

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Wood Plastic Composites (WPCs)

The term, wood plastic composites, refers to the material composed of plastic and wood of any form. Plastic, either thermoset or thermoplastic, is served as matrix while wood is applied as filler which the amount can reach 70% of the composites (Clemons. 2002). It is understood that the plastic in wood plastic composites is thermoplastic since thermoplastic is more preferred (Caulfield *et al.* 2005). Both of the composition are mixed and blended at the temperature beyond the melting point of the plastic but not exceed 220°C at which the wood component degradation occurs. The purpose of WPCs development is to create a material that can be used instead of wood product since neat wood is vulnerable to moisture, heat and sunlight (Pendelton *et al.* 2002). In manufacturing, WPCs have versatility in shapes (Soury *et al.* 2009), sizes and colors. The texture and decoration are desirously manipulable depending on processing method.

Due to the advantages in stiffness, light weight and processing flexibility, WPCs is favorably utilized in the area of wood applications (Bledzki *et al.* 1998, Markarian. 2005). Most of WPCs market share arises from the building product, as shown in figure 1, but the other applications such as automotive parts have shown an increase of market trend in the short coming years.

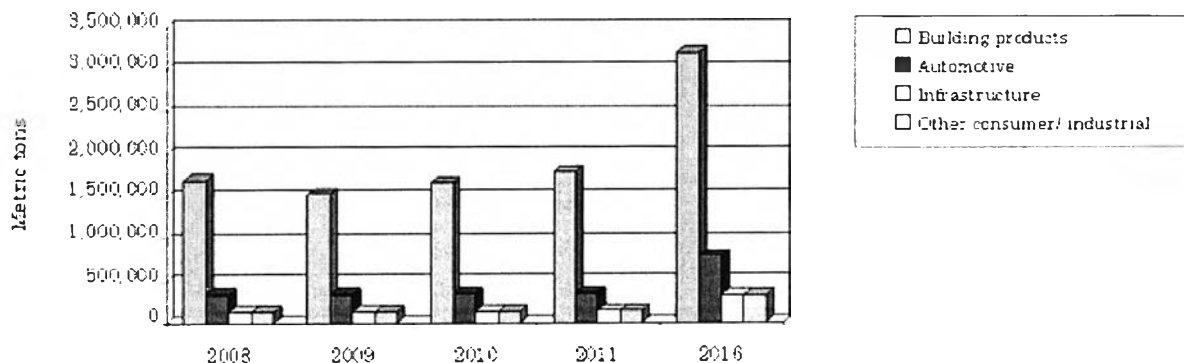


Figure 2.1 Global market for applications for WPCs from 2008 – 2016. (<http://bccresearch.blogspot.com/2011/11/global-market-for-wood-plastic.html>)

WPCs are not only applied for construction area, but also the automotive interior and home furnishing product. The majority of WPCs consumption is in USA, but the market proportion in Europe and Asia is expected to rise since deforestation and global warming become major crisis. The awareness of consumer and manufacturer in green product promotes WPCs as an eco-friendly material. As shown in table 1.1, the carbon emitted from producing the household product from WPCs and steel. The frame made from WPCs clearly releases less carbon than steel and becomes more environmental friendly.

Table 2.1 Carbon emissions from two Minneapolis Homes (Lippke *et al.* 2004)

Carbon Emissions from Two Minneapolis Homes (metric tons)		
	Wood Frame House	Steel Frame House
Carbon emissions during manufacture, use, and demolition	434	443
Carbon sequestered in wood products	489	258
Net carbon emissions	(55)	185

2.2 Wood Flour

Wood component used in WPCs is often in the form of dry particles (wood flour) or very short fiber. However, the relatively high bulk density, availability and free flow nature of wood flour compared to wood fiber is attractive to WPCs industries. In general, wood flour is a wood waste or by product obtained from wood operation which makes it has a low cost (Caufield *et al.* 2005). Wood flour is also produced directly from two steps method. The first step is size reduction which is done by the equipments such as hammer mill or chipper. The wood flour obtained is further grounded in to the fine powder with the typical particles size of 10 to 80 mesh.

The research indicates the species of wood has a very slightly effect to the properties of WPCs, it can be used individually or in combination with other species. The quality of interface between wood component and matrix is much more

considered since it determines the ability to of transferring stress and therefore the strength of the composites (Bledzki *et al.* 1998). Since most of the plastics used in WPCs are hydrophobic, the modification of wood flour in order to increase the homogeneous dispersion in matrix is important.

