier content (factor B) on the die swell ratio of the sample. Figure 1 illustrates changes in the die swell ratio as each factor moves from the chosen reference, with all other factors held constant at the middle of the design space (the coded zero level of each factor). It can be clearly seen from the perturbation graph that wood flour content and acrylic modifier content were the two important variables affecting the die swell, whereas the addition of a low level of plasticizer had no effect on die swell. Since the two main factors affecting the die swell of the materials (factors A and B) are also part of the only significant interaction (interaction AB) (Equation 8), it would be inappropriate to investigate these factors individually because the effect of one factor will depend upon the level of the other [23].

Figure 3.2 shows the interaction graph of the variation of die swell ratio as a function of the interaction between wood flour content and acrylic modifier content. The die swell ratio increased with the increased acrylic modifier content, regardless of the addition level of wood flour. However, the extent of die swell ratio increase due to the addition of acrylic modifier was more prominent for the unfilled PVC matrix than for the composites. This behavior is clearly seen by comparing the magnitude of the difference between the lowest (0 phr) and highest (8 phr) acrylic modifier content lines (Figure 3.2). Without wood flour the difference is large (coded value -1 or neat PVC), while the



Deviation from Reference Point

Figure 3.1. Perturbation plot of die swell against three investigated variables. A represents the wood flour content; B is the acrylic modifier content; and C is the plasticizer content.



Wood flour content

Figure 3.2. Die swell ratio as a function of the interaction between wood flour content and at 0 and 8 phr acrylic modifier (K-400) content.

difference decreases with increased wood flour content (coded value +1 or composite with 50 phr wood flour). The die swell ratio was considerably reduced by adding wood flour into the PVC matrix. These results imply that the die swell ratio can be reduced by increasing wood flour content in the PVC matrix.

Statistical Analysis of the True Viscosity

The same two-level factorial design was used to evaluate the effects of wood flour content, acrylic modifier content, and plasticizer content on the true melt viscosity of the neat PVC and PVC/wood-flour composites.

Since the shear rate encountered in the extruder during processing is in the range of 10^2 to 10^3 s⁻¹ [25], melt viscosity was measured for each composition in the design matrix at three different shear rates of 500, 1200 and 2000 s⁻¹ (Table 3.2). A normal probability plot of the residuals for each of the shear rates indicated there was non-normal variance. ANOVA requires equal variance of the residuals to detect differences in the treatment means. In this situation, a mathematical transformation is commonly performed on the entire data set to stabilize the variance of the residuals. For each shear rate, a power transformation was applied to the data set. The lambda value which normalized the variance of the residuals was different for each shear rate, and was negative in each case. These values were computed by the Design Expert software, using a Box-Cox plot. The adequacy of the generated models was very high with high R², adjusted R² and adequate precision values generated for the relationship at each shear rate (Table 3.3). ANOVA results showed that the curvature for the model was insignificant ("Prob > F" less than 0.05), at each of the tested shear rates (see Appendix B). The derived power regression equations describing the relationships between the true viscosity and different variables (in terms of coded factors) at various shear rates were:

at 500 s⁻¹ (Viscosity)^{-0.5} = +0.068 - 5.54 x 10⁻³ A - 3.03 x 10⁻³ B +7.22 x 10⁻³ C + 5.69 x 10⁻³ AB - 4.81 x 10⁻³ AC
(9)

at 1200 s⁻¹

$$(Viscosity)^{-1} = +6.23 \times 10^{-3} - 1.04 \times 10^{-3} \text{ A} - 0.39 \times 10^{-3} \text{ B} + 1.31 \times 10^{-3} \text{ C} + 0.89 \times 10^{-3} \text{ AB} - 0.91 \times 10^{-3} \text{ AC}$$
(10)

where A, B, and C are the coded variables that represent wood flour content, acrylic modifier content, and plasticizer content, respectively.

The above-described equations indicate that wood flour content, acrylic modifier content and plasticizer content are the main effect factors, while wood flour content/acrylic modifier content (interaction AB) and wood flour content/plasticizer content (interaction AC) are the significant two-factor interaction terms. Since these are power models with a negative lambda value, a positive algebraic sign of each factor in Equations 9-11 denotes a decrease in viscosity, whereas a negative algebraic sign denotes the opposite. As can be seen in the above equations, both wood flour content and acrylic modifier content had a negative sign, indicating an increased effect on the viscosity of the materials. In other terms, the true viscosity increased as the wood flour content or acrylic modifier content increased in the composites. In contrast, the effect of plasticizer content (factor C) was positive implying that the viscosity of the composites decreased with even the low level of plasticizer content.

The two-level factorial design also revealed powerful interactions between wood flour content and acrylic modifier content (interaction AB) as well as wood flour content and plasticizer content (interaction AC) (Equations 9-11). The wood flour content/acrylic modifier content interaction (interaction AB) had a negative sign, indicating a positive effect on the true viscosity, while an opposite trend was observed for wood flour content/plasticizer content interaction (interaction AC). As was previously mentioned, it would be inappropriate to investigate these factors individually since the effect of one factor will depend upon the level of the other factor in the model. The interaction graphs based on Equations 9-11 are illustrated in Figure 3.3.

The viscosity of neat PVC matrix and PVC/wood-flour composites decreased with increased plasticizer content, regardless of the presence of acrylic modifier and extrusion shear rate investigated. However, the effect of plasticizer in decreasing the viscosity was more pronounced in neat PVC than in the composite. This behavior was expected due to the plasticization effect induced by the plasticizer. When a plasticizer is incorporated into a PVC matrix, the polar groups of the plasticizer bond with the polymer dipoles, and the non-polar parts act as shields between polymer dipoles, thus resulting in less cohesion overall, with consequent increased freedom of molecular movement [27]. As a result, the chain flexibility or mobility increases, the matrix softens and flow



Figure 3.3. True viscosity at different shear rates: (a,b) at 500 s⁻¹ (c,d) at 1200 s⁻¹ and (e,f) at 2000 s⁻¹ as a function of the interaction between wood flour and at 0 and 4 phr plasticizer content: (a,c,e) no acrylic modifier and (b,d,f) 8 phr acrylic modifier.

properties are enhanced. As expected from the theory of particle suspension, the addition of wood flour increased the viscosity of the polymer matrix, regardless of plasticizer content and shear rate (Figure 3.3 a,c,e). It is believed that the presence of 50 phr wood flour in the PVC matrix restricted molecular motion, imposing more resistance to flow [9].

The viscosity of the neat PVC and the composite was a strong function of the acrylic modifier content, independent of the plasticizer content and shear rate. However, two distinct trends were observed: The addition of acrylic modifier significantly increased the viscosity of the neat PVC [8], while it decreased the viscosity of the composites (Figure 3.3 b,d,f). To further study this unusual behavior, a DMA analysis was conducted on the neat PVC and composite with and without acrylic modifier. Table 3.4 shows the generated DMA data. Irrespective of the temperature the storage and loss moduli of neat PVC increased with the addition of acrylic modifier (Table 3.4), implying that the addition of acrylic modifier increased the melt elasticity and viscosity of the neat PVC matrix. By contrast, the addition of acrylic modifier decreased the storage and loss moduli of the composites. These results are in good agreement with those reported by Guffey and Sabbagh [22], who showed that addition of CPE to PVC/wood-flour composites reduced the viscosity. The probable reason for the acrylic modifiers opposite effect observed on viscosity of PVC and composite may be due to its entanglement effect. Acrylic modifiers have relatively high molecular weight (200,000 to 3 million) compared to PVC (up to 85,000) [7]. When these compounds are melt mixed with PVC, their long polymer chains entangle the short PVC chains, increasing the overall PVC melt elasticity and viscosity (Figure 3.4) [7]. However, when wood flour is present in the
system, it may hinder the interaction between acrylic modifier and PVC, reducing the entanglement effect.

Wood tures	-Flour Com	posites. /C Pa) Loss	PVC with 8 modi (GI	phr acrylic ifier Pa) Loss	Com (G	posite Pa)	Composite acrylic 1 (G) Storage	with 8 phr nodifier Pa) Loss
' ≍ ∣	odulus	Modulus	Modulus	Modulus	Modulus	Modulus	Modulus	Modulus
	2.95	0.17	4.22	0.64	7.72	0.78	3.58	0.31
	2.62	0.27	3.57	0.72	6.61	0.92	3.19	0.33
	1.69	0.64	2.45	0.85	3.91	1.38	2.71	0.58

Table 3.4 Effect of Acrylic Modifier on the Storage Modulus (Elastic Modulus) and Loss Modulus (Viscous Modulus) of Neat PVC and PVC/Wood-Flour Composites.



Figure 3.4. Entanglements of PVC Chains and Acrylic Modifier [7]

CONCLUSIONS

Using a factorial design approach, this study examined the effect of different formulation variables on the viscoelastic properties of PVC/wood-flour composites measured online on a conical twin-screw extrusion capillary rheometer. The following conclusions can be drawn from the experimental results:

Wood flour content and acrylic modifier content were the two important variables affecting the die swell ratio, whereas the addition of a low level of plasticizer had no effect. The die swell increased with increased acrylic modifier content, regardless of the addition level of wood flour. This was a probable result of increased melt elasticity of the polymer. However, the die swell ratio was considerably reduced by adding wood flour into the PVC matrix as a result of reduced normal stresses and lower coefficient of thermal expansion.

The true viscosity of neat PVC and PVC/wood-flour composites decreased with the plasticizer content, irrespective of the acrylic modifier content due, to the plasticization effect of the plasticizer. However, the addition of acrylic modifier significantly increased the viscosity of unfilled PVC due to increased melt elasticity. Unlike for neat PVC, the true viscosity decreased as the acrylic modifier content increased in the composites.

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CHAPTER 4

CONTINUOUS EXTRUSION OF MICROCELLULAR FOAMED PVC AND ITS WOOD FLOUR COMPOSITES USING SUPERCRITICAL CO₂

ABSTRACT

The aim of this study was to produce microcellular foamed PVC and its wood flour composites in a continuous extrusion process using supercritical CO_2 as a blowing agent. An extrusion foaming setup was built to accomplish this goal. Various material composition and processing parameters were studied to determine their effects on the morphology of the foamed samples. Although foamed PVC samples could be produced from this setup, their processing-property relationships could not be determined due to a lack of steady-state conditions during the foaming process.

Keywords: Microcellular foaming, Polyvinyl chloride, Supercritical fluid, Extrusion

INTRODUCTION

Wood plastic composites (WPCs) represent a unique and growing share of the building products market. With advantages including durability, visual appeal, customizability, ease of installation and cost effectiveness compared to solid wood and other traditional building materials, WPCs are gaining market share in a variety of applications. Several companies have launched innovative lines of exotic-looking decking, railing systems, privacy fencing and complimentary accessories in recent years that have improved consumer acceptance of, and desire for, WPCs. If these trends continue, the market can be expected to grow and develop in new directions. For example, the market for extruded WPCs was approximately \$1 billion in 2005 and the market is expected to grow at 14% through 2010 [1, 2].

WPCs use wood flour or fiber as a filler or reinforcing agent in the plastic matrix. Wood flour has several advantages over conventional fillers (talc and calcium carbonate), advantages include low density, low cost and less abrasiveness to processing equipment. A variety of polymers have been used in manufacturing WPCs including polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS) and acrylonitrile butadiene styrene (ABS). These polymers may be virgin or recycled, and in either case, may be filled with wood that has been reclaimed from other uses.

PVC is one of the most-used polymers used in manufacturing WPCs on a volume basis, although the market is led by polyethylene. PVC wood composites offer several advantages over polyolefin-based wood composites such as increased weatherability, high stiffness, ease of customizing the final product properties by changes in formulation, and good paintability of the final product. The specific gravities of polyolefins and PVC

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are higher than that of solid wood. When combined into WPCs, the resulting composite materials have higher specific gravity than solid lumber. Compared to polyolefin-based WPCs, the PVC wood composites are even denser, because PVC is denser than polyolefins. The high specific gravity of PVC wood composites makes them heavier for shipping, handling and end use applications. Addition of wood to the PVC also significantly reduces the impact strength of the PVC matrix. These drawbacks have been addressed by producing microcellular-foamed structures in WPCs. This reduces the density of the composites. Additional advantages of microcellular foamed WPCs include reduced material costs and increased mechanical properties, such as impact strength [3, 4]. The combination of property enhancement and cost reduction makes microcellular foamed WPCs attractive for use in a variety of innovative applications, not limited to building products.

