

**Characterization of Phenol Formaldehyde Adhesive and Adhesive-Wood Particle
Composites Reinforced with Microcrystalline Cellulose**

by

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Abstract

The use of lignocellulosic materials as reinforcement in polymer adhesives has increased considerably over the past few years. Lignocellulosics, also known as natural fibers are more attractive to use compared with synthetic reinforcements because they are biodegradable, less costly and have acceptable specific strength. Phenol formaldehyde (PF) adhesives are the most widely utilized binders used in the wood composites industry. Although PF is more moisture resistant and gives acceptable strength properties, it is also known for its significant brittleness. This could be overcome by reinforcement.

The first part of this study aimed at reinforcing Phenol formaldehyde adhesive with microcrystalline cellulose (MCC) at different loading rates (0 – 10% wt). The viscosity of the adhesive system after reinforcement was evaluated. To determine the cure properties and thermal stability of the adhesive/cellulose composite, thermal analysis using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) was conducted. The strength of the cellulose reinforced adhesive system was evaluated using lap shear tests. Fourier transform infrared (FTIR) spectroscopy was used to investigate possible interactions between cellulose and the adhesive matrix.

Results from this portion of the study showed that cellulose reinforcement lowers the cure temperature as well as the thermal stability of the neat PF adhesive. Lap shear tests revealed an increase in shear strength with the addition of cellulose. The necessary cure temperatures and optimal MCC loadings from the first study were then utilized in the design of the second study.

In the second study, two particle sizes, two species, and two MCC loadings were utilized to determine the effects of these factors on the mechanical and physical properties of particleboard. A 15% PF loading was used to accommodate the high surface area of the 10% MCC loading. Sweetgum and southern yellow pine were the two species used and a 0.15 cm mesh sieve was used to separate the large particles from the small particles. The mechanical (Modulus of elasticity and modulus of rupture) and physical (thickness swell) properties of the boards were investigated.

The results revealed that control boards (untreated PF with southern yellow pine and sweetgum wood particles) had better mechanical (both modulus of elasticity and modulus of rupture) properties than boards manufactured with 10% MCC. It was found that addition of MCC to particleboard resulted in debonding of the adhesive from the cellulose matrix as indicated by the lower mechanical properties. This was attributable to the difference in viscoelastic properties and consequent springback of the wood and cellulose components within the matrix. A future study to reduce springback is necessary if MCC is to be used for the improvement of particleboard mechanical properties. On the other hand, increases in particle size had a positive effect on mechanical properties of boards produced and may be a cost effective way of dialing in particleboard mechanical properties to meet industry standards. Finally, sweetgum exhibited better dimensional stability and competitive mechanical properties than southern pine. Since sweetgum is an underutilized hardwood that is abundant in regions that include southern pine, use of sweetgum in composite board production may help to alleviate pressures on natural resources that are likely to occur as other biobased manufacturers compete for southern pine raw material.

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Chapter 1 Introduction

Wood composites describe a unique group of materials that combine two or more physically different materials with the aim of achieving enhanced properties that cannot be attained when each material is used individually. Wood is the primary raw material used, and the bond necessary to hold them together is produced by an adhesive. Worldwide, there has been growing concerns about ways of efficiently utilizing forest trees, residues and underutilized tree species. This will reduce the burden of overdependence on conventional trees species used for lumber and structural applications. Wood composite engineering makes this possible. Composite panels like particleboard, oriented strand board, plywood, laminated veneer lumber (LVL) have become more desirable and attractive to use because they combine material properties in ways not found in natural designed materials such as lumber. Wood composites are lightweight, have high stiffness and their properties can be engineered to meet specific applications, thereby reducing their weight and the amount of energy used.

Common adhesives used for binding wood materials in the composites industry include phenol formaldehyde (PF), urea formaldehyde (UF), diphenylmethane diisocyanate (MDI) and melamine urea-formaldehyde (MUF). PF is the most widely used because of its good mechanical properties as well as moisture resistance (Knop and Scheib, 1979; Lei et al., 2006). Despite these characteristics, PF lends itself to significant brittleness when cured (Mu et al., 2004). Also, PF like many others is petroleum derived, as such raises concerns relating to its sustainability, ecofriendliness and environmental health.

Over the past couple of decades, growing awareness of biodegradability, formaldehyde emissions, green chemistry, depleting petroleum resources and manufacturing ecofriendly materials have become drivers of research aimed at producing newer materials which are more environmentally friendly and not petroleum based. Composites materials, especially biobased composites, fit into this trend. Substitution of petroleum derived products with 100% biobased materials will not be attainable immediately. However, a promising alternative is to combine petroleum based materials with biobased materials to engineer products with specific properties such as work performance and cost that meet real world applications. When petroleum derived or biobased adhesives are reinforced with biobased fibers/fillers, a “biocomposite” is produced. ASTM, the American Society for Testing and Methods (2003) defines a filler as a relatively non-binding substance added to an adhesive binder to improve its working properties, strength and/or other qualities. If fillers/reinforcements are used, they would also add to the volume of the product, reducing the amount of petroleum derived material used.

In the past, synthetic fillers such as glass, aramid and carbon have been used because of their high reinforcement potential. For instance, tensile strength values in the range of 3000-4759 MPa have been reported for glass, aramid and carbon fibers (Bledzki and Gassan, 1999). Although they have high strength values, synthetic fibers used as reinforcement in adhesives are less desired. This is because compared to natural fibers, synthetic ones are more expensive, abrasive, toxic and not easily degradable (Azizi et al., 2004). It has been shown that biofibers like sisal, hemp, jute, flax, oil and banana can be utilized as fillers in synthetic polymers (Bledzki et al., 1998; Mohanty et al., 2002; Jacob et al., 2006). In the wood composites industry, additives such as wood flour, wheat flour and bark residues can be incorporated into plywood adhesive systems to improve their working and/or strength properties (Sellers et al., 1990; Oh et al., 1997).

Natural fibers have low density, are non toxic or abrasive and are easily degradable (Maya and Sabu, 2008; Goussé et al., 2004). Although the tensile strength of jute, flax and hemp fibers are low, wood fibers have strengths that are comparable to glass fibers (Bledzki and Gassan, 1999). In these biobased fibers (wood or non woody), cellulose is a primary constituent that provides the reinforcing effect.

Cellulose is a polysaccharide consisting of a linear chain of several hundred to over ten thousand β (1 \rightarrow 4) linked D-glucose units. Commercially, cellulose fibers are mostly obtained from wood and cotton feed stocks. Cellulose fibers have been studied as reinforcement especially in thermoplastic composites (Woodhams et al., 1984; Felix and Gatenholm, 1991; Arbelaiz et al., 2005). Native cellulose comprises amorphous (low order) and crystalline (high order) regions. Crystalline cellulose is stronger and stiffer than amorphous cellulose. The result is better strength when used as fillers (Gardner et al. 2008). Microcrystalline cellulose (MCC), also known as Avicel (commercial name), is a highly crystalline cellulose (~70%) obtained by the acid hydrolysis of native cellulose (Azizi et al., 2005). Acid hydrolysis isolates the crystalline regions of cellulose from the amorphous parts. There have been some studies on MCC as reinforcing filler in plastic composites (Bai and Li, 2009; Kiziltas et al., 2010). A few studies have reported on the reinforcement potential of MCC in thermosetting adhesives (Matos Ruiz et al., 2000). Nakagaito & Yano (2008) worked on reinforcing PF adhesive with pulp and with microfibrillated cellulose (MFC). Their findings revealed that, Young's modulus of pulp and MFC-based composites were similar and about 18–19 GPa; however the bending strength of the composites peaked at 370 and 260 MPa for MFC and pulp reinforced composites respectively.

A literature review reveals no documented studies on utilization of microcrystalline cellulose (MCC) as reinforcement in PF adhesives for the manufacture of wood particle based

composites. This study therefore investigated the substitution of microcrystalline cellulose into a PF adhesive matrix to promote increased mechanical properties and thermal stability. The main objectives of this project were twofold:

1. Engineer and characterize the thermal and mechanical properties of a PF-Microcrystalline cellulose based composite.
2. Leverage these findings towards the optimization of a wood particle to PF-Microcrystalline cellulose based wood composite.

To achieve these objectives, the following sub objectives were carried out:

1. Reinforce PF adhesive with MCC at different loadings.
2. Investigate the mechanical and thermal properties of the adhesive-cellulose system using DSC, TGA and Lap shear tests.
3. Blend the adhesive-microcrystalline cellulose mixture with wood particles to manufacture particleboards and subsequently test for their mechanical strength.

Chapter 2 Literature Review

2.1 Introduction to Wood Composite Products

In the past, wood was only used in solid form as large timbers/lumber for structural applications. The overdependence on natural forests for this raw material led to gradual depletion and increased prices of large diameter trees. Growing social demand for wood and wood based products resulted in the need to find newer wood resources and/or more efficient utilization of current resources. Wood based composites were developed which enabled one to utilize the entire tree. The term wood composite is used to describe all products manufactured by binding together woody materials such as strands, particles, fibers or veneers with non woody materials like adhesives and /or wax (Walker, 2006).

Wood based composites and panel products have several advantages over solid wood. First, the processing of these woody materials into smaller components efficiently utilizes waste material, small diameter and underutilized logs. Additionally natural defects like knots and slope of grain can be reduced, removed or evenly distributed within the composite. Particle size can also be reduced which further increases composite uniformity. Increased uniformity is beneficial and makes the prediction of engineering performance easier due to lower strength and stiffness variation (Marra, 1979). The mechanical properties of wood based composites are derived from the particulate nature of the woody raw material (Youngquist, 1999).

2.1.1 Density Classification of Wood Composite Products

Suchsland and Woodson (1986) have classified various wood composite boards based on particle size, density and process type (Figure 2.1). Typically different wood particle sizes

process parameters will yield different densities and consequent product properties. Currently engineered wood panels are categorized into five based on the physical processes used in their manufacture: plywood, oriented strand board, particleboard, hardboard and cellulosic fiberboard (Simpson and TenWolde, 1999). Wood composites have several structural and industrial applications including interior and exterior flooring, roof sheathing, wall sheathing, furniture and concrete forming.

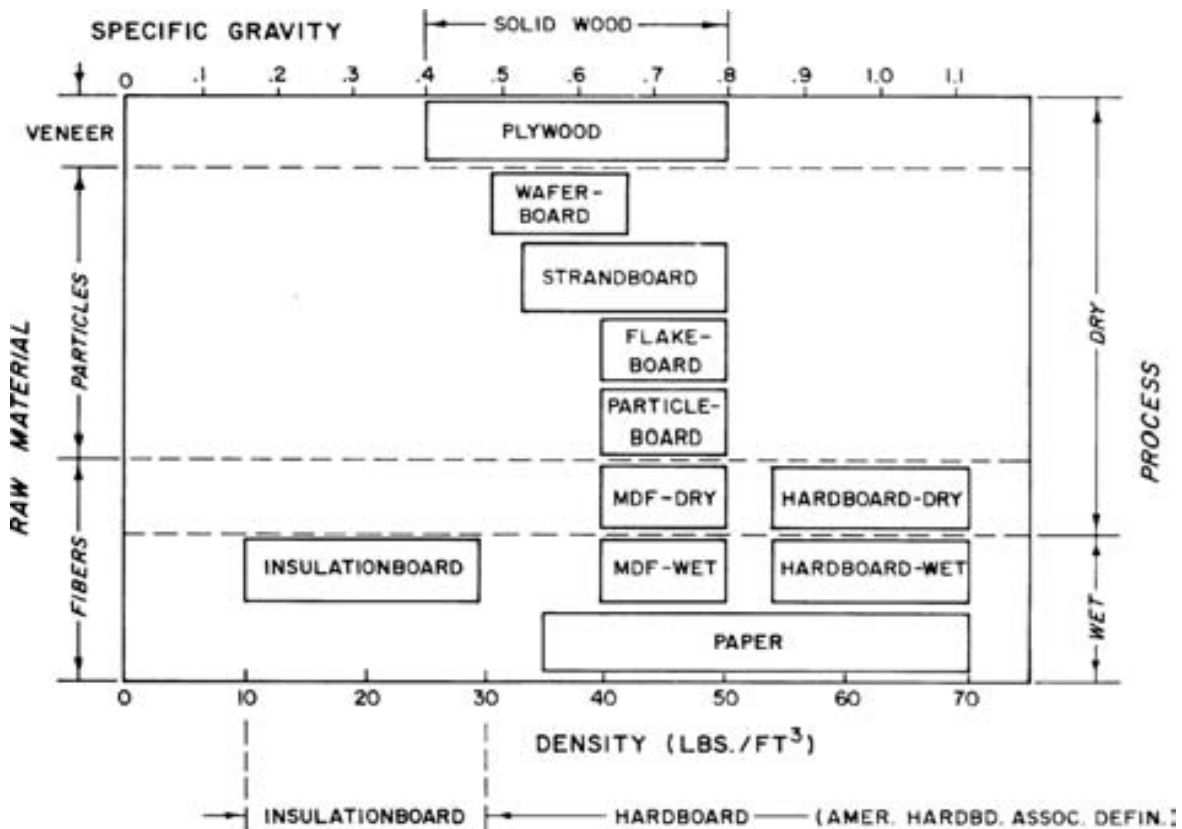


Figure 2.1 Classification of Wood Composite Board Materials by Particle size, Density and Processing Principle (Suchsland & Woodson 1986).

