

ABSTRACT

YUHAN WANG. A Novel Method to Produce a Multi-components Wood Plastic Composite. (Under the direction of Dr. Joel J. Pawlak).

Wood is a natural polymeric composite material that people have been working on manipulating and mimicking its wonderful useful properties for hundreds of years. Artificial polymeric materials such as polyethylene (PE), polypropylene (PP), polystyrene (PS), have also been created with desirable properties. There are on-going efforts to combine artificial polymers and natural polymers (composed of wood fiber, lignin, fibril cellulose (MFC), and starch) together to maximize their useful properties and minimize their undesirable properties. The resulting heterogeneous composite is called wood plastic composite (WPC).

A mathematical model was first set up for understanding the theoretical relationship of mechanical properties between the plastic matrix and natural material. The model indicated that micro fibril cellulose (MFC) theatrically supposed to contribute the most to the mechanical properties to WPC.

Two components, literature reported polyethylene and polypropylene based WPC were first extruded. Different weight percentage of different natural materials including hardwood fiber, softwood fiber and micro-fibrillated cellulose (MFC) were added into WPC with or without the addition of compatibilizer. Mechanical properties including tensile strength and tensile modulus were tested and compared. The thermal properties of the extruded WPC samples were determined with a thermogravimetric analysis (TGA) and a Pekin-Elmer Pyris-1 differential scanning calorimeter (DSC). The result showed that hardwood fiber is the most suitable natural material among the three candidates. The sample of 50 weight percent HW and 5 weight percent polypropylene grafted (MAPP) **PP based WPC** exhibited the best mechanical properties.

LDPE based WPC exhibited relatively lower mechanical properties. Due to the lower melting point, **LDPE based WPC** is more flexible, easier to process and possible for later multi-components extrusion.

LDPE-PSA based WPC was the upgraded version of **LDPE based WPC**, while a certain amount of corn starch was also added to the WPC. **LDPE-PSA based WPC** exhibited a better mechanical properties compared to **LDPE based WPC** that contained the same weight percentage of hardwood fiber. With the addition of more starch (up to 27 weight

percent), the mechanical strength increased by approximately 40%. Furthermore, modulus increased with the addition of starch up to 20 weight percent. Adding more starch beyond 20 weight percent resulted a decrease of homogeneity and decreased the modulus.

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A Novel Method to Produce a Multi-components Bio-renewable Wood Plastic Composite

by
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requirements for the degree of
Master of Science

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DEDICATION

I am dedicating this thesis to my parents and my dog. Their love, patience and encouragement helped to complete this work.

BIOGRAPHY

Yuhan Wang grew up in Wuhan, China. He came to United State in September 2008. He finished his bachelor degree in North Carolina State University major in chemistry and minor in chemical engineering. After graduation, he continued his study in the group of Dr. Joel Pawlak.

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Preface

Wood is a natural polymeric composite material that people have been working on manipulating and mimicking its wonderful useful properties for hundreds of years. Artificial polymeric materials such as polyethylene (PE), polypropylene (PP), polystyrene (PS), have also been created with desirable properties. There are on-going efforts to combine artificial polymers and natural polymers (composed of wood fiber, lignin, micro fibril cellulose (MFC), and starch) together to maximize their useful properties and minimize their undesirable properties. The resulting heterogeneous composite is called wood plastic composite (WPC). WPC can be categorized as either wood-based or plastic-based. Wood-based WPC was introduced in the early 1960s. To make wood-based WPC, wood is first immersed in solution containing monomers, heated and irradiated in order to initiate the polymerization and crosslink of the monomers from the solution with the wood. The challenge of wood-based WPC is the trade-off between the improved properties and the cost, since the process requires huge amount of heat and energy input, and this makes the process less practical (Zhang, 2013). In the current marketplace, the most common artificial fiber board is the medium density fiber board (MDF). MDF production involves bonding small wood chips, referred to as fibers in the MDF industry, with urea-formaldehyde resin and wax to increase its strength and water resistance. MDF is cheaper, more flexible, and more stable in dimensions than its natural wood counterparts. However, the high density and unavoidable urea-formaldehyde content impede the utilization of MDF in the future. There are numerous reports of consumers getting cancers of inhaling formaldehyde released from their new decorated MDF flooring or furniture.

Comparing with MDF, WPC is a composite has a number of positive attributes. For example, it avoids the need for the urea-formaldehyde, can be formed with recycled or sustainable polymers, and can have a wider variety of characteristics. Manufacturing a WPC that is competitive in properties to MDF has three challenges: the price, strength and stability. The manufacture of MDF is relatively mature now comparing with WPC. Therefore, advances in MDF manufacturing typically focus on cost reduction making MDF a

very affordable product. It will take significant advances in manufacturing in material formulation for WPC to directly compete with the properties and cost of MDF.

The formaldehyde resins bonds the wood chips of MDF tightly together which make MDF relatively strong but also heavy. For making a green composite, WPC does not contain any organic resins. On the other hand, the defects in the WPC undermine the connection between the plastic matrix and natural wood fiber. As a result, the force transmission from the plastic matrix to the wood fiber is relatively poor. Therefore, WPC typically do not achieve the theoretical strength of the composite.

The ultimate goal of this project is create a WPC that has improved strength and approaches the theoretical strength and modulus values for the composite. This will allow for the WPC to be used as a substitute for MDF. In order to improve the stress transfer from the matrix to the fibers, an agent is needed to bring the plastic matrix and natural content together. This agent is so-called the compatibilizer. A literature review for the history of compatibilizer is first conducted in this thesis. The review of the choices of compatibilizer and their effects on different materials is useful to set a starting point of this project. In addition, a review of the process method and other additives for further enhancement of WPC is also conducted. Overall, the literature review provided extensive knowledge and understanding of the effects of compatibilizer and other reagents on the strength of wood plastic composite.

The project was broken down into three tasks. In the first task, a theoretical model was developed to create a general sense of relationship between the strength and the content of natural fibers and plastic matrix. Hardwood (HW) and softwood fiber (SW) are used as examples for natural contents. The model was under the assumption that there were no defection and force was transmitted completely and efficiently in WPC.

In the second task, different combinations of natural materials and plastic matrixes were mixed without compatibilizer. The goal of the second task is to conduct a comparison between the theoretical model in the first task and experimental values. It also helped draw a baseline of the starting mechanical and thermal properties of WPC which could be used for understanding of such properties with compatibilizers in future work

In the third task, the already known combinations from the second task were retested with different compatibilizer. The results were compared with the results from the second task to show the effects of compatibilizer. Beside the addition of compatibilizer, other additives such as nanoclay was also added to test if they can further enhance the properties.

Chapter 1

Literature review.

1.1 Common compatibilizers and chemical mechanisms in WPC

Combining natural polymer and artificial products together does not result in their physical properties being added together. It is similar of embedding an artificial limb into body which will cause incompatibility. Because of the heterogeneity between the two kinds of materials to be combined, the WPC is heterogeneous, and external mechanical forces cannot be transmitted well throughout the composite. The lack of bonding and interactions, under ordinary processing conditions and in the absence of chemical additions, result in deficient shear and friction between the wood particles. An adhesive is necessary to glue these two components together. The compatibilizer is then introduced, and it serves as the adhesive that improves the bonding between natural and artificial polymers. (Figure 1). The most widely used or studied compatibilizer is maleic anhydride (MAH) (Figure 1). (Lippomen, 2012) MAH is typically introduced in a grafted form, such that the MAH has already been reacted with polyethylene (PE) or polypropylene (PP) before its used in the manufacture of WPCs. This grafting process increased the miscibility between the MAH and the artificial PE phase. Once heat is applied, a ring-opening reaction will proceed, along with the hydroxyl groups on the natural polymer side. An ester bond will then form. In addition, the functional groups in MAH and starch will form intermolecular hydrogen bonding to enhance the adhesion of wood and plastic.

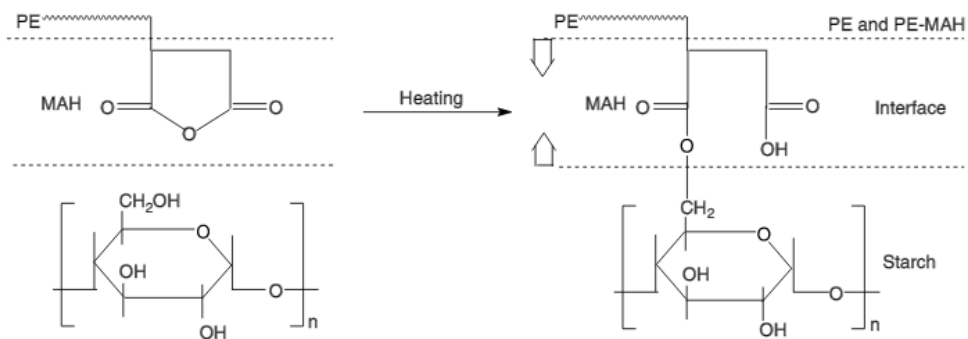
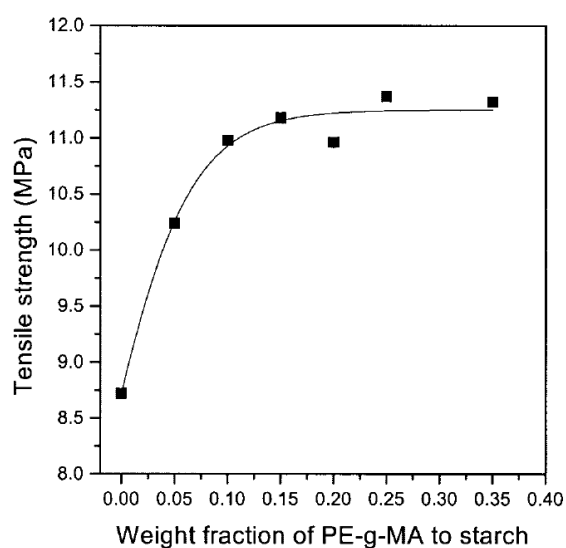
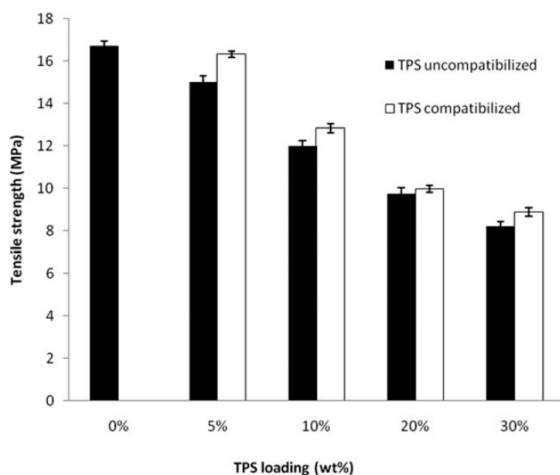


Figure 1. Maleic Anhydride (MAH) bonding mechanism (Lipponen, 2012).

There is typically a saturation point with respect to compatibilization. Before the saturation point, the tensile strength will increase with the addition of MAH. After reaching the saturation point, the tensile strength will level off and the interfacial tension will hence reach its minimum point. (Lippomen, 2012) The saturation point varies with different natural polymers. For the case of corn starch, the saturation point of MAH is approximately 10% of starch weight for the blend of starch and low density PE (at a ratio of 25:100). Figure (2I)



I.

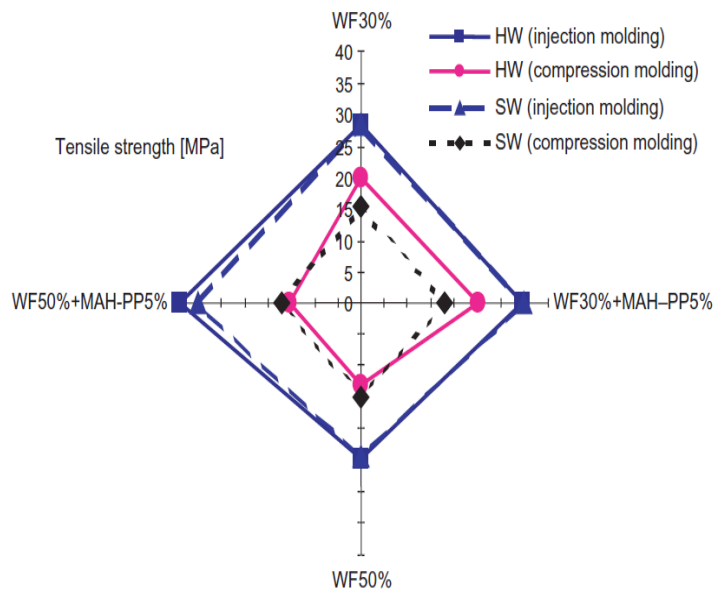


II.

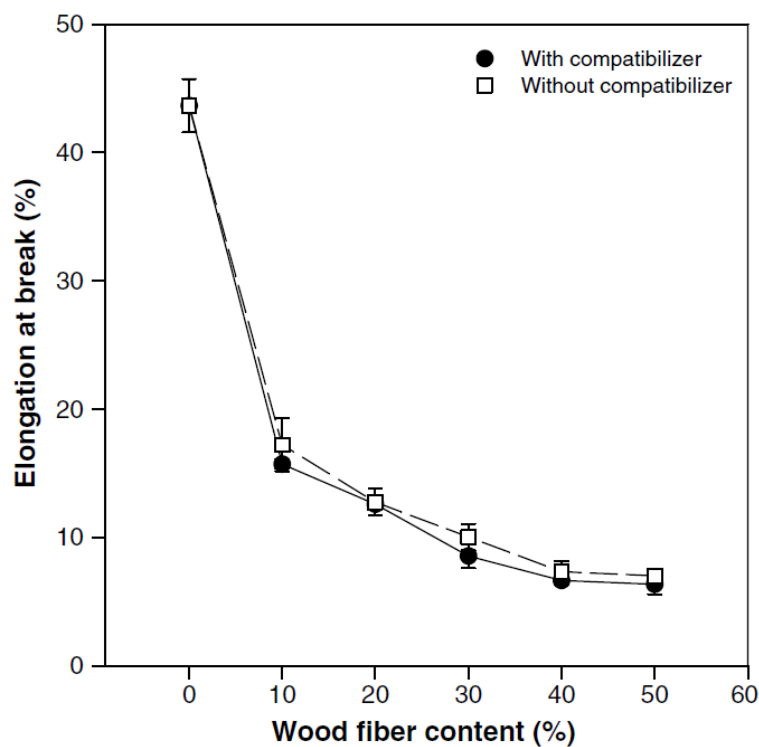
Figure 2. I. Plot of tensile strength of starch and LDPE (25:100) blends versus the concentration of PE-g-MA; II. Tensile strength of the HDPE /TPS blends with and without PE-g-MA as a function of TPS loading. (Liu, et.al., 2012)

The ratio between the filler and plastic is another key factor affecting the strength. As shown in Figure 2 II, increasing the starch content up to 30% results in a decrease of the tensile strength (Wang, 2003). This is due to the theory that large starch particle formation increased the stress-concentration, which will ultimately cause the reduction of tensile strength. (Kahar, 2012).

Similarly, this theory applies to wood fiber, where a content of 50 weight percent in the WPC reached the maximized tensile strength for the composite. One major trade-off about adding wood fiber is that an excessive amount of wood fiber will lead to less elongation, making a more brittle product. (Bledzki, 2004). (Figure 3)



I.



II.

Figure 3. I. Tensile strength of hard- and soft-wood-fiber-PP composites with and without compatibilizer in both processes. II. Elongation at break of wood-fiber-PP composites.

(Bledzki, 2004)

Other compatibilizers include ethylene-methacrylic acid, and 1-4 isocyanate. These compatibilizers are either highly toxic or highly selective to specific components. For example, 1-4, isocyanate is a good compatibilizer for wood/PP component. The carbon atom from the $N=C=O$ portion of the isocyanate attacks the lone pairs of oxygen on wood side and quickly forms a covalent bond (Figure 4). However, 1-4 isocyanate is toxic, highly explosive, and highly reactive which makes it impractical for industrial manufacturing.

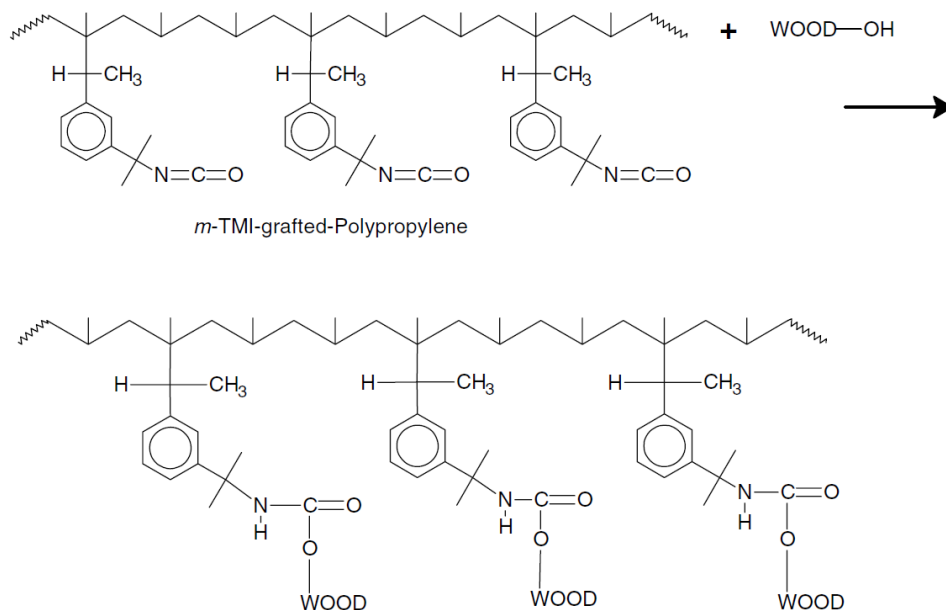


Figure 4. Coupling mechanism of *m*-TMI grafted polypropylene. (Lipponen, 2012).

As shown in Figure 1, the maleic anhydride group is attached on the side chain of the polypropylene grafted MAH. On one hand, it is easy to manipulate and miscible with the plastic matrix. On the other hand, since the attachments are on the side chains, it is possible that polypropylene grafted MAH (MAPP) would be detached through high heat and shear force. Based on this limitation, Arkema Chemical (Colombes, Paris, France) invented a new compatibilizer called Lotader. Lotader terpolymers are reactive polyolefins and contain certain amount of MAH or glycidyl methacrylate. Comparing with grafted MAH, Lotader embeds the MAH group on the backbone of the terpolymers, which offers more effective support on extrusion and coating. (Figure 5)

Lei and Wu used Lotader AX8900 and MAH as a combinational compatibilizer for enhancing the strength of polyethylene based WPC. In their work, high density polyethylene (HDPE), Lotader AX 8900 and poly (ethylene terephthalate) (PET) were first mixed and injected into extruder. Afterwards, the product was pelletized and extruded with polyethylene grafted maleic anhydride (MAPE) and wood flour. Based on their result, the addition of 2

weight percent Lotader AX 8900 increased the tensile strength from 21 MPa to 27.7 MPa and modulus from 0.64 GPa to 1.64 GPa.

Altun *et al.* compared the effects of two different types of Lotader compatibilizers on the strength of HDPE based WPC. The paper provided the structures of Lotader 2210 and Lotader AX 8900 (Figure 5).

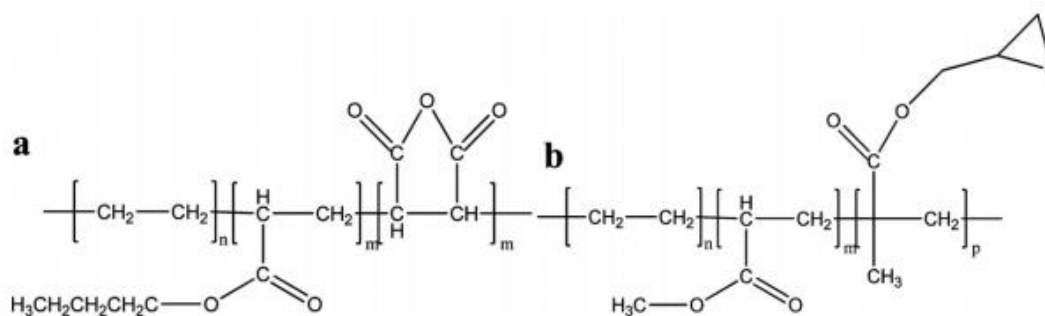


Figure 5. The chemical structure of compatibilizers. (a) Lotader 2210 and (b) Lotader AX 8900 (Altun, 2012).

As shown in Figure 5a, the maleic anhydride groups were located on the backbone of the terpolymer which make the compatibilizer more stable under heat and shear force. Altun compared the different effects of Lotader 2210 (end with MAH group) and Lotader AX8900 (end with glycidyl methacrylate group) on the strength of WPC. Their results confirmed that Lotader 2210 provided a better reinforcement in strength than Lotader AX 8900. With the addition of 10 weight percent of Lotader 2210, the tensile strength of WPC increased from 11.3 MPa to 14.4 MPa and the modulus increased from 0.38 GPa to 0.76 GPa. One thing to be noted that rather than extrude the WPC with compatibilizers, the author soaked the wood fiber into the solution of compatibilizer/chloroform to conduct a better disperse before extrusion. The chloroform was later removed at 50 °C.