The simplest way to introduce a microcellular structure into samples is to use a batch foaming process. Polymers of differing morphologies such as HDPE [5, 6], PP [6], PVC [7], PS [8], PC [9], etc., have been foamed using this technique. Most of the research on microcellular foaming of PVC and its composites has used the batch process. The relationships between void fraction and mechanical properties of batch foamed PVC and its composites have been investigated with varying results [10, 11]. An in-depth study is still needed to evaluate the dependence of mechanical properties on the characteristics of microcellular foamed PVC.

In spite of the ease and simplicity of batch foaming, this process is not likely to be implemented in the industrial production of foams because it is not cost-effective. The microcellular batch foaming process is time consuming due to the multiple steps involved in the production of foamed samples - particularly the sample saturation step, which can last from several hours to days. To overcome these drawbacks, a continuous process of manufacturing microcellular foam using an extrusion technique was proposed by several researchers [12-15].

Park et al. [16] studied the effects of different processing parameters on the morphology of high impact polystyrene (HIPS) foams using an extrusion technique. They found that melt temperature had a significant effect on cell coalescence, which could be prevented by selecting the correct melt and die temperatures. Reducing the die temperature from 170 to 135 °C increased the volume expansion ratio of the foam, mainly because lower temperatures reduced the gas loss. Further decrease in temperature had a negative effect on the volume expansion ratio of the foamed HIPS samples because of the increased stiffness of the polymer matrix.

Zhang et al. [17] used the single and tandem extrusion processes to foam microcellular HDPE/wood fiber composites using CO_2 as a blowing agent. They showed that increasing wood fiber content deteriorated the cell morphology in terms of both cell size and number. Similarly, when the CO_2 content was increased above 1 wt. % there no improvement in the cell structure and morphology was observed. It was also shown that the addition of 5 wt. % coupling agent dramatically improved the cell structure in the composites. This was attributed to improve bonding between the wood fiber and HDPE matrix due to the presence of the coupling agent.

The continuous extrusion process has been successfully used for several polymers and their composites, but to date there has been no available literature on using this process for PVC and its wood composites using online injection of supercritical fluid as the blowing agent. The limited research done on extrusion foaming of PVC and its composites has been mainly focused on chemical blowing agents, though the use of moisture as a foaming agent has also been reported in the literature [18]. Chemical blowing agents require extra care during dry blending to avoid migration, which results in density variations in the final product. Apart from this, chemical blowing agents have several other disadvantages including difficulties in adjusting online foam densities [19]. Physical blowing agents such as carbon dioxide (CO_{2}), nitrogen (N_2) and argon (Ar) are economical and eco-friendly, which makes them a favorable alternative to chemical blowing agents.

One challenge to producing PVC composite foams is overcoming the increase in the viscosity of the PVC matrix when wood flour is added. Increased viscosity hinders the bubble formation and growth and generally results in poor foam quality in terms of cell size and density [20, 21]. Our prior work (chapter 3) showed that the melt viscosity of PVC/wood-flour composites could be successfully altered by the addition of acrylic foam modifier [22].

Applying the continuous extrusion process technique to PVC and its wood flour composites, along with the use of supercritical CO_2 as a blowing agent, would result in an efficient, environmentally-friendly and cost-effective process. Thus, the goal of this study was to manufacture microcellular foamed PVC and its composites in a continuous extrusion process using supercritical fluids.

EXPERIMENTATION

Materials:

PVC, K value-57 (OxyVinyls) was used as a matrix in this study (Table 4.1). Tin stabilizer (PlastiStab 2808) from OMG Americas was used as a heat stabilizer. Calcium stearate (Synpro, Ferro Corp.) and paraffin wax (Gulf Wax) were used as lubricants. Different acrylic processing aids (Paraloid K-125, Paraloid K-175, Rohm and Haas Co.) were also used in the formulations. Acrylic foam modifier (Paraloid K-400, Rohm and Haas Co.) was used to facilitate the foaming process. Wood flour from hardwood maple (American Wood Fibers) was used as filler. CO₂ was used as a physical blowing agent.

Continuous Foaming Process:

The ingredients were weighed at the addition levels described in Table 4.1 and were mixed in a high intensity batch mixer (Papenmeier, TGAHK20) for 10 min at room temperature. Before compounding, wood flour was dried in an oven for 48 hrs at 105° C to a moisture content of less than 1%. The compounded mixture was then fed through a 19 mm single screw extruder with an L/D ratio of 25:1 (C. W. Brabender Instruments Inc.) (Figure 4.1). Supercritical CO₂ gas was injected at different concentrations into the extruder under high pressure between the second and third zones of the barrel. The concentration of the gas was precisely controlled by a positive displacement syringe pump (ISCO 260D). A static mixer (Omega FX 84441S) was attached at the end of the extruder to ensure homogenization of the solution of polymer melt and the blowing gas, followed by a custom designed nozzle die (Figure 4.1).

Ingredients	Concentration (phr)
PVC K-57	100
Tin stabilizer	2
Calcium stearate	1.5
Paraffin wax	2
Paraloid K-120	0-2
Paraloid K-175	0 – 2
Paraloid K-400	0 – 8
Wood flour	0 - 30

 Table 4.1. Formulations Used in Manufacturing Microcellular Foamed PVC and its

 Wood-Flour Composites



Figure 4.1. Schematic of Continuous Microcellular Foaming Process

Thermodynamics of Foaming:

The concentration of gas and the time required to induce foaming in a polymer depend on the solubility and diffusion coefficient of the gas in the polymer matrix. Both the solubility and diffusivity of the gas vary, depending on the processing parameters such as temperature and pressure. The diffusion coefficient increases with temperature, which can be expressed by the following Arrhenius type equation [23]:

$$D = D_o \exp(-\Delta E_D / RT)$$

where D is the diffusion coefficient, D_o is the diffusion coefficient constant, E_D is the activation energy, R is the universal gas constant and T is the temperature.

Muth et al. [24] showed that increasing the temperature and pressure of the system resulted in higher diffusivity of CO_2 gas in PVC polymer. Raising the temperature of PVC from 40 to 70 °C increased the diffusivity of CO_2 gas from 0.7 x 10⁻¹¹ m²/s to 2.51 x 10⁻¹¹ m²/s at 20 MPa pressure. As a result, saturation time for a sample of thickness 2mm is reduced from 40 hours at 40 °C to 11 hours at 70 °C, and could be further reduced to several minutes at elevated temperatures. The time required by the gas to diffuse into the sample can be calculated by the following equation [23]:

$$t_d \approx l_d^2 / D$$

where t_d is the diffusion time, l_d is the diffusion thickness/distance and D is the diffusion coefficient.

The higher temperatures and pressures used in the extrusion foaming process are expected to lower the time required for sample saturation. It will be important to select the proper processing speed, which will provide long enough residence time during extrusion to ensure the complete saturation of the polymer with blowing gas to form a single phase solution.

For the extrusion foaming process to be successful, an adequate amount of blowing gas must be dissolved in the polymer. Gas solubility in a polymer increases with increasing pressure, but decreases with increasing temperature. The relationship between the solubility or concentration of the gas and pressure can be expressed by Henry's Law:

C = H*P

where C is the gas saturation concentration, H is the Henry's Law Constant and P is the saturation pressure.

From Henry's law it is clear that high pressure must be maintained during processing to increase the solubility of the gas in the polymer. This becomes even more critical at high temperatures. Muth et al. also demonstrated that at 20 MPa pressure, an increase in temperature from 40 to 70 °C reduced the CO_2 solubility in PVC by nearly 15%. Similarly, an increase in temperature from 100 to 200 °C reduced the solubility of CO_2 in polystyrene from 7.17 wt. % to only 4 wt. % at 12.6 MPa pressure [25]. There is no solubility data available in the literature for PVC at elevated temperature and pressure. However, based on the lower temperature data for PVC, the solubility of CO_2 in PVC at extrusion temperatures is expected to be reduced even further. High pressure within the extruder barrel will be required to maintain adequate saturation of the polymer with blowing gas for foaming the PVC.

Physical Characterization of Foams:

Microcellular foam can be characterized by the proportion of voids in the foamed sample, which is known as the void fraction. The void fraction (V_f) is an indication of the foam density. It was calculated using the following equation:

$$V_f = 1 - \frac{\rho_f}{\rho}$$

where ρ_{f} and ρ are the densities of the foamed and unfoamed sample, respectively.

The density of the samples was determined by the water displacement method as per ASTM standard D-792 and was calculated by the following formula:

$$Density\left(g/cm^{3}\right) = 0.9975\left(\frac{M_{a}}{M_{w}}\right)$$

where M_a and M_w are the weights of samples measured at room temperature in air and water, respectively.

SEM Analysis:

Scanning electron microscopy (SEM) was used to study the morphological characteristics of the extruded foamed samples. This analysis shows the cell density and cell size in the foamed samples, which are major criteria in characterizing microcellular foam. The cell density (N_f) was determined by the following formula:

$$N_f = \left[\frac{nM^2}{A}\right]^{3/2} \left(\frac{1}{1 - V_f}\right)$$

where n is the number of cells in the area A, and M is the magnification factor of the micrograph.

SEM analysis was performed on fracture surfaces of cryogenically fractured foam samples. A JEOL JSM-6400 scanning electron microscope equipped with a LaB6 gun was used to collect the SEM images. An accelerating voltage of 12KV was used. The samples were gold coated in a sputter coater before collecting the images.

RESULTS AND DISCUSSION

Experimental Setup:

Extruding continuous, perfect foam requires constant feeding, conveying, melting and mixing of the polymeric material before it reaches the injection stage. To accomplish this, a 19 mm single screw extruder with a 25:1 L/D ratio (C.W. Brabender) was used (Figure 4.1). The extruder had three separate heating zones to effectively control the temperature of the polymer melt. After melting the polymer material, the blowing agent was continuously injected at a constant flow rate and pressure to produce a uniformly foamed product. A positive displacement pump (ISCO D260) with a custom designed injection port and flow restrictor (Mott Corporation) was used to achieve the constant flow rate and gas pressure. To ensure adequate mixing of the polymer and CO₂ after injecting the blowing agent, the injection port was placed between the second and third zones of the extruder barrel (Figure 4.1). The injection port consisted of a three inch blank melt bolt with a hole drilled through it to permit the passage of gas. To successfully inject the gas into the extruder, the gas pressure had to be higher than the actual barrel pressure. Otherwise, the polymer would flow towards the injection port and block it, preventing the blowing agent from flowing through the extruder. Supercritical CO₂ is a highly compressible fluid; this results in variation of the flow rate due to changes in the barrel pressure. This can be avoided by injecting the blowing agent at very high pressure, compared to the pressure in the extruder barrel. This pressure gradient was maintained with a flow restrictor, which is nothing but a fine metal membrane. The flow restrictor created resistance for the gas flow and thus maintained its high pressure. It also prevented the polymer from entering the injection port and

blocking it. The flow restrictor was machined into the very bottom of the injection port (blank melt bolt). Once the gas was effectively injected into the extruder, it had to be mixed with the polymer melt. A specially designed mixing area on the screw was used to achieve the mixing. This section of the screw provided extra shear, resulting in better mixing. To further increase the mixing and form a homogeneous solution of polymer and gas, a 6-element static mixer (Omega FMX8441S) was attached to the extruder (Figure 4.1). The element of the static mixer had a left and right helix, ensuring a vigorous and homogenous mixing of polymer melt and gas. To keep the blowing agent soluble in the polymer melt it had to be maintained at high pressure. A custom designed nozzle die was connected at the end of the static mixer (Figure 4.1). A 1 mm diameter nozzle was used to achieve a high pressure drop at the die opening, which results in thermodynamic instability by reducing the gas solubility in the polymer/gas solution. This instability created the phase separation and initiated the nucleation of numerous cells in the polymer matrix, which was then immediately cooled to preserve the cell structure. This experimental setup was based on the process described by Park et al. [18].

Microcellular Foaming of PVC:

As described above, the setup of an extrusion system for continuous foaming of polymers and composites using supercritical fluid as a blowing agent is very complex and involves many variables. To ensure that the experimental setup was adequate to foam polymeric materials, HDPE was used as a baseline. Other researchers have demonstrated the continuous foaming of HDPE in similar extrusion setups [19, 25]. Conditions described in these studies were used as the basis for foaming HDPE. These included die

temperatures ranging from 140 - 175 °C, extrusion speeds of 20-40 rpm and gas flow rates between 0.1 - 2 ml/min.