2.2 Particleboard

By definition, particleboard (also called chipboard) is an engineered wood product manufactured from lignocellulosic materials in the form of discrete wood fragments and a

synthetic adhesive which is then bonded together under heat or pressure (Bowyer et al., 2007). Dry wood particles are sprayed with a binder resin, blended and then formed into a loose sheet that is further pressed under heat at high temperatures resulting in bonding of wood particles. The addition of the binder resin provides the entire interparticle bond. The size of the particles used in manufacture differentiates particleboards from other types of wood-based panel products such as plywood, oriented strandboard (OSB), fiberboard, and hardboard

2.2.1 Particleboard Types

Depending on the kind of mat layering or configuration used, there are four types of particleboard panels: random (no distinct layers), graduated (gradual transition between layers), three-layer (finer particles in the face layers and coarse particles in the core), and five- or more layer particleboards (finer particles in the face, slender and flat particles in the intermediate layers, and coarse particles in the core layers). Three-layer particleboard is most commonly reported in literature and utilized in industry (Wong et al., 1999; Hiziroglu and Holcomb, 2005; Nemli and Dimerel, 2007; Claude et al., 2008). The coarse core materials provide the bulk of particleboard while the fine face materials provide smooth surfaces for laminating, painting, overlaying, or veneering (Wong et al., 1998, Nemli and Çolakog, 2005; Nemli et al., 2005). Although average mechanical strength properties of particleboards are generally lower than that of natural lumber, they are more consistent, thus their mechanical properties can be predicted more accurately.

2.2.2 Uses of Particleboards

Particleboards have several applications including floor underlayment, housing, TV and stereo cabinets, shelving table tops, furniture, sliding doors, pool tables and vanities (Bowyer et al., 2007, Maloney, 1993; Nemli et al., 2005). Particleboards are mainly used indoors because

they do not have enough water repellency. If particleboards utilized Phenol Formaldehyde instead of conventional Urea Formaldehyde resins, then it can be used for outdoor purposes. But due to the small particle size, strength may be a problem and reinforcement of the matrix would be useful. Typically, their surfaces are coated or laminated to improve their water repellency and also formaldehyde emission.

2.2.3 Materials Used in Particleboard Production

Several particleboard manufacturers use raw materials from industrial wood residues (such as sawdust, shavings, offcuts and slabs) and roundwood (logging residues, thinning and non commercial species) (Lehman and Geimer, 1974; Falk, 1997; Blanchet et al., 2000; Lehtikangas, 2001; Walker, 2006; Nemli and AydIn, 2007; Nemli et al., 2008; Hermawan et al., 2009). Wood species like Norway spruce, Scots pine (Boonstra et al., 2006), beech, pine and poplar (Nemli et al. 2007) have also been worked on. As the demand for wood products increase, researchers have to look at possible alternatives to natural wood such as agricultural residues like can readily be utilized as substitute raw materials for the production of particleboard like wheat straw and corn pith (Wang and Sun, 2002; Boquillon, 2004), waste tea leaves (Shi et al., 2006), kenaf (KalaycIoglu and Nemli, 2006), egg plant (Guntekin and Karakus, 2008), waste grass (Nemli et al., 2009).

2.2.4 Manufacture of Particleboards

The general steps for particleboard include raw material preparation, screening by size, drying, blending with resin and some wax or production additives, forming the resinated material into a mat, hot pressing and finishing is described in Figure 2.2. The particleboard manufacturing process typically begins with the preparation of the furnish or raw material (i.e. chips, saw dust, planar shavings). At the mill, logs are debarked first, sawn into smaller chunks and then

comminuted into long and thin consistently sized particles using hammer mills, flakers or refiners (Youngquist, 1999). The type of particleboard to be manufactured determines the size of

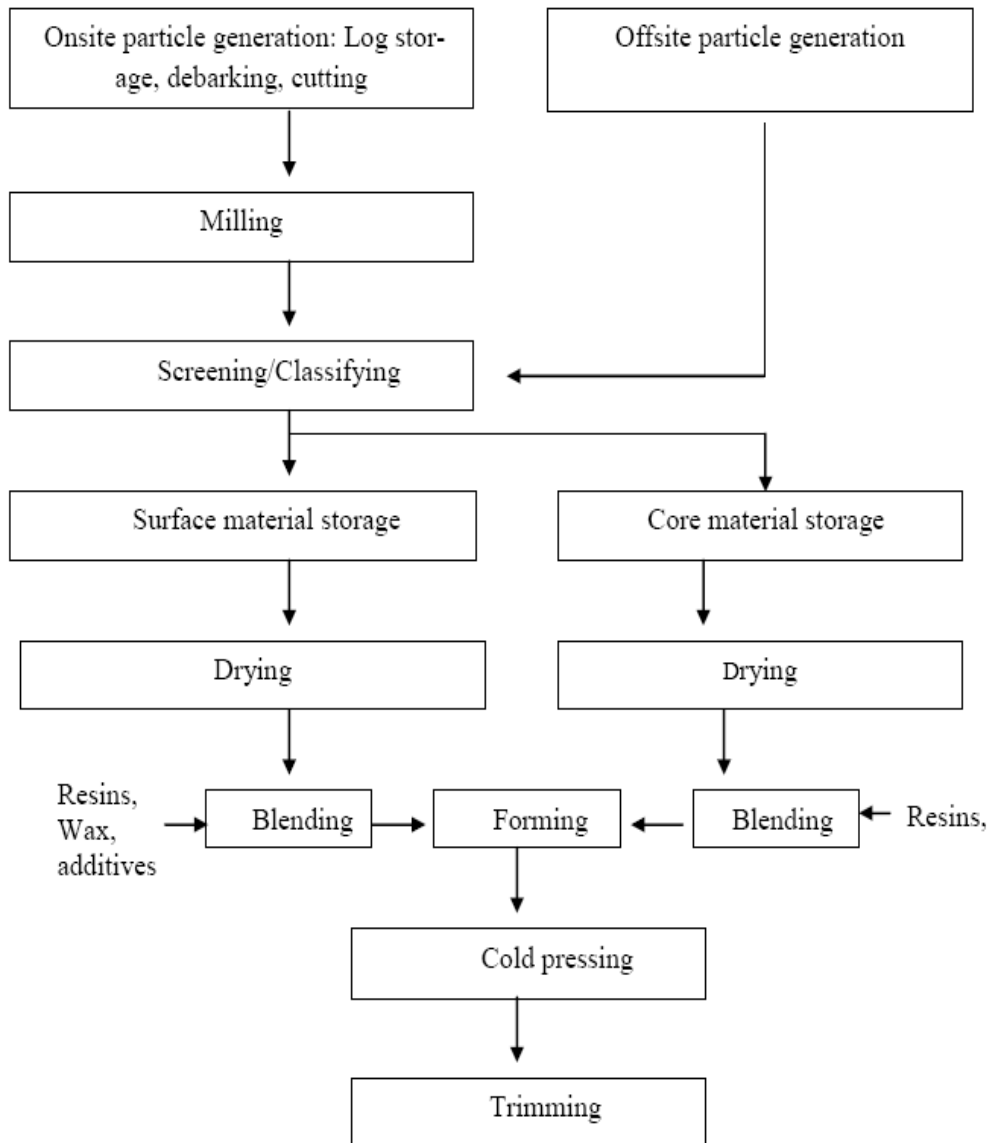


Figure 2.2 General Process for Particleboard Manufacture

the furnish. For instance, three layered boards have thicker and coarser core particles in the center layer while finer and smaller sized particles are used for the surface layer. A vibrating or

gyrating screen is then used to separate finer sized particles from oversized particles into surface and core materials respectively; and conveyed into storage bins.

The high moisture content of the furnish ranging from 10% to 200% is reduced (usually in rotary dryers) to a lower moisture content typically between 7% and 12%. The moisture content of particles is critical for hot pressing (Youngquist, 1999). Excessive moisture content will cause excessive pressure resulting in a “blow” which has a negative effect on resin bonding; while overly dry material will lower its internal bonding strength. It is therefore crucial to carefully control the operating parameters of temperature and time in the dryer to achieve different hot-presses temperatures for different particleboard products; for instance by increasing the temperature and/or time to produce drier particles for the core material rather than for the surface material. Following drying, the particles are sieved and transferred to blenders in which adhesives and/or waxes and other additives are sprayed onto them from a high pressure spraying nozzle (atomizer) to achieve fine resin droplet size. Urea–formaldehyde (UF) adhesives are commonly used for particleboard manufactured for indoor use, whereas phenol–formaldehyde (PF) adhesive are utilized in particleboards for structural purposes where moisture might be present for short durations of time. Adhesives used in the particleboard manufacturing are thermosets; thus they cure when heat is applied to them and cannot return back to their original liquid state. Wax can be added at 0.3 - 1% of the oven-dry weight of the particles for short term moisture resistance (Youngquist, 1999).

The resinated wood particles are then formed into an even and consistent mat over a moving conveyer belt. Mat-formation is either batch-wise or continuous. The mat is typically cold-pressed prior to trimming and hot pressing, to reduce mat thickness. Hot-pressing is the most critical stage of making particleboard panels since it controls the thickness and thus the

density of the final particleboard products. Hot-pressing brings the particle surfaces together for bonding, and provides heat to cure the thermosetting adhesives. Two types of hot-presses are reported: batch hot-press and continuous hot-press. The total press time is around 2 and a half minutes for a continuous hot-press and can be up to 5 minutes for a multi-opening batch press. The operating temperature ranges from 300 °F to 360 °F. The moisture content of the mat before hot-pressing is typically about 8 to 12%. The hot-press is typically heated by steam generated from a wood-burning boiler in the particleboard plant.

After hot-pressing, particleboard panels are cooled before finishing. Finishing involves trimming, sanding, laminating and packaging. The edges of particleboard panels are trimmed to design specifications. Trimming reduces the size of a particleboard by 0.5 – 8% of its weight depending on the panel size and process employed. Trimmed material is usually recycled for core particles of future panels.

2.2.5 Physical and Mechanical Properties of Particleboards

Based on their final densities, particleboards have been classified as H- high density ($>800\text{kg/m}^3$), M- medium density ($640\text{-}800\text{ kg/m}^3$), LD- low density ($< 640\text{kg/m}^3$), D- manufactured for home-decking and PBU- used as underlayment. When the letters are followed by digits, the digits refer to the grade of the panel within that classification. The general properties required for the classifying particleboards as stipulated by the American National Standard Institute A208.1 (ANSI/A208.1, 1999) is described in Tables 2.1 and 2.2

Several mechanical properties are commonly important for general wood based composites including static bending, tensile strength parallel to the surface, tensile strength perpendicular to the surface (internal bond), shear strength, edgewise shear and glue line shear. For particleboard, the mechanical and physical properties most evaluated include static bending

Table 2.1 Property Requirements Specified by the American National Standards Institute A208.1 (ANSI/A208.1, 1999) for Various Classes of Particleboard Products.

Grade	MOR (MPa)	MOE (GPa)	Internal Bonding (MPa)	Hardness (N)
H-1	16.5	2400	0.90	2225
H-2	20.5	2400	0.90	4450
H-3	23.5	2750	1.00	6675
M-1	11.0	1725	0.40	2225
M-S	12.5	1900	0.40	2225
M-2	14.5	2225	0.45	2225
M-3	16.5	2750	0.55	2225
LD-1	3.0	550	0.10	NS
LD-2	5.0	1025	0.15	NS

MOR = modulus of rupture, MOE = modulus of elasticity, NS = not specified.

1 MPa = 145 lb/in²; 1 N = 0.22 lb.

Grade M-S refers medium density; “special” grade added to standard after grades M-1, M-2, and M-3. Grade M-S falls between M-1 and M-2 in physical properties.