2.3 Silicate Clay

The silicate clay favorably used in composites is in the family of 2:1 phyllosilicates. Their crystal structure consist of two dimensional layers where a central octahedral sheet composed of alumina is fused with two external tetrahedral silicate sheet, as shown in figure 2 (Pavlidou *et al.* 2008). The thickness of clay layer is around 1 nm and the lateral dimension varies from 300 Å to several microns, depending on source and method of clay preparation. Since the individual layer of clay is relatively small comparing to the surface area, the layers show the tendency to agglomerate themselves to form a stack. The space or gap between each layers in the stack called interlayer or gallery. The substitution within the layer structure generates permanent negative charges which are balanced with alkali or alkali earth cations such as Na⁺, Li⁺ and Ca²⁺. These exchangeable cations locate at the gallery and hold stack together with weak forces. Consequently, the substitution or intercalation of small molecules at the gallery is facile.

The most favorably used silicate clays are montmorillonite, hectorite and saporite. Their chemical formulas are given in table 3.1.

The negative charges of clay layers and the capacity to exchange ions can be measured and quantified by the specific property known as Cation Exchange Capacity (CEC) and expressed in meq/100g. This property is highly dependent on the substitution on silicate layer and therefore on the source where the clay is formed. The charges on the clay surface is not locally constant on each layer, as it localizes from layer to another, and must be consider as an average value. The majority of these exchangeable ions are located at the gallery. When these cations are ion-exchanged with organic cations, which are more bulky, it usually results in a larger interlayer spacing.

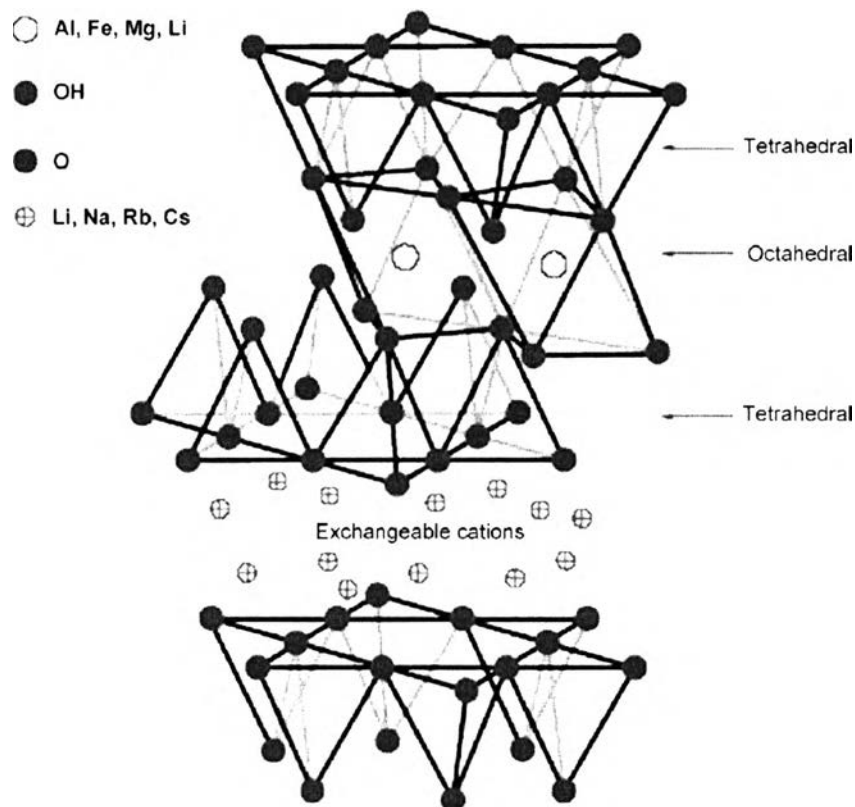


Figure 2.2 The structure of 2:1 layer silicate.

Bentonite is clay mostly consisted of montmorillonite which the CEC value is in the range of 70-100 meq/100g. depending on the composition and source. It can be categorized into three types.

1. Natural Sodium Bentonite: It is bentonite clay which has sodium as major exchange cations. Natural sodium bentonite is characterized by high swelling, high liquid limit and high thermal durability.

2. Natural Calcium Bentonite: It is bentonite clay which the exchange cations are mostly calcium. Compared to sodium bentonite, the swelling and liquid limit properties are lower but calcium bentonite is much more available worldwide.

3. Sodium Activated Bentonite: It is synthetic bentonite clay produced by the substitution of calcium ions by sodium ions with the properties similar to natural sodium bentonite.