Successful microcellular foamed samples of HDPE were obtained under various combinations of temperature, gas flow rate and extrusion speed. Steady state conditions of constant pressure, temperature and gas flow rate were attained over this range. Steady state conditions are crucial for foam characterization, since, as mentioned previously, CO_2 gas is highly compressible. The density of CO_2 gas is directly proportional to the pressure and inversely proportional to the temperature. Thus, any changes in pressure and temperature will change the net mass flow rate of the gas. This makes it difficult to characterize the processing-property relationships of the foamed samples, as the exact amount of CO₂ used to manufacture the samples is not known. SEM micrographs of representative samples of microcellular foamed HDPE were taken to visualize the morphology of the samples (Figure 4.2). The top image (Figure 4.2a) shows microcellular sized bubbles that are distributed fairly evenly throughout the sample. This implies that the designed setup can produce good quality microcellular foams. Figure 4.2b shows the cell wall area at higher magnification. This figure provides evidence of even smaller bubbles that are very evenly distributed throughout the cell wall area. These bubbles are less than a micron in size. HDPE foamed very well in the extrusion process using CO_2 as a blowing agent, which suggested that the extrusion foaming setup was properly designed to achieve continuous microcellular foaming of polymers using a supercritical fluid blowing agent.



Figure 4.2. SEM Micrographs of HDPE at (a) 100X and (b) 10,000X

Unlike HDPE, PVC was not easily foamed using the continuous extrusion process with CO_2 . The injection of supercritical fluid CO_2 into the extruder did not provide even gas pressure in the extruder during foaming. It was not possible to reach and maintain steady state conditions where the pressure was held constant and the material would exit the die as a foam. Instead, the pressure fluctuated greatly throughout the experiments, resulting in some partially foamed samples that were rapidly ejected from the die under high pressure. The various combinations of barrel temperature, die temperature and extrusion speed that were tested for foaming PVC are listed in Table 4.2. The gas content was varied from 0.5 - 5 wt. %. The inability to reach and maintain steady state conditions may have been due to the high melt viscosity of PVC melt compared to HDPE, which could result in very high pressure drops in the static mixer and die. This pressure drop reduces the solubility of the gas in the polymer and foams the polymer matrix well before the die exit. The released gas inside the extruder system expands due to the high temperature and lack of high pressure, creating a huge empty pocket in the system and thus breaking the continuous extrusion of polymer. This released gas exits the die intermittently, shooting the polymer from the die at high pressure. Attempts were made to suppress this behavior by changing the viscosity of the PVC melt.

Our previous research [24] (Chapter 3) showed that additives such as foam modifier, plasticizers and filler have a significant effect on the melt viscosity of the PVC melt. Based on that study, the batch composition of the PVC was altered in favor of lower melt viscosity by adding 4 and 10 phr of DEHP plasticizer. Various combinations of extruder screw speed, barrel temperature and die temperature (listed in Table 4.2) were again tested with these formulations to determine whether lower melt viscosity might

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Zone 1 (°C)	Zone 2 (°C)	Zone 3 (°C)	Die (°C)	Screw Speed (RPM)
160	180	175	150-180	10-30
160	185	180	150-180	10-30
180	190	185	150-180	10-30
175	190	180	150-180	10-25
175	180	175	160-175	10-20

Table 4.2. Different Processing Conditions used to Manufacture MicrocellularFoamed PVC and Its Composites

lead to steady state conditions and improved foaming. However, none of these tests were successful, as steady state conditions were never achieved with PVC. Other polymers such as polystyrene (both regular and high impact) and polyethylene of various melt flow rates were also tested in this extruder setup to see whether these variables would have an effect on foaming. Surprisingly, all polymers tested, other than PVC, were able to be foamed successfully in this setup. The success obtained with other polymers suggested that the PVC polymer itself was likely the obstacle to foaming. The complex processability of PVC, including difficulty in controlling its melt viscosity, was one probable reason for the difficulties in foaming. Another possible problem might have been insufficient mixing of the polymer melt and gas due to the small mixing zone in the extruder. This could be eliminated by using a longer L/D ratio extruder. Lack of a proper flow restrictor, which could maintain a high enough pressure difference between the barrel and gas pressure, may be another reason why the PVC did not consistently foam.

Some foamed samples were collected from the extruder, but these were not obtained at steady state conditions. SEM micrographs were collected for foamed samples produced with varying content of CO_2 (Figures 4.3 and 4.4). Since the pressure and mass flow rate were not stable at any time during the run, the effects of various processing conditions and material composition could not be systematically compared.

Any trends observed during non-steady state conditions were not necessarily reflective of actual behavior of the foam. An overall view of the foamed PVC sample at 3 wt. % CO₂ content (Figure 4.3a) showed randomly distributed large and small bubbles



Figure 4.3. SEM Micrographs of PVC foamed at 3 wt. % CO₂ (a) 20X and (b) 50X

throughout the sample. This indicated that the polymer and gas were not mixed properly and a homogeneous solution was not formed, which resulted in uneven foaming of the sample. A magnified view of the same sample (Figure 4.3b) illustrates a broken cell structure that was consistent throughout the sample. This can result either from high foaming temperature or from premature foaming inside the machine before exiting the die. To study whether this was a result of temperature, a wide range of die temperatures were studied, ranging from 135 to 175 °C. Samples collected at various temperatures over this range displayed similar cell morphology. Thus, we concluded that the pressure inside the machine was not high enough to maintain the solubility of the CO_2 gas in the polymer melt, resulting in premature foaming of the samples. High pressure in the system could not be maintained due to the excessive pressure drop in the static mixer and die, resulting from the high viscosity of the PVC melt. In the SEM micrographs of samples foamed with 2 and 1 wt. % of CO_2 , respectively (Figure 4.4a and 4.4b), larger bubbles were formed at the lower mass flow rate of CO_2 . None of the SEM images show bubbles that were uniform in size. While some of the bubbles appear to be microcellular, many are larger than that.

Since steady state conditions were not achieved, it was not possible to assess the effects of processing conditions or material composition on the foam structure of the PVC with any certainty. For the several reasons discussed above, including the lack of sufficient mixing after the gas was introduced into the extruder, we were unable to attain the initial goals of this experiment.



Figure 4.4. SEM Micrographs of PVC foamed at (a) 2 wt. % CO2 and (b) 1 wt. %

CO₂

CONCLUSIONS

The goal of this study was to produce microcellular foamed PVC and its wood flour composites through a continuous extrusion process using supercritical CO₂ as the blowing agent. A continuous extrusion setup for microcellular foaming was developed in this study. Polymers such as HDPE and PS were successfully microcellular foamed under steady-state conditions with these this setup. However, when PVC was foamed, steady-state conditions could not be achieved. This may be due to insufficient mixing of polymer and blowing gas and to a lack of high enough pressure to keep the gas soluble in the polymer. SEM images revealed uneven cell size and extreme cell wall breakage within the PVC foams. This confirmed that there was a lack of proper mixing and premature foaming in the extruder, due to the lack of high pressure needed to maintain the solubility of CO₂ gas in the polymer melt. Attempts were made to control this behavior by testing various processing conditions and material compositions. However, none of these attempts were able to produce good quality microcellular foamed samples under steady-state conditions.

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CHAPTER 5

NOVEL COUPLING AGENTS FOR PVC/WOOD-FLOUR COMPOSITES^{*}

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^{*}This paper was the winner of the 2005 Best Student Paper Award presented by the SPE Vinyl Division

ABSTRACT

Effective interfacial adhesion between wood fibers and plastics is crucial for both the processing and ultimate performance of wood-plastic composites. Coupling agents are added to wood-plastic composites to promote adhesion between the hydrophilic wood surface and hydrophobic polymer matrix, but to date no coupling agent has been reported for PVC/wood-fiber composites that significantly improved their performance and was also cost-effective. This paper presents the results of a study using chitin and chitosan, two natural polymers, as novel coupling agents for PVC/wood-flour composites. Addition of chitin and chitosan coupling agents to PVC/wood-flour composites increased their flexural strength by approximately 20%, their flexural modulus by approximately 16%, and their storage modulus by approximately 33-74%, compared to PVC/wood-flour composite without the coupling agent. Significant improvement in the composite performance was attained with 0.5 wt% chitosan and while 6.67 wt% chitin.

Keywords: PVC, PVC/wood-flour composites, coupling agent, chitin, chitosan, dynamic mechanical analysis, flexural properties.
INTRODUCTION

Wood-plastic composites (WPCs) have emerged as an important family of engineering materials. They are partially replacing solid pressure-treated wood and other materials in a variety of applications [1]. Although WPCs are superior to the neat polymers in terms of material cost and stiffness, their strength performance (tensile, flexural, and impact) is generally lower compared to the unfilled polymers [2,3]. The decreased strength is likely a result of the natural incompatibility of the hydrophilic wood fibers (high surface tension) and the hydrophobic polymer matrix (low surface tension) [2-5]. Phase incompatibility yields very weak interactions and thus a weak interface (poor interfacial adhesion) between the fiber and the matrix.

One approach to designing WPCs is to modify the wood fiber surface with coupling agents to improve the strength [6]. Coupling agents convert the hydrophilic surface of wood fibers to a more hydrophobic surface. Thus, the surface tension of the wood fibers is reduced and approaches that of the molten polymer. As a result, wetting and adhesion are improved via mechanisms such as diffusion and mechanical interlocking between treated fibers and the polymer matrix [6].

Due to its strong effect in altering the hydrophilic surface of wood fibers to a more hydrophobic one, maleic anhydride functionalized polyolefin is commonly used as a coupling agent for polyolefin/wood-fiber composites [4,6]. Similarly, to enhance the interfacial adhesion between wood fibers and a PVC matrix, the second largest plastic used to manufacture WPCs, several investigators have assessed the effects of various fiber treatments, including different types of isocyanates, maleic anhydride, silanes, etc. as coupling agents [7-9]. Most mechanical properties of the composites were improved by these chemical treatments, compared to those of composites with non-treated fibers. However, the properties of the composites were inferior to those of unfilled PVC, suggesting that, unlike in polyolefin/wood-fiber composites, converting the hydrophilic surface of wood fiber to hydrophobic is not effective for enhancing the adhesion of PVC to wood fibers.

Previous studies, however, demonstrated that when PVC is used as the matrix in WPCs, acid-base interactions, in which one phase acts as an electron donor (base) and the other acts as an electron acceptor (acid), are a significant factor in enhancing interfacial adhesion [2,3]. Therefore, surface modification of wood fibers to be used with PVC should be designed to modify the acid-base interactions at the matrix/fiber interface in order to improve the performance of these composites. For example, by changing the acidic characteristics of wood fibers through surface modification with γ -amino propyltriethoxy silane (Figure 5.1), PVC/wood-fiber composite with equal tensile strength and greater modulus than unfilled PVC was developed [2]. The use of the aminosilane successfully modified the wood surface, and facilitated the interaction between the wood and PVC according to Lewis acid-base theory [2].

In spite of these benefits, γ -amino propyltriethoxy silane has not been extensively used as a coupling agent for PVC/wood-fiber composites, mainly due to its high cost but also due to the difficulty in evenly coating the surface of wood fibers, owing to its sensitivity to hydrolysis and self-condensation. Consequently, aminosilane is not a desirable coupling agent in this application.



ЮH

Modified Wood

Figure 5.1. γ -Amino Propyltriethoxy Silane Reaction Mechanism with Wood and . PVC [2]

ЮH

Thus, the objective of this study was to explore the use of amine-containing natural polymers such as chitin and chitosan as cost-effective and novel coupling agents for PVC/wood-fiber composites.

Literature Review on Chitin and Chitosan

Chitin (Figure 5.2a) is the second most abundant natural polymer after cellulose and is extracted from the shells of crustaceans. Chitosan (Figure 5.2b) is obtained by Ndeacetylation of chitin. These polymers are widely available, non-toxic, biocompatible, and lower in cost than many synthetic coupling agents. The acetyl amine functionality of chitin, and the amine functionality of the chitosan, should permit these polymers to interact with wood and PVC in a manner similar to the aminosilane, and so enhance the interfacial adhesion between PVC and wood fibers, while potentially improving other properties, and also be more cost-effective.





Several investigators have reported the use of chitin and chitosan as additives in different polymers for various applications [10-16]. In one study, the interfacial adhesion between chitin fibers and polycaprolactone (PCL) was increased by an irradiation treatment of the composites. This resulted in an overall increase in mechanical properties of the composite compared to composite prepared from untreated chitin fiber. This increase in interfacial bonding was attributed to a free-radical grafting reaction [10]. Chitosan has also been reported to have been crosslinked to a polymer matrix [11]. However, that process used formaldehyde as a cross linking agent, which is a known carcinogen and hazardous to the environment.

Biodegradable composites were also prepared by incorporating chitin flakes ranging from 0-30 wt% into a plasticized starch matrix using an injection molding process. Chitin flakes increased the elastic modulus, tensile stress and water resistance of the composites when compared to the unfilled starch [12]. Biodegradation of the synthetic polymers can also be increased by incorporating a natural biodegradable polymer such as chitosan [13].