1.2 Surface treatment agent and other additives in WPC

Surface treatments for WPC

Heat treatment

Due to the hydrophilic property of the natural content and hydrophobic nature of the matrix, fibers will clump and agglomerate during extrusion. As a result, fiber clumps become defects that locally reduce the strength of composite and force transmission in the system. This reduces the overall modulus and strength of the composite materials. In order to make Wood Plastic Composite (WPC) stronger, surface treatments are necessary. Heat treatment refers to preconditioning the wood fibers at high and moist environment. A common technique is to use hot steam (180 °C to 230 °C) to condition the fiber. Through heat and moisture, the hemicellulose is removed, crystallinity of cellulose is increased while the polymerization index is decreased. (Pelaez, 2013)

Andrusky *et al.* (2008) extruded conditioned wood flour (WR) with Poly- Propylene (PP). As a result, the tensile modulus was increased from 1868 MPa (unconditioned) to 2178 MPa (conditioned). The tensile strength was increased from 16 MPa (unconditioned) to 19.5 MPa (conditioned).

Hosseinaei *et al.* (2012) conditioned the fibers at varied temperature and found that as the condition temperature increased, the tensile strength increased. As reported, the tensile strength increased from 24.1 MPa (140 °C) to 26.9 MPa (170 °C). The tensile modulus increased from 4505 MPa (140 °C) to 5363 MPa (140 °C).

Mechanical Treatment

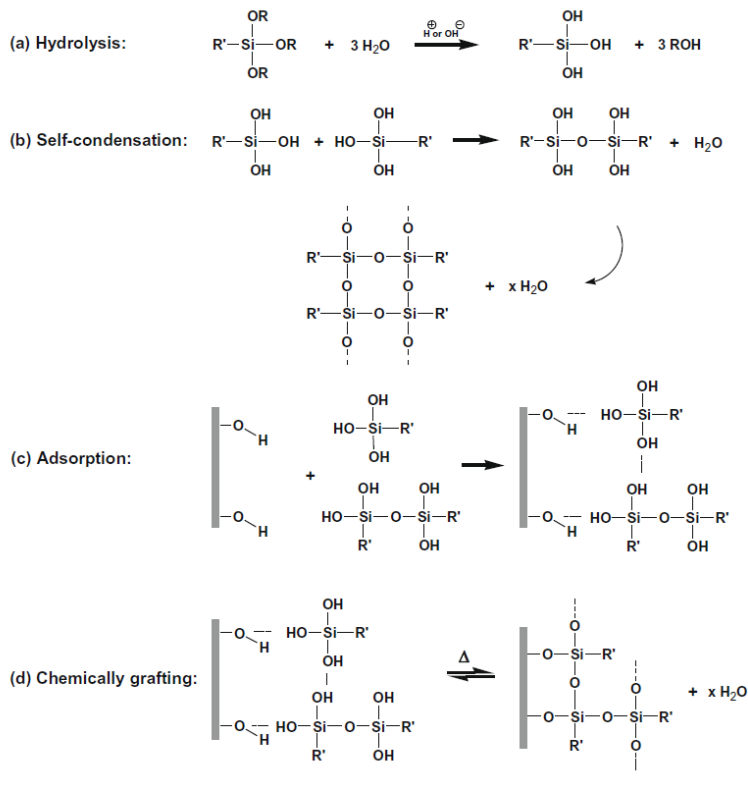
Kinetic treatment refers to use high frequency radio plasma to make the fiber particles move inside the WPC. As a result, the fiber particles will be distributed more evenly in the system. Such treatment will decrease amount of defects in WPC and therefore increase the strength. (Dong, 1993)

Chemical Treatment

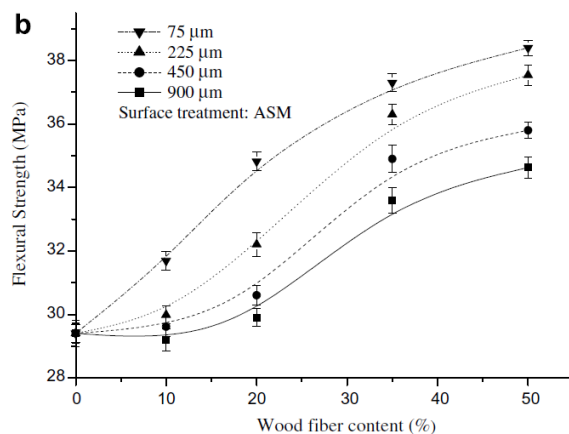
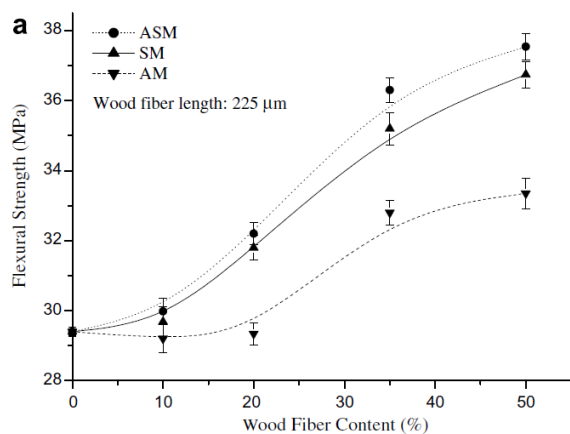
Common coupling agents are polyvinyl and silane. Sodium hydroxide (NaOH), silane and MAH are usually used as a combination treatment (NSM). NaOH has the ability to

remove the impurities such as hemicellulose or small lignin and extractives on the wood fiber surface. (Xie, 2004). Such treatment helps expose and disperse the wood fiber to compatibilizers and increase the sites for bonding. The functions of silane are mainly made up by four steps (Figure 6 I). The silane monomers are first hydrolyzed in the presence of either acid or base. During the hydrolysis process, the self-condensation of silane monomers take place at the same time. The rate of condensation can be controlled by the pH of the hydrolysis system. In order to free as much silane monomers as possible, the rate of self-condensation should be minimized. The silanol monomers are then bonded with hydroxyl groups on the wood side to form the hydrogen bonds. Finally, under heating conditions, the hydrogen bonds can be converted to $-\text{Si}-\text{O}-\text{C}-$ bonds to further increase the strength. (Cui, 2008) As shown in Figure 15 II a, ASM exhibits the highest flexural strength. In Figure 6 II b, 75 μm wood fiber exhibits the highest flexural strength, which is in agreement with the theory mentioned earlier. (Cui, 2008).

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I



II

Figure 6. I. Interaction of silane with natural fibers by hydrolysis process. (Xie, et.al. 2004).

II. Flexural strengths of wood fiber composites as a function of wood fiber content with (a) different surface treatment methods and (b) different fiber lengths (Cui, et.al., 2008).

The pretreatment of the natural content is now common in industry. A pre-wash through NaOH is necessary for better contacts between the natural content and compatibilizers. The treatment with silane is still expensive and complicated which make it less acceptable in industry.

Nanoclays and Nanoxide addition

Nanoclays and Nanoxide have been well studied and are currently regarded as the most suitable nanofillers to WPC due to their high aspect ratio and large surface area. As shown in Figure 7, the clay may increase the overall tortuosity of the system and packed the fibers and plastic matrix together. The permeability of the composite may decrease with addition of clay and act as fillers to enhance the stiffness of the system. (Turku, 2014). There are various nanoclays that are commercially available on the market. The one that has been most commonly used is **cloisite Na⁺** (Tjong, 2006) In comparison with original cloisite, the addition of sodium ions improves its swelling such that it can be easily inserted into organic cations. (Tjong,2006)

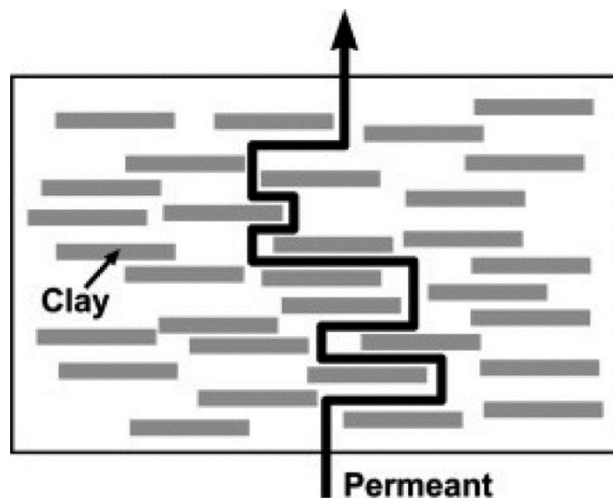


Figure 7. Tortuous pathway of a permeant in a clay nanocomposites (Turku, 2014)

Tabari *et al.* (2011) have examined the effect of **cloisite Na⁺** addition on the WPC of PP/wood flour/MAH. The WPC was extruded with three weight percent of **cloisite Na⁺** and

five weight percent of MAH. An improved tensile strength of 10 MPa and tensile modulus of 1.1 GPa was observed.

Such improvement was due to the restriction of mobility of polymer chains (Deka, 2011) and better intercalation between fibers and matrix (Faruk, 2008) that supplied by the nanoclay layer. The less mobility of polymer chains and better intercalation will result as an enhancement of the modulus of the matrix. It has little effect on the bonding between the fibers and matrix.

Other fillers

Besides nanoclay, there are many other fillers that have been added into the WPCs to enhance their thermal and mechanical properties. Micro-crystalline cellulose (MCC) and carbon nano-tube (CNT) are the two most popular additives recently explored.

Faruk and Matuana (2008) blended PVC/Wood flour/chitin/CNT for manufacturing WPC. One thing to be noted that chitin is a better compatibilizer than MAH in the case of a PVC matrix. With the addition of five weight percent of CNT into the system, the tensile strength increased from 28 MPa to 40 MPa. The issue with CNT is that CNT is expensive and hard to produce in comparison with nanoclay.

Ashori and Nourbakhsh (2009), instead of using nanoclay, blended MCC with wood flour and polypropylene. With the addition of 8weight percent of MCC, the tensile strength increased from 18 MPa to 39 MPa. The authors did not explain the potential mechanism behind this improvement, and further study is necessary.

Foaming additives

Foaming WPC may modify the WPC properties such as increased the impact strength, reduced weight and density. Such modification may create more potential application for WPC such as the dashboard of vehicles. Common foaming additives are categorized by the thermal properties (endothermic, exothermic endothermic/exothermic). (Bledzki, 2005)

Zhang *et al.* compared all three methods and concluded the exothermic method would create the best foam structure from PP matrix. It was reported that the density was decreased 30% by foaming and surface roughness was decreased by 70%.

1.3 Wood plastic composite molding process

Compression molding

Compression and injection moldings are the two most typical methods to process wood plastic composite. (Faruk and Bledzki 2007) As mentioned earlier, compression molding was unable to provide competitive strength as the injection mold provided. Such difference is due to different layer orientations retained by compression molding. (Bledzki, 2004) The compression molding is also less efficient and more costly than injection mold which make it impractical in industry.

Injection molding

Compared to the compression molding, injection molding is more interchangeable. An extruder is typically used to optimize the injection molding process while a plastic resin is heated, melted and conveyed by screws in a barrel. The process is typically downstream and most effective in plastic production. (Bledzki, 2004) Injection molding provided a much more uniform orientation than compression molding. On the other hand, the shear force of provided by extruders is much higher than the compression molding. Such high shear force aggravates the degradation of plastic and shorten the fibers which ultimately decreases the overall strength. (Ku and Wang 2011)

Two-step process

One of the major issue while adding nanoclay into the WPCs is the difficulty to thoroughly disperse the nanoclay into the system. This difficulty is due to absence of solvent in the whole process. Poor distribution of nanoclay increases the overall heterogeneity and leads to poor force transmission in the system. In order to optimize the disperse, a two-step compounding process was introduced.

Faruk and Matuana (2008) first introduced the two-step compounding process. In their first step, nanoclay was extruded with HDPE to set up a new matrix for the natural phase. The HDPE/Nanoclay matrix was then mixed with wood flour and MAH to create such a “two-steps” compounding of WPC. They reported that the “two-steps” compounding

increased the mechanical properties of the WPC significantly comparing with the “one-step” WPC.

Lee *et al.*(2010) proposed a masterbatch process in which instead of blending the nanoclay with plastic phase, they compounded the nanoclay with MAH in a ratio of 1:9. The author claimed that the masterbatch method promoted the interaction of OH group on the nanoclay with the maleic anhydride groups on MAH. Such interaction increased the opportunities of forming ester and hydrogen bonds between nanoclay and MAH which therefore disperse the nanoclay uniformly in the system.

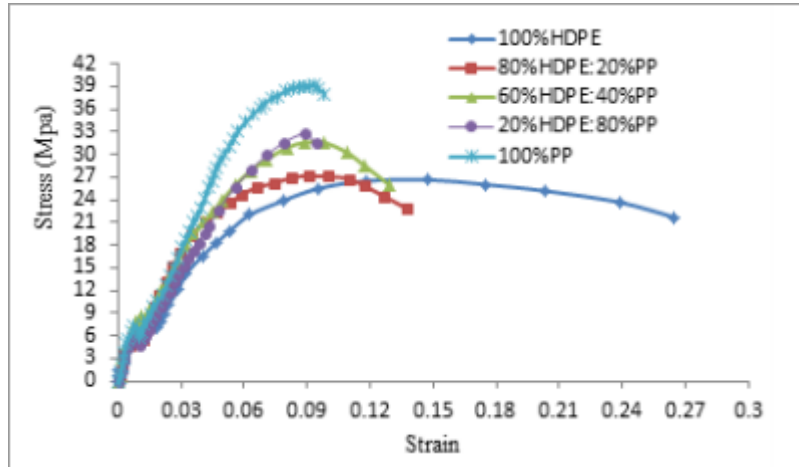
Yeh and Gupta (2010) raised a question about the masterbatch method and pointed out that there would be competing reactions between OH groups on both nanoclay and wood fibers with the maleic anhydride group on MAH. The author introduced their two-steps method, which blended PP/wood flour/MAH in the first step and added nanoclay and three times more MAH (based on the weight of nanoclay) into the system in the second step. This method provided an excess MAH environment to guarantee the formation of ester bonds between both nanoclay/MAH and wood fiber/MAH. Their result showed a 25% strength increase from their “two-steps” method comparing with the “single-step”. They proposed that this improvement was due to the absence of a competing reaction between nanoclay and fibers. The modulus, however, decreased slightly which author explained as excessive destruction of fibers microstructure since they had passed through the extruder twice.

1.4 Choices of matrix and natural content

Different researchers chose different materials as their starting materials. For the plastic matrix, common candidates are LDPE, HDPE, and PP. For the natural content, wood residue flour (WR), hardwood fiber (HW), softwood fiber (SW), and starch (SA) are common choices. Different materials are best suited for particular applications. Combining natural materials and plastic matrixes together would create different process challenges such as temperature and machine operating limitations. The review of these combinations would provide comprehensive knowledge on the advantages and disadvantages of them.

Plastic Matrix

Salih *et al.* (2013) blended LDPE and HDPE with PP and tested the mechanical properties of the blends. As shown in Figure 1, tensile tests were conducted at various ratios of LDPE: PP and HDPE: PP blends.



I.

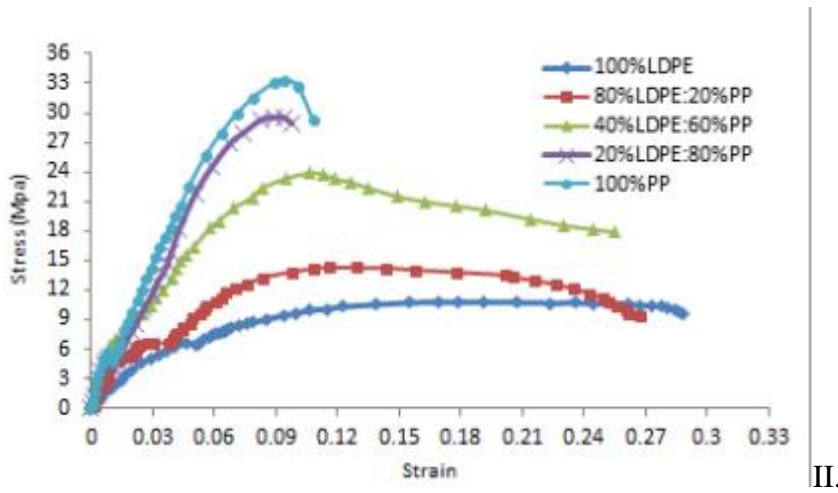


Figure 8. I Stress-strain curve of HDPE : PP polymer blends. II. Stress-strain curve of LDPE : PP polymer blends Salih *et al.* (2013).

With the addition of polyethylene into the blends, tensile strength decreased and elongation break increased. HDPE had a less significant effect on the properties of PP. As shown in Figure 8I, the addition of HDPE decreased the maximum stress, but had little effects on the strain. On the other hand, blending LDPE and PP had a significant effect on the PP properties. As shown in Figure 8II, the addition of LDPE decreased the stress and increased the strain significantly.

From Salih's work, it can be confirmed that when choosing plastic matrix, PP would provide more strength and rigidity, while LDPE would provide more flexibility. There are also other commercial plastic been used as matrix such as polystyrene, polyethylene terephthalate and polyvinyl chloride (Yong, 2010). These polymers are chosen to cooperate with different natural content to meet special requirements.

Natural content

Compared to the polymer matrix, the choices for natural content are more abundant. Researchers blend all kinds of plant fibers with polymers to test which one gives the most significant improvement. As mentioned, common natural phase for WPC are softwood fibers (SW), hardwood fibers (HW), starch (SA), and wood flour (WR) are easier to manipulate in

industry because of their powder-like form. SW, HW and also cotton fibers are more fluffy and hard to pre-mix with compatibilizers.

It is still uncertain that whether longer fiber length would provide more strength to WPC. Theoretically, the longer the fiber was, the stronger the WPC would be. Based on the formula provided by Ashby (1983), the density and elastic modulus would increase with the increase of the cross sectional area of fiber perpendicular to the applied force. Whereas the cross section area is direct proportion to the fiber length.

$$\rho_c = \frac{A_f}{A_T} \rho_f + \frac{A_m}{A_T} \rho_m$$

Where ρ_c is the density of the composite, ρ_f is the density of the fiber, ρ_m is the density of the matrix, A_f is the cross sectional area of fiber perpendicular to the applied force, A_m is the cross section area of the matrix perpendicular to the applied load, and A_T is the total cross sectional area (A_f plus A_m).

$$E_c = \frac{A_f}{A_T} E_f + \frac{A_m}{A_T} E_m$$

Where E_c is the elastic modulus of the composite, E_f is the elastic modulus of the fiber, E_m is the elastic modulus of the matrix.

Nonetheless, the experimental results did not always correspond to this theory. As shown in Figure 2 II, the flexural strength of the composite decreased with the increase of fiber length, whereas the one extruded with 75 μm (shortest) fiber actually gave the best strength. (Cui, et.al., 2008)

Sebastien Migneault *et al.* brought the debate to a higher level. Sebastien and his colleagues blended HDPE with fixed amount of fibers that possessed different fiber lengths. 40 weight percent short (0.196 mm), medium (0.304 mm) and long (0.481 mm) wood fibers were mixed with 60% wt percent of HDPE respectively in same condition. The flexural strength increased from 37.8 MPa (short) to 43.5 MPa (long). The tensile modulus increased from 2.83 GPa (short) to 2.99 GPa (long). Sebastien pointed out that with longer fibers, good quality WPC was produced qualified with higher tensile and flexural modulus and better water absorption. (Migneault, 2008)

Compared to wood fibers, starch (SA) gives relatively low contribution to the strength of WPC. As shown in Figure 9, the addition of starch had little positive effect on the strength of WPC. Even with the addition of polyethylene grafted MAH, the strength barely reached to the original strength of HDPE at five weight percent of starch. (Liu, et.al., 2012)

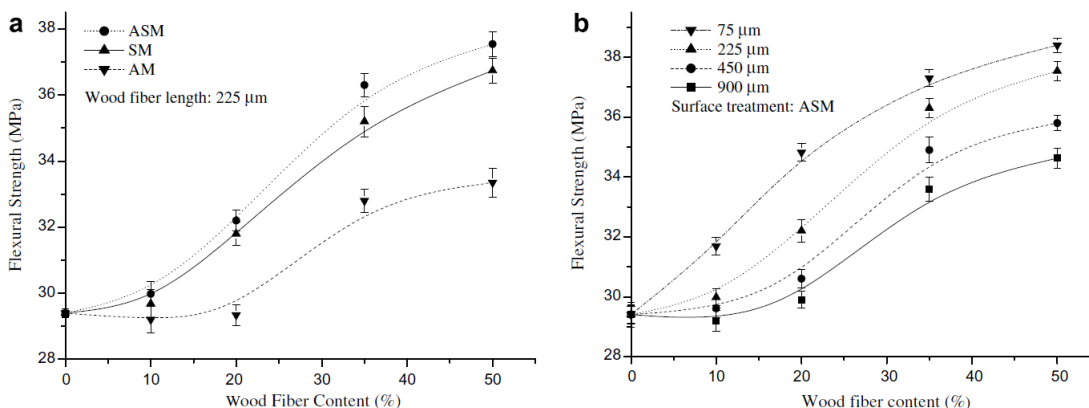


Figure 9. Flexural strengths of wood fiber composites as a function of wood fiber content with (a) different surface treatment methods and (b) different fiber lengths (Cui, et.al., 2008).