Table 2.2 Chemical formulas and characteristic parameters of commonly used 2:1 phyllosilicates

2:1 Phyllosilicates	General formula	CEC (meq/100g)	Particle length (nm)
Montmorillonite	$M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$	100	100-150
Hectorite	$M_x(Al_{6-x}Li_x)Si_8O_{20}(OH)_4$	120	200-300
Saponite	$M_xMg_6(Si_{8-x}Al_x)O_{20}(OH)_4$	86.6	50-60

M: monovalent cation; x: degree of isomorphous substitution (between 0.5 and 1.3)

2.4 Polypropylene

Polypropylene (PP) is one of the most widely used polyolefin. Because of PP does not have any polar groups on its backbone, it is very hydrophobic and does not compatible with hydrophilic additives like clay and wood flour which respectively contain silanol and hydroxyl groups on their surface. Consequently, the homogeneous dispersion of both fillers could not be achieved by simply mixed with PP. To make clay dispersed well in PP matrix, two major methods of modifying clay have been developed. The first method is melt intercalation using a polar functional oligomer or polymer as a compatibilizer, in other words, coupling agent. In this method the organoclay is first blended with the compatibilizer in melt stage. Then the resulting modified clay is melt-blended with PP. When the miscibility of the composites is achieved, the exfoliation of clay takes place. The second method is intercalating polymerization with catalyst supported on clay surface. The gallery gap of clay is increased by the growth of polymer chain until exfoliation is finally achieved. Albeit the second method is very promising, the most environmental friendly and practical for current industry is based on direct polymer insertion with modified clay.

In the same case with clay, the homogeneous dispersion of wood flour is achieved by the aid of compatibilizer. For polyolefin, maleic anhydride grafted on polyolefin such as maleated polyethylene and propylene is the most widely used coupling agent.

2.5 Compatibilizer

Wood plastic composites are normally produced by adding wood particles as filler into a polymer matrix. Most of the polymers are non-polar which make them incompatible with wood component, therefore, weak adhesion between matrix and filler is occurred. Consequently, the aggregation, phase separation and poor mechanical properties are achieved. In order to improve the adhesion of the two components, compatibilizer, substances added in small amount to enhance the compatibility between two phases, are introduced to the composites.

Compatibilizers, in other word coupling agents, provide compatibility through the reduction of interfacial tension of those two phases. Among the compatibilizer used in WPCs, maleic anhydride is favorably used since it contains two carboxylate groups (-COO-) which are able to be grafted on the wood surface via esterification. Moreover, on MA heterocyclic ring, the α,β -unsaturated double bond can be used for conjugation with polymer matrix, resulting in a strong adhesion at the interface (Lu *et al.* 1998). Li *et al.* (2004) has proposed the esterification reaction between hydroxyl groups on wood fiber and anhydride of maleated polyethylene chain (figure 2.3). Myers and coworkers (1990) studied the effect of maleated polypropylene (MAPP) coupling agent on the mechanical properties of WPCs. The flexural strength and modulus are increased with the addition of 1% MAPP. The peel force test indicates the enhancement in wetting and penetration of polypropylene into wood particle which provides an effective mechanical interlocking.

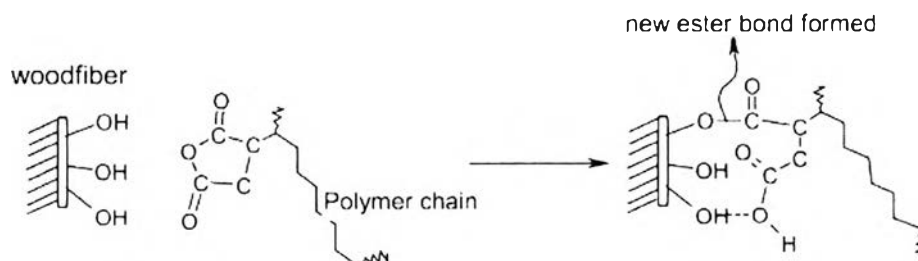


Figure 2.3 Esterification of maleated polyethylene and wood fiber.

2.6 Mechanical Properties

Ichazo *et al.* (2001) studied the mechanical properties of WPCs by preparing wood flour with different treatments, including the effect of adding maleic anhydride grafted polypropylene as a compatibilizer. All the composites have a mixture ratio of wood: PP at 40: 60 by weight with the wood particle size of 20+40 mesh. The result of mechanical testing is shown in Table 6.1. The treatment of wood flour with NaOH, compared with untreated wood flour, increase the tensile modulus without any significant change in other properties. The silane coupling agent demonstrated the result in the same trend with NaOH, however, the impact strength decreased unexpectedly. The addition of Polybond 3150 and 3200, which are the maleated polypropylene, resulted in the significant improvement of mechanical properties, still the impact strength showed the tendency to decrease.