Chitosan is also used in the wood industry. For example, chitosan forms a Schiff base when reacted with aldehyde compounds. This property of chitosan can be very useful in reacting with the formaldehyde released from the glue line of plywood, thus reducing the overall emission of formaldehyde to the environment. Hence, chitosan can be used as a functional coating reagent for wood [15]. The use of chitosan as an environmentally friendly adhesive for wood has also been reported in the literature. Glue

made from chitosan showed excellent water resistance and was proposed as a replacement for synthetic adhesives [16].

Research has not been carried out to examine the effectiveness and efficiency of chitin and chitosan as adhesion promoters in PVC/wood-fiber composites. These compounds present an opportunity for compatibilizing PVC and wood-fiber in composites in a way that would be novel, low cost and readily available.

EXPERIMENTAL

Materials

Chitin and chitosan, two natural polymers were used as coupling agents. PVC (K value-66) was used with 40 mesh size wood flour from a hardwood maple species as filler. The complete formulations of the rigid PVC/wood-flour composites are given in Table 5.1.

Ingredients	Content (phr)		
PVC K-66 (OxyVinyls)	100		
Tin stabilizer (PlastiStab 2808- from OMG Americas)	2		
Calcium stearate (Synpro, Ferro Corp.)	1.5		
Paraffin wax (Gulf Wax)	2		
Paraloid K-120 (Rohm and Haas Co.)	2		
Paraloid K-175 (Rohm and Haas Co.)	2		
Paraloid KM-334 (Rohm and Haas Co.)	10		
Chitin or Chitosan (TCI America)	Variable ¹		
Wood flour (American Wood Fibers)	75		

Table 5.1. Formulations Used in PVC/Wood-Flour Composites.

¹The concentrations of chitin and chitosan varied from 0 to 10 wt. % based on the weight of wood flour in the composites.

Composite Manufacturing

All components of the formulation given in Table 5.1 were added to a high intensity mixer (Papenmeier, TGAHK20) and mixed at room temperature for 10 min. Prior to compounding, the wood flour was dried in an oven for 48 hrs at 105°C to a moisture content of less than 1%. The compounded and mixed formulation was then extruded through a 32 mm conical counter rotating twin-screw extruder with an L/D ratio of 13:1 (C. W. Brabender Instruments Inc.) into 10 mm diameter rods. The temperature profile during extrusion was set at 190°C for all zones and the extrusion speed was maintained at 40 rpm. The extruded rods were compression-molded into panels in a hydraulic press (Erie Mill Co.) at 190°C for 5 minutes under 6200 KPa pressure. The mold was then cooled to room temperature.

Property Testing

The samples for flexural testing were cut from the compression molded panels and conditioned at 23 °C \pm 2 and 50% \pm 5 relative humidity in a walk-in conditioning room for 48 hours before testing. The flexural test was carried out on an Instron 4206 with series IX software as per ASTM D790. The crosshead speed was 1.9 mm/min. At least eight samples were tested for each formulation. Tukey HSD test of multiple comparisons was used to determine significant differences between the averages of the batches. The effects of chitin and chitosan content on the flexural strength and flexural modulus of the composites were compared at P < 0.05 to determine the statistical significance. Dynamic mechanical analysis (DMA) was carried out on a Perkin Elmer (DMA 7e) instrument in the three-point bending mode to determine the storage modulus (elastic modulus), loss modulus (viscous modulus) and tan delta of the samples. The test was performed in the temperature sweep mode from 25°C to 150°C under a helium atmosphere at a frequency of 1 Hz and at a heating rate of 5°C/min.

RESULTS AND DISCUSSIONS

Flexural Properties

Figure 5.3 and 5.4 show the flexural strength and modulus of the neat rigid PVC and composite without and with various coupling agent contents.

As expected, without coupling agent the addition of wood flour into the PVC matrix reduced the flexural strength of the composite compared to the neat PVC (Fig. 5.3a and 5.3b). Poor interfacial adhesion between wood flour and PVC matrix may be one of the reasons for the inferior flexural strength of the composites [4,6].

The incorporation of coupling agents into the formulations had a positive effect on the flexural strength of PVC/wood-flour composites. Both chitin and chitosan significantly improved the strength of the PVC/wood-flour composites compared to composites without coupling agents (Figure 5.3a and 5.3b). Different letters above the bars indicate significant differences between the uncoupled composite and composites with chitin or chitosan, while the same letter indicates no statistically significant difference at P < 0.05. The observed increase in flexural strength of the composites may be attributed to the improved interfacial adhesion between the wood flour and the PVC matrix [4,6]. This improved interface resulted in more effective stress transfer from the matrix to the fiber.

The enhanced interfacial adhesion that occurs between wood flour and the PVC matrix with the addition of coupling agents may be explained by the potential of chitin and chitosan to alter the acid-base interactions at the interface between the wood flour



Figure 5.3. Flexural strength of PVC and its composites with varying concentration of coupling agent: (a) chitin and (b) chitosan. Different letters above the bars indicate significant differences between the uncoupled composite and composites with chitin or chitosan at P < 0.05.



Figure 5.4. Flexural modulus of PVC and its composites with varying concentration of coupling agent: (a) chitin and (b) chitosan. Different letters above the bars indicate significant differences between the uncoupled composite and composites with chitin or chitosan at P < 0.05.

and the PVC matrix [2,3]. When these biopolymer coupling agents were incorporated into the formulation, hydrogen bonds may have been formed between the hydroxyl groups of the wood flour and chitin/chitosan coupling agents. As a result, the acidic nature of the wood is moderated, and the wood surfaces that are bonded to the aminocontaining biopolymer have a more basic character. On processing, strong interfacial adhesion between the chlorine-containing PVC and amino groups on the surface of wood flour is promoted, which results in the significant increases measured in the mechanical properties of the composites [2]. Chemically, chitosan also has the potential to form covalent bonds with PVC through an S_N1 or S_N2 reaction between the amine group of chitosan and the chlorine atom of PVC, eliminating HCl. The covalent bond would provide additional stability to the interface of the composite. This would likely not be a dominant phenomenon since chitosan and PVC are both polymers, which increases both the steric hindrance and the activation energy needed for the reaction.

The flexural strength of coupled composites increased with the addition of either chitin or chitosan, with the extent of the increase depending on the amount of added coupling agent. On addition of 6.67 wt. % of chitin to the composite the flexural strength was approximately 54 MPa, compared to 45 MPa for the composite without a coupling agent, and 57 MPa for the neat PVC (Figure 5.3a). Chitosan was more efficient in enhancing the strength of PVC/wood-flour composites, giving a flexural strength of 53 MPa at 0.5 wt. % concentration, with no additional increase in properties attained on addition of more chitosan (Figure 5.3b). This difference can be attributed to molecular structures of chitosan that contain more reactive amino groups (Figure 5.2). In addition,

chitosan may have formed some direct covalent bonds to PVC, which would enhance the flexural strength of the composite. Chitin cannot react in this manner due to the presence of the less reactive secondary amine in the acetylamino group.

The flexural modulus was also significantly improved with the composite containing 6.67 wt. % chitin having a flexural modulus of 3.7 GPa compared to 3.2 GPa and 2.2 GPa for the uncoupled composite and neat rigid PVC, respectively (Figure 5.4a). Again, the different letters above the bars indicate significant differences between the uncoupled composite and composites with chitin or chitosan, while the same letter indicates no statistically significant differences with the coupling agent at P < 0.05. The composite modified with 0.5 wt. % chitosan had a flexural modulus of 3.5 GPa (Figure 5.4b). Without a coupling agent, the addition of wood flour into the PVC matrix significantly increased the flexural modulus of the composites, as expected from the rule of mixtures [5], but the addition of both chitin and chitosan significantly increased the stiffness is also attributed to the improved interfacial adhesion between the PVC matrix and the wood flour. Other investigators have reported similar results [4]. Greater improvement in stiffness was observed with chitin in the composites.

Overall, the bending strength of rigid PVC/wood-flour composites with 6.67 wt. % (~5.0 phr) chitin or 0.5 wt. % (~0.4 phr) chitosan matched that of unfilled PVC whereas their stiffness outperformed that of neat PVC.

Dynamic Mechanical Properties

Figure 5.5 illustrates the DMA curve of composite without coupling agent. Although not shown, similar curves were obtained for neat rigid PVC and composites with 6.67 wt. % chitin and 0.5 wt. % chitosan. These specific concentrations of coupling agents for DMA study were selected on the basis of the optimum flexural properties discussed in previous section. Table 5.2 summarizes the storage modulus (E'), loss modulus (E'') and tan δ peak max values for the neat rigid PVC, composite without and with 6.67 wt% chitin and 0.5 wt% chitosan coupling agents obtained from DMA curves.

Both the storage modulus (E' or elastic component of the material) and the loss modulus (E" or viscous component of the material) increased with the addition of wood flour into PVC matrix, regardless of both the type of coupling agent used and testing temperature. Increased storage modulus (E') due to the addition of wood flour into PVC matrix implies an increase in the load bearing capacity of the composites. This trend correlates well with the flexural test data. The addition of wood flour increased the viscosity of the polymer matrix, i.e. the loss modulus E". It is believed that the presence of 75 phr wood flour in the PVC matrix restricted molecular motion of the matrix [5].

Composites prepared with chitin and chitosan showed a greater increase in both storage modulus and loss modulus compared to the uncoupled composite. The increased storage modulus (E') is attributed to a better wood flour-matrix adhesion. This enhanced interfacial adhesion may also restrict the free motion of the PVC chains, resulting in an increased viscosity of the composites and the corresponding increase in loss modulus (E''). Greater improvement in E' and E'' was observed with chitin in the composites. The glass transition temperature (tan δ peak max) of PVC was not significantly affected when wood flour was added into the PVC matrix, irrespective of the type of coupling agent used.



Figure 5.5. DMA curve of rigid PVC/wood-flour composite without coupling agent.

Table 5.2. Effect of Coupling Agent on the Dynamic Mechanical Properties of NeatRigid PVC and PVC/Wood-Flour Composites.

Samples	Storage Modulus, E' (GPa)			Loss Modulus, E" (GPa)			Tan δ Peak Max
	30°C	50°C	70°C	30°C	50°C	70°C	(°C)
PVC	2.8	2.5	1.9	0.5	0.4	0.4	90.5
Composite	4.6	3.5	2.6	0.6	0.5	0.5	88.5
Composite with 6.67 wt. % chitin	8.0	5.9	3.8	1.3	0.9	0.8	90.9
Composite with 0.5 wt. % chitosan	6.1	5.2	3.5	1.0	0.9	0.8	90.5

CONCLUSIONS

Chitin and chitosan were used as coupling agents for rigid PVC/wood-flour composites. Both polymers gave composites having a flexural strength greater than the uncoupled composite and rivaling those of neat PVC, and had a flexural modulus that exceeded the flexural modulus of both the PVC and the uncoupled PVC/wood-flour composite. The chitosan was more effective in improving the properties compared to the chitin, which may be due to the presence of more reactive amine groups in the backbone of chitosan. The optimum wt. % for addition of chitin was 6.67 wt. %. Addition of chitosan also improved the flexural strength and modulus of the composites up to 0.5 wt. %, with higher amounts giving no additional increase. A DMA study showed that the addition of chitin and chitosan also increased the E' and E'' of the composites. The increase in properties by addition of chitin and chitosan was attributed to increased interfacial adhesion between the modified wood surface and the PVC matrix, which may occur through acid-base interactions between the chlorine-containing PVC and amino groups on the surface of wood flour.

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CHAPTER 6

EFFECTS OF WOOD FLOUR AND CHITOSAN ON MECHANICAL, CHEMICAL AND THERMAL PROPERTIES OF POLYLACTIDE

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ABSTRACT

Composites of polylactide (PLA, 100-60 wt. %) and wood flour (0-40 wt. %) were prepared to assess the effects of wood filler content on the mechanical, chemical, thermal, and morphological properties of the composites. The polysaccharide chitosan (0 – 10 wt. %) was added as a potential coupling agent for the PLA-wood flour composites. Addition of wood flour significantly increased the flexural modulus and the storage modulus of PLA-wood flour composite, but neither the wood flour nor chitosan had an effect on the glass transition temperature (T_g). Fourier transform infrared (FTIR) spectra did not show any evidence of covalent bonding, but chitosan at the interface between wood and PLA is thought to have formed hydrogen bonds to PLA carbonyl groups. SEM images of fracture surfaces showed fiber breakage was far more common than fiber pullout in the composites. No evidence of discrete chitosan domains was seen in SEM micrographs. When added at up to 10 wt. % (based on wood flour mass), chitosan showed no significant effect on the mechanical, chemical, or thermal properties of the composites, with property changes depending on wood flour content only.