Table 2.2 Property Requirements Specified by the American National Standards Institute A208.1 (ANSI/A208.1, 1999) for Various Grades of Particleboard Flooring Products.

Grade	MOR (MPa)	MOE (MPa)	Internal Bonding (MPa)	Hardness (N)
PBU	11.5	1725	0.40	2225
D-2	16.5	2750	0.55	2225
D-3	19.5	3100	0.55	2225

(modulus of rupture and modulus of elasticity), internal bond, thickness swell and linear variation with change in moisture content. These properties are generally measured according to

the American Society for Testing and Materials ‘Standard and Methods of Evaluating the Properties of Wood-Base Fiber and Particle Panel Materials,’ ASTM D 1037.

2.2.5.1 Static Bending

Static bending measures two important properties: modulus of rupture (MOR) and modulus of elasticity (MOE). MOR is considered the accepted measure of strength of a panel. Simply, it describes the maximum load carrying capacity of a member in bending. This usually occurs in the extreme upper and lower surface of the member when true stress distribution is considered.

MOE on the other hand refers to the stiffness of the material under load and measures the deflection of the material under stress. Both MOR and MOE are measured parallel to the face of the panel and due to lack of fiber alignment; it is assumed that the perpendicular direction will yield equivalent results. When a supported particleboard beam of span L and with a concentrated load P applied at the center of the span, the maximum deflection, MOE and MOR are mathematically calculated as follows:

$$\text{MOR (MPa)} = \frac{3PL}{2bd^2}$$

$$\text{MOE (GPa)} = \frac{P_1 l^3}{4bd^3} Y_1$$

where P is maximum load (N), P_1 is the load at proportional limit (N), b is the width of the specimen (mm), d is the thickness of the specimen (mm), Y_1 is the deflection corresponding to P_1 (mm), and L is the span (mm).

2.2.5.2 Internal Bond

Internal Bond (IB), also known as tensile strength perpendicular to the surface measures the strength of the adhesive in the wood composite at a given composite density. This is carried

out by pulling the test specimen apart with the direction of the load as nearly perpendicular to the horizontal axis of the board as possible.

2.2.5.3 Thickness Swell

Water absorption and thickness swell are evaluated by submerging the product specimen horizontally under distilled water, and the increase in weight and dimension due to the absorption of is measured after 2 and 24 hours.

2.2.6 Parameters Affecting Board Properties

2.2.6.1 Density

The density of the furnish has a profound effect on the physical properties of particleboard. Low density wood species produce particleboards with higher strength compared to that of higher density (Moslemi, 1974; Vital et al., 1974; Wong et al., 2003). This can be explained by the fact that low-density wood has a relatively high compaction ratio when hot-pressed into a board, resulting in better contact among the particles. The density of the resultant panel after hot pressing also affects the mechanical properties of the board. At the hot press, interaction between heat, pressure and moisture leads to a non uniform deformation of the materials and subsequently an uneven density distribution along the thickness of the board is formed. Wong et al., (1999) studied formation of the density profile and its effects on the properties of particleboard. Their results revealed that in uniform vertical density profile boards, MOR and MOE are highly correlated to the board mean density. Their study also showed that at equal mean density level, the MOR and MOE of the conventional particleboards are higher than boards with uniform vertical density (homo-profile) due to the higher density near the faces. However, the reverse is true for IB, owing to the presence of the low density core in the former.

2.2.6.2 Moisture Content

The moisture content (MC) and its distribution during manufacture and within the thickness of the formed mat plays a very important role in panel mechanical and physical properties. A higher MC in the face layer will result in a higher densification towards the surface. There is an upper limit after which additional increases in moisture content will result in blow outs within the panel. Higher surface densities will have a positive impact on bending strength and stiffness. Conversely, a furnish of uniform MC will exhibit a lower density toward the surface resulting in lower mechanical properties. Several researchers have studied the influence of mat MC on particleboard properties (Halligan and Schniewind, 1972; Papadopoulos, 2006; Han et al., 2006). For instance, Wong et al., (1998) studied the effect of moisture content (MC) on the formation of density profile and board properties. They produced particleboards at three different closing speeds, while mats were produced such that the MC of the core and surface layer was equal in one treatment while in another treatment; the surface layer had a higher MC. Their findings demonstrated an increase in MOE when particles of higher MC were placed in the surface.

2.2.6.3 Adhesive Content

Urea formaldehyde (UF) and Phenol formaldehyde (PF) are two common adhesives used in the United States. Increasing the adhesive level increases the mechanical properties of the board. However, adhesive is expensive and as such must be used sparingly or in the production of specialty products. All strength properties (modulus or rupture, modulus of elasticity and internal bonding) have been shown to increase with increased adhesive content (Lehmann, 1970; Kelly, 1977; Ashori & Nourbakhsh, 2008).

2.2.6.4 Particle Size

Particle geometry describes shape and size dimensions of particles used in particleboard production. This parameter creates a significant impact on the properties of the boards. Particle size plays a more important role in the development of board properties than the actual mechanical properties of the panels (Suchsland, 1990). For instance, a variation of particle shape and size significantly influenced overall panel properties of cement bonded composites (Frybort et al., 2008). Also, recent studies have shown that particle shape, size, fines content affected mechanical properties such as linear expansion as well as internal bond strength of samples (Miyamoto et al., 2002; Sackey et al., 2008) showed that particle shape affected the linear expansion of particleboard.

2.2.7 Adhesives Used in Particleboard Manufacture

The American Society for Testing and Materials (ASTM D 907-00, 2002) defines an adhesive as a substance capable of holding materials together by surface attachment. Wood adhesives are classified into two broad categories: natural and synthetic adhesives. Natural adhesives (also known as bioadhesives) are made from organic sources like vegetable matter, starch (dextrin), natural resins or from animals e.g. casein or animal glues. Animal glues like blood albumen have been used in the plywood industry, but now are largely replaced by synthetic glues. Synthetic adhesives on the other are man-made and further classified into thermoplastic or thermosetting adhesives based on their response when exposed to heat. A thermoplastic adhesive turns soft and formable when heated, but regains its rigidity when cooled below its softening point many times without degradation. Examples of thermoplastic adhesives used in the wood composite industry include poly (ethylene-vinyl acetate), Poly (vinyl acetate) (PVA), Polyacrylate, polyethylene and polyvinyl chloride (PVC) (Ashori, 2007).

Upon heating, thermosetting adhesives will become soft, but cannot return to their original state upon cooling. At present, the particleboard industry depends more on synthetic thermosets, such as urea formaldehyde adhesive and phenol formaldehyde to manufacture panels. These account for up to 32% of manufacturing costs in the glued-wood composites industry (Sellers, 2000).

2.2.7.1 Phenol Formaldehyde Adhesives

Phenol formaldehyde adhesives are formed by a step growth reaction which may be either acid or base catalyzed. The reaction pathway varies and is dependent on the catalyst type. There are two types of phenol formaldehyde: resols and novolacs. Resols are synthesized under basic pH conditions with excess formaldehyde, whereas novolacs are carried out in acidic pH conditions with excess phenols. Phenol is reactive towards formaldehyde at the ortho and para sites (sites 2, 4 and 6) allowing up to 3 units of formaldehyde to attach to the ring. This forms a hydroxymethyl phenol, which is not usually isolated in novolacs but is found in resoles. The hydroxymethyl group is capable of reacting with either another free ortho or para site, or with another hydroxymethyl group. The first reaction forms a methylene bridge, and the second forms an ether bridge. The reaction scheme for preparing these two PF resins is shown in Figure. 2.3. (Blomquist et al., 1981). Base catalysed phenol formaldehyde resins are made with formaldehyde to phenol ratio of greater than one (usually around 1.5). Phenol, formaldehyde, water and catalyst are mixed in the desired amount, depending on the resin to be formed, and are

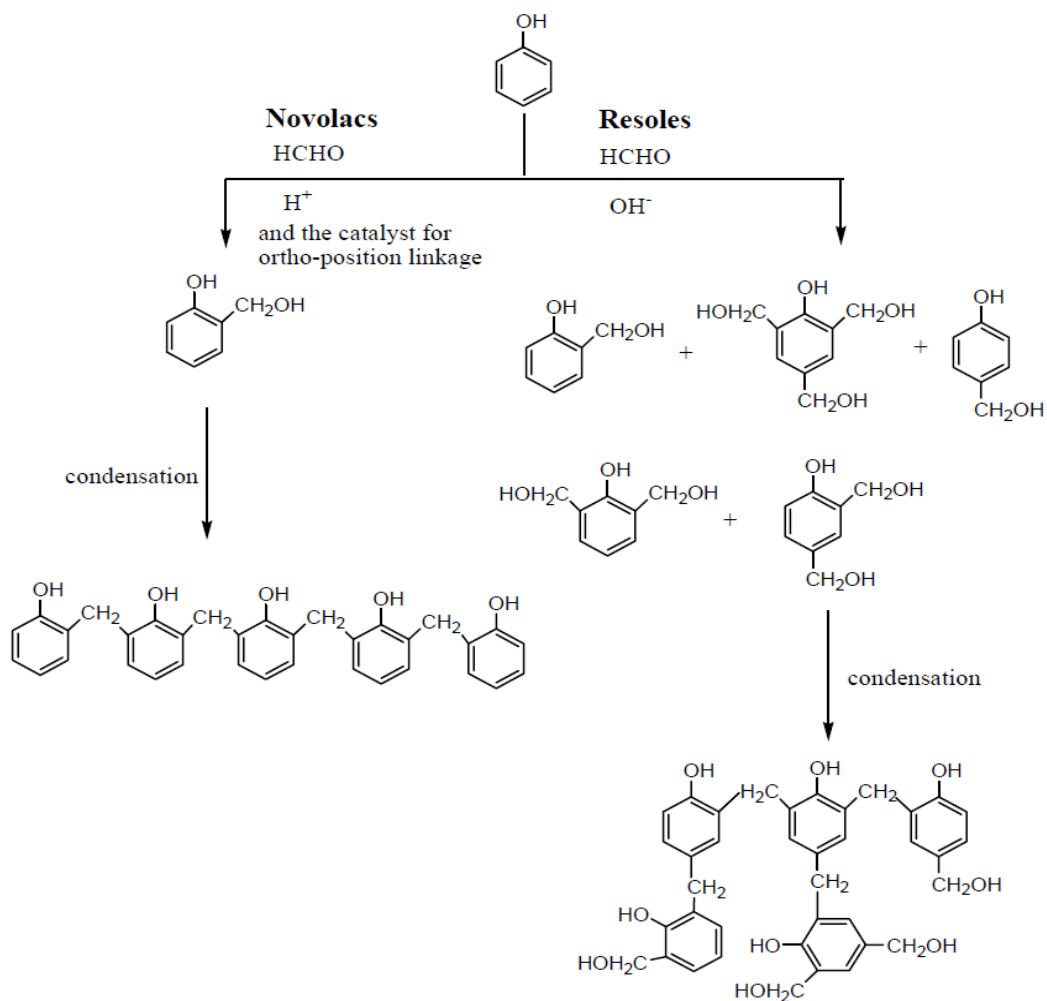


Figure 2.3 Reaction Scheme for Preparing Novolac and Resole PF Adhesives

then heated. The first part of the reaction, at around 70 °C, forms hydroxymethyl phenols. This results in thick reddish-brown resin. The rate of the base catalysed reaction initially increases with pH, and reaches a maximum at approximately a pH = 10. Acid catalysed phenol formaldehyde resins are made with a molar ratio of formaldehyde to phenol of less than one. Owing to the molar ratio of formaldehyde to phenol, they will not completely crosslink (polymerize) without the addition of a crosslinking agent. Additional amounts of formaldehyde therefore has to be added to further react the adhesive, prior to wood bonding to achieve

crosslinking of the adhesive system. Other possible enhancements will be the use of catalysts such as divalent metal acetates. This allows phenols to be predominantly linked at ortho-positions, thus resulting in novolacs with a linear structure. Because novolacs require a two step process, almost all commercially used PF adhesives are now resols (Koch, 1987).

Phenolic adhesives are preferred in a wide range of applications because they have several desirable characteristics, such as superior mechanical strength, heat resistance and dimensional stability, as well as, high resistance against various solvents, acids and water (Knop et al., 1985; Kopf and Little, 1991; Gardziella et al., 2000). Phenol Formaldehyde (PF) adhesives are the major thermosetting adhesives used for bonding panels for exterior applications and also in the manufacture of Oriented Strand board (OSB), softwood plywood and wafer boards (White, 1995).