Table 2.3 Results of the mechanical test of PP/WF* composites

Material	E (MPa)	σ_r (Mpa)	ε_r (%)	IS (J/m)
PP	1148±33	25±1	23.4±8.7	26±2
PP/untreated WF	3016±193	37±1	3.1±0.1	15±1
PP/treated WF with NaOH (1/2 h)	3211±89	38±1	2.7±0.3	15±1
PP/treated WF with NaOH (1h)	3125±141	38±1	2.6±0.1	16±1
PP/treated with silane	3177±310	36±1	2.7±0.1	12±1
PP/WF/Polybond 3150	3270±159	39±1	1.2±0.1	13±1
PP/WF/Polybond 3200	3010±228	43±1	2.1±0.1	11±1

*WF in 40%, particle size (20+40) mesh.

Bledzki *et al.* (2003) studied the mechanical properties of WPCs prepared from different type and geometry of wood components. Hard wood, soft wood and long wood fibers, together with wood chip, have been blended with polypropylene with the addition of maleated polypropylene. The composites composed of wood chip demonstrated the high tensile properties compared to those composed of fiber, however, the WPCs contained hard wood fiber showed the highest impact strength.

These results indicated that the type and geometry of wood particle have an influence in mechanical properties.

The effect in mechanical properties arises from incorporating clay into wood-polypropylene composites has been studied by Lee *et al.* (2008). The addition of clay slightly increased the tensile modulus and impact strength.

Zhong *et al.* (2007) studied the effect of organoclay in the wood-polyethylene system. They found that the incorporating of clay resulted in increment of flexural strength when more amount of clay is added, but the flexural strength began to drop when the concentration of clay exceeded 3%. The authors claimed that the failure arisen from the deboning of fillers and more compatibilizer is needed to improve the properties.

Hemmasi *et al.* (2010) studied the effect of nanoclay and coupling agent on the clay dispersion and mechanical properties of the WPC composites. The result showed that the flexural modulus increase when the increase of clay content up to 3 phc (per hundred compound), as shown in figure 6.1. The other properties such as tensile modulus and impact strength also showed the same tendency. The authors concluded that the present of nanofiller with high aspect ratio do have an influence in enhancement of mechanical properties.

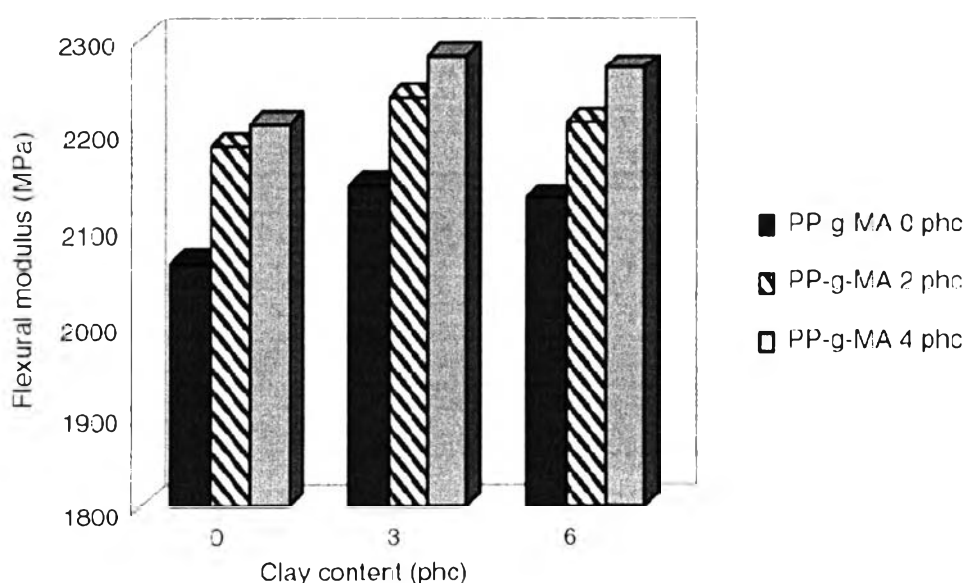


Figure 2.4 Flexural modulus of sample vs. clay content at different PP-g-MA levels.

2.7 Water absorption

It is recognized that neat wood is susceptible to the attack of moisture which usually follows by fungus. The rain or vapor in atmosphere could penetrate into the wood particle and water molecules are trapped between the chains of cellulose. The entrapment of water creates a massive stress which consequently causes a major crack. Another problem arises from water absorption is the invasion of fungus which could potentially damage and deteriorate the wood (Pendelton *et al.* 2002). Wood treatment could prolong the service life, but the absorption of water is inevitable.