Keywords: Polylactide, Thermal properties, FTIR, Coupling agent and Biocomposites

INTRODUCTION

Recently, biopolymers have become popular due to both increased social and economic pressure to conserve petroleum resources. Biopolymers offer environmental benefits such as biodegradability, reduced greenhouse gas emissions, and renewability of the base material [1, 2]. Polylactide (PLA) has properties that are comparable to many commodity polymers (e.g. PP, PE, PVC, PS) such as high stiffness, clarity, gloss and UV stability [3, 4], but is a biobased polymer, often made from corn. PLA is still costly compared to PP, but does have a low cost compared to other readily available biopolymers that have similar properties.

Biopolymers in combination with natural fibers represent a growing share of the composites market for various applications. The major advantages of using natural fibers as reinforcements or fillers are their low cost, low density, high specific strength and less abrasiveness to processing equipment compared to conventional inorganic fillers [5-7]. Natural fiber-filled biopolymers are often referred to as "green" composites as they are completely biodegradable and renewable.

The mechanical properties of composite materials depend on several factors such as the interfacial interaction between the matrix and fiber; type, aspect ratio and concentration of fiber, etc. Although cellulosic fibers have been shown to be good reinforcing agents for polymer composites, poor dispersion and weak interfacial bonding of the hydrophilic fibers with the hydrophobic polymer matrix leads to poor strength properties, compared to neat polymer. Poor dispersion is inherent to cellulosic materials due to hydrogen bonding between the fibers but only weak dispersion forces between the filler and the polymer [7-9]. Several researchers [10-15] have studied PLA composites with different nonwood cellulosic fibers. Compared with unfilled PLA, decreased strength properties were found for PLA composites made from different natural fibers [10, 15, 16]. This was a function of natural fiber content and was attributed to poor interfacial adhesion between the filler and matrix. Oksman and coworkers [13] found that PLA/flax fiber composites have superior mechanical properties compared to PP/flax fiber composites, and hence have the potential to replace PP/natural fiber composites in many industrial applications. They also reported the need for better interfacial adhesion between the polymer matrix and natural fibers to improve overall mechanical properties of the composites. Similar results were obtained by other researchers when bamboo [14], cellulose [15] and recycled newsprint fibers [10] were used.

To overcome the poor interfacial adhesion between filler and matrix, researchers using bamboo fiber esterified the fiber with maleic anhydride and successfully used this for PLA/bamboo fiber composites [14]. Addition of 5% esterified bamboo fiber resulted in nearly 21% improvement in the tensile strength and 10% improvement in tensile modulus, while addition of more compatibilizer had no further effect on properties. Although the esterified bamboo fiber increased the properties of the PLA composite, this approach had several drawbacks including the additional step of manufacturing reactive fibers before processing of the composites, and the use of a solvent-based process to produce the reactive fibers, which is less desirable economically and environmentally. In a similar, effort another researcher used maleated PLA as a coupling agent. Reported results suggest this would be effective in PLA/natural fiber composites [17]. However, maleated PLA is not available commercially and would be expensive and time consuming to produce as a part of a composite manufacturing process. A commercially available natural product is desirable as a coupling agent for "green" composites.

Our previous work showed that natural polymers such as chitin and chitosan can be successfully used as coupling agents for PVC/wood-flour composites [18]. Addition of chitosan and chitin increased the flexural strength and flexural modulus of PVC/woodflour composites as a result of increased interfacial adhesion between the polymer matrix and the wood flour. This increase was attributed to acid-base interaction between the PVC and coupling agent.

Unlike PVC, PLA cannot undergo acid-base interaction with chitosan, but Honma et al. [19] demonstrated that both OH and NH₂ groups from chitosan (Figure 6.1) could hydrogen bond with the carbonyl group of poly(ε -caprolactone) (PCL). Both PCL and PLA are aliphatic polyesters with significant structural similarity (Figure 6.1). Furthermore, it is theoretically possible that a reaction could occur between the amine groups of chitosan and the ester groups of PLA, forming a covalent bond between the chitosan and PLA (Figure 6.2) [20]. Similarity between the chitosan and cellulose structure (Figure 6.1) indicates these compounds should be highly compatible and readily hydrogen bond with each other. We hypothesized that the addition of chitosan would increase the interfacial adhesion between PLA and wood flour, resulting in a stronger composite product.

Chitosan has not previously been studied as a wood-PLA coupling agent. Furthermore, although several different cellulosic fibers have been used to manufacture PLA composites, there have been limited studies that used wood as a filler for PLA









Figure 6.1. Structures of (a) Polylactide (b) Poly(E-caprolactone) (c) Cellulose and (b) Chitosan.



Figure 6.2. Possible Chemical Reaction between Amine and Ester Group

composites [21]. Wood fiber is readily available in the US as a waste product of other wood manufacturing processes and is often very inexpensive when compared with other natural fibers [6]. Although wood is similar to other cellulosic fibers there are also differences, most notably in the ratios of lignin and hemicelluloses to cellulose [5]. Thus, its strength is known to be different from those of other natural fibers [5].

Therefore, the specific goals addressed in this paper are: 1) determine the effects of various concentrations of wood flour on the properties of PLA/wood composites and 2) evaluate the efficacy of chitosan as a coupling agent in PLA/wood composites. These goals were addressed through analysis of the mechanical, chemical and thermal properties of PLA/wood composites prepared with varying wood content (0 - 40 wt. %). PLA/wood flour composites with 40 wt. % wood were then prepared with chitosan (0 - 10 wt. % based on wood flour content) and similarly tested to determine whether chitosan was effective in improving the composite properties.

EXPERIMENTATION

Materials

Polylactide (PLA) 4042-D containing 94% *L*-lactide (Nature Works LLC, Minnetonka, MN) was used as a matrix. Maple wood flour (4020) of 425 μ m average size (American Wood Fibers, Schofield, WI) was used as a filler. Chitosan (TCI America, Tokyo, Japan) was used as a coupling agent. Chitosan flakes were pulverized into a powder (< 250 μ m) in a Kleco 4200 pulverizer (Garcia Manufacturing, CA) at room temperature before compounding. All other ingredients were used as supplied.

PLA/Wood Flour Composite Manufacturing

Before compounding, wood flour was dried in an oven for 48 hrs at 105 °C to a moisture content of less than 1%, and PLA was dried at 75 °C for 24 hrs. Formulations used 0-40 wt% of dried wood flour, 100-60 wt. % dried PLA, and chitosan added at 0-10 wt. % based on wood flour mass. The exact formulations are given in Table 6.1.

The polymer, wood flour and chitosan were weighed at the desired addition level and premixed in a glass beaker. The mix was then melt compounded in a microcompounder (DSM Research, Netherlands) at 190 °C for 4 minutes at a mixing speed of 100 rpm. The micro-compounder had a total volume of 15 cc and was equipped with corotating intermeshing conical twin screws of L/D ratio 18 to ensure homogeneous melt mixing of the material. The molten compounded material was then immediately transferred to a plunger-based mini-injection molding machine through a heated cylinder to mold the test samples. Temperature of the heated cylinder was maintained at 183 °C, while that of the mold was controlled at 40 °C.

Experiment No.	PLA (%)	Wood Flour (%)	Chitosan ¹ (%)
1	100	0	0
2	80	20	0
3	70	30	0
4	60	40	0
5	60	40	1
6	60	40	2.5
7	60	40	5
8	60	40	10

Table 6.1. Individual Batch Composition

¹ Chitosan content is based on the weight of wood flour

Mechanical Property Testing

An Instron 4206 (Norwood, MA) Universal testing machine equipped with series IX software was used to test flexural properties of the samples as per ASTM standard D790 [22]. The injection molded samples were conditioned at $50\% \pm 5$ relative humidity and 23 °C \pm 2 in a walk-in conditioning room for 48 hours before testing. Sample dimensions were 60 mm x 12 mm x 3 mm. The average of at least seven samples was reported for each formulation.

Statistical Analysis

Tukey's test of multiple comparisons was used to determine significant differences between the averages of the batches. The effects of wood flour content and chitosan content on the flexural strength and flexural modulus of the composites were compared. P < 0.05 was used to determine statistical significance.

Dynamic Mechanical Analysis (DMA)

DMA was carried out on a TA Instruments DMA Q800 (New Castle, DE) analyzer using a dual cantilever fixture to determine the storage modulus (elastic modulus), loss modulus (viscous modulus) and tan δ of the samples. The test was performed in the temperature sweep mode from 30 °C to 100 °C at a frequency of 1 Hz and a heating rate of 2°C/min. The sample dimensions were 60 mm x 12 mm x 2 mm. At least three samples for each batch were tested.

Surface Analysis

FTIR spectroscopy was performed on a Shimadzu IRPrestige-21 (Columbia, MD) spectrometer in attenuated total reflectance (ATR) mode. Samples were pulverized in a Kleco-4200 pulverizer (Garcia Manufacturing, CA) to a powder, which was placed in the sample holder. Each spectrum consists of 50 scans collected at a resolution of 4 cm⁻¹ over the range of 4000 - 650 cm⁻¹. Shimadzu IRsolution software was used to analyze the collected spectra.

Scanning Electron Microscopy (SEM)

Fracture surfaces of tested (flexural test) specimens were observed using a JEOL JSM-6400 (Tokyo, Japan) scanning electron microscope equipped with a LaB6 gun. An accelerating voltage of 12KV was used. The samples were gold coated in a sputter coater before collecting the images.

RESULTS AND DISCUSSION

Mechanical Properties

The addition of wood flour to the PLA matrix appears to be slightly reducing the flexural strength of the PLA/wood flour composites, compared to unfilled PLA (Figure 6.3a). Based on Tukey's t-test (P > 0.05 in all cases) this decrease was not statistically significant. Interestingly, decreased strength properties, compared with unfilled PLA, has been reported by other authors using natural fibers including bamboo, newsprint and cellulose [10, 14, 15]. Since there was no significant drop in strength properties when wood was added to PLA, wood appears to be a better filler for PLA than other natural fibers. An increase in the standard deviation of the samples was observed as the wood flour content increased, which was likely a result of reduced mixing efficiency at higher wood flour loading, and could likely be decreased by increasing mixing intensity.

The addition of wood flour to the PLA matrix significantly increased its flexural modulus, irrespective of the wood flour content used (Tukey's t-test, P < 0.05 in all cases) (Figure 6.3b). Adding 20 wt. % wood flour increased the flexural modulus of the PLA from 3180 MPa to 4249 MPa, which represented an improvement of ~34%. At 40 wt. %, the modulus increase was approximately 87% compared to unfilled PLA. This behavior was expected, based on the rule of mixtures, as the modulus of wood fiber is higher than that of the polymer.

The rule of mixtures is a mathematical equation that relates a property of a composite to the properties of each component and volume fractions of the components in the composite. Using the rule of mixtures, the modulus of the composite product can be estimated by the following equation [23]:

$$\mathbf{E}_{c} = \mathbf{E}_{f} \mathbf{V}_{f} + \mathbf{E}_{m} (1 - \mathbf{V}_{f})$$

where E_c , E_m and E_f are the moduli of composite, matrix and fiber respectively and V_f is the volume fraction of fiber. The modulus of fiber used in the calculation was 20 GPa, which represents a general value for wood fiber [23].

The flexural modulus of the composite increases with increasing fiber volume and follows the predicted trend, however at much lower values (Figure 6.4). The prediction from the rule of mixtures is based on several assumptions such as: fibers are uniform and unidirectionaly oriented, perfect bonding between the fiber and matrix exists, and applied load produces equal strain in the fiber and matrix. In the experimental samples, it is unlikely that the assumptions hold true, which accounts for the decreased values compared to those predicted for the system. Weak interfacial adhesion between the wood flour and the matrix, uneven size of the wood flour used in this work, and random orientation of the fibers in the composite were likely responsible for the experimental values being lower than predicted. An increase in the standard deviation of the samples was also observed for flexural modulus as the wood flour content increased (Figure 6.3b) which was likely a result of reduced mixing efficiency at higher wood flour loading.

Chitosan had no significant effect on either the flexural strength (Figure 6.5a) or on the modulus (Figure 6.5b) of the composite (Tukey's t-test, P > 0.05 in all cases). This implied that chitosan was not a suitable coupling agent for PLA-wood composite, possibly due to incompatibility between chitosan and PLA. An incompatibility between chitosan and PLA was reported by Suyatma et al. [24]. They studied blends of chitosan and PLA prepared at room temperature by a solution blending technique. The


Figure 6.3. Flexural Properties of PLA and its Composites with Varying Concentration of Wood Flour (a) Flexural Strength and (b) Flexural Modulus. Different letters above the bars indicate statistically significant differences at P < 0.05.