2.2.8 Thermal Analysis of PF Adhesives and their Composites

One of the most important variables affecting the properties of thermosetting resins is the degree of cure. Thermosets are crosslinked through the curing process resulting in significant changes in the mechanical and physical properties. Various methods are available for the determination of the degree of cure, including spectroscopic, chromatographic techniques and thermal analysis. Thermal analysis methods are a group of techniques in which specific physical properties of a material are measured as a function of temperature, and include thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and thermomechanical analysis (TMA). Thermal analysis is an important analytical method in understanding the structure–property relationships and thermal stability of the composite materials (Focke et al., 1991; Pearce, 1997). Since cellulose fibers are going to be incorporated

in the molten adhesive to form composites upon polymerization, there is a need to evaluate the thermal characteristics of the resulting composites since the introduction of the fibers will strongly affect the maximum processing temperature and retention time of the materials during processing. Also, the degree of resin cure affects wood composites performance. For instance, DSC has been utilized to determine the relationship between formulation parameters and physical properties of PF resols (Christiansen & Gollob, 1985). Two peaks were found; the first peak was attributed to the addition of free formaldehyde to phenolic rings while the second peak was assumed to be due to the condensation reaction of methylolated phenols. DSC has also been used in comparing novolacs with resol resins (Chow & Steiner, 1979), as well as the curing kinetics of phenol formaldehyde resin and wood-resin interactions in the presence of wood substrates (He & Reidl, 2004).

The presence of water also plays an important role during cure. For instance, it has been reported that at 100°C, the curing rate of aqueous adhesives such as PF decreases with increasing moisture. This was explained by the fact that the extra water acts as an energy barrier to cross linking (Chow and Hancock, 1969; Chow and Mukai, 1972). Contrary to this, other studies reported that moisture in phenolic moulding compounds can actually accelerate the curing rate and the degree of cure. This is due to the fact that moisture improves the flowability of the compounds by plasticization (Tonogai et al., 1978; Tonogai et al., 1980, Wang & Reidl, 1994).

2.2.9 Lignocellulosic Fibers/Natural Fibers as Reinforcements in Adhesives

Natural fibers also referred to as cellulosic fibers originate from plants. Plant fibers are composed of cellulose. Examples of plant fibers are bast (or stem or soft sclerenchyma) fibres, leaf or hard fibres, seed, fruit, wood, cereal straw, and other grass fibres (Saheb & Jog, 1999). Recently, a number of researchers have been involved in investigating the use of natural fibres as

load bearing constituents in composite materials (Joshi et al., 2004). The choice of such materials in composites manufacture has increased due to their relative cheapness, their ability to recycle and for a good strength per weight of material (Bledzki & Gassan, 1999). Thus natural fibers can be suitably substituted for synthetic ones in reinforcement of the polymer matrix (thermoset or thermoplastic) (Table 2.3). Natural fibers such as flax and softwood-Kraft have strength characteristics comparable to that of E-glass fibers (Bledzki & Gassan 1999).

Like synthetic fibers, the ability of natural fibers to reinforce the composite for improved mechanical properties derives from their architecture. Natural fibers consist of mainly cellulose

Table 2.3 Mechanical Properties of Natural Fibers in Comparison with Synthetic Ones

Fibre	Density (g/cm ³)	Tensile strength (MPa)	Young's modulus (GPa)	References
Cotton	1.5-6	287-597	5.5-12.6	Bledzki et al., 1999
Jute	1.3	393-773	26.5	Bledzki et al., 1999
Flax	1.5	345-1035	27.6	Bledzki et al., 1999
Hemp	-	690	-	Bledzki et al., 1999
Sisal	1.5	511-635	9.4-22	Bledzki et al., 1999
Softwood kraft	1.5	1000	40	Bledzki et al., 1999
Crystalline cellulose	1.5	-	138	Hollister, 2005
E-glass	2.5	2000-3500	70	Bledzki et al., 1999
Aramide	1.4	3000-3150	63-67	Bledzki et al., 1999
Carbon	1.4	4000	230-240	Bledzki et al., 1999

fibrils embedded in a lignin matrix. These cellulose fibrils are aligned along the length of the fiber, giving it rigidity and maximum tensile and flexural strength. Lignocellulosic fibers are composed of carbohydrates, lignin and some extraneous materials. The carbohydrate portion contains the cellulose, hemicelluloses and other sugars. Cellulose is principally the reinforcing material of the fiber and reinforcement quality can further depend on microfibril angle and crystallinity.

2.2.10 Structure and Composition of Cellulose

Cellulose, by far is the most common natural polymer, occurring in a wide variety of living plants. Cellulose consists of D-anhydroglucose ($C_6H_{11}O_5$) repeating units joined by 1, 4-b-D-glycosidic linkages at C1 and C4 position (Nevell & Zeronian, 1985). These linear cellulose chains, known as microfibrils are approximately 3.5×10 nm in cross-sectional dimension and of indeterminate length. Naturally occurring cellulose chains have a degree of polymerization DP of approximately 10 000 glucopyranose units in wood cellulose and 15 000 in native cellulose cotton (Sjostro'm 1993). The molecular structure of cellulose is responsible for its supramolecular structure and this determines many of its chemical and physical properties (Figure 2.4). Characteristic of lignocellulosic compounds is their high density of hydroxyl groups which makes them hydrophilic (water absorbing) in nature.

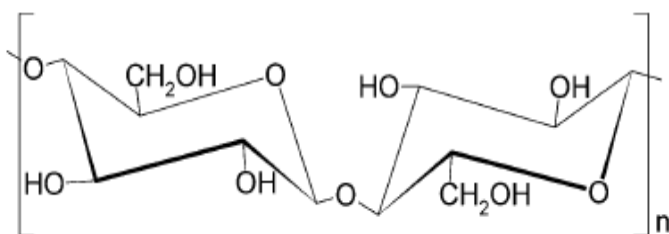


Figure 2.4 Chemical Structure of Cellulose

These hydroxyl groups govern the physical properties of cellulose. Solid cellulose forms a microcrystalline structure with regions of high order i.e. crystalline regions and regions of low order i.e. amorphous regions. The crystalline regions are up to several μ m long and a few nm wide. Because of their dimensions i.e. their high aspect ratio they are regarded as nano-crystals. Cellulose is resistant to strong alkali (17.5 wt %) but is easily hydrolyzed by acid to water-soluble sugars.

2.2.10.1 Preparation of Microcrystalline Cellulose

Nanotechnology is the science and control of matter at dimensions of roughly 1–100 nm, producing unique characteristics for novel applications. Typically, any cellulosic material could serve as a potential raw material source for the isolation of micro or nano-sized cellulosic structure. However, because of its great abundance, wood is preferred as the most suitable raw material for the preparation of nanomaterials.

The isolation of cellulose microcrystals, cellulose whiskers or other cellulosic structures in the nanoscale range (1-100nm) requires a two step approach involving chemical and/or mechanical operations. Different researchers have described different methods of separating cellulosic nano elements (crystals, whiskers, nanofibers etc) from wood and other natural sources (Azizi Samir et al., 2005; Oksman and Sain 2006; Ye 2007). However, the process of extracting microcrystalline cellulose elements from lignocellulosics can be simplified into four stages: delignification (pulping and bleaching), mechanical diminution, chemical diminution and dissolution.

Delignification is the initial process of extraction of cellulose crystals since lignin impedes the separation of wood into its component fibers (Moran et al., 2008). After pulping and bleaching, the remaining fibers consist of polysaccharides which are mainly cellulose. These fibers are a few mm long. These cellulose fibers can be used in composites, however greater strength properties are found at the nano scale. Microcrystalline cellulose is stronger than natural fibers but weaker than nanocellulose.

Mechanical refining involves passing the solids Kraft pulp fibers between rotating and stationary moving discs and high pressure homogenizing (Turbak et al., 1983; Zimmermann et al., 2004; Nakagaito & Yano 2003; Wang et al., 2007; Chakraborty et al., 2006; Svagan et al.,

2007). Refining crushes the fiber lumens while rupturing the S1 and S2 layers. . This results in microfibrilated cellulose (MFC) with a diameter range of 10-100nm. During refining, shear and compression forces act to aggregate nanoscale fibrils rather than individual crystal domains (Cheng et al., 2007).

In most cases, chemical diminution is carried out in conjunction with the mechanical treatment. Chemical diminution involves the hydrolyzing of pulp fibers in strong acids thereby removing the amorphous regions of the cellulose while leaving the crystalline portions in suspension (Dong et al., 1998; Edgar & Gray 2003; Wang & Ding 2004; Dufrense 2006; Lu et al., 2006). This produces cellulose microcrystals. The amorphous regions are removed because they act as openings for structural defects and are also responsible for the transverse cleavage of the micro fibrils into short monocrystals under acid hydrolysis (Battista et al., 1956; Marchessault 1961)

Dissolution involves using solvents to chemically treat cellulose. For instance, Oksman et al., (2006) were able to use a solvent to swell MCC thereby making its separation into nano fibers easier. The solvent employed was DMAc with Lithium Chloride (LiCl)

2.2.11 Cellulose Fibers and Composite Application

There has been an ongoing research aimed at utilizing cellulose fibers as load bearing elements in various polymeric composites (Eihchorn et al., 2001). The reinforcing efficiency of cellulosic fibers depends on the nature of the cellulose and its degree of crystallinity. For instance, wood in its natural state has elastic moduli of 10GPa, but increases to 40GPa when separated by the chemical pulping process, and a further 70GPa when disintegrated into micro fibrils by mechanical means (Figure 2.5) (Bledzki & Gassan, 1999). Cellulose nanocrystals have a high stiffness and modulus resulting in materials with lower density but better mechanical

properties. Sakurada (1962) reported nanocrystals to possess a Young's modulus of 250 GPa and strength of 10 GPa. Cellulose nano whiskers have also been reported to have elastic moduli as high as 130-250GPa (Noshino et al., 1995; Sturcova et al., 2005). This high strength property of cellulose nanocrystals makes it possible for them to be substituted for glass, carbon and other manmade fillers in the manufacture of biocomposites (Cheng et al, 2007; Zimmerman et al., 2004)

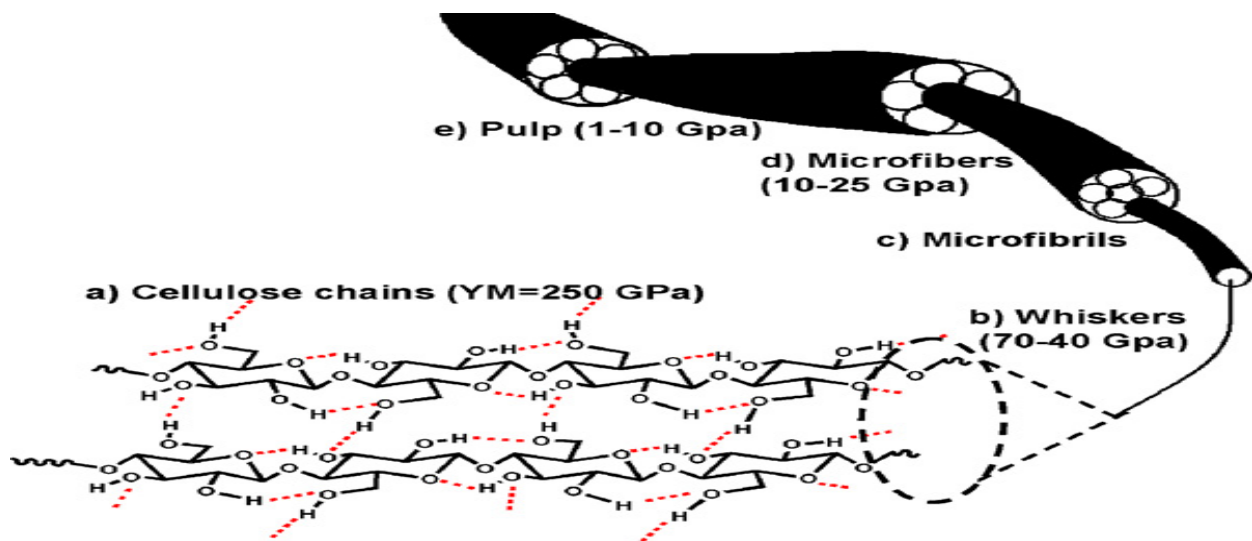


Figure 2.5 Schematic Representation of Cellulose Chemical Structure and Microfibril Formation (Kumar et al. 2009)

Nano scale cellulose fibers have attracted attention for reinforcing different polymers including thermoplastic and thermoset alike (Favier et al., 1995; Azizi et al., 2004; Yano & Nakahara 2004; Bhatnagar & Sain 2005; Oksman et al., 2006; Hubber et al., 2008.). Recent studies have revealed an increase in the mechanical strength of composites reinforced with nano cellulose in their polymer matrix (Dufrense et al., 1997; Lu et al., 2007; Oksman et al., 2006; Wu et al., 2007; Sain et al., 2005). This high reinforcing efficiency is due to the fact that, the nano cellulose will integrate in the polymer matrix much better due to their small size. Also, their larger surface area also reduces defects at the nano level (Ozgur & Oksman, 2008).