Glass fiber (GF)

Besides natural contents, glass fibers were used as a reinforcement to WPC. Comparing with natural fibers, the fiber length of GF is easier to manipulate. However, the compatibilization between GF and plastic matrix is poor. Hence, GF is usually added with wood flour (WR) or wood dust into WPC as a compensation for the zero fiber length of WR. (Tunjitpornkull, 2007) Tunjitpornkull blended wood saw dust, various amount of GF and PVC together and extrude the WPC. The results show that the stiffness and strength of the WPC increased with the addition of GF. The mechanical properties reached maximum points at 30 percent glass fiber loadings. (Tunjitpornkull, 2007)

Cellulose nanocomposites

Nanocomposite refers to a solid material which contain multiphase of additives that are in the nanoscale (less than 100 nm). As mentioned earlier, nanoclay may be used a nano-additives to enhance the strength of the overall system. Other than nanoclay, current popular nanoparticles are cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs). (Xu, 2013)

Comparing with CNCs, CNFs are a better additives for reinforcing WPC due to their larger aspect ratio. (Mariano, 2014) Jonoobi and his colleagues extrude CNF with PLA by twin screw extrusion. With the increased amount of CNF (up to five weight percent), the tensile modulus increased from 2.9 GPa to 3.6 GPa. The tensile strength increased from 58.9 MPa to 71.2 MPa. (Jonoobi, 2010)

Other nano-additives include nano-carbon fiber, carbon-nanotube and nano filled glass fibers. Different types of nano-additives fit various types of application. The main challenge with the nano technology is the high cost of these nano-materials.

Patent Statics

As Gardener mentioned, patent containing “wood plastic composite” have increased greatly in the last decade.(Figure 10) . As environmental awareness has grown, the importance of WPC to provide more environmentally friendly alternative to pure plastics seems to have grown. This is manifested in the rapid increase in the patent record for WPC.

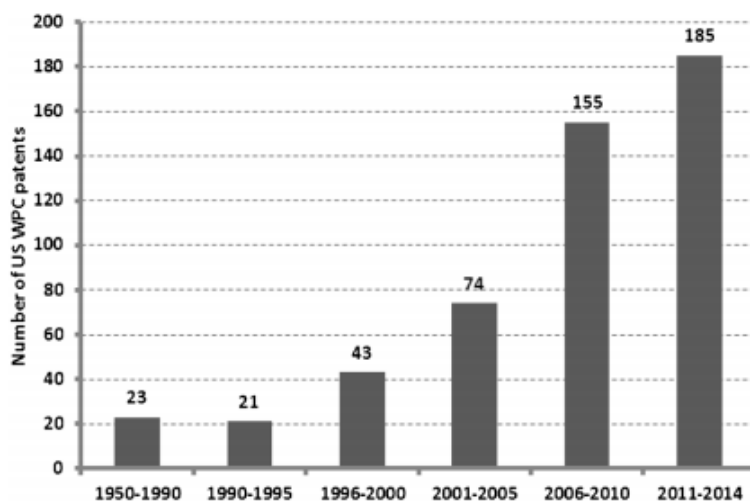


Figure 10. Total number of US patents related to wood–plastic composites since 1950

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Chapter 2

Theoretical extrusion and foaming model for WPC

2.1 Introduction

In wood plastic composites (WPC), the fiber dimensions have various effects on the modulus and strength of the composite. Longer fibers would provide more modulus and strength. On the other hand, longer fibers would create more opportunities for defects. Such defects were caused by uneven distribution of fibers, poor direction arrangements of fibers. These defects would lead to poor interfacial adhesion and force transmission. (Liu, et.al. 2012)

In order to better understand the relationship between the fiber lengths, plastic types vs. strength of WPCs, we have developed a model to predict the elastic modulus of foam materials made of both pure and composite materials. This will help guide the research in identifying the material properties required to achieve the desired levels of strength needed.

2.2 Foam Model Results:

The model was constructed using the general relationship for behavior of foams identified by Ashby (1983) in his review of the mechanical properties of cellular foam solids. This work brings together the body of knowledge at that time to explain generalized relationships between foam density and elastic modulus. These foam materials include both wood, metal foams, and plastic foams. The basic relationship between foam density and the elastic modulus is:

$$\frac{E}{E_s} = \left(\frac{p}{p_s}\right)^2$$

Where E is the elastic modulus of the foam, E_s is the elastic modulus of the solid material making up the foam, p is the density of the foam, and p_s is the density of solid material making up the foam.

The elastic modulus and density of the solid making up the foam is determined using a fibrous composite model with the matrix and fiber working in parallel. This assumes that strain is distributed equally between both the matrix material and the fibers added. The result is a weight averaging between the cross sectional areas of the fiber and matrix inside of unit element as shown in Figure 1. Using the respective volume (cross sectional area) fraction of the matrix and the fiber, as well as the density of these two materials, the density of the composite can be calculated:

$$\rho_c = \frac{A_f}{A_T} \rho_f + \frac{A_m}{A_T} \rho_m$$

Where ρ_c is the density of the composite, ρ_f is the density of the fiber, ρ_m is the density of the matrix, A_f is the cross sectional area of fiber perpendicular to the applied force, A_m is the cross section area of the matrix perpendicular to the applied load, and A_T is the total cross sectional area (A_f plus A_m).

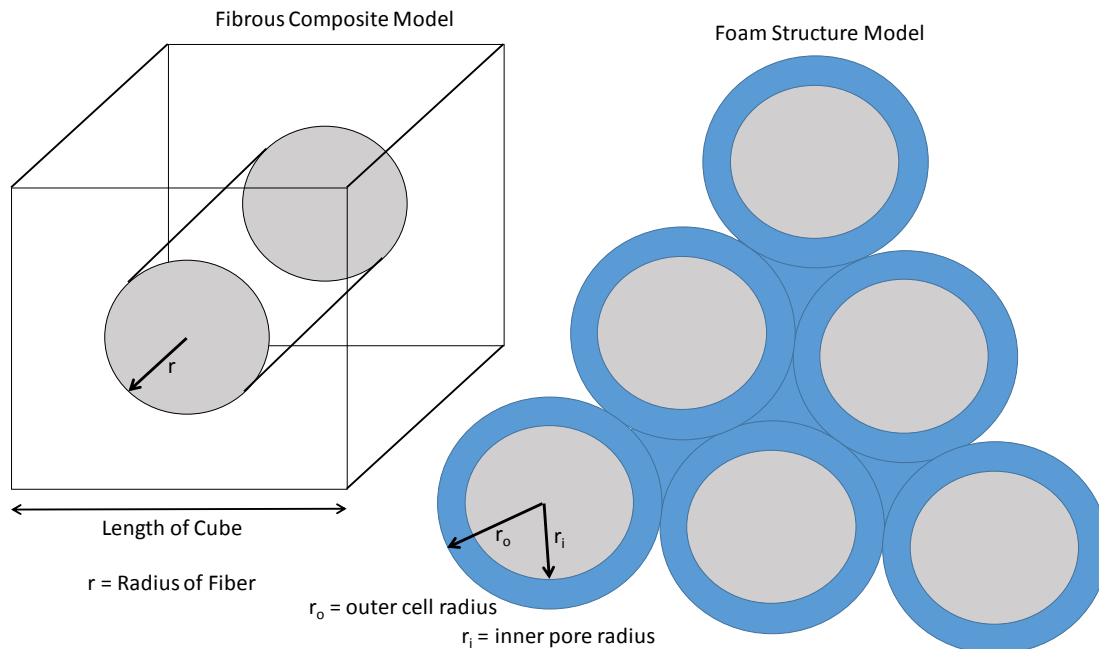


Figure 1: Fibrous composite model shows how the foam wall strength is determined from combination of the matrix and fiber. Foam structure model shows how the foam

structure is approximated to determine density. Note that the space between cells is considered negligible in this model.

The equation for the elastic modulus of the composite material making up the foam wall is as follows:

$$E_c = \frac{A_f}{A_T} E_f + \frac{A_m}{A_T} E_m$$

Where E_c is the elastic modulus of the composite, E_f is the elastic modulus of the fiber, E_m is the elastic modulus of the matrix, A_f is the cross sectional area of fiber perpendicular to the applied force, A_m is the cross section area of the matrix perpendicular to the applied load, and A_T is the total cross sectional area (A_f plus A_m).

The foam structure is determined by a simple bubble model. The concept is that the individual foam cell can be approximated as a bubble with a thick wall. This is then used to approximate the density of the foam, cf. Figure1: This approximation ignores the mass between individual cells.

$$\rho_{\text{foam}} = \frac{(V_o - V_i)\rho_c}{V_o}$$

Where V_o is the volume of a sphere characterized by radius r_o , V_i is the volume of a sphere characterized by radius r_i , and ρ_c is defined above.

This model is used to predict the elastic modulus of the foam material. Ideally, WPC can be formed that approximates the properties of wood, but can be manufactured in unique cross sections and have additional benefits related to plastics, ex. water resistance, dimension stability, rot resistance. Literature values for medium density fiberboard (MDF), softwood, hardwood, and balsa wood are shown in Table 1 for comparison purposes. As one can see, the elastic modulus of medium density fiberboard (MDF) is 4000 MPa. This value is significantly higher than LDPE (200 MPa (literature), 95 MPa (measured) and polypropolyene (PP) (2880 MPa). Thus, it will require the addition of a strengthening

material to achieve the desired level of elastic modulus. The basic approach will be to add fibrous material to create a fibrous composite for the foam wall.

TABLE 1: Reference literature values for various materials of interest.

	Modulus (MPa)	Density (kg/m ³)	Density (lbs/ft ³)	Modulus/Density (m ² /s ²)
MDF	4000	750	46.8	5.33
Softwood	16000	500	31.2	32.00
Hardwood	12000	700	43.7	17.14
Balsa Wood	3000	130	8.1	23.08
LDPE (measured)	95	910	56.8	0.10
LDPE (Lit.)	200	910	56.8	0.22
PP (Lit.)	2880	950	59.3	3.03
MFC	30000	1500	93.6	20.00

Three different reinforcing fibers were examined using the model. These were softwood fibers, ground softwood, and micro-fibrillated cellulose (MFC). Each of these material have the basic components characteristics as shown in Table 2.

TABLE 2: Basic components properties of fibers used in modeling.

Fiber Property	Softwood	Groundwood	MFC
Length (mm)	3	1	1
Eff. Diameter (um)	40	200	4
Elastic Modulus (MPa)	12000	16000	30000

2.3 Scenario 1 – MFC Cellulose and Poly-propylene

Figure 2 shows the effect of adding various amounts of MFC to poly-propylene (PP) on the elastic modulus and the density of the foam. The foam was held constant at a relative volume (void/ total) of 0.52. This means that 48 % of the foam material is composed of air.

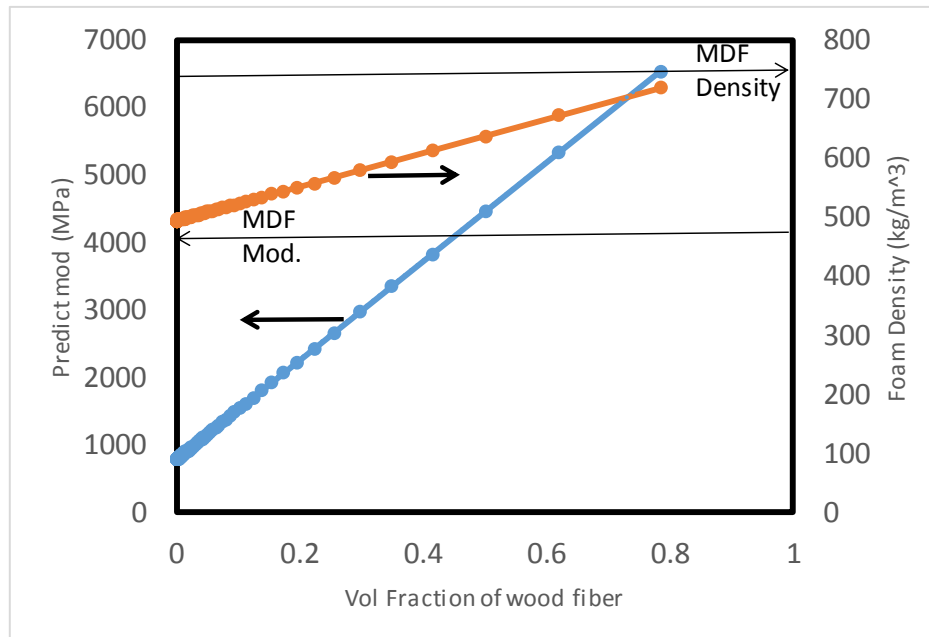


Figure 2: The elastic modulus and the density of a foam composite material with 0.52 relative volume (i.e. 0.48 void fraction). The composite material is made of poly-propylene and MFC.

Figure 2 shows the range of materials that will produce a foam with properties similar to MDF. This range can be identified by the lower horizontal line which defines the modulus of MDF (4000 MPa). Any mixture of MFC and matrix that produces a modulus above this line is advantageous. Thus, at ~0.5 volume fraction the composite foam material has a 4000 MPa and a density of ~600 kg/m³. This combination of materials and void volume has about a 20 % lower density than MDF and similar elastic modulus.

2.4 Scenario 2 – Poly-propylene and Softwood Fiber

Figure 3 shows the predicted elastic modulus and the density of a foam composite with a 48 % void volume. It is worth noting that according to the prediction, there is no reasonable combination of softwood fiber and poly-propylene that will achieve an elastic modulus equal to or greater than MDF.

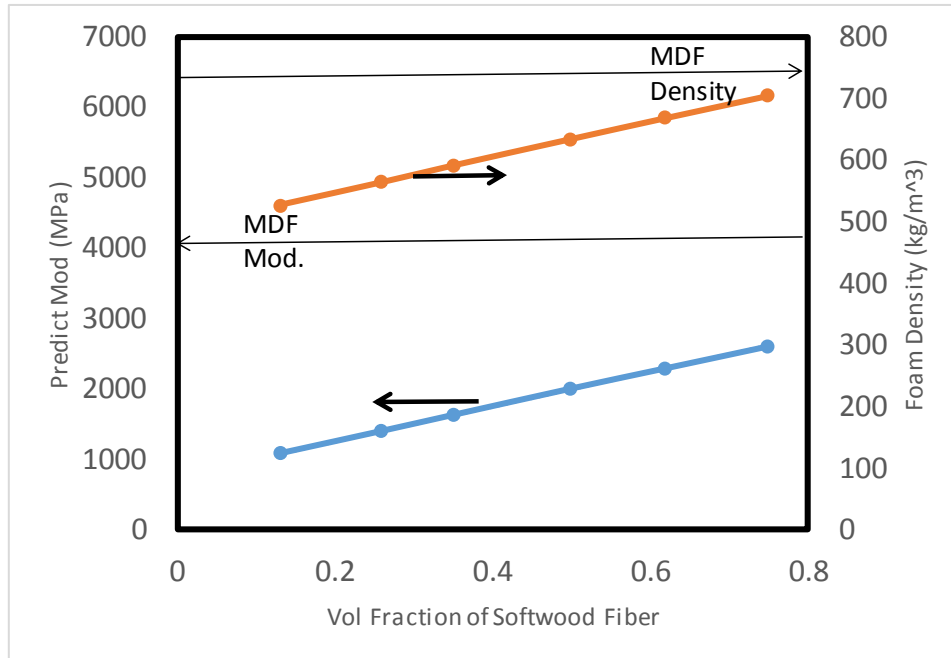


Figure 3: The elastic modulus and the density of a foam composite material with 0.48 void fraction. The composite material is made of poly-propylene and softwood fiber.

Using a composite material made of 75 % fiber and adjusting the void fraction of the foam to equal a density of 750 kg/m³, the predicted elastic modulus rises to 2940 MPa, which is about 75 % of the modulus of MDF. Thus, it appears that there is no practical advantage to pursuing this technology if the intention is to create an exact replacement for MDF with a wood fiber plastic composite.

2.5 Scenario 3 – Ground Softwood and Poly-propylene

In the modeling, the ground softwood, as compared to the softwood fiber, shows slightly higher elastic modulus at the same fiber volume fraction. This is attributed to higher modulus of the ground wood as compared to the softwood fiber. However, up to a 75 % volume fraction of the ground wood, the elastic modulus still does not achieve the elastic modulus of MDF. When the density is adjusted at 0.75 volume fraction of wood fiber to the

density of MDF (750 kg/m³), the elastic modulus of the foam is 3847 MPa, which is comparable to MDF.

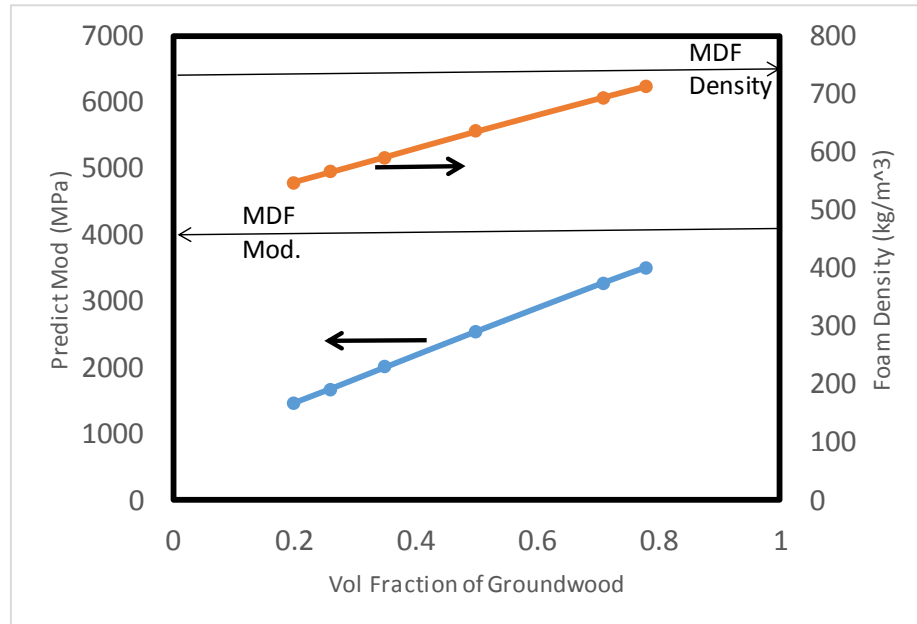


Figure 4: The elastic modulus and the density of a foam composite material with 0.48 void fraction. The composite material is made of poly-propylene and ground softwood.

2.6 Conclusion.

Only the MFC showed the combination of an increase in the elastic modulus and a lower density when compared to MDF. Thus, using the MFC/Poly-propylene combination of materials will have the greatest chance at achieving the combination of reduced weight and strength as desired by the marketplace. Alternatively, this indicates that it is imperative to investigate various matrix materials that can provide a greater elastic modulus in an extrudable form. Softwood fiber and ground wood are both predicted to create similar or slightly lower performance as compared to MDF.

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Chapter 3

Wood Plastic Composite extrusion with polyethylene as the matrix.

3.1 Introduction

From the result of Chapter 2, it was predicted that the combination of MFC and polypropylene would provide a competitive modulus compared with MDF. The result was underlying the assumption that the natural contents would bond completely with the plastic matrixes. This assumption is untrue because of the different properties possessed by plastic and natural content. Cellulose, which is mainly composed of linear D-glucose monomers, is polar and immiscible with hydrophobic non-polar polymer matrixes. (Kahar, 2012)

It is necessary to know how far the actual experimental results of the extrusion is from the theory model. In this section, HW (medium), SW (long) and MFC (short) were chosen as the natural content. Polyethylene grafted, maleic anhydrite (MAPE) was selected as the compatibilizers. Polypropylene (PP) was used as the plastic matrix for producing high mechanical performance WPC. The detailed method and experimental design were described in the follow.

3.2 Experimental Methods and Materials

3.2.1 Materials

Polymeric Matrix

Polypropylene was received from ENTC Polymers as pellets. Its melting temperature is 170 °C. Polypropylene grafted maleic anhydrite was purchased from Sigma-Aldrich.

Wood Fibers

Hardwood (HW) and softwood (SW) was used as the fiber resource from U.S. National Institute of Standards and Technology (AKR A.D.#18002). MFC was received from MeadWestvaco Corp. (Richmond, Virginia, USA). Approximately 26 g of HW and SW raw materials were placed in a disintegrator separately with 2 L of deionized water. (Figure 1a).