This is not the case with synthetic polymers which are highly water repellence. The encapsulation of plastic is believed to overcome the water absorption problem and WPCs is originally placed in the market as being decay resistance. However, the laboratory and field tests clearly demonstrate that WPCs do gradually absorb the water and eventually deteriorate. Wang *et al.* (2004) studied the water absorption of two commercial wood plastic composites product. The result showed that the moisture content is much higher at the surface than the interior. The authors also claimed that, comparing to neat wood, the rate of water uptake and deterioration of WPCs tend to be much retarded and the water entrapment is localized on the surface.

Ichazo *et al.* (2001) studied the relationship of wood content and water uptake. It is found that the increase of wood element increase the water absorption since the increment of wood enlarges the hydrophilic character of the composites and result in the high water retention.

The addition of clay into WPCs results in the reduction of water uptake. Lee and coworkers (2008) studied the effect of clay in physical properties of WPCs including the water absorption. The results demonstrated that the present of clay has a positive effect in improvement of WPCs performance.

2.8 Thermal Stability

The interest in natural reinforced polymer composites materials is rapidly growing, especially in terms of their industrial applications. Thermal stability is one of the most important parameter for WPCs as well as mechanical properties and water absorption. Salemane *et al.* (2005) studied the influence of wood powder size and content, as well as, the presence and the amount of maleic anhydride grafted polypropylene (MAPP) on the thermal property. As shown in figure 8.1, WPCs with the present of MAPP demonstrated higher thermal stability which is the results of strong interfacial interaction, when compare with neat PP and wood powder. The increase of MAPP content showed the tendency in thermal stability improvement.

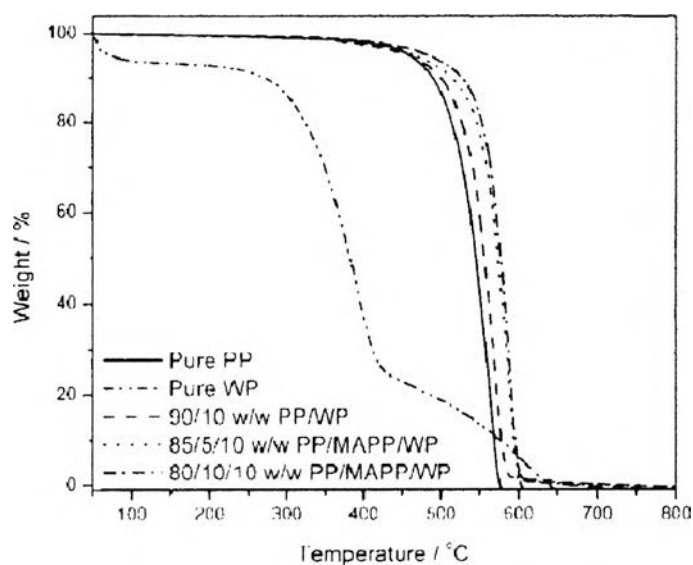


Figure 2.5 TGA curves for composites containing wood powder particles and different MAPP contents.

Coutinho *et al.* (1999) studied the performance of PP-wood composites. The addition of wood particles resulted in the increase of crystallization temperature and enhanced the thermal stability. The wood particle, in associated with MAPP, might be considered as a nucleating agent for PP. Since the SEM image (figure 8.2) showed that crystallization of PP occurred at the surface of wood particle, it is believed that the wood particle gain a barrier properties of both gas and moisture.

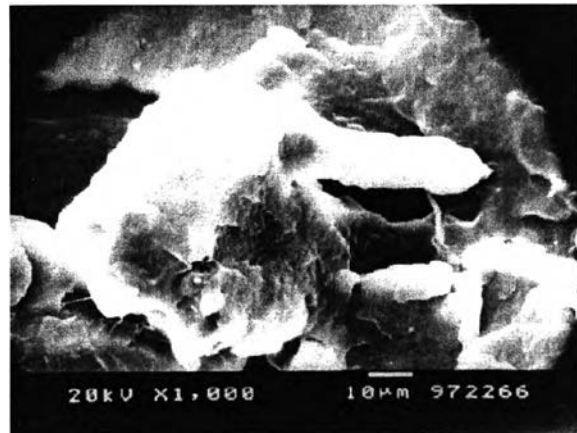


Figure 2.6 SEM micrograph the composite contains 20% of wood particle.