2.2.11.1 Modification of Cellulose Fibers

Although biofibers including cellulose have several merits (improved strength and mechanical properties), the extent to which they can be applied for industrial and commercial use is limited. This is due to their high surface interactions with one another relative to their interaction with PF resin and other matrix polymers. The mechanical performance of composites depends on the degree of fiber dispersion within the matrix polymer and the nature and frequency of fiber to polymer adhesion interactions. The presence of hydroxyl groups in the chemical structure of cellulose makes it hydrophilic (Yamane et al., 2006). Most polymers e.g. Phenol formaldehyde resins, are non polar (hydrophobic) and as such are incompatible with polar (hydrophilic) fibers, resulting in the formation of cellulose aggregates and poor dispersion within the polymer matrix. The presence of aggregates acts as defects within the composite. One way to improve the adhesion between the fiber and polymer matrix is to modify the cellulose surface. Methods on improving them include grafting hydrophobic groups on to them (Grunert & Winter, 2002) or coating them with surfactants (Heux et al., 2000). Recent technology shows that stable suspensions of cellulose nanocrystals can be made in dimethylformamide (DMF) without either addition of a surfactant or any chemical modification (Azizi Samir et al., 2004).

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Chapter 3 Thermal and Shear Strength Properties of Microcrystalline Cellulose (MCC) Phenol Formaldehyde Reinforced Composites

3.1 Introduction

The use of natural fibers offers an excellent opportunity to utilize waste materials and also produce new, low cost value-added products. Composites derived from natural and sustainable resources, especially cellulose have gained increased attention due to their several applications and advantages. Cellulose fibers, which are primarily derived from both woody angiosperms and gymnosperms, have many advantages including low cost, low density, high specific strength and modulus, biodegradability, low toxicity and availability as a renewable natural resource (Revol et al., 1992; Bledzki and Gassan, 1999; Bondeson et al., 2006; Panaitescu et al., 2007). Also, their properties compare favorably with other synthetic fillers (Mohanty et al., 2000; Curvelo et al., 2001). Various industries such as wood, automotive and biocomposites fields require a low density, high stiffness, low cost and thermal resistant element for composite reinforcement. The addition of cellulose has proven more attractive in recent years because of its ability to act as a natural reinforcement in thermoplastic and thermosetting resins (Ranby, 1951; Marcovich et al., 2001). Studies have indicated that when cellulose fibers are used as fillers together with either thermoplastic or thermosetting resins, the mechanical properties of composites usually improve when compared to non-cellulosic fillers (Helbert et al., 1996; Paul and Thomas, 1997; Wambua et al., 2003; Kiziltas et al., 2010). Factors influencing the mechanical performance of cellulose reinforced composites include the strength and modulus of the fiber, the strength and chemical

stability of the resin, as well as the effectiveness of the bond between resin and fibre in transferring stresses across the interface.

Microcrystalline cellulose (MCC) is highly crystalline and consists primarily of crystallite aggregates. Commercially known as Avicel, MCC has a potential as cellulose reinforcement/filler in many polymer matrices and composite manufacture. It is produced from high quality pulp by acid hydrolysis, which results in the removal of the amorphous regions leaving the crystalline regions intact (Marchessault et al., 1961; Matthew et al., 2005; Samir et al., 2005). Research shows that there is no significant differences among commercial grades of MCC and also the amount amorphous material in MCC samples do not exceed ~30% (Nakai, 1977; Rowe, 1994). The advantage of using cellulose fibers owes to its characteristic mechanical properties. Theoretical calculations for the modulus of MCC are estimated at 167 GPa (Bondeson et al., 2006). The lateral dimensions of MCC range from about 2–10 nm in diameter with a length that varies from 100 nm to several tens of micrometers. These dimensions therefore yield high aspect ratios and high specific surface area of about 150 m²/g (Eichhorn et al., 2001) compared to other conventional cellulose fibers. MCC has been employed as a reinforcing agent in several thermoplastics such as polylactic acid, polypropylene, polyethylene (Matthew et al., 2005; Petersson and Oksman, 2006; Cheng et al., 2007) as well as thermosetting resins like epoxy, phenolics and polyesters (Bledzki and Gassan, 1999; Shih, 2007). In all these instances, addition of these cellulose fibers resulted in significant improvements in mechanical properties including both tensile strength and tensile modulus.

However, the hydrophilic nature of natural fibers, its water absorption properties, lower dimensional stability as well as low thermal stability result in significant difficulties when incorporating them into hydrophobic resins. This can be overcome by chemical and physical

modification of cellulose fibers including acetylation, carboxylation, sulfonation, surfactants and grafting (John & Thomas, 2008)

Phenol formaldehyde (PF) adhesives are the major thermosetting adhesives used for bonding panels for exterior applications and also in the manufacture of Oriented Strand board (OSB), softwood plywood and wafer boards (Knop and Pilato, 1985, White 1995). Phenol-formaldehyde adhesives are formed by a step-growth polymerization reaction that can be either acid (novolacs) or base catalysed (resols). Phenolic adhesives are preferred in a wide range of applications due to their superior mechanical strength, heat resistance and dimensional stability, as well as, high resistance against various solvents, acids and water (Kopf and Little, 1991; Gardziella et al., 2000; Tonge et al., 2001). It is also accepted that wood products bonded with PF emit almost or no formaldehyde gas (Agarwal et al., 2000; Lin et al., 2004). Despite its several advantages, PF exhibits a characteristic brittle nature. A possible solution to this would be reinforcement with natural fillers. Currently, it is possible to reinforce PF through the addition of natural fibers including jute, oil palm fibers and sisal (Singh and Gupta 2005, Mu et al. 2009). Addition of MCC cellulose would be the next natural step in product development.

In the manufacture of wood composites, the performance of boards is affected by the degree of adhesive cure. Cure is affected by process and environmental variables such as temperature and relative humidity. Typically PF resins cure at temperatures above 150°C (Chow and Steiner, 1979). When cellulose has been incorporated into adhesives as fillers, the processing temperature of the resulting composites is restricted to less than 200 °C because cellulosic materials start to degrade near 230 °C and ensures a high enough temperature for adhesive cure (Samir et al., 2005). The interaction between wood and cellulose and, the cure properties of PF have been researched using differential scanning calorimetry (DSC) scans (Pizzi et al., 1994).

The study revealed that the presence of wood was shown to have a lower energy of activation than when PF adhesive was used alone. This was attributed mainly to the catalytic activation of the resin self-condensation induced particularly by carbohydrates such as crystalline and amorphous cellulose and hemicelluloses. Thermal analysis including DSC and thermogravimetric analyses (TGA) therefore served as important analytical tools in understanding the structure–property relationships and thermal stability of these composite materials.

The objective of this study was to investigate the influence of MCC filler loading on the mechanical properties of MCC filled Phenol formaldehyde composites. Microcrystalline cellulose was added to the PF adhesive system over a range of 0-10 wt%. The thermal behavior, as well as cure properties of the adhesive- microcrystalline cellulose matrix was studied using DSC and TGA. The shear strength of the reinforced PF adhesive was also determined following protocols from ASTM-D 1002 (2003). The flow property of the PF-MCC mixture was studied using a Brookfield viscometer and the interactions between the MCC and the phenolic resin was characterized by FT-IR spectroscopy.

3.2 Materials and Methods

3.2.1 Adhesive Polymer

The resin used was a commercial 13BO33 Liquid Phenol Formaldehyde (PF) solution intended for bonding wood based composites. Some of the properties of the adhesive determined in the Forest products laboratory (Auburn University) or obtained from source are described in Table 3.1. MCC was purchased from Sigma- Aldrich Chemicals, Inc., USA. The MCC used was powdery with a particle size in the range of 20-25 μ m and density 0.4 g/mL. It was stored in sealed containers before use to avoid moisture uptake from the environment.

Table 3.1 Properties of Phenol Formaldehyde Adhesive

Characteristics	Liquid PF adhesive (13BO33)
Appearance	Pale red to brown
Specific gravity	1.1-1.4 (1.225 measured in lab)
pH	10.5
Boiling point	~ 100°C
Solids content	54.957 (measured in lab)
Free formaldehyde content	< 0.1 by weight.

3.2.1.1 Determination of Solids Content

The solid content of the PF adhesive solution was measured by weighing a known amount of the adhesive into a pre- weighed Petri dish, then heating in an oven at 60°C for 30 min (Kopf and Little, 1991). After curing, the Petri dish was kept in a desiccator at room temperature for 2 hours and reweighed.

The solid content was calculated as follows:

$$\% \text{ Solid content} = \frac{\text{weight of oven dried adhesive}}{\text{weight of adhesive}} \times 100$$

3.2.1.2 Density Measurement

The density of the adhesive was also determined by measuring a known volume in a graduated cylinder and then measuring the mass of the cylinder with the known volume of adhesive. Density was calculated as:

$$\frac{\text{mass of adhesive}}{\text{volume of adhesive}}$$

3.2.2 Preparation of MCC Reinforced PF Matrix

All adhesive mixtures (PF and MCC) were prepared by mechanically mixing the aqueous PF with the microcrystalline cellulose at 0, 3, 6 and 10% (wt/wt) loading ratio for 10 min at room temperature. The particulate nature of MCC gives it a higher surface area which in turn makes it extremely viscous at loading rates higher than 10%. The adhesive solution was stored in a freezer until it was used in the experiment.

3.2.3 Thermal Properties (DSC and TGA)

3.2.3.1 Measurement of Cure Reaction Rates

The cure reaction rates of prepared samples were measured using a differential scanning calorimeter (TA Q200, TA instruments, DE, USA). The phenol formaldehyde resin liquid was removed from the freezer and were allowed to warm to room temperature. Two sets of sample preparations were analyzed; one liquid sample directly measured after preparation at ambient temperature and the second set of sample mixtures precured at 40°C for 48 hours before DSC measurements. The second was precured because using the liquid PF resin and mixtures directly caused significant amounts of blow outs in the DSC pans due to the buildup in pressure during heating. Samples of 10–15 mg were taken and placed in hermetically sealed aluminum capsules (TA high volume pans) that can withstand vapor pressures up to 10 MPa. Before the test, the temperature of the base heating block was maintained at 40°C. The total area under the exothermal curve, based on the extrapolated baseline at the end of the reaction, was used to calculate the reaction heat at a given temperature. Heat flow (W/g) was measured as a function of curing temperature using a dynamic DSC procedure. The samples were heated to complete cure as defined by the following equation (Myers et al. 1991):

Degree of cure (α) = $\Delta H(T) / \Delta H\text{-total}$

Dynamic scans were conducted using a heating rate of 5°C/min, and the scanning temperature ranged from 40 to 200°C.

3.2.3.2 Measurement of Thermal Degradation

The thermal degradation of the samples was also observed by means of a thermogravimetric analysis (Perkin Elmer model Pyris 1). Approximately 8.0-16.0 mg of a test sample was placed into an open experimental sample pan and combusted (30-800°C) in a nitrogen environment; with a flow rate of 50 mL/min and a heating rate of 10°C/min. Derivative TG (DTG) curves were used to express the weight-loss rate as a function of time.

3.2.4 Viscosity Measurements

The effect of adding cellulose on the flow properties of the untreated PF adhesive was measured at room temperature using a Rheometer (AR2000ex, TA Instruments, Newcastle, DE) with a #2 cylindrical spindle set according to ASTM D1084–97 (2003). Viscosity measurements were taken for both untreated PF and PF adhesive with the different cellulose loadings (i.e. 3%, 6% and 10%). Each sample was stirred and about 30 mg scooped on to the 25 mm disposable plate, ensuring all surface of plate is covered by sample. The upper cup was then lowered and the viscosity determined based on the formula below:

$$\text{Viscosity} = \frac{\textit{Shear stress}}{\textit{Shear rate}}$$

All samples were measured at room temperature (25°C).