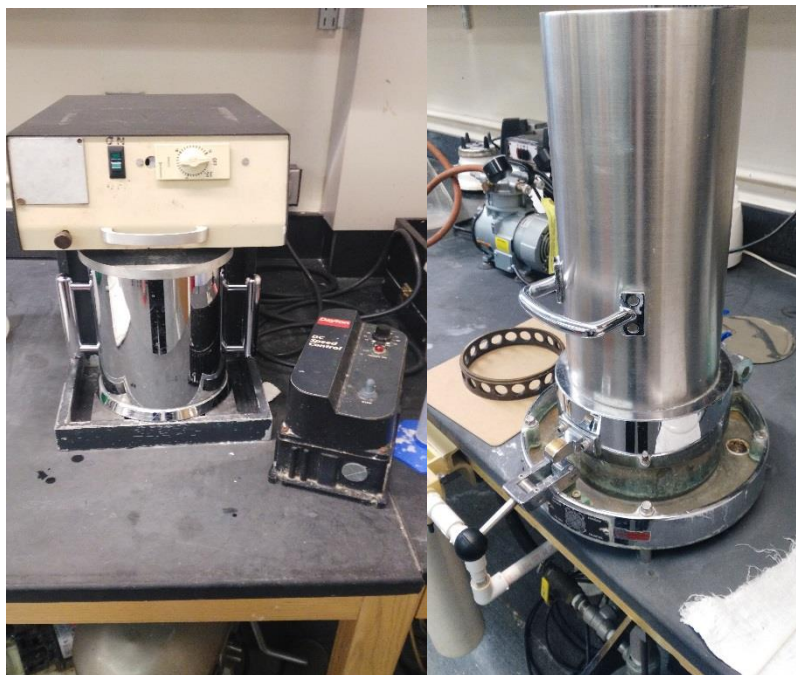
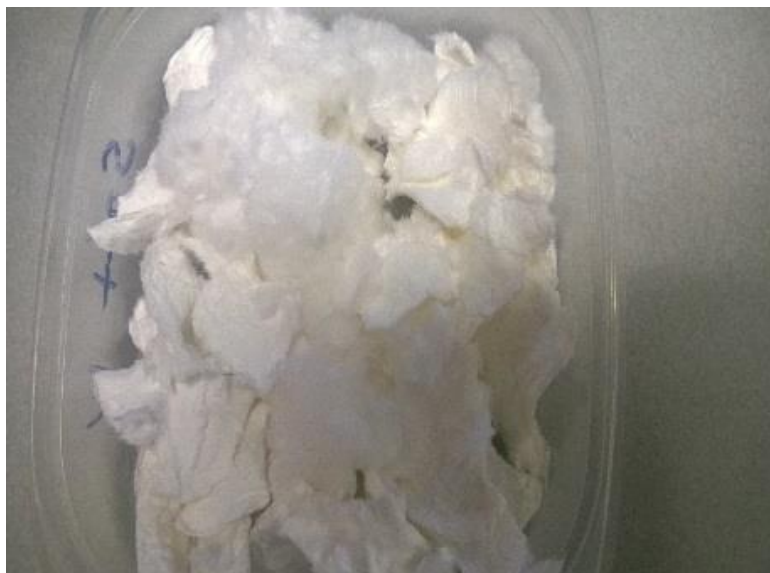


Figure 1. a. Pulp disintegrator. b. Handsheet maker

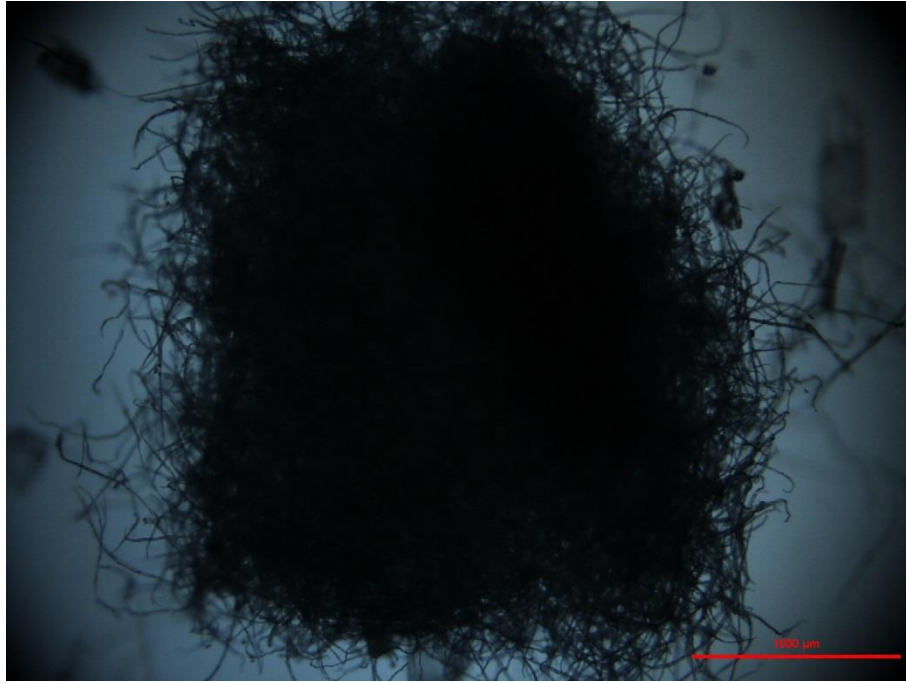
The mixtures were disintegrated for 3 minutes. The water in the mixtures were then removed through a handsheet maker (Figure 1b). The substrates were placed in a freeze dryer for 72 hours for further drying (Figure 2I) and were further blended and fluffed in a blender for 3 minutes (Figure 2II). The thoroughly disintegrated HW and SW were placed in the oven for 1 hour at 75 °C before using for extrusion.



I.



II.



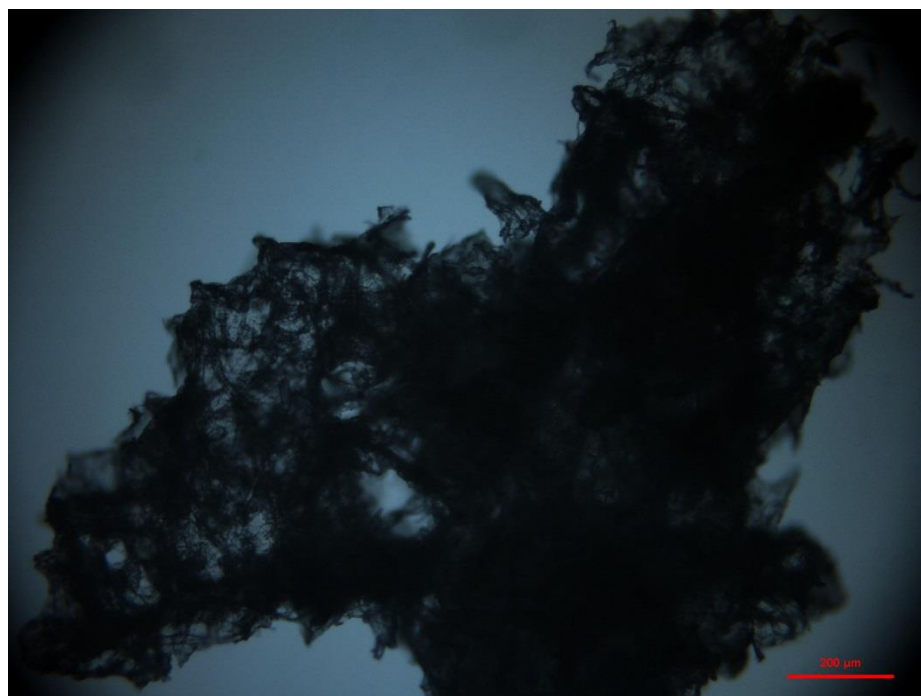
III.

Figure 2. I. Freeze dried SW sample; II. Thoroughly disintegrated SW sample; III.
Microscopic picture of hardwood fiber

Approximately 26 g of MFC solution was directly placed in the freeze dryer for 96 hours. It was then blended and disintegrated in a blender for 3 minutes and were placed in the oven for 1 hour at 75 °C before using for extrusion (Figure 3).



I.



II.



III.

Figure 3. I. Thoroughly disintegrated MFC sample, II Microscopic picture of MFC, III. DSM Xplore twin-screw extruder.

3.2.2 Extrusion

PP phase WPC. Six grams of PP pellets with the oven dried HW, SW and MFC (nominally at 4.7%, 9.1%, 13%, 16% and 33% by weight) were mixed by twin-screw extruder at 220 °C .To improve dispersion, the materials were circulated inside the extruder for five mins before extrusion It is also notable that PP was separated into two three gram batches and were added before and after the addition of natural fibers for reaching a better dispersion.

MAPP addition. Six grams of oven dried HW with MAPP (nominally at 3%, 5%, and 7% by weight of HW) and six grams PP pellets were mixed by twin-screw extruder at 220 °C. To improve dispersion, the materials were circulated inside the extruder for five minute before extrusion. The PP and MAPP were mixed and added first, followed by natural fibers for a better dispersion.

PP phase WPC at 200 °C. Six grams of PP pellets with the oven dried HW (nominally at 40%, 50%, 60% by weight) were mixed by twin-screw extruder at 200 °C. Five

percent by weight percent of MAPP were added to all the samples. To improve dispersion, the materials were circulated inside the extruder for five minute before extrusion. It is also notable that PP was separated into two 3 g batches and were added before and after the addition of natural fibers for reaching a better dispersion.

3.2.3 Dog-bone specimen preparation.

1.1 grams of all the extruded samples were input into the piston of a dog-bone mold instrument (DAKA, Raleigh, USA) at 200°C. The samples were placed in the piston for five minutes before injection.

3.3. Measurements

3.3.1 Thermal analysis.

The thermal degradation properties of the extruded **PP phase WPC** samples were determined with thermogravimetric analysis (TGA). For TGA, samples were heated from 20 to 500°C in a rate of 20°C/min.

3.3.2 Tensile properties

Five dog-bone shaped specimens (gauge length of 25 mm, width 4 mm and thickness 1.5 mm) were prepared from each extruded sample. The tensile tests were carried out with an Instron Universal Testing Machine at 23°C with a cross head speed of 2.5mm/min.

3.4 Results and discussion

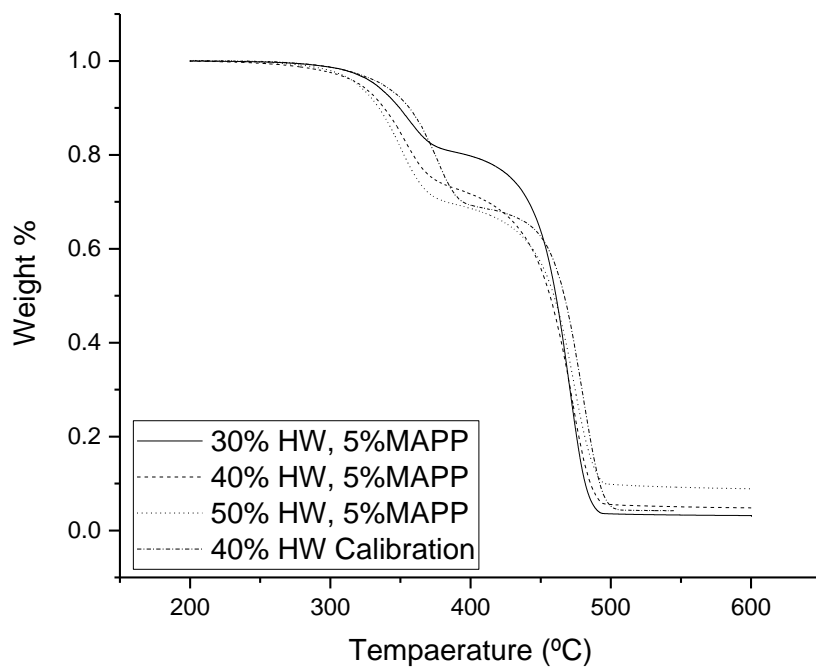
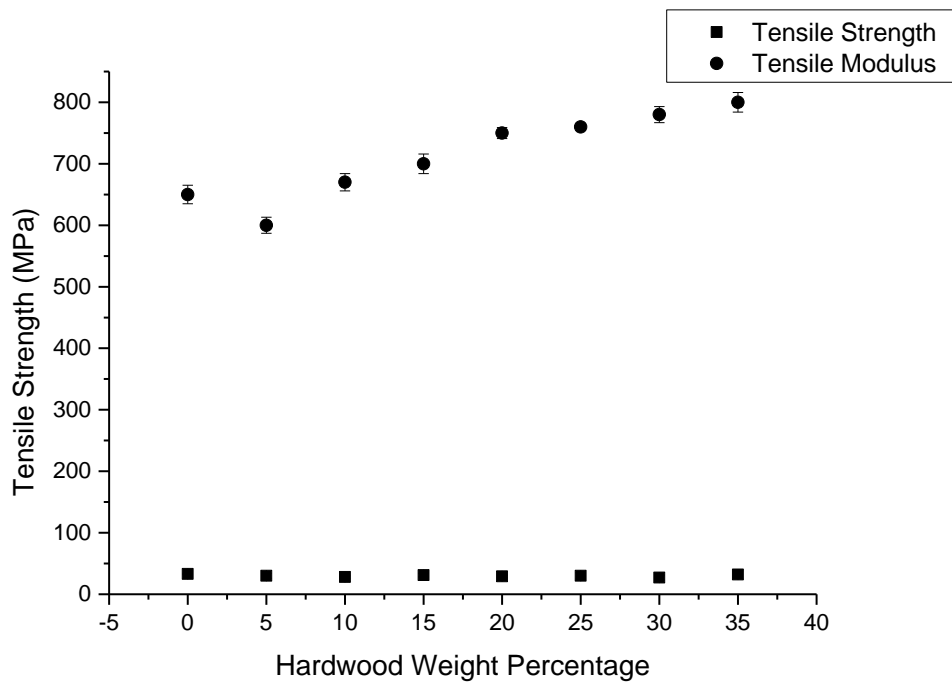
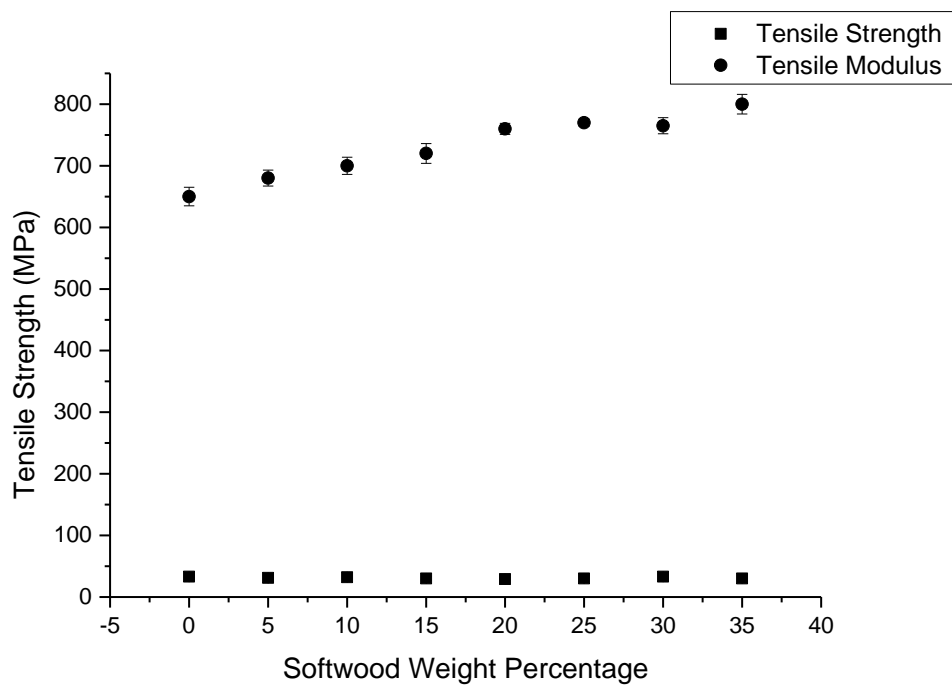


Figure 4. The TGA curves for PP phase WPC

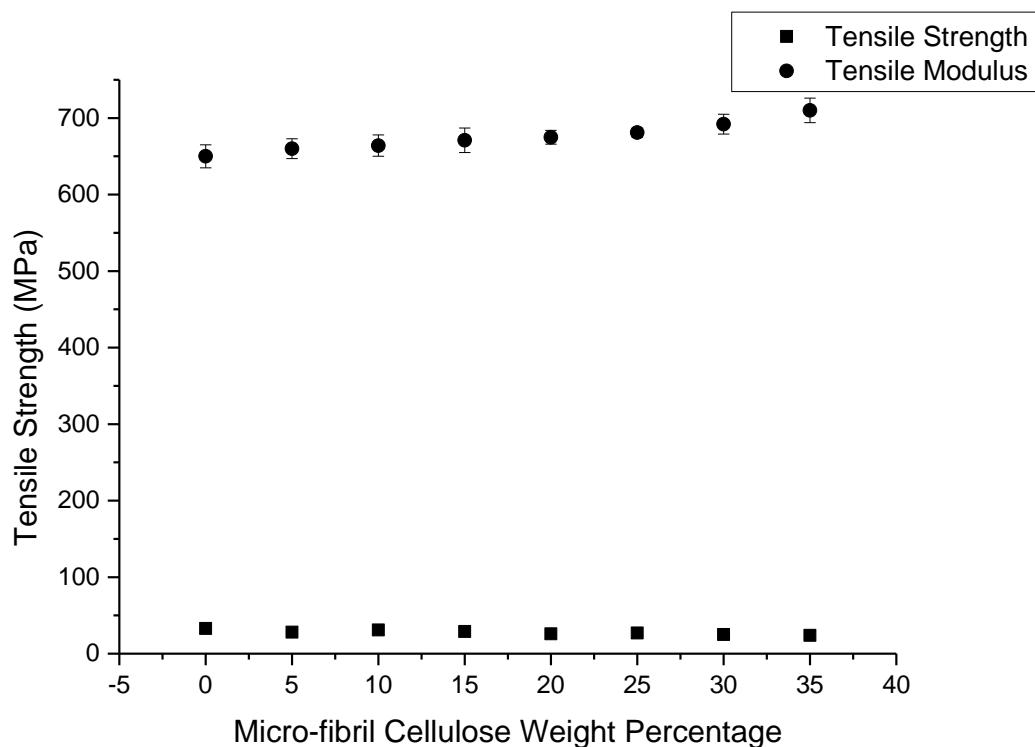
As shown in Figure 4, all the **PP phase WPC** samples exhibited the similar degradation trend. The a drop in weight at around 350°C which corresponded to the degradation natural fibers. As the weight percentage of the natural fibers increased, the amount of drop in weight increased accordingly. Due to the residue accumulated in the extruder chamber, the actual weight percentage of HW fiber in **PP phase WPC** is approximately 10% lower than the nominal value. (Figure 4.)



3a. Tensile properties for PP-HW.



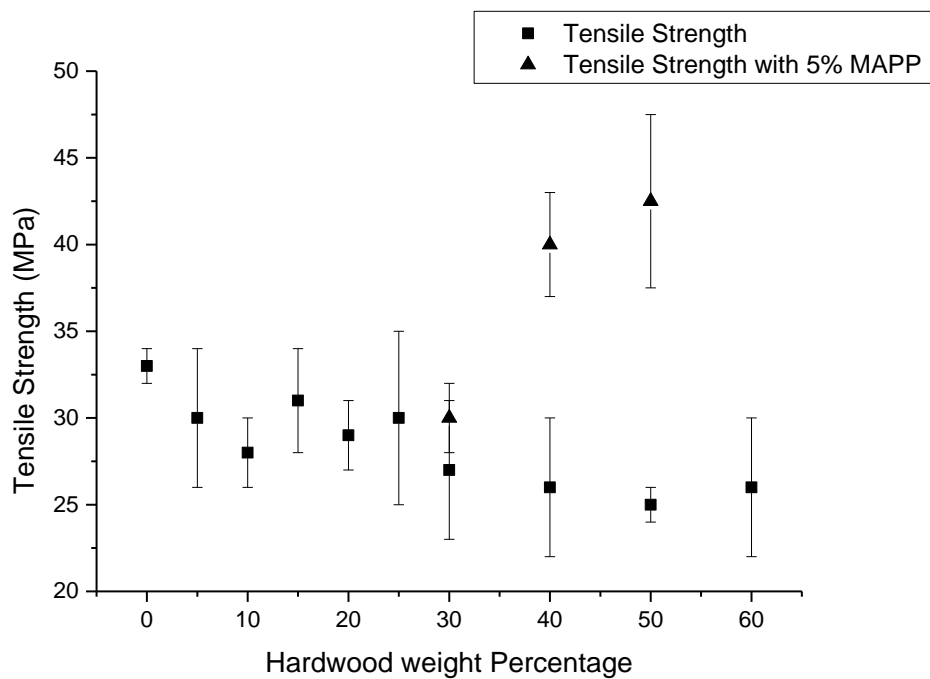
3b. Tensile properties for PP-SW.