Figure 6.4. Predicted and Experimental Values of Flexural Modulus with Increasing Volume of Fiber



Figure 6.5. Flexural Properties of PLA/Wood Flour Composites with 40 wt. % Wood Flour and Varying Concentration of Chitosan (a) Flexural Strength and (b) Flexural Modulus. Different letters above the bars indicate statistically significant differences at P < 0.05.

content of PLA in these blends was varied from 0 - 30 wt. %. Under these conditions, the chitosan/PLA blends were found to be incompatible. The temperature used to manufacture these blends may not have been sufficient for a reaction to occur between the chitosan and PLA. In the current work, an extrusion process at elevated temperature and high pressure was used, which was expected to provide better conditions for a reaction or interaction between PLA and chitosan. However, results of flexural testing did not support this.

FTIR Analysis

Several characteristic peaks representing chemical functional groups were detected in the FTIR spectra of PLA, wood and the wood/PLA composite with and without chitosan (Figure 6.6, Table 6.2). The strong peak in the spectrum of PLA (Figure 6.6a) at 1747 cm⁻¹ is due to C=O stretching of the carbonyl group, while the bending vibration of this group appears at 1265 cm⁻¹. The peaks at 866 and 754 cm⁻¹ represent the amorphous and crystalline phases of PLA, respectively. It is interesting to note that the intensity of the amorphous and crystalline peaks is nearly the same, which indicates the PLA is a semicrystalline material with nearly equal presence of both phases.

Compared to the spectrum of neat PLA, the spectrum of the composite containing 40 wt. % wood flour shows the presence of OH groups from the wood at 3332 cm⁻¹ (Figure 6.6c). Some reduction in peak intensity of the characteristic PLA peaks was expected in the composite spectrum as a result of wood flour addition, simply because of a dilution effect. However, comparing the ratios of characteristic peak intensity of PLA to the composite spectrum indicated that the intensity of the peak at 1749 cm⁻¹ in the

PLA (cm ⁻¹)	Wood (cm ⁻¹)	Peak assignments	References
	3331	OH stretching	[33, 34]
2993, 2943	2895	CH stretching	[3, 4, 33]
1747	1735	C=O stretching	[4, 33, 34]
1450		CH ₃ bending	[3, 4, 34]
1381, 1357	1400-1300	CH deformations	[3, 4, 33, 34]
1265		C=O bending	[3, 4, 34]
	1232	phenolic OH deformation	[33, 34]
1180, 1126, 1082		C-O stretching	[3, 4, 34]
1041		OH bending	[3, 4, 33, 34]
	1028	C-O and C-O-C stretching, OH bending	[33, 34]
866		PLA amorphous phase	[3, 4]
754		PLA crystalline phase	[3, 4]

Table 6.2. FTIR Band Assignment of Major Peaks in PLA and Wood Flour





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composite was further reduced, beyond that expected by dilution. In addition, the carbonyl peak was shifted very slightly compared to PLA alone (1747 to 1749 cm⁻¹). This may indicate an interaction between the carbonyl groups of PLA and hydroxyl groups of wood through hydrogen bonding [25-27]. The decreased intensity of the crystalline peak of PLA at 754 cm⁻¹ with respect to the amorphous peak at 867 cm⁻¹ suggests a reduction in the crystallinity of PLA with the addition of wood flour. Reduced crystallinity of PLA by addition of wood or other natural fibers has been reported in the literature [10, 21]. The composite spectrum did not show any new peaks that were not in the original wood or PLA spectra. Similarly, no major shifting or disappearance of peaks was observed. The composite spectrum was essentially an overlay image of both PLA and wood flour spectra, which was expected because the two dissimilar phases in the composite were only likely to interact through hydrogen bonding.

Similarly, addition of chitosan had no effect on the FTIR spectra of the composite (Figure 6.6d). The IR spectrum of the composite with 10 wt. % chitosan looked identical to the spectrum of the composite with no chitosan (i.e. Figure 6.6c). There was no evidence of chemical bonding between the amine group of chitosan and the ester carbonyl group of PLA (Figure 6.2), which should have been detected as a peak near 1650 cm⁻¹ for the amide carbonyl. This finding is in agreement with the flexural properties of the composites, where chitosan had no significant effect on mechanical properties. However, we were also not able to detect any of the primary characteristics of chitosan, such as the presence of amino groups (Figure 6.1), which would appear between 1600-1500 cm⁻¹ in the spectrum of the composite with chitosan. This might be due to the low concentration of chitosan used in the study, or due to limitations of the ATR

technique, which is highly surface sensitive, as the IR beam can only penetrate the sample 0.5-3 μ m depending upon the refractive index of the sample and crystal [28, 29].

Dynamic Mechanical Analysis

The temperature dependence of storage modulus and tan delta for unfilled PLA (curve a) and PLA wood composite with 20 wt. % (curve b) and 40 wt. % wood flour (curve c) is illustrated in Figure 6.7(I). The storage modulus significantly increased as wood flour was added to the PLA. This trend was similar to the results obtained in the flexural test and was expected on the basis of the rule of mixtures. Above T_g , at around 80 °C, the storage modulus starts to slightly increase again in both unfilled and filled PLA, due to a phenomenon known as cold crystallization [13]. This behavior in unfilled PLA cannot be seen because of the scale used (Figure 6.7(I)). During molding, the samples were quickly cooled from 183 °C (processing temperature) to 40 °C (mold temperature), which restricted the chain movement and thus prevented the formation of crystallites. When these samples were again heated above $T_{g}\xspace$ in the DMA test, the molecular motion within the chain increased and they tended to rearrange themselves to form crystallites. This process is referred to as cold crystallization. This increase in crystallinity gives added strength to the material, and thus an increase in the storage modulus.

The loss modulus (Figure 6.7(II)) peak represents the glass transition temperature (T_g) of the polymer. Addition of wood flour changed the T_g of the polymer by less than 1 °C. A similar trend of increased storage modulus with no significant change in the Tg of the PLA was observed by Huda et al. when cellulose fibers were added to PLA [13]. As



Figure 6.7. Temperature Dependence of (I) Storage Modulus and Tan Delta and (II) Loss Modulus of (a) PLA, (b) PLA Composite with 20 wt. % Wood Flour and (c) PLA Composite with 40 wt. % Wood Flour.

the T_g occurred over a range of temperature, it can be seen from the graphs that addition of wood flour broadened the loss modulus curves and increased the glass transition period. This was likely the result of disruption of the movement of the polymer chains by added wood flour. Presence of rigid wood flour hinders the large-scale motion of the polymer chains, which may lengthens the time of the transition from glassy to rubbery state [30]. Similar to the storage modulus, the loss modulus increased when the increasing content of wood in the composite. The increasing trend in loss modulus means that the composite can dissipate more energy into heat without deforming, which would indicate that the composite has greater resistance to flow under conditions of stress compared with unfilled PLA at T_g [31].

The tan δ peak height decreased significantly with the addition of wood flour, and showed a continued decreasing trend as the wood content was increased from 20 to 40 wt. % in the composite (Figure 6.7(I)). Tan δ was reduced as the addition of wood flour reduced the free volume of the polymer, restricting the molecular motion of the polymer chains. However, there was no change in the tan δ max temperature. This signifies that there was no strong interaction between wood and PLA, which correlates with the findings of the flexural and FTIR analysis. Additionally, the width of the tan δ peak increased with increased percentage of the fiber in the composite. Idicula et al. attributed this phenomena to molecular relaxations taking place in the composite which were not present in the matrix [32].

There was no significant change in storage modulus, tan delta or loss modulus with addition of chitosan to PLA/wood composite, irrespective of the amount added (Figure 6.8). This indicates that chitosan was not an effective coupling agent for PLA-



Figure 6.8. Temperature Dependence of (I) Storage Modulus and Tan Delta and (II) Loss Modulus of PLA composite with 40 wt. % Wood Flour and Varying Amount of Chitosan (a) 0%, (b) 2.5% and (c) 5%.

wood flour composites. This result agrees with the results of the flexural testing and FTIR analysis which indicated that there was no significant effect of adding the chitosan to the composites.

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Morphology

The SEM study was performed on fracture surfaces of samples from the flexural test. SEM images of PLA/wood flour composites containing 20 wt. % wood flour (Figure 6.9) were recorded at various locations across the fracture surface. Representative images from two different areas of the fracture surface are shown (Figure 6.9a and 6.9c). The SEM images suggest that the fibers were well dispersed in the matrix resulting in a homogenous composite. Several fibers can be seen in these images, many of which are broken at the surface of the sample. To better understand the mode of failure in the flexural samples, an area of each image (rectangle in Figures 6.9a and 6.9c) was further magnified to display the wood particles in greater detail (Figures 6.9b and 6.9d). Higher magnification (Figure 6.9b) shows two wood particles which have been broken off evenly with the surface of the polymer matrix. Fiber breakage indicates good interfacial adhesion between the wood and PLA matrix. Conversely, pullout of fibers from the matrix would indicate poor adhesion between the wood and polymer. There are some areas (Figures 6.9a and 6.9c) that show fiber pullout, but those are a minority compared with the number of fibers that were broken. Even the fibers which were pulled out left distinct imprints of the wood fiber surface instead of clean pullout in the matrix,



Figure 6.9. SEM Images of PLA Composites with 20 wt. % Wood Flour at Different Magnifications: (a, c) 100X and (b, d) 400X.

suggesting mechanical interlocking between the fiber and matrix. Good mechanical interlocking between PLA and wood flour was also observed through SEM recently by Mathew et al. [21] and was attributed to the surface roughness of the wood flour. An additional feature (Figure 6.9d) is what appears to be polymer filling the lumens of the wood fiber, which can be seen in the broken fiber. The polymer appears as parallel lines that seem to be holding the halves of the broken fiber together. If the PLA is able to flow into the hollow lumens of the wood particles and fill them, this would add strength to the composite. This, along with mechanical interlocking of the filler into the matrix, is likely responsible for the insignificant drop in flexural properties when wood was added to the PLA matrix.

The fracture surfaces of PLA/wood flour composites with 40 wt. % wood (Fig. 10) without chitosan (Figures 6.10 a and b) and with chitosan (Figures 6.10 c and d) show similar characteristics to those with 20 wt. % wood (Figure 6.9), i.e. more fiber breakage was seen than fiber pullout. Chitosan could not be differentiated from small particles of wood flour in these images, which may be a result of the small size of the chitosan particles used (less than 250 microns). Images of the fracture surface at higher magnification (Figure 6.10b and 6.10d) compared to the same areas under low magnification (Figure 6.10a and 6.10c) more clearly show fiber breakage both across the length and parallel to the length of the fibers. These SEM observations further support the findings from the flexural study that addition of wood had no destructive effect on the strength properties of the PLA, indicating that wood is a suitable filler for PLA in composites.



Figure 6.10. SEM Images of PLA Composite with 40 wt. % Wood Flour without (a, b) and with 10 wt. % Chitosan (c, d) at Different Magnifications: (a, c) 100X and (b, d) 400X.

CONCLUSIONS

Results of this study indicate that wood flour can be successfully used as a filler for PLA. The resulting composites will be renewable and biodegradable. The storage and flexural modulus of the PLA/wood composites were higher than those of unfilled PLA, regardless of wood content, but the strength properties were not improved by adding wood. FTIR analysis of the composites produced spectra that were essentially an overlay of the two component spectra, suggesting little interaction between the phases. The SEM study provided evidence that there was sufficient interfacial adhesion between the PLA matrix and the wood filler to cause the composite to fail mostly through fiber breakage, rather than fiber pullout. This was likely a result of mechanical interlocking between the wood fibers and PLA matrix, and the observed filling of the wood lumens by PLA.

Chitosan was tested as a natural, biodegradable coupling agent for PLA/wood flour composites. The results of this study did not show any significant improvement in the mechanical or thermal properties of the composites when chitosan was added. No differences were detected in the FTIR spectra of composites with chitosan, compared with composite spectra without chitosan. The lack of differences in the spectra suggest that no chemical bonding occurred between the wood and PLA. Since there were no improvements when chitosan was used, we can conclude that chitosan was not a suitable coupling agent for PLA/wood flour composites. However, PLA/wood flour composites without coupling agent have enhanced moduli compared to PLA alone.

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CHAPTER 7

SUMMARY AND RECOMMENDATIONS

Summary

The aim of this work was to advance wood composites technology and utilization through experimentation focused on improving WPCs properties and broadening the applications for WPCs. Research was focused on three goals which address current limitations of WPCs: i) development of a continuous extrusion process for microcellular foaming of polyvinyl chloride (PVC) and its composites using supercritical fluids to reduce the high density of the WPCs, ii) development of coupling agents for PVC and polylactide (PLA) based WPCs to overcome the poor compatibility between the wood and plastic, and iii) demonstrate that wood can be successfully used as a filler for biodegradable WPCs based on PLA. Reaching these goals will open up new areas for WPC utilization and expand composites technology.