3.2.5 Measurement of Shear Strength

The adhesive strengths of microcrystalline cellulose reinforced resin for wood-to-wood system were measured by the single lap-shear method and compared with that of untreated phenol formaldehyde resin following ASTM D-1002. Southern yellow pine (*Pinus spp*) flakes 1.27 cm wide, 0.162 cm thick and 10.61cm long (Figure 3.1) were used in the adhesion study as the wood-to-wood joints. Flakes were cut so that the grain was parallel to the length so as to ensure complete failure in the PF - cellulose composite only. The area of overlap for all samples was 1.27 cm X 2.54 cm and 0.162 mm. All flakes were conditioned at 62% RH, (22°C) for at least 24 hours before testing.

A lap shear joint was manufactured by bonding two smooth flakes together with MCC reinforced liquid PF adhesive on their smooth surfaces. The amount of adhesive, approximately 20 mg (± 2 mg) applied on the overlap area at one end of each flake was controlled to give a thin, uniform and continuous adhesive film. The two flakes were then lapped over the length of their coated ends. The sample flakes were glued in a hot press at a temperature of 150°C and a pressure of 10 N/cm² for 5 minutes. Six test samples were used for each adhesive mixture type as specified in ASTM D-1002 using a Zwick/Roell (Z010) at a loading capacity of 10KN at room temperature. Only 100% failure in the PF/cellulosic composites was sampled.

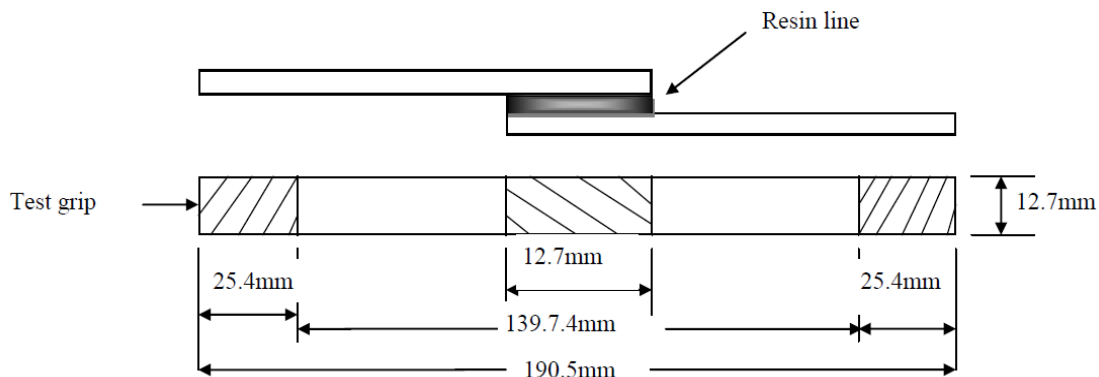


Figure 3.1 Diagram for Lap-Shear Test

3.2.6 Interaction between MCC and PF using FT-IR

FT-IR measurements were performed in a Perkin–Elmer Spectrum 400 instrument (Perkin Elmer Co., Waltham, MA) fitted with a single reflectance ATR diamond. The samples (PF and PF/MCC mixtures) were measured immediately after cure to avoid samples picking up moisture from the atmosphere. All measurements were made at room temperature (25°C). The contribution of CO₂ in air, moisture, and oxygen was eliminated by measuring the background spectra before every test sample. Each spectrum was recorded over 4 scans, in the range from 4000 to 650 cm⁻¹ with a resolution of 4 cm⁻¹.

3.2.7 Data Analysis

All statistical analysis of data sets was performed using SAS statistical software package (Version 9.1, SAS institute Inc., Cary, NC, 2010-2011). Microsoft Excel (Microsoft Office XP Professional, 2007) was used for initial data analysis and plotting of graphs.

3.3 Results and Discussion

3.3.1 Effect of Addition of MCC on Viscosity of PF

The results of the viscosity measurements of the untreated and filled PF adhesives are presented in Figure 3.2. The change in initial viscosity of untreated PF adhesive gives an indication of the effect of MCC on the flow properties of the adhesive before curing. As was expected, the addition of MCC to the adhesive matrix increased the viscosity significantly with the initial viscosity almost quadrupling with the addition of 10% MCC. This trend was statistically significant with the slope being different from zero. The larger surface area of the MCC resulted in noticeable effects in the properties of the resin even at lower loadings (<10%) (Eichhorn et al., 2001). If the viscosity was higher, it would be difficult to achieve an efficient distribution of the adhesive if it has to be sprayed to make any form of composite.

The result of the viscosity test is similar to the findings of Waage et al., (1991) who investigated the influence of fillers and extenders (wheat flour, pecan shell and clay) on the viscosity and physical properties of phenol-formaldehyde adhesives. Their results revealed increases in viscosity at loading rates of 25% wheat flour, 33% pecan shell and 33% clay. They further explained where the viscosities were higher; the resin mixtures could be warmed at 40°C to give acceptable spraying properties.

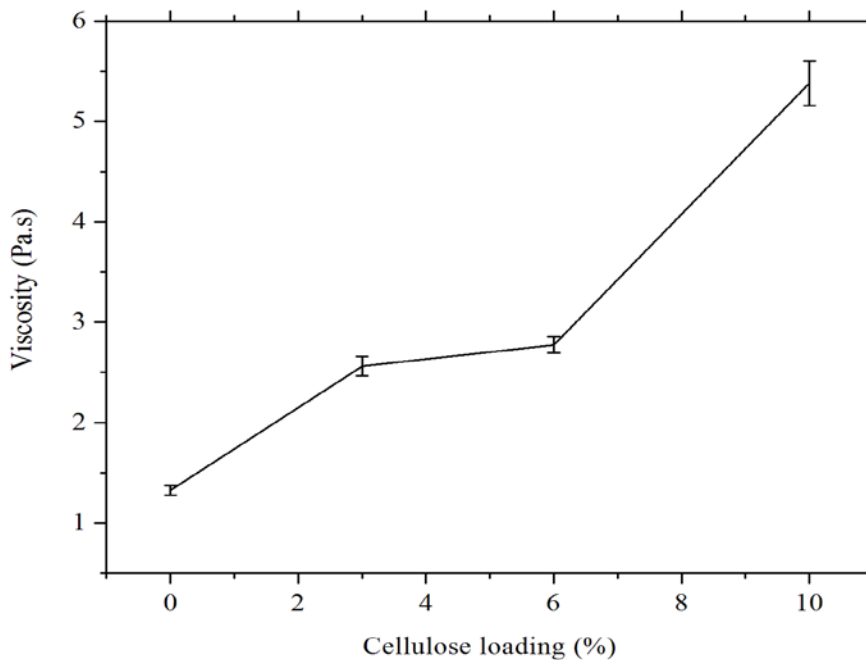


Figure 3.2 Effect of Cellulose Loadings on the Viscosity of PF Before Curing

3.3.2 Effect of MCC on Cure Properties of PF

Differential scanning calorimeter was used in studying the cure properties of the liquid phenol formaldehyde adhesive. The nature and method of preparation of the adhesive before running them through the DSC had an effect on the results. Liquid samples of the PF adhesive and PF/MCC samples for the DSC measurements were used. This resulted in significant blow

outs in the DSC aluminum lids. Since these were liquid adhesives, during the heating process, there was a high pressure build up owing to the escape of the solvents within the adhesive. This caused internal bubbling and resulted in blow outs in the DSC pans.

The results of the DSC run are presented in Figure 3.3. From Figure 3.3 it can be seen that the thermograms consist of two endothermic peaks which ranged from 115°C - 140°C and 140°C to 160°C in the case of the neat PF, and 100°C - 120°C and 130°C to 155°C for the MCC filled PF adhesives. The PF/MCC mixtures showed endothermic cure peaks similar to the untreated PF adhesive. The area under the broad peaks corresponds to the degree of cure based

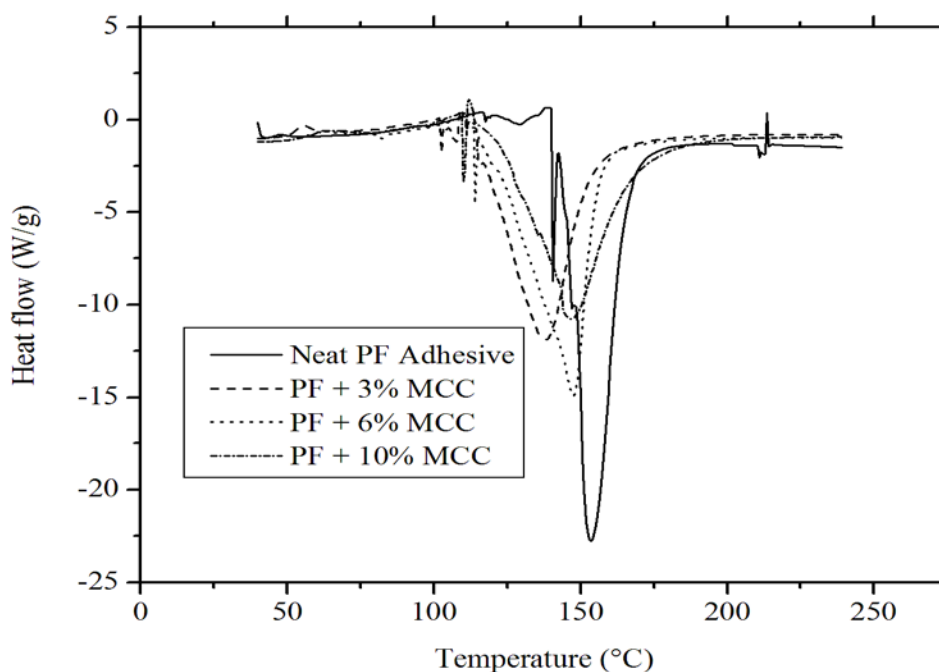


Figure 3.3. DSC thermograms of Liquid Neat PF, PF + 3% MCC + 6% MCC and PF + 10% MCC

on the assumption that heat flow (dH/dt) is proportional to the reaction rate (dR/dt) and that polymerization during cure represents the total degree of energy in the thermodynamic system

(Park et al., 1999). Comparatively, cure temperature ranges became wider and the peak heights shorter when MCC was added. When MCC was added to the PF adhesives, the cure (polymerization) peak for PF reduced from 153°C to 138°C, 149° and 147°C for addition of 3%, 6% and 10% MCC respectively. It can be seen that the addition of the MCC to the PF resin causes significant reduction in the cure temperatures of the untreated PF adhesive. The onset of cure and maximum cure temperatures were significantly lowered with the addition of MCC.

From Figure 3.3, the peaks within the ranges 115°C - 140°C and 100°C - 120°C for untreated PF and PF/MCC respectively, correlate with that found in literature. For instance, Christiansen and Gollob (1985) observed two exothermic peaks at 98-129°C and 139-151°C) for liquid phenol formaldehyde adhesives. The authors related the first peak to the methylation reaction, and the second one to the condensation reaction of PF adhesive. Typically two types of reactions are associated with resol PF cure; an addition reaction (methylation) and condensation (crosslinking) reaction. Methylation is a nucleophilic which involves the addition of formaldehyde into phenol ring while the condensation is a cross-linking (cure) reaction by methylated phenol into polymer molecules. Although the adhesive used for this experiment is a commercial PF with a low formaldehyde content (<0.1), peaks at 100°C-120°C are possibly attributable to methylation reaction.

The addition of MCC to the untreated phenol formaldehyde lowered their cure temperatures as well as the reaction rate of the PF/MCC samples. He and Reidl (2004) studied the interactions between chemical groups of PF and wood. They observed that the most important interactions are the ones between PF and cellulose and lignin since these two materials are the main components of wood. It has been reported that cellulose reacts with formaldehyde under acidic conditions (novolacs) to form ethers (Kottes et al., 1986). However, Allan and

Neogi (1971), Myers (1985), Bo and Reidl (2004) have concluded that no chemical reaction or a very small extent of reaction occurs between cellulose and formaldehyde or phenol formaldehyde adhesives under either neutral or alkaline conditions (resols). Contrary to this, Alma and Basturk (2001) have reported that cellulose reacts with phenol under special conditions (Figure 3.4).