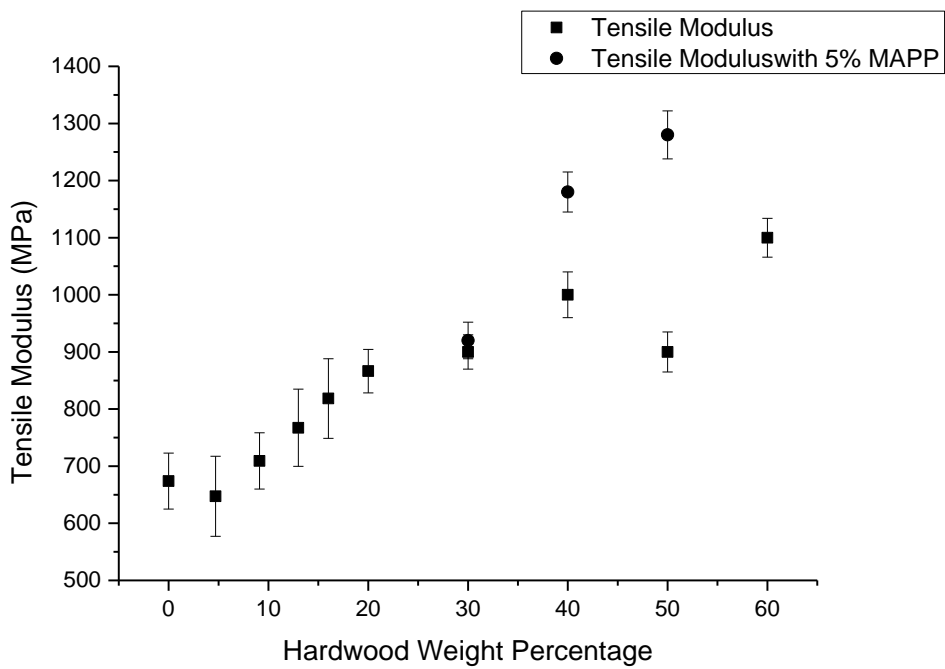
3c. Tensile properties for PP-MFC.

Figure 3. Tensile properties for PP based WPC.

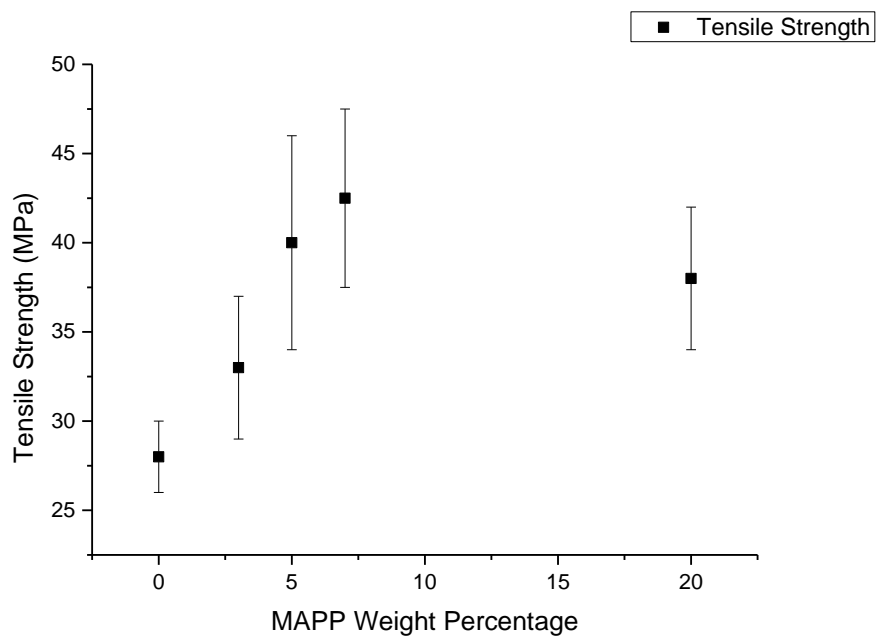
PP based WPC exhibited a good tensile strength and modulus which is attribute to physical properties of polypropylene. As similar, increased amount of natural fibers increased the modulus but had little effects on the tensile strength. As shown in Figure 3a, 3b and 3c, the tensile strength slightly decreased with the increase amount of natural content, whereas the modulus kept increasing which was probably due to the modulus contribution from natural content. Hardwood fiber provide most modulus support among these three candidates, where the modulus increased from 700 MPa to 900 MPa.



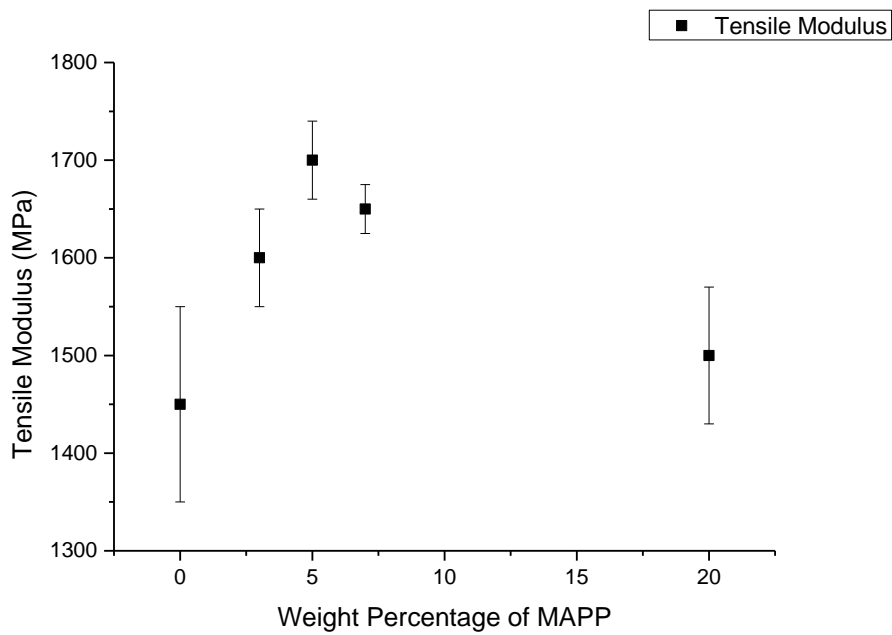
4a. Tensile strength properties for PP-HW with MAPP addition.



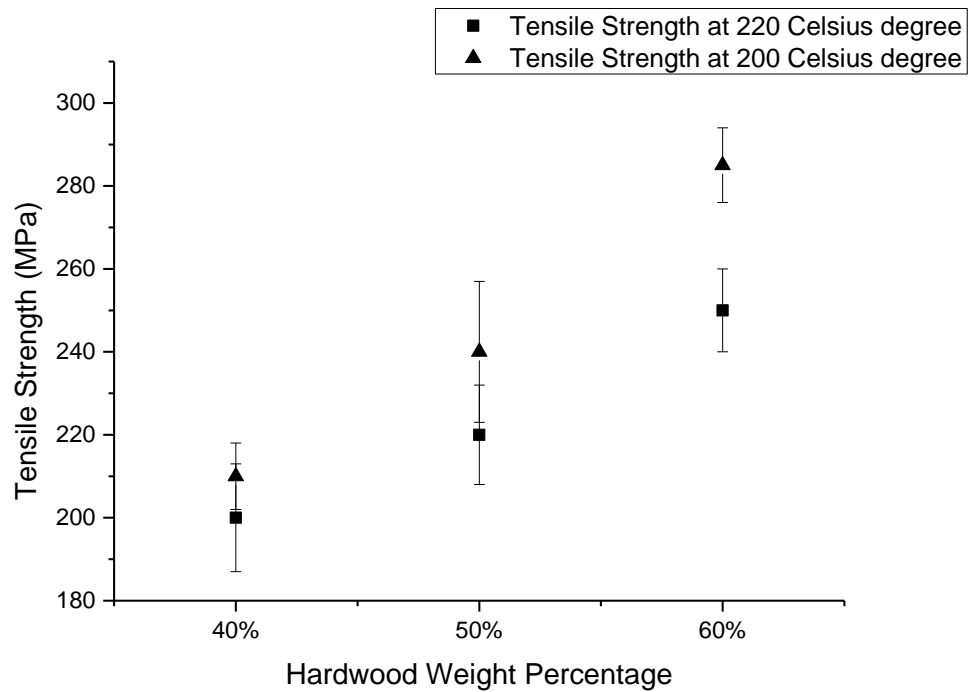
4b. Tensile modulus properties for PP-HW with addition of MAPP.



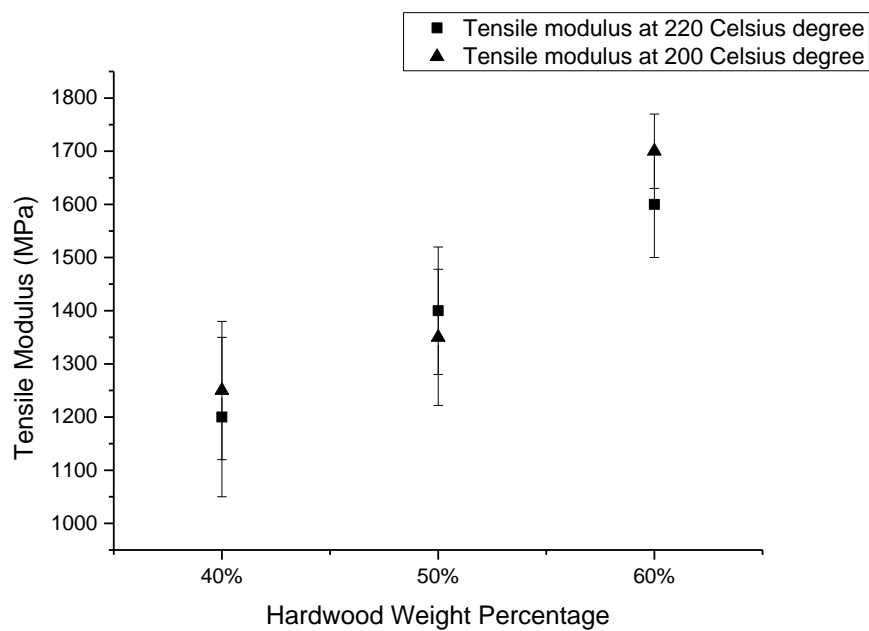
4c. Tensile strength properties for PP-HW with addition of MAPP.



4d. Tensile modulus properties for PP-HW with addition of MAPP.



4e. Tensile strength at different extruded temperature.



4f. Tensile modulus at different extruded temperature.

Figure 4. Tensile properties for PP based WPC with MAPP addition

As shown in Figure 4a and 4b, the addition of only hardwood fiber into the WPC decreased the tensile properties, which can be attributed to poor force transmission between two phases. With addition of MAPP, the tensile strength increased by approximately 25% and tensile modulus increased by approximately 30%. The MAPP maximized the tensile properties at five weight percent (4c and 4d). At this point, it can be confirmed that MAPP reached a saturated condition, and further addition would increase the heterogeneity and decrease the strength. As shown in Figure 4e, identical weight percent of HW were extruded at both 200 °C and 220 °C. At 200 °C, the tensile strength increased from 200 N to 250 N (40% HW) and 220 N to 290 N (60% HW). The tensile modulus stayed at nearly the same level after decreasing the extrude temperature. The improvement of tensile strength was probably due to the slower degradation of the cellulose at 200 °C. Such deceleration would protect more hydroxyl groups for bonding with MAPP. The homogeneity was therefore increased which resulted of the increase of tensile strength.

3.5 Conclusion

PP served as a good plastic matrix. Adding natural content without any compatibilizer decrease the homogeneity of the **PP based WPC**. No significant increased tensile strength were observed, this is probably due to the deflections in the system. It is also notable that MFC weakened the tensile strength of the system most which is probably due to the poor dispersion caused by the abundant amount internal hydrogen bonds in MFC. (Mohanty, 2005). Furthermore, 50 weight percent of HW with PP would provide the highest modulus.

Adding MAPP into **PP based WPC** increased the overall homogeneity and reinforced the overall mechanical strength. With addition of MAPP, the tensile strength increased by approximately 25% and tensile modulus increased by approximately 30%. The MAPP reached maximized the strength at 5 weight percent

Relatively lower extruding temperature would lead to decelerate of degradation of cellulose, which provided more hydroxyl groups to be bonding with the maleic anhydride

groups on MAPP. On the other hand, as the temperature decrease, the melting flow index (MFI) of PP also decrease. Lower MFI would prevent HW fiber penetrating into the PP matrix, which would result the defections in the system. The optimized temperature for **PP based WPC** required further study.

References

- Rowell, R. M., Lange, S. E. and Jacobson, R. E., 'Weathering Performance of PlantFiber/Thermoplastic Composites', *Molecular Crystals & Liquid Crystals* 353, 2000, 85.
- Salih,S. , Hammood A. and ABD alsalam A. Comparison of the Characteristics of LDPE : PP and HDPE : PP Polymer Blends. *Modern Applied Science* (2013) 1913-1852.

Chapter 4

WPC extrusion with polyethylene as the plastic matrix

4.1 Introduction

Based on the result acquired from Chapter 3, it can be confirmed that the plain mix of natural content and polypropylene (PP) does not provide any tensile strength enhancement to the WPC. The absence of bonding between the natural phase and plastic phase caused the poor force transmission in the system. (Rowell, et. al 2000) Furthermore, maleic anhydride (MAH) is effective in increasing the overall bonding characteristic in the WPC.. In addition, the results showed that hardwood fiber (HW) acted as the most suitable natural phase among the three candidates (HW, SW, and MFC), because HW contributed most modulus in WPC.

In this chapter, low density polyethylene (LDPE) and HW were blended with and without polyethylene grafted maleic anhydride (MAPE). Compared to PP, LDPE has relatively a low mechanical properties. On the other hand, LDPE has a lower melting point which make the extrusion possible at a lower temperature. In Chapter 3, extrusion at a lower temperature with PP showed improved tensile strength. This may be attributed to the partial degradation of the wood fibers during extrusion at higher temperatures. . The detailed method and experimental design are described in the following sections.

4.2 Experimental Methods and Materials

4.2.1 Materials

Polymeric Matrix

LDPE was received from purchased from Sigma Aldrich (Cas No. 9002-88-4) as pellets. Its melting temperature is 115 °C.

Wood Fibers

Hardwood (HW) was purchased from U.S. National Institute of Standards and Technology. The natural content were pretreated identically as described in Chapter 3.

4.2.2 Extrusion

LDPE based WPC. Six grams of LDPE pellets with the oven dried HW, SW and MFC (nominal additions at 4.7%, 9.1%, 13%, 16% and 33% by weight) were mixed by DSM Xplore twin-screw extruder (Xplore, Netherlands) (Figure 3b) at 130 °C. To improve dispersion, the materials were circulated inside the extruder for five minutes before extrusion. It is also notable that LDPE was separated into two three gram batches and were added before and after the addition of natural fibers for reaching a better dispersion.

MAPE addition. Four grams of LDPE pellets with HW (nominal additions at 0%, 4.7%, 9.1%, 13%, 16% and 25% by weight) and MAPE 5 % by weight were mixed by twin-screw extruder at 130°C. Two grams of starch was then added to all the samples. To improve dispersion, the materials were circulated inside the extruder for five minutes before extrusion.

4.2.3 Dog-bone specimen preparation.

One gram of all the extruded samples were input into the piston of a dog-bone mold instrument DaKa (Raleigh, NC, USA) at 200°C. The samples were placed in the piston for five minutes before injection.

4.3. Measurement

4.3.1 Thermal analysis.

The thermal properties of the extruded **LDPE phase WPC** samples were determined with a thermogravimetric analysis (TGA) and a Pekin-Elmer Pyris-1 (Raleigh, NC, USA) differential scanning calorimeter (DSC). For TGA, samples were heated from 20 °C to 500 °C in a rate of 20 °C/min. For DSC, samples were heated from 40 °C to 200 °C, cooled at 40°C, and then reheated to 200 °C at a rate of 10 °C/min. The peak temperature of the second heating curves was termed the melting temperature (T_m).

4.3.2 Tensile properties

Five dog-bone shaped specimens (gauge length of 25 mm, width 4 mm and thickness 1.5 mm) were prepared from each extruded sample. The tensile tests were carried out with an Instron Universal Testing Machine at 23 °C with a cross head speed of 2.5 mm/min.

4.4 Results and discussion

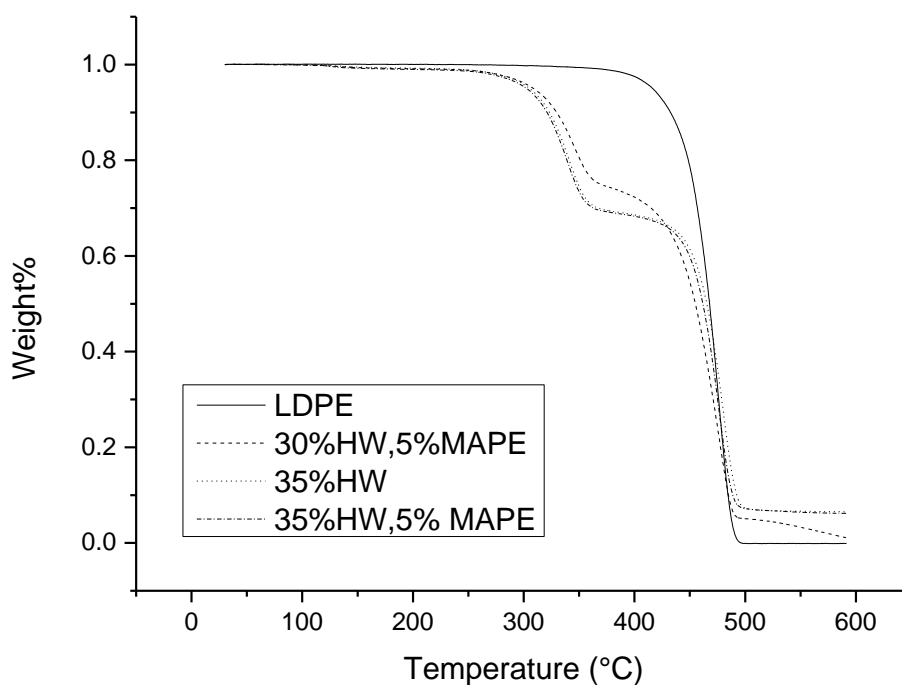
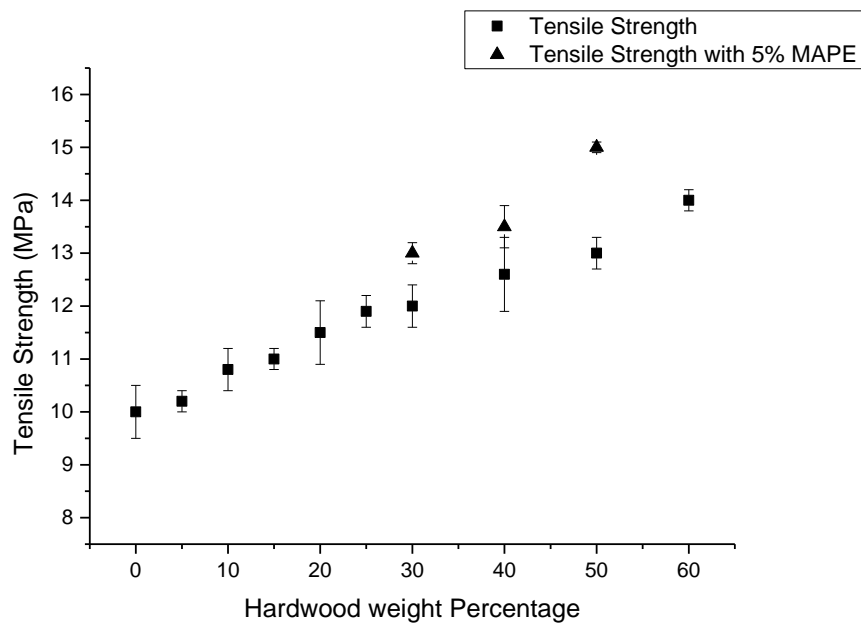
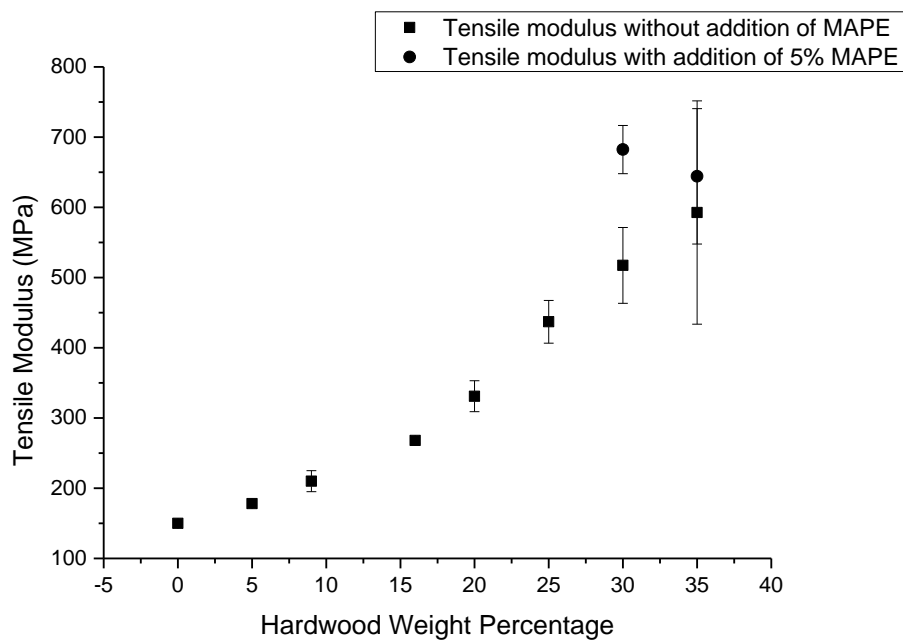


Figure 1. The TGA curves for LDPE phase WPC

As shown in Figure 1, all the **LDPE phase WPC** samples exhibited the similar degradation trend. The drop in the mass at around 350°C were corresponded to the degradation natural fibers. As the weight percentage of the natural fibers increased, the magnitude of the drop increased.