The following conclusions were drawn from this work:

Complex relationships between wood flour, acrylic modifier and plasticizer on the die swell and true viscosity of PVC and PVC wood flour composites have been identified and explored. Understanding the relationships between key processing variables is critical in producing high-quality products, and is vital for implementing an extrusion processing method for microcellular foaming.

A greater understanding of the conditions necessary for foaming PVC and its wood composites was developed. Although PVC was not microcellular foamed in the extrusion system using supercritical CO_2 as the blowing agent, understanding the role of

mixing and pressure on the PVC foam has lead to the generation of new ideas on how to successfully foam this polymer.

Chitin and chitosan were successfully used to compatibilize PVC wood flour composites. These efficient, cost effective coupling agents improved the compatibility between the wood and PVC, resulting in better composite properties. Although both compounds improved the composite properties, chitosan was more effective than chitin. Use of these coupling agents can improve PVC wood composite products at a lower cost and they are simpler to use than the current alternatives.

This work demonstrated that wood was an effective filler for PLA composites. Adding wood to the PLA increased both the flexural and storage moduli, compared to unfilled PLA. These composites are natural and biodegradable, and will expand the use of WPCs in applications such as packaging and the automotive industry. Chitosan did not improve the properties of the composites, but this investigation lead to greater information about PLA reactivity with amine containing polymers.

Taken together, these results have added to the current state of the knowledge on both PVC and PLA wood flour composites. The property improvements and increased understanding of wood polymer composites meet our original aim of advancing wood composites technology. This knowledge increases the potential applications for WPCs in new areas. Information gained from this work also provides a basis for future studies.

Recommendations

Based on the results of this research, the following recommendations for future work are suggested:

- 1. The viscosity measurements done as part of the rheology study were performed in an extrusion capillary rheometer. This type of rheometer is known to operate at high shear rates. A complimentary study at low shear rates should be performed using a conventional rheometer, such as cone and plate, to fully understand the effects of material composition over a wide range of shear rates.
- 2. Results of the rheological study revealed complex interactions between acrylic foam modifier and components of the PVC wood flour composite. The behavior in the composite was opposite from that observed in the unfilled PVC. In the PVC, melt viscosity was observed to increase, which is typical behavior when acrylic foam modifiers are added to PVC. The reasons for the decreased viscosity in the composite with acrylic foam modifier are not well understood, and should be investigated in detail.
- 3. The foaming setup developed as a part of this work was not effective for producing microcellular foamed PVC at steady-state conditions, even though microcellular foams of other polymers were successfully produced using this equipment. This was likely due to insufficient mixing of polymer and blowing gas to produce microcellular foam. A setup utilizing an extruder with a larger L/D ratio could improve the foamability of PVC with supercritical CO₂ as the blowing agent. Another suggestion would be to use a different flow restrictor

which would maintain a higher pressure differential between the barrel and the blowing gas. Better control of the static mixer temperature may also improve the ability to produce microcellular foamed PVC with this setup.

4. When chitin and chitosan were used as coupling agents for PVC wood flour composites, improved properties were observed. The increase in the properties was attributed to possible acid-base interactions between the coupling agents and the PVC wood flour composites. A detailed investigation of surface properties of the composites with and without coupling agent should be carried out to better characterize the mechanism for improved adhesion. Inverse phase gas chromatography or contact angle measurements could be used for these experiments.

- 5. Chitin and chitosan are known as anti-fungal agents. This aspect of chitin and chitosan was not within the scope of this research. A study could be done to assess the effectiveness of chitin and chitosan as anti-fungal agents for PVC wood composites.
- 6. In the PLA-wood flour composite study, 40-mesh size maple flour was used as the filler for PLA. This wood flour was an effective filler for PLA. The effects of other mesh sizes and species of wood flour on the properties of PLA are unknown and should be studied.
- 7. One goal of the PLA-wood flour composite study was to evaluate chitosan as a natural coupling agent for these composites. While the results of the study

reaffirmed the need for an effective coupling agent for these composites, chitosan did not improve the composite properties. Maleated polymers are known to be effective couplers for other composite systems. Maleated PLA should be investigated as a coupling agent to improve the properties of these composites.

APPENDIX A

Wood:

Wood is one of the major natural fibers used in making composites and is also a focus of this research. Wood is used in several forms in manufacturing composites such as flour (particles), flakes, fibers and pulp. Wood is a cellular, fibrous material available abundantly in nature and can be broadly classified as softwood and hardwood [1, 2]. The wood from gymnosperm (conifer) trees is generally called softwood, e.g. pine, cedar, spruce, larch, douglas fir, etc. The wood from angiosperm (deciduous) trees is generally referred to as hardwood, e.g. maple, oak, teak, aspen, ash, etc. The terms softwood and hardwood and hardwood should not be confused with the literal meaning of soft and hard, as some softwoods are harder and denser than hardwood and some hardwoods are softer than softwood [1, 3]. The structure and chemical composition of the wood varies greatly with species. Table A.1 shows the difference in chemical compositions of softwood and hardwood.

Chemical Component	Softwood (%)	Hardwood (%)
Cellulose	40-45	45-50
Hemicellulose		
i. galactoglucomannan	15-20	-
ii. arabinoglucuronoxylan	10	-
iii. glucuronoxylan	-	20-30
iv. glucomannan	-	1-5
Lignin	26-34	22-30
Extractives	0-5	0-10

Table A.1. Chemical Composition of Wood

Cellulose is a crystalline, high molecular weight polysaccharide and is a key component of wood or any natural fiber. Cellulose consists of a long chain of beta glucose. Due to the high presence of hydroxyl groups, cellulose has an affinity for water. Microfibrils or microcrystals of cellulose are formed by hydrogen bonding of several individual cellulose chains. These microfibrils are primarily responsible for the tensile strength of the fiber [1-3].

Hemicellulose is similar in structure to cellulose but with low molecular weight and is amorphous in nature. These characteristics make hemicellulose more prone to hydrolysis than cellulose. Hemicellulose is composed of several heteropolymers such as xylan, glucomannan, arabinose and others. Hemicellulose and cellulose are largely responsible for the hydrophilic nature of wood [1-3].

Lignin is the second most abundant component of the wood. It acts as a binder in wood and is mainly responsible for the strength of the wood. Lignin is a complex natural cross-linked polymer whose definite structure is still not known [1-3].

Extractives account for 0-10% of the composition of wood, depending on the species. Various extractives in the wood include oils, fats, resins, fatty acids, waxes, tannins, etc. Extractives from the wood can be removed by a solvent extraction process if needed. The type and amount of extractives can have a significant effect on the manufacturing process and final properties of the composites [1-3].

Freshly cut wood contains around 50% by weight of moisture or water. Broadly, the water in the wood can be classified into two forms, free and bound. The water in the

cell lumen is called free water as it is not chemically bonded to wood and can be easily removed on drying. The water present in the cell walls is bound by hydrogen bonding and therefore called bound water. Bound water needs extra energy in terms of heat for removal [1, 2]. Dry wood can contain moisture ranging from 1 - 10 % by weight. It is very important to dry the wood before using it for manufacturing composites. If not dried properly the moisture in the wood is released during processing under high temperature and pressure, causing several problems in both the manufacturing process and the end product properties and quality. For example, moisture released during processing can cause unwanted foaming and voids in the composite, reducing its mechanical properties and aesthetics.

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Polyvinyl Chloride:

Polyvinyl chloride (PVC) is a synthetic polymer that consists of repeating units of vinyl chloride monomer (Figure B.1). The preparation of this monomer was first reported by Regnault in 1835. Baumann reported preparation of PVC polymer in a sealed vacuum tube under sunlight in 1872 [1]. Today's commercially available PVC is polymerized by a free radical polymerization mechanism using suspension (80% of production), emulsion (12%) or bulk/mass (8%) polymerizing techniques.



Figure A.1. Structure of PVC (where n = 700 - 1500)

PVC is mostly amorphous in nature, but has a small amount of crystallinity. It is a polar polymer due to the presence of chlorine atoms. PVC has a glass transition temperature of around 80°C. It has limited thermal stability and starts to decompose at as low as 100°C, and tends to adhere to metallic surfaces when heated [2]. As a result, PVC is extremely difficult to process alone and requires the incorporation of several additives to ease the processing and to tailor the end product properties. Various additives used in PVC processing include: stabilizers, lubricants, plasticizers, processing aids, impact modifiers and fillers. Flexibility in formulating the PVC to achieve desired properties gives it a popularity and acceptability for a wide range of products ranging from rigid pipes for construction to flexible tubing for medical applications. On the other hand, these additives complicate the recycling process of PVC. Since each product manufactured from PVC contains different type and amount of additives, recycled PVC contains an unknown mix of additives. This makes it difficult to obtain desired properties in products made from recycled PVC.

References:

- 1. Brydson, J.A., *Plastics Materials*. 7th ed, Oxford ; Boston: Butterworth-Heinemann. xxvii 920p. (1999).
- 2. Titow, W.V., *PVC Technology*. 4th ed, London ; New York: Elsevier Applied Science Pub. xxx, 1233 p. (1984).

Polylactide:

Polylactide (PLA) is a renewable and biodegradable linear polyester (Figure C.1) formed from lactic acid. PLA was first polymerized in 1920 but was not commercialized until recently. NatureWorks LLC (previously known as Cargill Dow LLC) is a major producer of PLA from corn starch in the US, producing 140,000 metric tons per year. The general process of making lactic acid involves the fermentation of dextrose, which can be made from several different sources such as biomass or corn. The presence of chiral carbon atoms results in two different forms of lactic acid: L-form and D-form. PLA can be polymerized by several different techniques, the most common of which is ring-opening polymerization of lactide dimer. Polymerization of PLA is a stepwise process. The first step involves the low molecular weight polylactic acid into lactide dimers using a catalyst. Finally, these lactide dimers are further polymerized through ring opening polymerization into PLA [1].

Lactide dimer exits in three different forms: L-lactide formed from two L-lactic acid molecules, D-lactide formed from two D-lactic acid molecules and meso-lactide formed from one each of L-lactic acid and D-lactic acid. Desired properties in the PLA can be achieved by varying the ratio of different forms of the lactide. The polymer that consists of more than 93% of L-form lactic acid is semicrystalline in nature, while a lower content of the L-form (50 – 93%) results in an amorphous polymer [1]. Microorganisms used in fermentation of dextrose produce predominantly L-lactic acid. As a result, most commercially produced PLA consists of L-form. However, some

quantity of meso-lactide is almost always present, which makes PLA a copolymer of Land meso-lactide.



Figure A.2. Polymerization of Polylactide

Another process to produce PLA is through direct condensation polymerization of lactic acid. Although direct condensation polymerization is simple in theory, in practice it is hard to get solvent-free high molecular weight polymer from this process. Additional chemicals are needed to get high molecular weight polymer, which adds extra cost to the overall process.

References:

1. Auras, R., Harte, B., and Selke, S., "An Overview of Polylactides as Packaging Materials", *Macromolecular Bioscience*, **4**(9): 835-864 (2004).

APPENDIX B

Response: Die swell ratio

ANOVA for Selected Factorial Model Analysis of variance table [Partial sum of squares]

	Sum of		Mean	F	
Source	Squares	DF	Square	Value	Prob > F
Model	0.52	3	0.17	79.21	0.0005 significant
A	0.17	1	0.17	78.00	0.0009
В	0.31	1	<i>0.31</i>	140.45	0.000 3
AB	0.042	1	0.042	19.17	0.0119
Curvature	4.050E-003	1	4.050E-003	1.85	0.2458 not significant
Residual	8.775E-003	4	2.194E-003		·
Cor Total	0.53	8			

The Model F-value of 79.21 implies the model is significant. There is only a 0.05% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.

In this case A, B, AB are significant model terms.

Values greater than 0.1000 indicate the model terms are not significant.

If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The "Curvature F-value" of 1.85 implies the curvature (as measured by difference between the average of the center points and the average of the factorial points) in the design space is not significant relative to the noise. There is a 24.58% chance that a "Curvature F-value" this large could occur due to noise.

Std. Dev.	0.047	R-Squared	0.9834
Mean	1.34	Adj R-Squared	0.9710
C.V.	3.51	Pred R-Squared	N/A
PRESS	N/A	Adeq Precision	19.622
Case(s) wit	h leverage of 1.0000:	Pred R-Squared and PRESS statistic	not defined

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 19.622 indicates an adequate signal. This model can be used to navigate the design space.