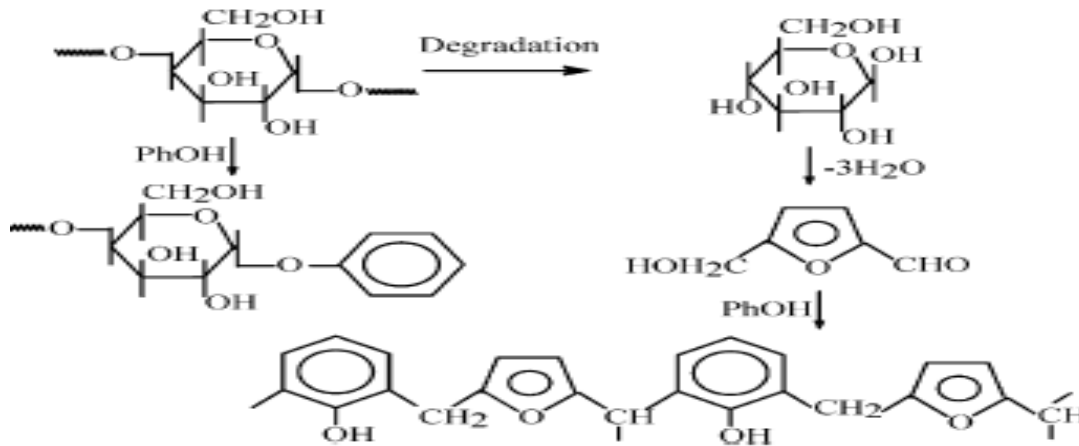


Figure 3.4 Reaction of Cellulose with Phenol (He & Reidl, 2004.)

It is therefore plausible to say that, the reductions in cure temperatures and their enthalpies when MCC was added to the untreated PF adhesive are due to possible interactions between chemical groups of the PF and the MCC. These interactions might have caused the low cure temperatures and enthalpy of the PF/MCC samples. It is believed that the interaction between PF and MCC lowered the peak cure temperatures.

Also, there is a phase change from a homogenous to a heterogeneous when PF is mixed with cellulose (He and Reidl, 2004). In other words, the addition of the cellulose changes the neat PF from a continuous phase to a dispersive one. In a homogenous PF curing system, all PF molecules come together to form a large crosslinked network. On the other hand, in the PF/MCC matrix, PF exists as many spots dispersed on the surface of the MCC powder. They further

explained that curing reactions of each spot are carried out as bulk PF resin does, but these spots are not able to link together with each other and then a part of the functional groups remains unreacted resulting in retardation in condensation reaction. It is possible that the addition of cellulose to the PF system results in barriers to the PF cure. Thus in neat PF adhesive, the PF oligomers molecules have unrestricted space to polymerize allowing for complete cure and maximum reaction enthalpy. On the other hand, as cellulose is added, the polymerization may be restricted by the distance between cellulose polymers resulting in lower reaction enthalpy and resultant maximum cure temperature.

3.3.3 Thermal Degradation of MCC/PF Matrix

The thermal behaviour (i.e. pyrolysis and thermal degradation) of the neat PF and PF reinforced adhesives was measured with the TGA at a heating rate of 10°C/min and in nitrogen atmosphere between 30°C and 800°C. The thermogravimetric (TG) curves and as well as their corresponding derivative thermogravimetric curves (DTG) for the untreated and reinforced PF adhesives are shown in Figures 3.5 and 3.6. A critical look at the TGA thermograms reveals degradation at four different stages of the heating process; i.e. around 150°C, 230°C, 430°C and 530°C. However there are slight differences in the amounts of solid residue after the heating or pyrolysis process. The untreated PF adhesive had 52% residue while the 3%, 6% and 10% MCC filled PF had solid residue content of 48%, 48% and 45% respectively. While the untreated PF adhesive was slightly more resistant to extreme temperatures (700C), it is unlikely that the adhesive will see this temperature in most service applications.

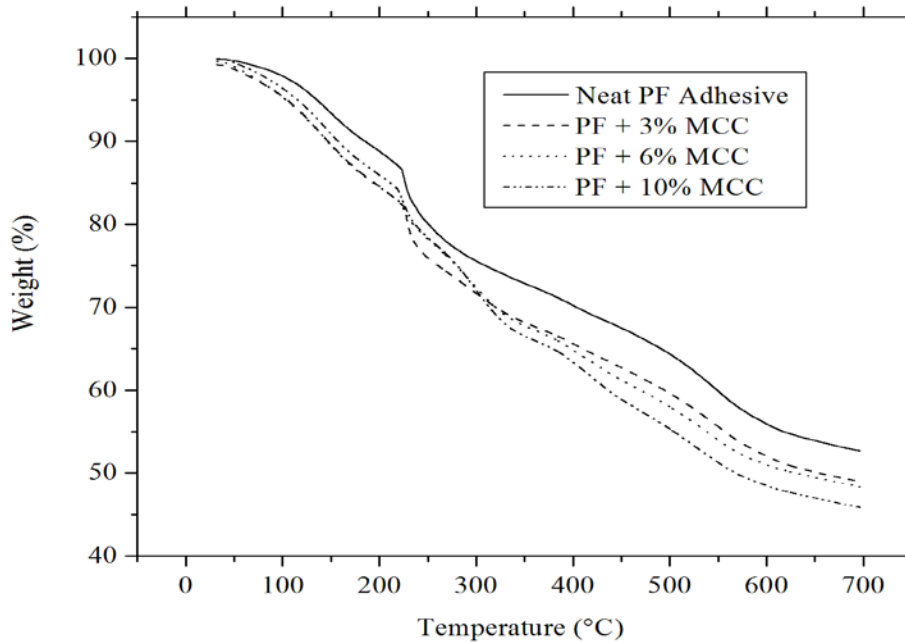


Figure 3.5 Thermogravimetric (TG) Curves for PF and MCC Reinforced PF Adhesive

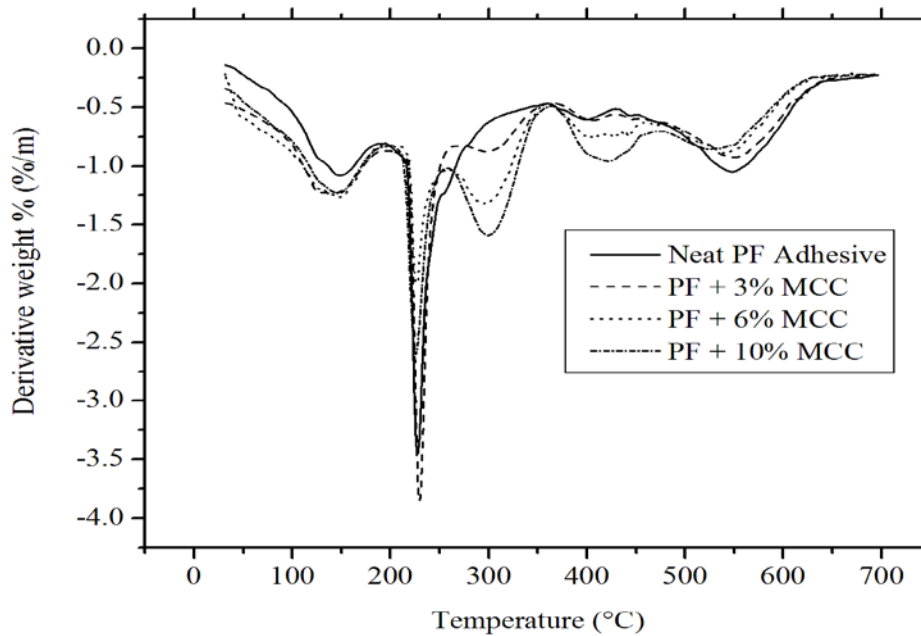


Figure 3.6 Derivative Thermogravimetric (DTG) Curves for PF and MCC Reinforced PF Adhesive.

There have been several attempts to explain the thermal degradation mechanism of Phenol formaldehyde adhesives (Chen et al., 2004; Kim et al., 2004). Generally, the thermal degradation of PF consists of three distinct stages. In this study, the following 3 temperatures 230°C, 430°C and 530°C were observed to represent the primary peaks associated with PF adhesive degradation. This was similar to Chen et al., (2008) who observed three overlapped peaks at 245°C, 418°C and 545°C in the DTG curves for a commercial resol PF adhesive. The first peak temperature in this study (230°C) was attributable to additional cross-links that are formed and small exposed groups of the cured resin are removed (Chen et al., 2008). The additional cross-links are as a result of condensation reactions between functional groups of the cured PF adhesive. The condensation reaction is between a phenol and a methylene group to form a carbon-hydrogen crosslink. The second peak temperature in this study was 430°C and this was attributable to the second stage where methylene bridges decompose or are broken into methyl groups with the formation of both phenols and cresols (Chen et al., 2008). The degradation of phenols occurs in the third stage (530°C). This involves the removal of hydrogen atoms from the ring structure and subsequently the evolution of hydrogen gas. Also, from Figure 3.6 there peaks in the region of 300°C for all MCC/PF samples which hitherto had not appeared in the neat PF adhesive sample. The peaks at 300°C correspond with the thermal degradation of the microcrystalline cellulose with the MCC/PF matrix (Alvarez, 2004)

The results obtained from the TGA thermograms also showed that the untreated PF had the highest initial decomposition temperature (160°C) and best overall thermal stability compared with the MCC filled PF adhesives. Moreover, when comparing the solid residue of the four types of resins, the untreated PF had better solid residue/char content (52%) after 700°C. This shows that the thermal behavior of the untreated PF is better than that of the 3%, 6% and

10% MCC filled resins. While the yield/residue was better for PF, the addition of cellulose only decreased the overall yield in minor amounts. This suggests that the reinforcement of PF adhesive results in only minor losses in final thermal degradation. This is explained by the fact that the charred layer acts as insulation and thus a physical barrier to heat transfer (Lin et al., 2004).

3.3.4 Effect of the addition of MCC on the shear strength of PF adhesives

The reference parameter that is most frequently used to investigate the bond strength of an adhesive in wood is shear strength because it's the most common interfacial stress encountered during service conditions (Pizzo et al., 2003). The bond strength of thermosetting adhesives develops during the curing process and is usually initiated by increased pressure and temperature. The shear strength properties of the untreated PF and PF/MCC samples were studied following protocols from ASTM D-1002 (2003) for lap shear strength. Figure 3.7 describes the relationship between increasing cellulose loading and tensile shear. From the graph it is observed that the addition of MCC to the PF system resulted in substantial increases in the shear strength. In particular, a rapid increase in strength occurred from the 3% to 6% MCC addition. After 6% MCC addition, further increases in cellulose loading resulted in only minor improvements in tensile shear.

Singha and Thakur (2008) reported increases in strength properties of Hibiscus sabdiriffa fiber reinforced PF resins up 30%. They explained that the increase in strength properties was due to chemical bonding between the methylol groups of the resin and the hydroxyl groups of the cellulose (Joseph et al., 1996; Singha and Thakur, 2008). Higher strength increases at higher fiber loadings is possible because there is more fiber-to-fiber contact at higher loadings. Also when subjected to load, fibers with the reinforced resin act as load carriers thereby uniformly

distributing the stress within the reinforced matrix (Singha & Thakur, 2008). The lower strength values at lower loadings is attributed to the fact that the fibers are not uniformly distributed resulting in high stress concentrations at a particular cellulose fiber and a more rapid failure resulting in lower strength values. However, at higher loadings maximum and uniform orientation of the fibers occurred.

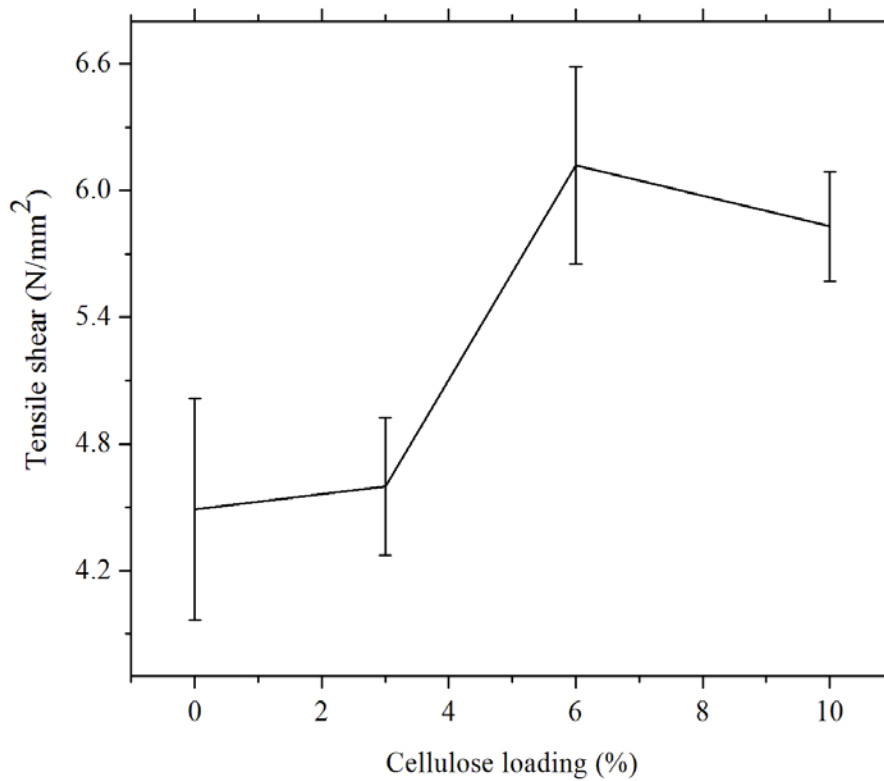


Figure 3.7 Effect of Cellulose Loadings on Shear Strength of PF Adhesive

3.3.5 FTIR Analysis of PF and MCC/PF Composites

The composition of polymeric materials can be readily determined by measuring their infrared spectra using a Fourier transform infrared (FT-IR) spectrometer and then comparing the results with a commercially available or specifically prepared spectral data base (Stuart, 2002).