2a. Tensile strength for LDPE based WPC.



2b. Tensile modulus for LDPE based WPC.

Figure 2. Tensile properties for LDPE based WPC.

As shown in Figure 2, increased amount of HW fibers increased the tensile modulus. On the other hand, adding more than 20 weight percent HW increased the tensile modulus significantly. By adding 35 weight percent of HW, the tensile strength increased from 0.075 kN to 0.11 kN; the tensile modulus increased from 150 MPa to 750 MPa. MAPE further increased the mechanical properties. For 35 weight percent of WPC, adding 5% of MAPE increased the tensile strength by 10% and tensile modulus by 8%.

As mentioned in last chapter, adding only HW to PP decreased the tensile strength from 200 N to approximately 165 N. Compared to **PP based WPC**, the strength of **LDPE based WPC** increased with addition of HW (without MAPE) from 75 N to 100N. This is probably due to the lower extrusion temperature slow down the degradation of HW fiber whereas the fibers contributed more strength into the system. As shown in Figure 3, the LDPE based WPC is a much lighter color than PP based WPC which indicated the slower degradation of HW in LDPE.



Figure 3. (Left to right): 30 weight percent HW LDPE based WPC, 30 weight percent HW PP based WPC and 50 weight percent HW PP based WPC.

4.5 Conclusion

For **LDPE based WPC**, the tensile strength increased with the addition of only hardwood fiber which is opposite to **PP based WPC**. Blending hardwood fiber (more than 20 weight percent) into LDPE with or without MAPE, increased both tensile strength and

tensile modulus. Such difference is probably due to the lower processing temperature for **LDPE based WPC** (135 °C) . Hardwood fiber degraded slower at lower temperature and contributed more strength into the system. Adding 5 weight percent MAPE further improved the mechanical properties by approximately 10%.

References

Mohanty A, Misra M, Drzal LT, editors. Natural fibers, biopolymers and biocomposites. Boca Raton, FL: CRC Press, Taylor and Francis Group; 2005.

Kahar, A.W.M., H. Ismail, and N. Othman. "Effects of Polyethylene-Grafted Maleic Anhydride as a Compatibilizer on the Morphology and Tensile Properties of (Thermoplastic Tapioca Starch)/ (High-Density Polyethylene)/(Natural Rubber) Blends." JOURNAL OF VINYL & ADDITIVE TECHNOLOGY 10(2012): 65-70.

Chapter 5

Wood fiber, Low Density Polyethylene, Starch Composite Extrusion.

5.1 Introduction

In Chapter 3 and 4, polypropylene and polyethylene grafted maleic anhydride was shown to increase the strength and uniformity for both PP and LDPE matrix. This is also shown by previous author (Bledzki, 2004). However, such enhancement is limited. There are few effective compatibilizer other than maleic anhydride. The natural fiber weight percentage is also limited at about 50 weight percent. When adding more than 50 weight percent natural fiber, the fiber agglomerate forming defects and reducing tensile properties. In order to further increase the strength of WPC, it is necessary to find another component that has the capability to bond fiber and matrix tighter.

Nanoclay (appendix) and plasticized starch (PSA) were chosen as the candidates. In this chapter, plasticized corn starch was used as an additional component and low density polyethylene (LDPE) was used as plastic matrix. The point of choosing SA was attempting to mimic the formation of tree. Trees were mainly composed by cellulose, hemicellulose, lignin and extractives. Conceptually, the plastic matrix acts as the lignin, plasticized starch as hemicellulose and the hardwood fiber as cellulosic component. The advantage of this composition is that a higher fraction of renewable raw material can be used, while maintain the manufacturing characteristic of traditional WPC. In this chapter, we attempt to create a higher renewable content WPC with improved mechanical properties. These materials were examined by SEM, thermal properties and mechanical properties.

5.2 Experimental Methods and Materials

5.2.1 Materials

Low density polyethylene was purchased from purchased from Sigma Aldrich as pellets (Cas No. 9002-88-4). Its melting temperature is 115 °C. The natural content were pretreated identically as described in Chapter 2. Glycerol was purchased from Sigma Aldrich (Cas No.

56-81-5). Hardwood (HW) was purchased from U.S. National Institute of Standards and Technology. The natural content were pretreated identically as described in Chapter 3.

5.2.2 Mix of glycerol and starch (PSA)

Sixty gram of starch and 40 gram of glycerol were first mixed in a beaker using a glass rod for 10 mins. The mixture was then placed in a vacuum dryer for 24 hrs before using.

5.2.2 Extrusion

Starch as a constant. Four grams of LDPE pellets with Hardwood (nominally at 0%, 4.7%, 9.1%, 13%, 16% and 25% by weight) were mixed by twin-screw extruder at 130°C. Two grams of plasticized starch (PSA) was then added to all the samples. To improve dispersion, the materials were circulated inside the extruder for five minutes before extrusion

HW as a constant. Four grams of LDPE pellets with 25 weight percent HW and MAPE five weight percent were mixed by twin-screw extruder at 130°C. PSA mixture was added at 0%, 5%, 10%, 15%, 20% and 27% by weight(nominally). To improve dispersion, the materials were circulated inside the extruder for five minutes before extrusion

5.2.3 Dog-bone specimen preparation.

1.1 grams of all the extruded samples were input into the piston of a dog-bone mold instrument (DAKA, Raleigh, USA) at 150°C. The samples were placed in the piston for five minutes before injection.

5.3. Measurement

5.3.1 Thermal analysis.

The thermal properties of the extruded **LDPE phase WPC** samples were determined with a thermogravimetric analysis (TGA) and a Pekin-Elmer Pyris-1 (Raleigh, NC, USA)

differential scanning calorimeter (DSC). For TGA, samples were heated from 20°C to 600°C in a rate of 20°C/min. For DSC, samples were heated from 40°C to 250°C, cooled to 40°C, and then reheated to 250°C at a rate of 10°C/min. The peak temperature of the second heating curves was termed the melting temperature (T_m).

5.3.2 Scanning electron microscopy (SEM) morphological characterization

A composite sample was dropped directly into liquid nitrogen and fractured with a pre-chilled razor blade held in a vice-grip. The fractured pieces were picked out of the liquid nitrogen using a pre-chilled forceps and placed in a desiccator to thaw to reduce the condensation of water on the surface of the material. All composite materials, fractured by the Instron Testing Machine and in liquid nitrogen, were mounted with the fractured surfaces facing up. All specimens were coated with Gold–Palladium for 45 s in a Denton Desk II sputter coating unit (Denton Vacuum USA, Raleigh, NC). Specimens were viewed in a FEI Verios 460L field emission scanning electron microscope (Raleigh, NC, USA) at 2 kV.

5.3.3 Tensile properties

Five dog-bone shaped specimens (gauge length of 25 mm, width 4 mm and thickness 1.5 mm) were prepared from each extruded sample. The tensile tests were carried out with an Instron Universal Testing Machine at 23°C with a cross head speed of 2.5mm/min.

5.3.4 Water uptake procedure

Three specimen of each sample were oven dried for 24 hours and weight. The specimen were then placed in deionized water. The samples were removed at desired intervals and weighed until the equilibrium state was reached. The water uptake of the samples was calculated as follows:

Water absorption (%)

$$= \frac{\text{weight after immersion} - \text{oven dry weight}}{\text{oven dry weight}} \times 100\%$$

5.4 Results and discussion

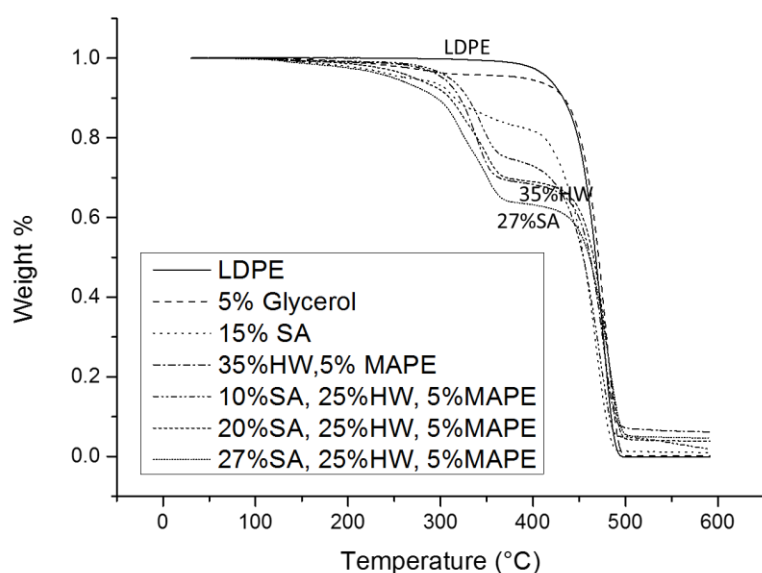


Figure 1. The TGA curves for LDPE –PSA based WPC

As shown in Figure 1, all the **LDPE-PSA based WPC** samples exhibited the similar degradation trend. The drops in mass at around 300°C were corresponded to the degradation natural fibers and starch. The degradation of glycerol started at about 100°C. As the weight percentage of the natural content increased, the natural drop in weight increased similarly. The actual total weight percentage of natural content is approximately 10% less than the nominal value. This is due to the residue left in the extruder from every last trial. It is notable that the degradation of glycerol result a grey color of WPC. As shown in Figure 2, as the SA weight percent increased, the WPC specimen were darker.

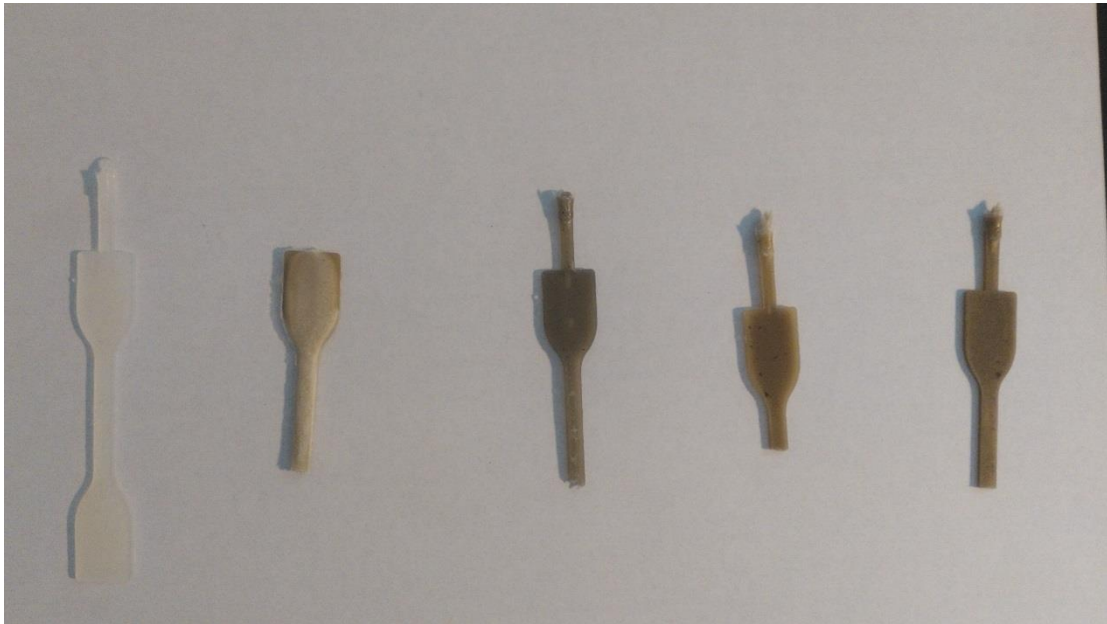


Figure 2. LDPE-PSA based WPC samples. (Left to Right): LDPE; 15% SA, 25% HW; 20% SA, 25%HW; 27% SA, 25% HW; 5% Glycerol.

As shown in Figure 3, all the **LDPE phase WPC** samples exhibited the similar melting characteristics. Peak separation took place at around 115°C which is due to the melting of LDPE. Neither hardwood fiber nor plasticized starch has any significant effects on the melting process of LDPE.

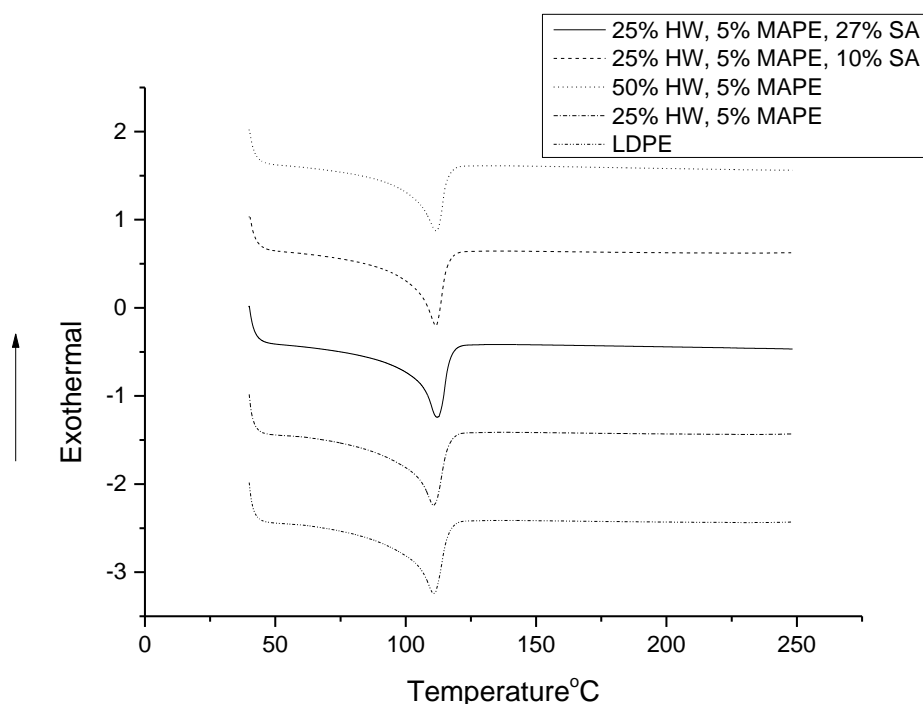
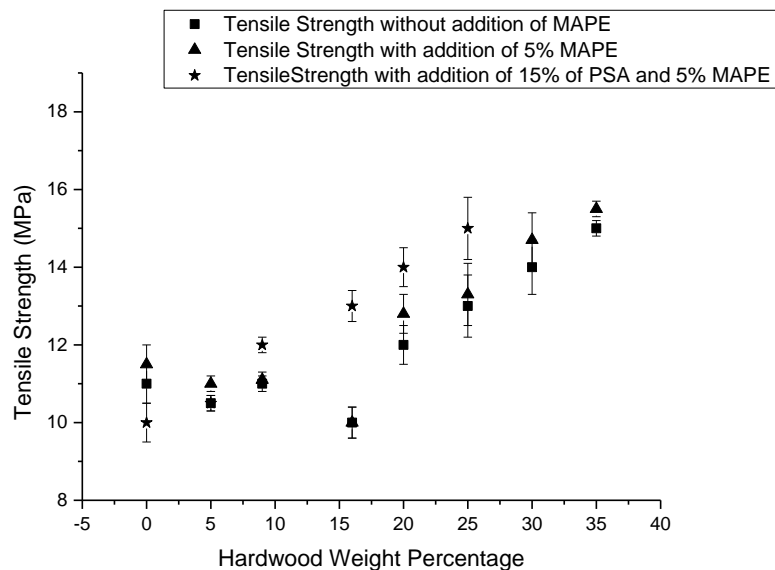


Figure 3. The DSC curves for LDPE-PSA based WPC.

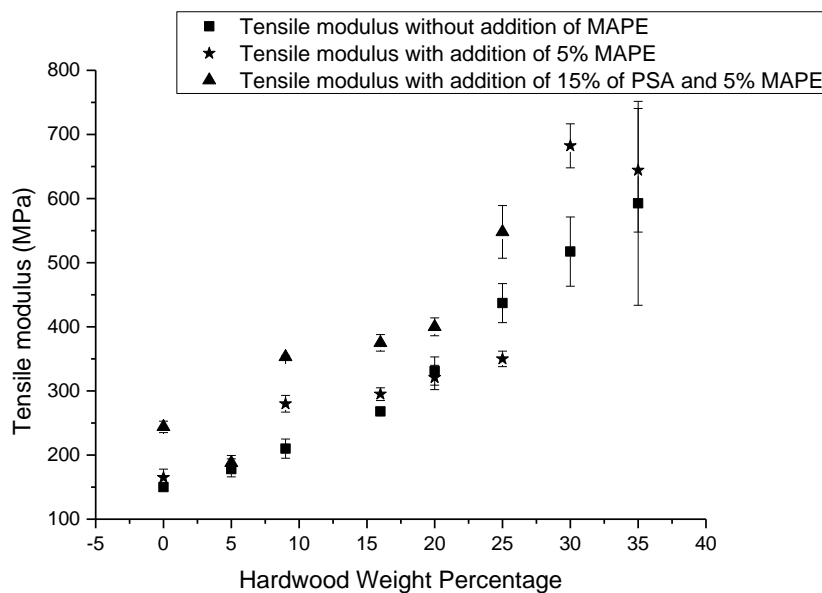
As shown in Figure 4a, the addition of starch into the LDPE/HW first decreased at tensile strength at low HW weight percent. As the HW weight percent increased, the addition of starch increased strength significantly. However, as shown in Figure 4a, adding only starch has negative effect on the strength of WPC. With the addition of 15 weight percent starch, the strength decreased from 0.075 kN to 0.062 kN. The tensile modulus increased approximately 50% (200 MPa) with the addition of 15 weight percent starch (Figure 4b). With the addition of starch, the heterogeneity of WPC decreased which resulted of the decrease of tensile property. However, starch probably improved the restriction of mobility of polymer chains and intercalation between fibers and matrix which ultimately increased the mechanical properties.

As shown in Figure 4c, with the addition of more starch, the tensile strength increased from 0.91kN to 1.65kN. The modulus started to decrease after adding more than 20 weight percent starch. This is probably because that starch was unable to contribute in modulus as

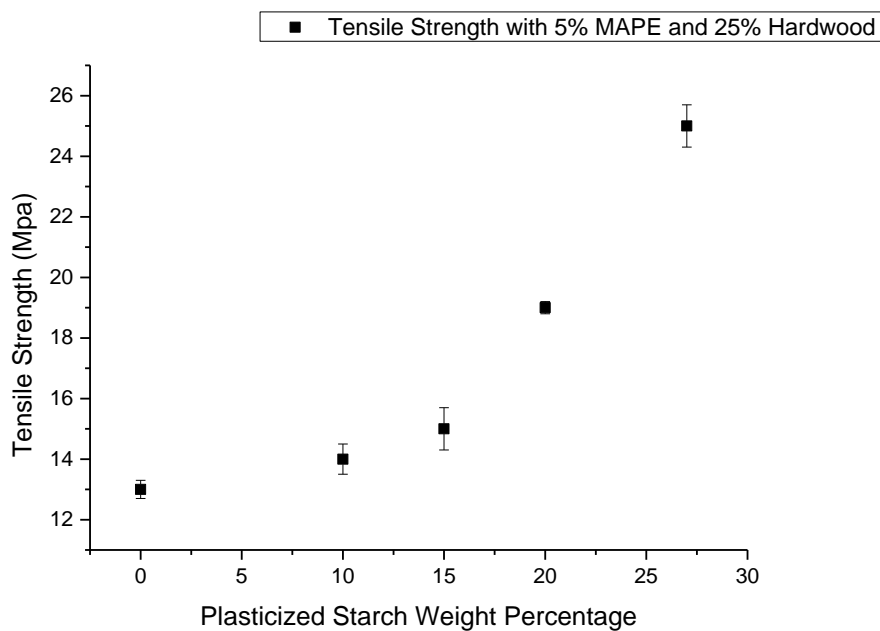
the hardwood fiber did, whereas adding more starch increase the heterogeneity of the overall system. This also explained the large standard deviation of tensile modulus at 20% and 27% of starch. (Figure 4d).