	Coefficient		Standard	95% CI	95% CI
Factor	Estimate	DF	Error	Low	High
VIF					_
Intercept	1.34	1	0.017	1.30	1.39
A-Wood flour	-0.15	1	0.017	-0.19	-0.10
1.00					
В-К - 400	0.20	1	0.017	0.15	0.24
1.00					
AB	-0.072	1	0.017	-0.12	-0.027

1.00					
Center Point	-0.068	1	0.050	-0.21	0.070
1.00					

Final Equation in Terms of Coded Factors:

Die swell	=
+1.34	
-0.15	* A
+0.20	* B
-0.072	* A * B

Final Equation in Terms of Actual Factors:

=	Die swell
	+1.22000
* Wood flour	-2.95000E-003
* K - 400	+0.067188
* Wood flour * K - 400	-7.25000E-004

Response: Viscosity (500)

Transform:	Power	Lambda: -	0.5	Constant:	0	
ANOVA for Sel	lected Factor	ial Model				
Analysis of vari	ance table [P	Partial sum of so	quares]			
-	Sum of		Mean	F		
Source	Squares	DF	Square	Valu	e	Prob > F
Model	1.181E-003	3 5	2.362E-004	651.7	74	0.0015 significant
A	2.453E-004	4 1	2.453E-004	676.7	79	0.0015
В	7.366E-00	5 1	7.366E-005	5 203.2	22	0.0049
С	4.172E-004	4 1	4.172E-004	¢ 1151.0	06	0.0009
AB	2.593E-004	4 1	2.593E-004	¢ 715.4	45	0.0014
AC	1.856E-004	4 1	1.856E-004	512.1	17	0.0019
Curvature	6.535E-000	5 1	6.535E-006	5 18.0)3	0.0512 not significant
Residual	7.249E-001	7 2	3.625E-007	7		-
Cor Total	1.188E-003	3 8				

The Model F-value of 651.74 implies the model is significant. There is only a 0.15% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C, AB, AC are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The "Curvature F-value" of 18.03 implies there is curvature (as measured by difference between the average of the center points and the average of the factorial points) in the design space.

There is only a 5.12% chance that a "Curvature F-value" this large could occur due to noise.

Std. Dev.	6.020E-004	R-Squared	0.9994
Mean	0.068	Adj R-Squared	0.9979
C.V.	0.88	Pred R-Squared	N/A
PRESS	N/A	Adeq Precision	78.224
Case(s) w	with leverage of 1.0000:	Pred R-Squared and PRESS statistic	not defined

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 78.224 indicates an adequate signal. This model can be used to navigate the design space.

	Coefficient		Standard	95% CI	95% CI	
Factor	Estimate	DF	Error	Low	High	VIF
Intercept	0.068	1	2.129E-004	0.067	0.069	
A-Wood flow	ur-5.537E-003	1	2.129E-004	-6.453E-003	-4.622E-003	1.00
B-K - 400	-3.034E-003	1	2.129E-004	-3.950E-003	-2.119E-003	1.00
C-DOP	7.222E-003	1	2.129E-004	6.306E-003	8.137E-003	1.00
AB	5.693E-003	1	2.129E-004	4.778E-003	6.609E-003	1.00
AC	-4.817E-003	1	2.129E-004	-5.733E-003	-3.901E-003	1.00
Center Point	-2.711E-003	1	6.386E-004	-5.459E-003	3.620E-005	1.00

Final Equation in Terms of Coded Factors:

(Viscosity (500)) ^{-0.5}	=
+0.068	
-5.537E-003	* A
-3.034E-003	* B
+7.222E-003	* C
+5.693E-003	* A * B
-4.817E-003	* A * C

Final Equation in Terms of Actual Factors:

=	(Viscosity (500)) ^{-0.5}
	+0.070626
* Wood flour	-2.56551E-004
* K - 400	-2.18196E-003
* DOP	+6.01940E-003
* Wood flour * K - 400	+5.69345E-005
* Wood flour * DOP	-9.63434E-005

Response: Viscosity (1200)

Transform:	Power elected Factor	Lambda: -	1	Constant:	0		
			•				
Analysis of val	riance table [H	Partial sum of so	quares				
	Sum of		Mean	F			
Source	Squares	DF	Square	Valu	Ie	Prob > F	•
Model	3.649E-00	5 5	7.298E-006	5 1675.2	20	0.0006	significant
1	4 8.563E-00	61	8.563E-006	5 1965.0	66	0.0005	-
1	B 1.232E-00	61	1.232E-006	5 282 .8	84	0.0035	
(C 1.369E-00	5 1	1.369E-005	5 3143.2	20	0.0003	
Al	B 6.320E-00	6 1	6.320E-006	5 1450.2	70	0.0007	
AC	C 6.681E-00	61	6.681E-006	5 1533 .2	58	0.0007	
Curvature	e 6.950E-00	8 1	6.950E-008	15.9	95	0.0573 not	significant
Residua	1 8.713E-00	9 2	4.357E-009)			
Cor Tota	l 3.657E-00	5 8					

The Model F-value of 1675.20 implies the model is significant. There is only a 0.06% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C, AB, AC are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The "Curvature F-value" of 15.95 implies there is curvature (as measured by difference between the average of the center points and the average of the factorial points) in the design space. There is only a 5.73% chance that a "Curvature F-value" this large could occur due to noise.

Std. Dev.	. 6.600E-005	R-Squared	0.9998
Mean	6.196E-003	Adj R-Squared	0.9992
C.V.	1.07	Pred R-Squared	N/A
PRESS	N/A	Adeq Precision	120.373
Case(s)	with leverage of 1.0000:	Pred R-Squared and PRESS statistic	not defined

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 120.373 indicates an adequate signal. This model can be used to navigate the design space.

	Coefficient		Standard	95% CI	95% CI	
Factor	Estimate	DF	Error	Low	High	VIF
Intercept	6.227E-003	1	2.334E-005	6.126E-003	6.327E-003	
A-Wood flo	ur-1.035E-003	1	2.334E-005	-1.135E-003	-9.342E-004	1.00
B-K - 400	-3.925E-004	1	2.334E-005	-4.929E-004	-2.921E-004	1.00
C-DOP	1.308E-003	1	2.334E-005	1.208E-003	1.409E-003	1.00
AB	8.888E-004	1	2.334E-005	7.884E-004	9.892E-004	1.00
AC	-9.139E-004	1	2.334E-005	-1.014E-003	-8.135E-004	1.00
Center Point	-2.796E-004	1	7.001E-005	-5.808E-004	2.160E-005	1.00

Final Equation in Terms of Coded Factors:

(Viscosity) ⁻¹	=
+6.227E-003	
-1.035E-003	* A
-3.925E-004	* B
+1.308E-003	* C
+8.888E-004	* A * B
-9.139E-004	* A * C

Final Equation in Terms of Actual Factors:

(Viscosity) ⁻¹	=
+6.32031E-003	
-4.03832E-005	* Wood flour
-3.20321E-004	* K - 400
+1.11109E-003	* DOP
+8.88821E-006	* Wood flour * K - 400
-1.82772E-005	* Wood flour * DOP

Response: Viscosity (2000)

Transform: ANOVA for Se	Power elected Fact	Lambda: - orial Model	1.5	Constant:	0		
Analysis of var	iance table	[Partial sum of se	quares]				
	Sum of		Mean	F			
Source	Squares	S DF	Square	Valu	e	Prob >]	F
Model	8.899E-0	007 5	1.780E-007	3473 .2	22	0.0003	significant
A	1 2.277E-0	007 1	2.277E-007	4442.	90	0.0002	
E	B 1.055E-0	008 1	1.055E-008	205.	95	0.0048	
(C 3.554E-0	007 1	3.554E-007	6934.	84	0.0001	
AE	B 1.094E-0	007 1	1.094E-007	2134.	27	0.0005	
AC	C 1.869E-0	007 1	1.869E-007	3648.	12	0.0003	
Curvature	e 8.691E-0	11 1	8.691E-011	1.1	70	0.3226 no	t significant
Residua	1 1.025E-0	2 10	5.124E-011				•
Cor Tota	1 8.901E-0	07 8					

The Model F-value of 3473.22 implies the model is significant. There is only a 0.03% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C, AB, AC are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.
The "Curvature F-value" of 1.70 implies the curvature (as measured by difference between the average of the center points and the average of the factorial points) in the design space is not significant relative to the noise. There is a 32.26% chance that a "Curvature F-value" this large could occur due to noise.

Std. Dev	. 7.159E-006	R-Squared	0.9999
Mean	6.754E-004	Adj R-Squared	0.9996
C.V.	1.06	Pred R-Squared	N/A
PRESS	N/A	Adeq Precision	163.744
Case(s)	with leverage of 1.0000:	Pred R-Squared and PRESS statistic	not defined

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 163.744 indicates an adequate signal. This model can be used to navigate the design space.

	Coefficient		Standard	95% CI	95% CI	
Factor	Estimate	DF	Error	Low	High	VIF
Intercept	6.765E-004	1	2.531E-006	6.656E-004	6.874E-004	
A-Wood flou	ur-1.687E-004	1	2.531E-006	-1.796E-004	-1.578E-004	1.00
B-K - 400	-3.632E-005	1	2.531E-006	-4.721E-005	-2.543E-005	1.00
C-DOP	2.108E-004	1	2.531E-006	1.999E-004	2.217E-004	1.00
AB	1.169E-004	1	2.531E-006	1.060E-004	1.278E-004	1.00
AC	-1.529E-004	1	2.531E-006	-1.638E-004	-1.420E-004	1.00
Center Point	-9.888E-006	1	7.593E-006	-4.256E-005	2.278E-005	1.00

Final Equation in Terms of Coded Factors:

(Viscosity (2000)) ^{-1.5}	=
+6.765E-004	
-1.687E-004	* A
-3.632E-005	* B
+2.108E-004	* C
+1.169E-004	* A * B
-1.529E-004	* A * C

Final Equation in Terms of Actual Factors:

=	(Viscosity (2000)) ^{-1.5}
	+6.34845E-004
* Wood flour	-5.31025E-006
* K - 400	-3.83114E-005
* DOP	+1.81816E-004
* Wood flour * K - 400	+1.16924E-006
* Wood flour * DOP	-3.05735E-006

Samples	Flexural Strength MPa	Flexural Modulus MPa
PVC	52.96 <u>+</u> 2.97	2168.6 <u>+</u> 74.9
Composite	44.51 <u>+</u> 2.09	3086.0 <u>+</u> 146.6
Chitin ¹		
2.5 wt. %	49.04 <u>+</u> 2.78	3521.9 <u>+</u> 148.2
5 wt. %	52.39 <u>+</u> 3.27	3379.1 <u>+</u> 236.9
6.67 wt. %	54.23 <u>+</u> 4.65	3667.5 <u>+</u> 232.8
7.5 wt. %	54.09 <u>+</u> 2.10	3545.5 <u>+</u> 251.7
10 wt. %	53.79 <u>+</u> 1.92	3557.3 <u>+</u> 171.9
Chitosan ¹		
0.5 wt. %	53.05 <u>+</u> 3.86	3497.1 <u>+</u> 244.5
1.0 wt. %	50.27 <u>+</u> 2.49	3282.9 <u>+</u> 219.2
1.5 wt. %	51.75 <u>+</u> 2.53	3457.1 <u>+</u> 221.7
2.5 wt. %	50.24 <u>+</u> 1.66	3375.1 <u>+</u> 245.0

 Table B.1. Mechanical Properties of the PVC/wood-flour Composites made with different concentration of coupling agent compared with the control sample.

¹chitin and chitosan wt. % were based on the weight of the wood flour.

PLA (%)	Wood Flour (%)	Chitosan ¹ (%)	Flexural Strength (MPa)	Flexural Modulus (MPa)
100	0	0	99.64 <u>+</u> 1.6	3180.3 <u>+</u> 60.8
80	20	0	97.97 <u>+</u> 0.7	4249.3 <u>+</u> 138.4
70	30	0	97.40 <u>+</u> 1.9	5020.6 <u>+</u> 111.1
60	40	0	96.13 <u>+</u> 4.1	5953.1 <u>+</u> 210.8
60	40	1	96.91 <u>+</u> 1.4	6107.9 <u>+</u> 151
60	40	2.5	97.74 <u>+</u> 2.4	5945 <u>+</u> 122
60	40	5	98.37 <u>+</u> 2.5	5919.4 <u>+</u> 138.5
60	40	10	99.06 <u>+</u> 2.5	6040.6 <u>+</u> 172.6

Table B.2. Mechanical Properties of the PLA/wood-flour Composites made with different concentration of coupling agent.

Chitosan content is based on the weight of wood flour

	NCHAM STATE UNVERSITY LIBRARIES 3 1293 02845 8580	