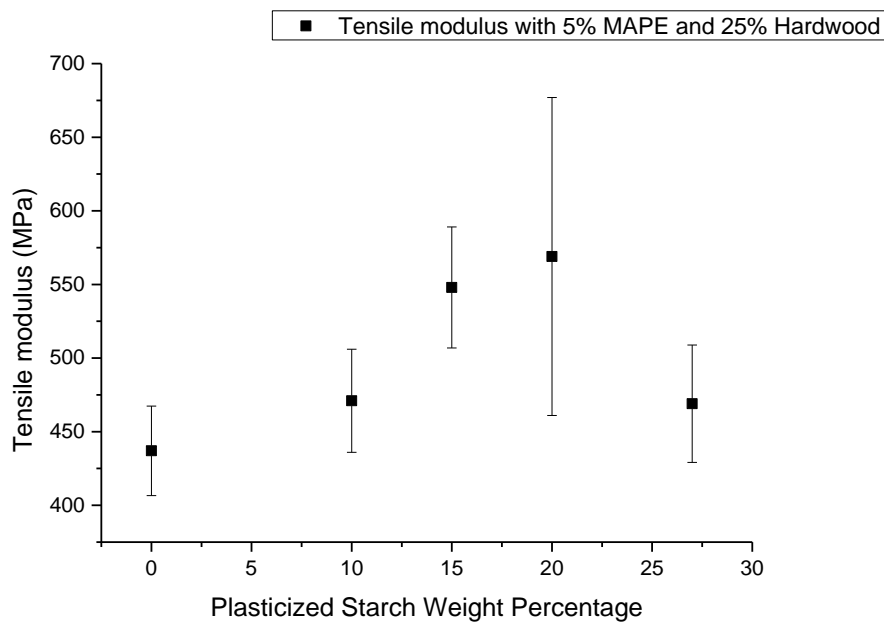
4a. Tensile Strength for LDPE-HW-SA.



4b. Tensile Modulus for LDPE-HW-SA.



4c. Tensile Strength for LDPE-HW-SA (constant 25 weight percent HW)



4d. Tensile Modulus for LDPE-HW-PSA (constant 25 weight percent HW) Figure 4. Tensile properties for LDPE-PSA based WPC.

As shown in Figure 5b, adding only plasticized starch (PSA) into LDPE would only agglomeration into the system which ultimately decreased the tensile strength. The weight percentage of PSA increased from Figure 5d to 5c, whereas the hardwood weight percent was fix at 25%. As shown in Figure 5d, the hardwood fiber and starch distribute evenly in the matrix. With the addition of PSA increasing (5e and 5f), the agglomeration of PSA increased. A bonding characteristic between two hardwood fibers was observed in Figure 5f. Such bonding was possibly caused by the addition of starch, which ultimately resulted in an increase of tensile properties.

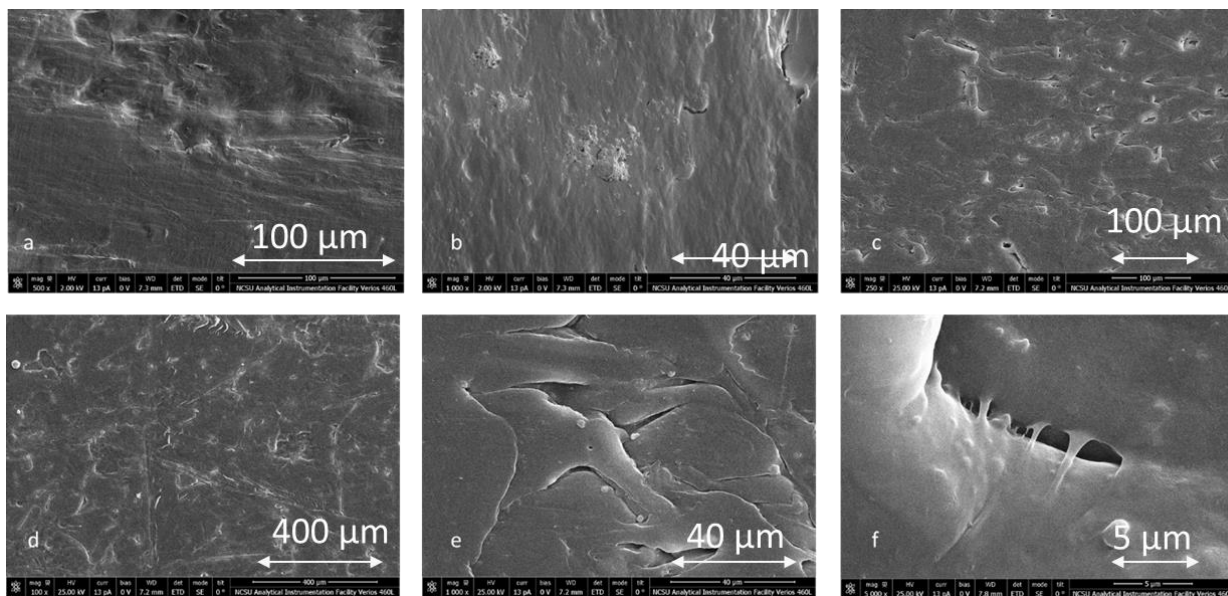


Figure 5. SEM image LDPE-PSA based WPC (a: LDPE; b: 20% PSA; c: 25% HW; d: 10% PSA and 25% HW; e: 20% PSA and 25% HW; f 27% SA and 25% HW). All sample contains 5% MAPE.

As shown in Figure 6, the water uptake increased as the time elapsed. Increasing hardwood percentage had little effect on the water uptake percentage, whereas adding more starch increased the water uptake significantly. This is probably due to the water soluble property from both amylose and amylopectin. In order to increase the water repellent property of **HW-PSA-LDPE WPC**, additional coating is needed. Further study is required to optimize the properties.

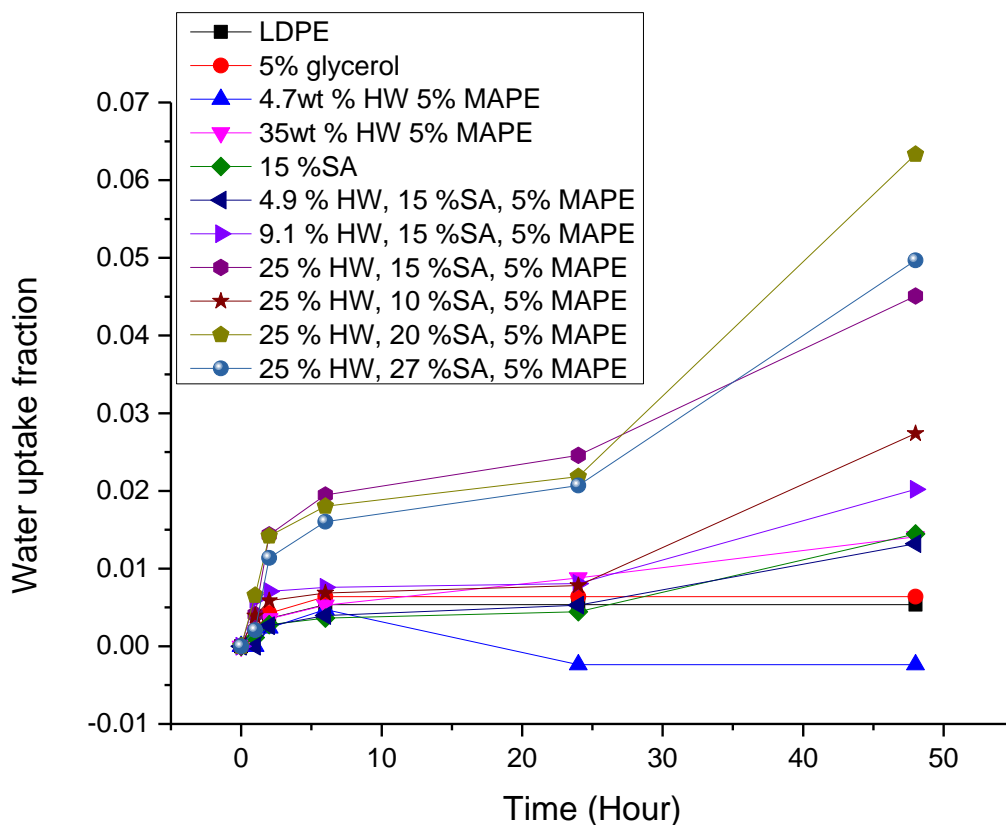


Figure 6. The water uptake percentage of WPC samples

5.5 Conclusion

Three components WPC including starch, hardwood fiber and low density polyethylene was successfully extruded. Adding solely plasticized starch (PSA) to LDPE had negative effect to the tensile strength. Adding solely HW improved the tensile strength, but the improvement is limited. Adding both HW and PSA WPC broke the limitation and further increased the tensile strength by approximately 40%. Furthermore, modulus increased with the addition of starch up to 20 weight percent. Bonding characteristics between two fibers were observed at 27 weight percent PSA sample which is possibly caused by PSA. Adding more starch beyond 20 weight percent resulted in an increase of agglomeration and decreased the modulus.

Chapter 6

Conclusion

The project was finished with the successfully extrusion of three types of wood plastic composite (WPC) ----Polypropylene (PP) based, low density polyethylene (LDPE) based and low density polyethylene – starch (LDPE-PSA) based WPC. Five weight percent of maleic anhydride significantly improved the mechanical properties of all WPC samples. Three types of WPC had their own advantages and disadvantages.

PP based WPC possessed the high durability. With the addition of 40 weight percent of hardwood fiber and five weight percent of polypropylene grafted maleic anhydride (MAPP)), the strongest WPC was made. It has the highest melting point 170 °C, highest tensile strength 0.285kN and highest tensile modulus 1850 MPa. On the other hand, the unavoidable degradation of natural materials at high temperature limited the possible of further development of **PP based WPC**.

LDPE based WPC had a relatively lower mechanical properties. They were more flexible, easier to degrade and had the potential for further development.

LDPE-PSA based WPC is the upgraded version of **LDPE based WPC**. With the addition of PSA, the natural content percentage increased. The WPC therefore is more bio-friendly and renewable for the future. Starch (25 weight percent) also increased the strength of **LDPE based WPC** by 40%. Furthermore, modulus increased with the addition of starch up to 20 weight percent. Adding more starch beyond 20 weight percent resulted a decrease of homogeneity and decreased the modulus. Further study is needed for understanding the mechanism behind such improvement of mechanical property. The maximized tensile strength and modulus for all based WPC were summarized in Table 1.

Table 1. The maximized tensile strength and modulus for all the natural candidates and plastic matrix

	Tensile Strength (MPa) for HW addition	Tensile Strength (MPa) for SW addition	Tensile Strength (MPa) for MFC addition	Tensile Modulus (MPa) for HW addition	Tensile Modulus (MPa) for SW addition	Tensile Modulus (MPa) for MFC addition
Polyethylene	12.14			685.21		
Polyethylene with 5% MAPE	14.15			599.43		
Polypropylene	33.32	28.14	31.21	788.34	754.21	677.31
Polypropylene with 5% MAPP	51.2				1885.41	
Polyethylene with 5% MAPE and 25% Plasticized starch	25.21			564.12		

Appendices

Appendix A- extrude PP based WPC with nanoclay.

Introduction

As was mentioned earlier in literature review, the nanoclay may increase the overall tortuosity of the system and packed the fibers and plastic matrix together. The permeability of the composite may decrease with addition of clay and act as barriers to enhance the strength of the system. There are various nanoclays that are commercially available on the market. The one that has been most commonly used is **cloisite Na⁺** (Tjong, 2006). In comparison with original cloisite, the addition of sodium ions improves its swelling such that it can be easily inserted into organic cations. (Tjong,2006)

As described in many others work, we attempt to repeat the addition of nanoclay into our **PP based WPC**. The result was however contradictory to the literatures result. The experimental details were described in the following.

Experimental

Materials

Polymeric Matrix

Polypropylene was received from ENTC Polymers as pellets. Its melting temperature is 170 °C. HW and SW was purchased from U.S. National Institute of Standards and Technology.

Wood Fibers

HW and SW was purchased from U.S. National Institute of Standards and Technology. MFC was received from Main University. The natural content were pretreated identically as described in chapter 3.

Extrusion

PP phase WPC with Nanoclay. Six grams of pp pellets with the oven dried HW, SW and MFC (40%, 50%, 60% by weight) respectively, were mixed by twin-screw extruder at 200 °C . Five percent by weight percent of MAPP and nanoclay **Chloiste Na⁺** were added to all the samples. To improve dispersion, the materials were circulated inside the extruder

for 5 mins before extrusion It is also notable that PP was separated into two 3 g batches and were added before and after the addition of natural fibers for reaching a better dispersion.

Dog-bone specimen preparation.

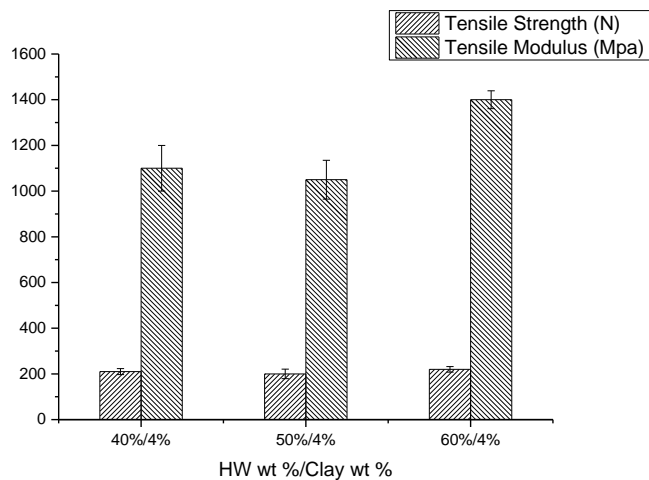
1.1 grams of all the extruded samples were input into the piston of a dog-bone mold instrument (DAKA) at 200°C. The samples were placed in the piston for 5 min before injection.

Measurement

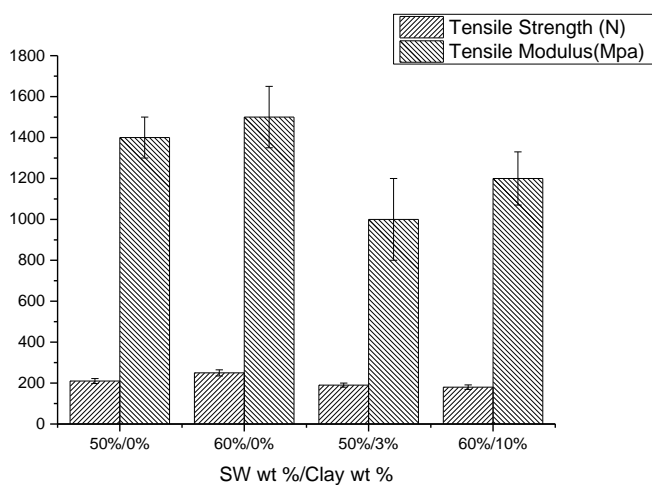
Tensile properties

Five dog-bone shaped specimens (gauge length of 25 mm, width 4 mm and thickness 1.5 mm) were prepared from each extruded sample. The tensile tests were carried out with an Instron Universal Testing Machine at 23°C with a cross head speed of 2.5mm/min.

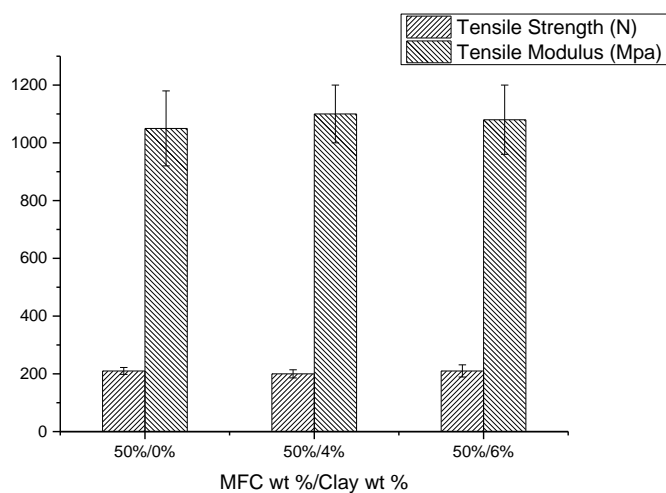
Result and discussion



a.



b.



c.

Figure 1. Mechanical properties of PP based WPC with Nanoclay. a, tensile properties with HW addition; b, tensile properties with SW addition; c, tensile properties with MFC addition.

As shown in Figure 1, adding clay into the system does not result of any significant improvements for all natural content candidates. The granules came out of extruder became thinner with clay. The MFI increased and significant increase of flow property was observed.

Conclusion

The addition of nanoclay does not increased the tensile properties as described in the literatures. More study is need in future. Adding nanoclay increased the melting flow index which probably would save significant amount of energy consumption in industry scaled extrusion.

Appendix B- extrude PP based WPC with starch.

Introduction

As was mentioned earlier in literature review, the starch was used also as a natural content candidate. The goal of extruding starch based WPC is to create a bio-degradable composite. Before extruding starch with LDPE, starch was first attempted to extrude with PP. Since the melting point of PP is too high (170 °C), the starch was degraded completely in the extrusion. Detailed experimental designs were described in the following

Experimental

Materials

Polymeric Matrix

Polypropylene was received from ENTC Polymers as pellets. Its melting temperature is 170 °C. Starch was placed in the oven at 100 °C for 24 hours before using. The oven-dried starch was then mix the glycerol in a ratio 6:4.

Extrusion

PP phase WPC with Nanoclay. Six grams of pp pellets with the oven dried starch (40%, 50%, 60% by weight) respectively, were mixed by twin-screw extruder at 200 °C . Five percent by weight percent of MAPP was added to all the samples. To improve dispersion, the materials were circulated inside the extruder for 5 mins before extrusion It is also notable that PP was separated into two 3 g batches and were added before and after the addition of natural fibers for reaching a better dispersion.

Result and discussion

The starch was completely burned in the extrusion and failed to produce any products. Smelly adhesive gel was formed at the end. In order to extrude starch, the temperature must be lowered to at most 140 cent degree.

Appendix C- extrude WPC with Nomaco provided LDPE pellets.

Experimental

Materials

Polymeric Matrix

LDPE was received from purchased from Nomaco as pellets. Its melting temperature is 110 °C.

Wood Fibers

Hardwood (HW) and softwood (SW) was purchased from U.S. National Institute of Standards and Technology. MFC was received from MeadWestvaco Corp. (Richmond, Virginia, USA). Approximately 26 g of HW and SW raw materials were placed in a disintegrator separately with 2 L of deionized water. (Figure 1a).

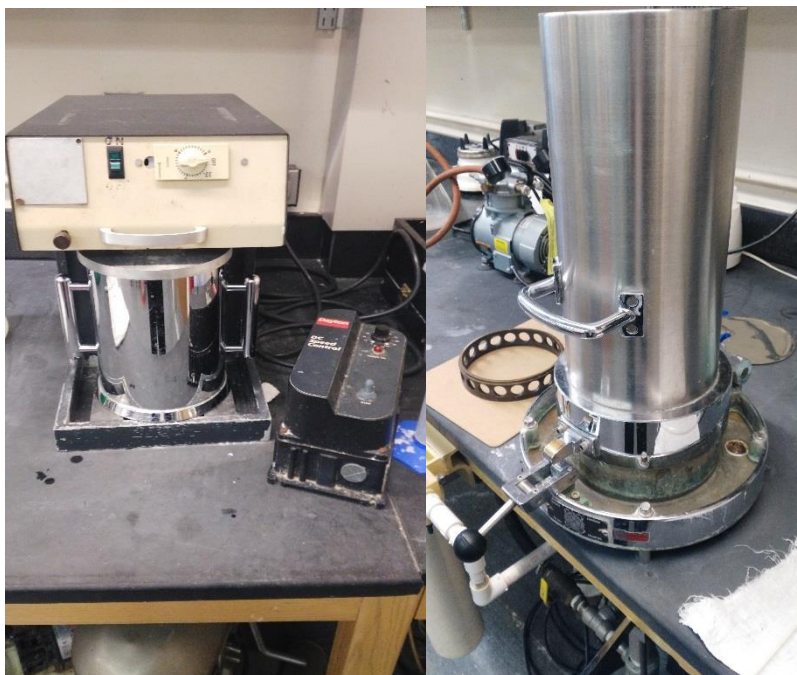
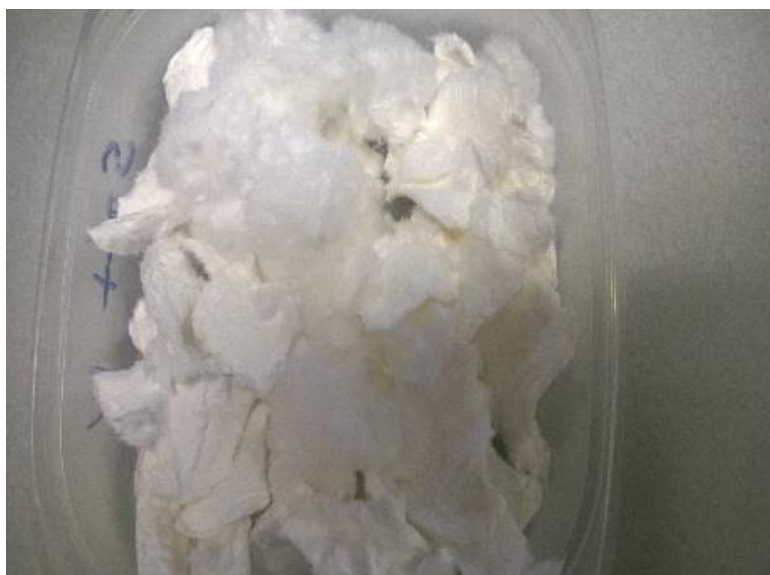


Figure 1. a. Pulp disintegrator. b. Handsheet maker

The mixtures were disintegrated for 3 minutes. The water in the mixtures were then removed through a handsheet maker (Figure 1b). The substrates were placed in a freeze dryer for 72 hours for further drying (Figure 2a) and were further blended and disintegrated in a lab scale blender for 3 minutes (Figure 2b). The thoroughly disintegrated HW and SW were placed in the oven for 1 hour at 75 °C before using for extrusion.



a.



b.

Figure 2. a. Freeze dried SW sample; b. Thoroughly disintegrated SW sample.

Approximately 26 g of MFC solution was directly placed in the freeze dryer for 96 hours. It was then blended and disintegrated in a lab scale blender for 3 minutes and were placed in the oven for 1 hour at 75 °C before using for extrusion (Figure 3).



a.



b.

Figure 3. a. Thoroughly disintegrated MFC sample, b. DSM Xplore twin-screw extruder.

Extrusion

LDPE phase WPC. Six grams of LDPE pellets with the oven dried HW, SW and MFC (4.7%, 9.1%, 13%, 16% and 33% by weight) were mixed by DSM Xplore twin-screw extruder (Xplore, Netherlands) (Figure 3b) at 200 °C and under an force of 1.5KN/mm². To improve dispersion, the materials were circulated inside the extruder for 5 mins before extrusion. It is also notable that LDPE was separated into two 3 g batches and were added before and after the addition of natural fibers for reaching a better dispersion.

Dog-bone specimen preparation.

1.1 grams of all the extruded samples were input into the piston of a dog-bone mold instrument DaKa (Raleigh, NC, USA) at 200°C. The samples were placed in the piston for 5 min before injection.

Measurement

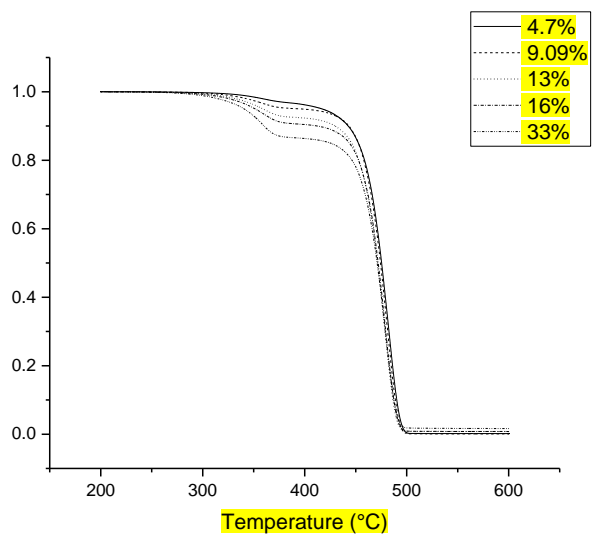
Thermal analysis.

The thermal properties of the Extruded **LDPE phase WPC** samples were determined with a thermogravimetric analysis (TGA) and a Pekin-Elmer Pyris-1 (Raleigh, NC, USA) differential scanning calorimeter (DSC). For TGA, samples were heated from 20 to 500°C in a rate of 20°C/min. For DSC, samples were heated from 40 to 200°C, cooled at 40°C, and then reheated to 200°C at a rate of 10°C/min. The peak temperature of the second heating curves was termed the melting temperature (T_m).

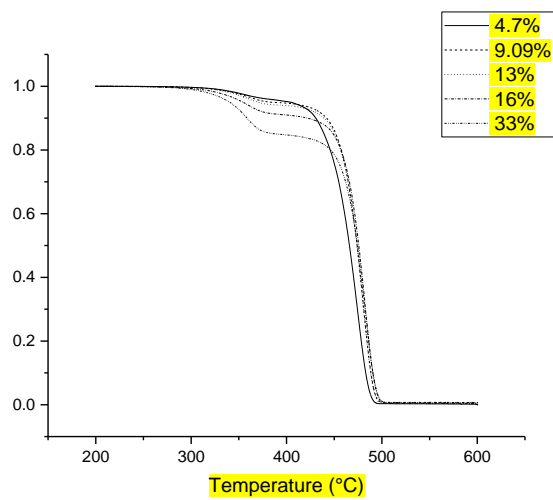
Tensile properties

Five dog-bone shaped specimens (gauge length of 25 mm, width 4 mm and thickness 1.5 mm) were prepared from each extruded sample. The tensile tests were carried out with an Instron Universal Testing Machine at 23°C with a cross head speed of 2.5mm/min.

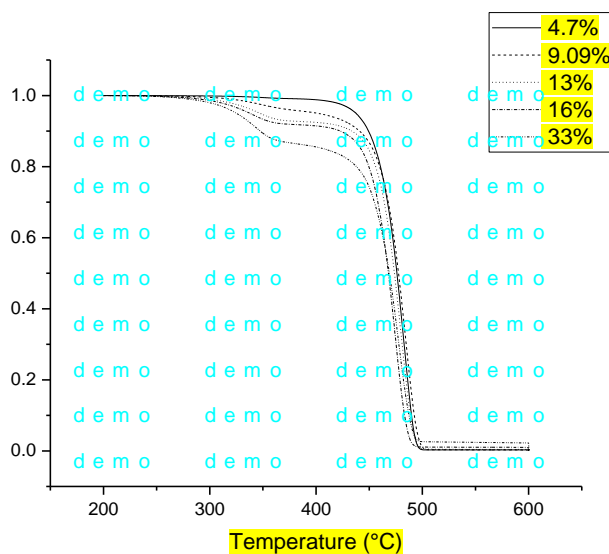
Result and discussion



3a. TGA curves for LDPE-HW.



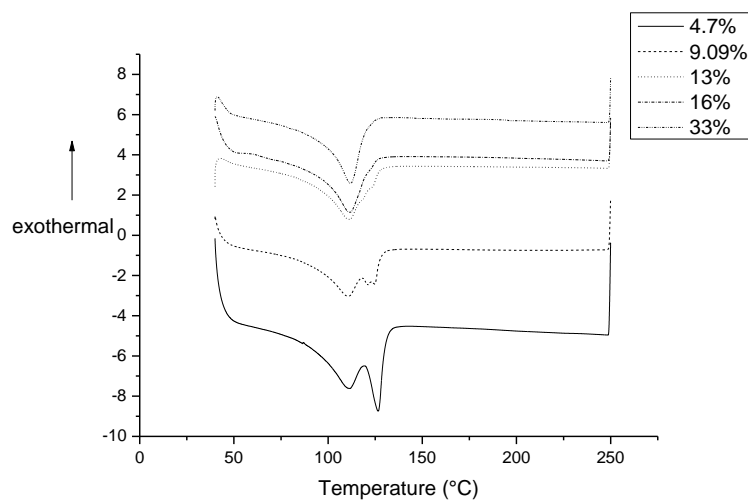
3b. TGA curves for LDPE-SW.



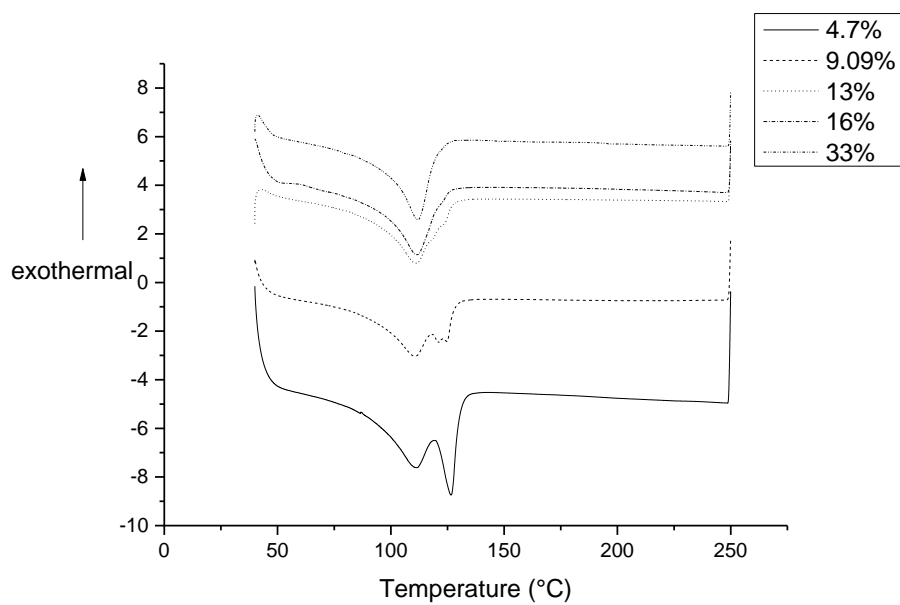
3c. TGA curves for LDPE-MFC.

Figure 3. The TGA curves for LDPE phase WPC

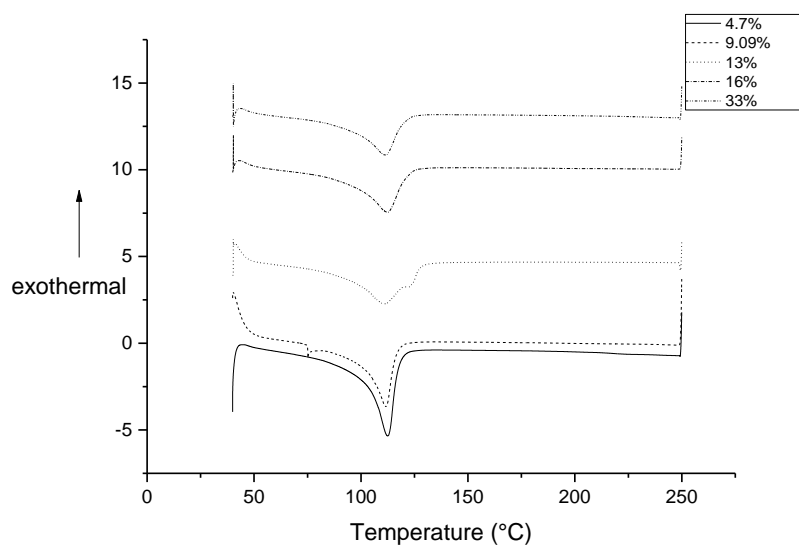
As shown in Figure 3, all the **LDPE phase WPC** samples exhibited the similar degradation trend. The inclines at around 350°C were corresponded to the degradation natural fibers. As the weight percentage of the natural fibers increased, the slope increased.



4a. DSC curves for LDPE-HW.



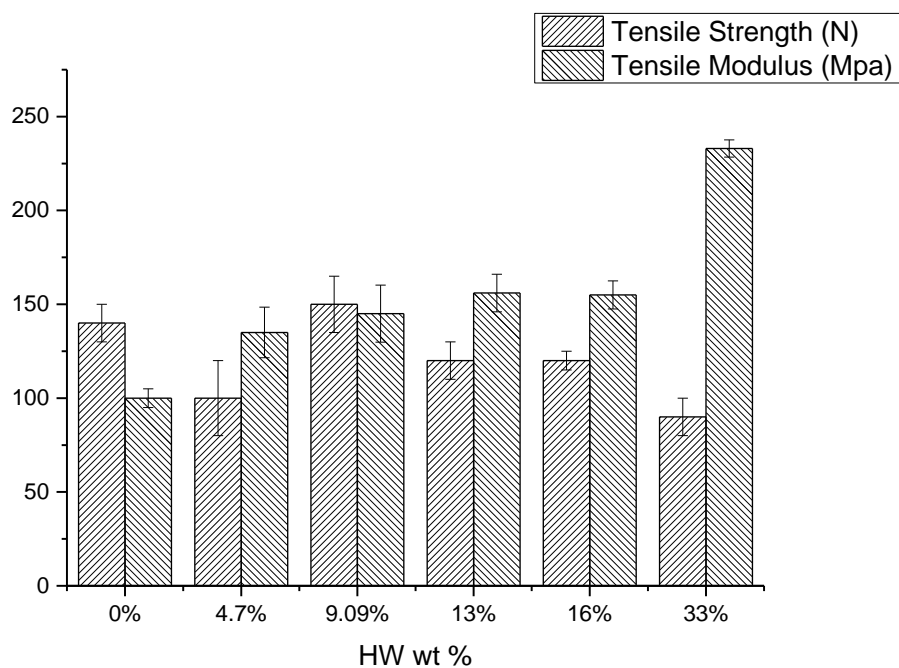
4b. DSC curves for LDPE-SW.



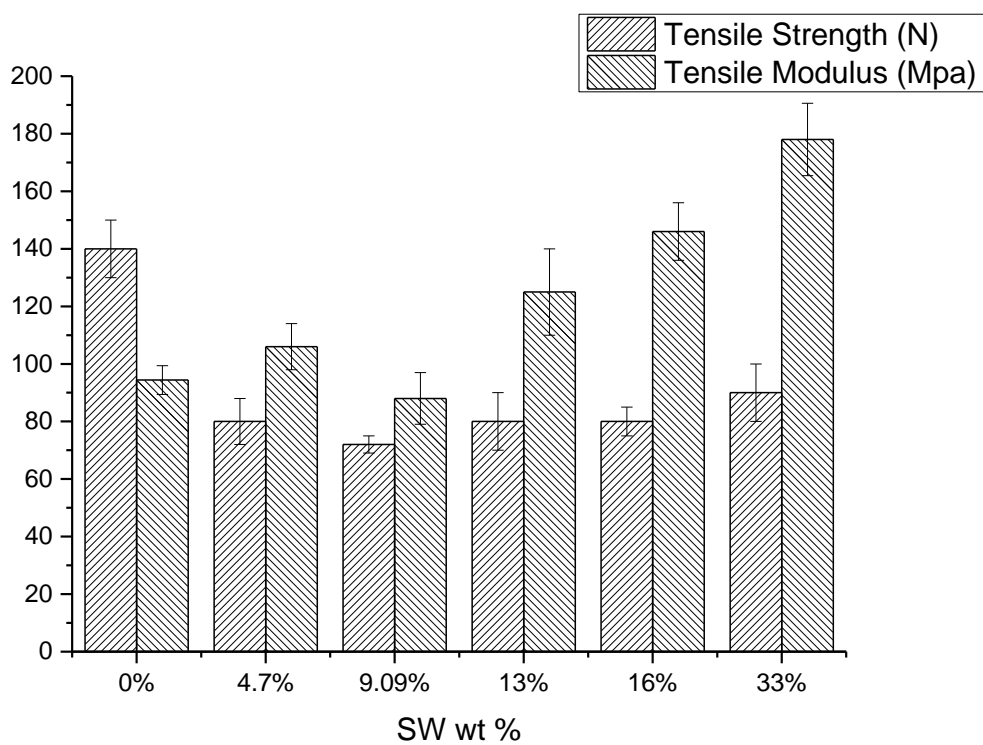
4c. DSC curves for LDPE-MFC.

Figure 4. The TGA curves for LDPE phase WPC

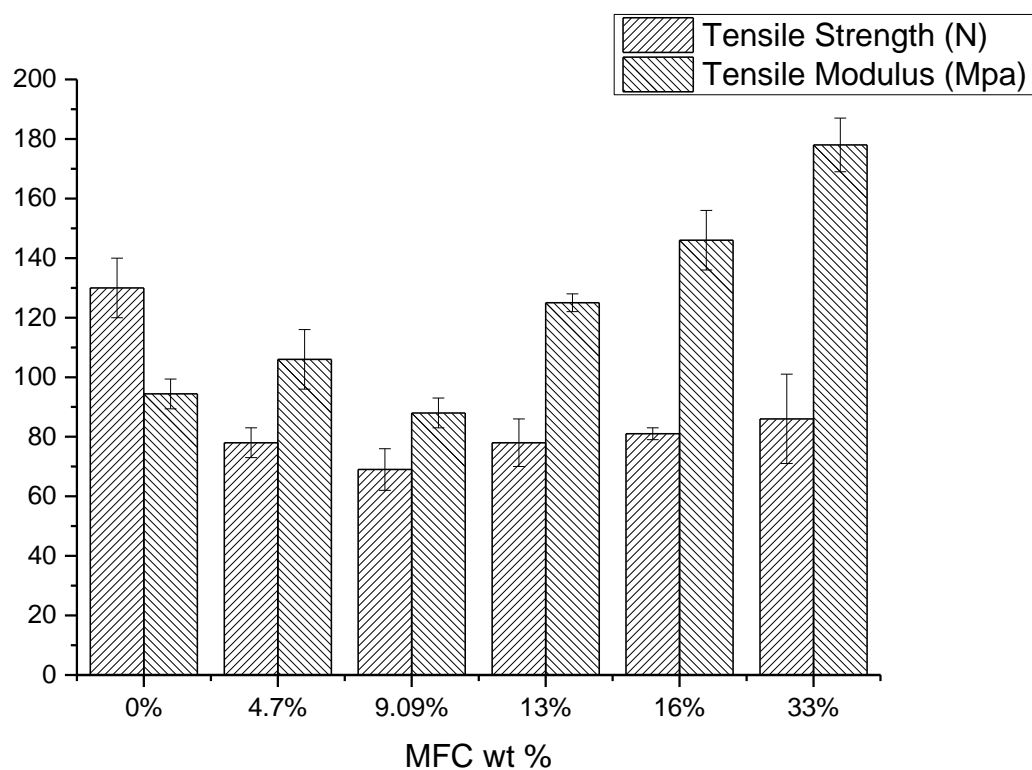
As shown in Figure 4, all the **LDPE phase WPC** samples exhibited the similar melting characteristics. Peak separation took place at around 120°C. The separation disappeared at higher weight percentage of natural fibers. This is probably due to the heterogeneity change of the composites during the addition. At higher natural fiber concentration, the samples exhibited a higher homogeneity.



5a. Tensile properties for LDPE-HW.



5b. Tensile properties for LDPE-SW.



5c. Tensile properties for LDPE-MFC.

Figure 5. Tensile properties for LDPE phase WPC.

Table 1. Summary of mechanical properties

	Tensile strength (KN)			Modulus (MPa)		
	HW/LDP E	SW/LDPE	MFC/LDP E	HW/LDP E	SW/LDP E	MFC/LDP E
0%/100%	0.14±0.01	0.14±0.01	0.14±0.01	100±5.1	100±5.1	100±5.1
4.7%/95.3 %	0.1±0.02	0.08±0.008	0.08±0.005	135±13.5	140±8.2	105±10.2

9.1%/90.9 %	0.15±0.01 5	0.072±0.00 3	0.076±0.00 7	145±15.2	148±9.4	90±5.2
13%/87%	0.12±0.01	0.08±0.01	0.08±0.002	156±10.5	245±15.3	125±3.3
16%/84%	0.12±0.00 5	0.08±0.005	0.081±0.00 4	155±7.5	195±10.2	150±10.2
33%/67%	0.09±0.01	0.092±0.01	0.09±0.015	233±4.6	251±12.6	180±9.4

As shown in Figure 5, the addition of natural fibers into the LDPE increased the modulus. On the other hand, the influence on the tensile strength is inconclusive. There was no significant trend by increasing the percentage of natural content. (Table 1.) It is also notable that MFC weakened the tensile strength of the system most which is probably due to the poor dispersion caused by the abundant amount internal hydrogen bonds in MFC.

Conclusion

The results were contradictory to the former modeling summary because the addition of MFC weakened the WPC the most. The MFC was not able to be thoroughly dispersed in the WPC. Flocs could be observed by eyes. These clumps were probably due to the abundant amount of hydrogen bonds in the MFC. These hydrogen bonds held the MFC fibers together and prevent them to be dispersed by extruder. The HW, however, exhibited the best dispersion and weakened the WPC the least. At this point, it could be concluded that increasing amount of natural fiber will increase the modulus of the WPC.

The material LDPE was found to contain potential foaming agent which broke the internal structure WPC significantly. The LDPE was discard and standard LDPE from Sigma-Aldrich was later chosen to be the matrix.