FT-IR identifies types of chemical bonds (functional groups). The wavelength of light absorbed is characteristic of the chemical bond. By interpreting the infrared absorption spectrum, the chemical bonds in a molecule can be determined. FT-IR was used to examine possible interactions between the microcrystalline cellulose and phenol formaldehyde adhesive. In this experiment, powdered samples of the MCC were used whereas the untreated PF and PF/MCC mixtures were cured before use. The spectra for the MCC and PF/MCC mixtures are presented in Table 3.2. Characteristic peaks were assigned based on a literature review (Holopainen et al., 1998; Poljanšek & Krajnc, 2005). Figure 3.8 shows typical raw spectra for MCC powder as well as the PF adhesive with different cellulose loadings. The baseline corrected spectra for these samples is also presented in Figure 3.9.

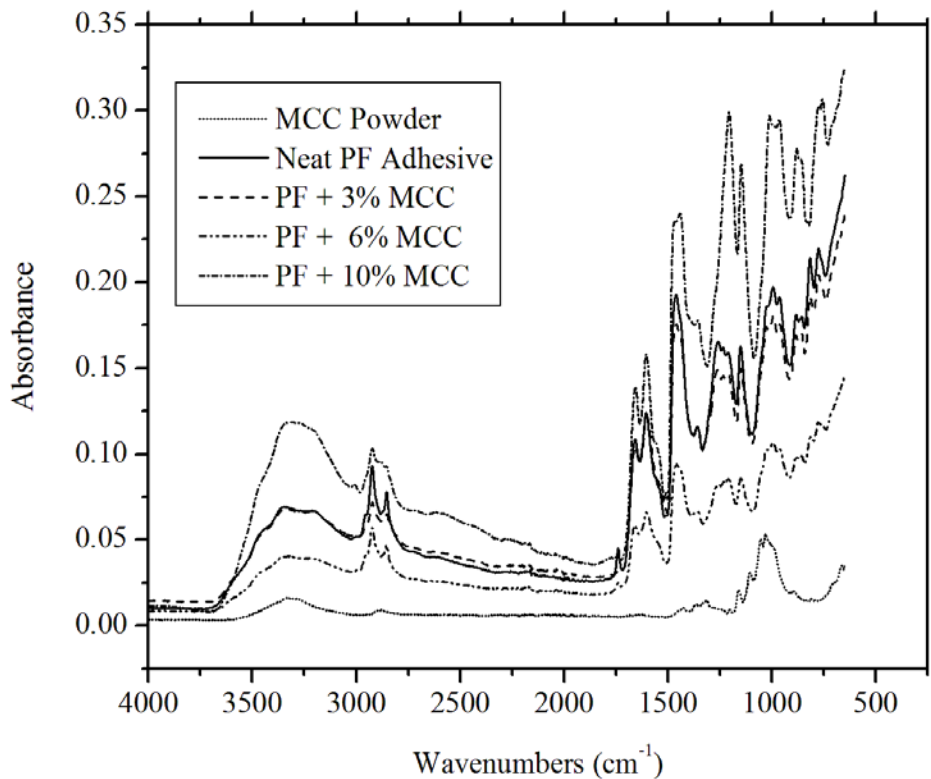


Figure 3.8 FT-IR Graph of Absorbance versus Wavenumber for MCC and PF composites

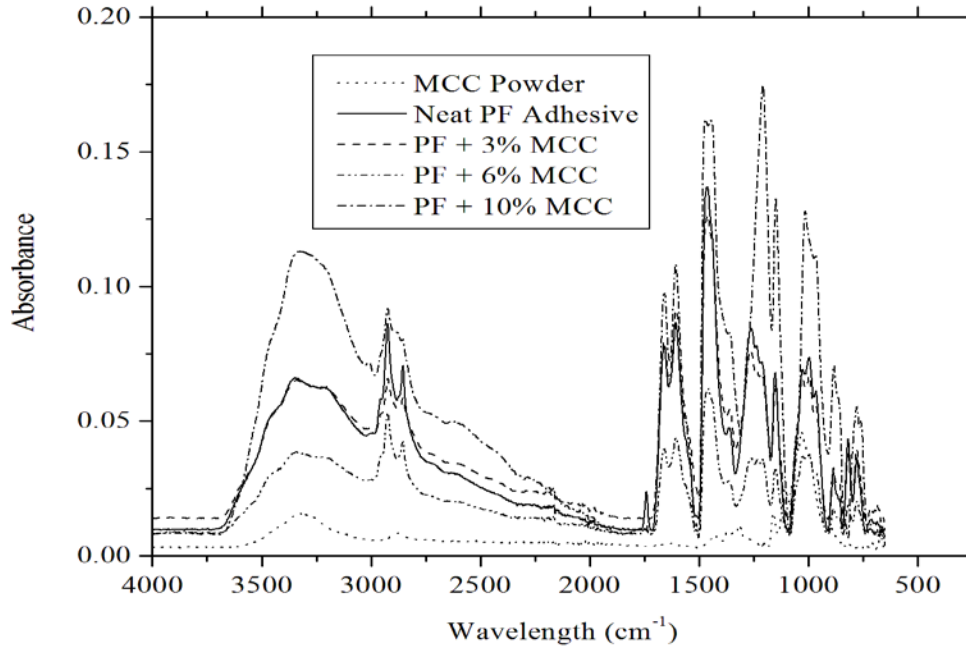


Figure 3.9 Baseline Corrected FT-IR Graph of Absorbance versus Wavenumber for MCC and PF Composites

It can be seen that all samples (both MCC and PF/MCC) presented two main absorbance regions. The first absorbance peaks were in the low wavelengths range of $700\text{--}1700\text{ cm}^{-1}$ while the second band of peaks occurred at higher wavelength range of $2700\text{--}3500\text{ cm}^{-1}$. For microcrystalline cellulose (MCC), the bands at 3348 and 1374 cm^{-1} is attributed to the hydrogen bonded O-H stretching vibration and O-H in plane bends respectively. Peaks at 2900 , 1432 , 897 cm^{-1} correspond to C-H stretching vibration while those at 1030 and 900 cm^{-1} corresponded to C-H in plane deformation and C-H out of plane vibration stretching respectively (Table 3.2). Absorbance bands which correspond to the PF adhesives are 1633 , 1478 and 1116 cm^{-1} for the C=C aromatic ring, C-H methylene bridge and C-O-C methylene-ether bridge, respectively

Table 3.2 FT-IR assignment of PF adhesive with MCC

Sample	Wavenumber, cm^{-1} observed in Literature	Wavenumber, cm^{-1} observed	Functional group
MCC	3348	3336.4	O-H stretching vibration
	2900	2889.5	-C-H stretching vibration
	1432	1431	-C-H
	1374	1367.4	O-H in-plane bend
	1030	1031.4	-C-H in plane deformation
	900	903.09	C-H out of plane in position ring stretching due to b-linkage
	897	839.17	-C-H
PF Resin	3400	3464	O-H stretch
	2925	2926	-CH ₂ - in phase stretching vibration
	2850	2855	-CH ₂ - out of phase stretching vibration
	1722	1743.7	C = O stretch (overlapped with OH scissors of water)
		1633	C = C aromatic ring
	1610	1609.3	C = C aromatic ring
	1460	1464.8	-CH ₂ - deformation vibration
	1450	1464.8	C = C benzene ring obscured by -CH ₂ - methylene bridge
	1378	1364	O-H in plane (Phenolic)
	1237	1239.7	asymmetric stretch of phenolic C-C-OH
	1153	1152.3	C-O stretch (methylol)
	1023	1021.3	-C-OH
	1000	1021.3	aliphatic hydroxyl
	992	997.7	C-H
	976	997.77	1,2,4-substituted benzene ring
885	880.17	CH out-of-plane, isolated H	
760	779	CH out of plane, ortho-substituted	

(Holopainen et al., 1998; Poljanšek & Krajnc, 2005). In the case of this study, these peaks showed up at wavelengths 1663, 1464 and 1152cm^{-1} respectively (Figure 3.8). Related peaks associated with phenols include bands at wavelengths 1378, 1237cm^{-1} and that for formaldehyde also includes 2855, 1743.7, 1021.3 and 997.7cm^{-1} . Functional groups corresponding to these wavelengths have been explained in Table 3.2. From Figure 3.8, it can be seen that the intensity

of the –OH stretching of the PF adhesive decreased with 3 and 6% MCC loading. However, the intensity of OH stretching with the addition of 10% MCC resulted in an increase. Such decreases in OH peak intensities suggest possible reactions between the OH groups of the cellulose and methylol groups of the PF adhesive (De et al., 2007). This was explained by the fact that the OH groups of the cellulose are consumed through covalent bonding when the composite cures. However, since the addition of 10% MCC increased OH peak intensity rather than decrease, the results of the experiment become inconclusive.

3.3.6 Conclusions

The effect of the addition of MCC on the thermal and strength properties of resol liquid phenol formaldehyde adhesive has been investigated. The important points obtained from this experiment can be summarized as follows:

1. The addition of cellulose to untreated PF adhesive increases the viscosity of the adhesive
2. The cure temperature of the untreated PF adhesive reduced significantly with the addition of MCC. This was an indication of a significant interaction between cellulose and PF adhesive.
3. The thermal stability of the untreated PF adhesive was reduced only slightly with the addition of MCC. The addition of cellulose only had minor impact on thermal degradation. This was explained by the fact that the untreated PF yields more solid residue resulting in char and consequent insulation. However, the reduction in thermal stability with addition of cellulose was low and negligible in service applications.
4. The shear strength of the PF adhesive increased nonlinearly with cellulose loading.

3.3.7 References

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Chapter 4 Effect of addition of Microcrystalline Cellulose on the Mechanical and Physical Properties of Particleboards

4.1 Introduction

Wood based composites allow for complete utilization of the tree resulting in better use of our timber resources. Worldwide, there has been a growing demand for composite wood products such as ply-wood, oriented strandboard (OSB), hardboard, particleboard, medium-density fiberboard and veneer board products (Sellers, 2000). Consumption of particleboard has grown from 9 million m³ in 1965 to 70 million m³ in 1997 (Buongiorno, 2003). Furthermore, global production is projected at 84.1 million m³ in 2013. In North America, 76 particleboard mills produced 10.952 million m³ in 1998, accounting for 19% of the total wood composites produced (Sellers, 2000 & 2001). ‘Particleboards’ are composite panels manufactured from discrete lignocellulosic materials, preferably wood. These materials are usually low quality trees, mill residue, wood shavings and agricultural materials such as wheat, or rice straw (Garay et al., 2009; Nemli et al., 2009; Li et al., 2010). A synthetic thermosetting adhesive is often used to bind these particles together. The interparticulate bond required to hold these particles together is developed during the hardening or curing process, which is usually carried out in a hot-press at a defined pressure, temperature and time (Chen and Beale, 2000). When compared to conventional lumber, particleboards have lower mechanical strength. However particleboards have several advantages over natural wood including easier engineering of their properties, more consistency in properties, and absence of solid wood defects such as knots that are removed during manufacturing (Maloney, 1996).

Particleboard panels are incorporated into various end uses such as cabinets, housing, floor underlayment, stair treads shelving, home construction, furniture, core material and structural sheathing (Maloney, 2003; Nemli et al., 2005). Known problems associated with particleboard manufacture include their moderate strength properties and increased swelling potential when exposed to moisture. Controlling both of these properties may be important for products such as floor underlayment where high mechanical properties and low swelling ability are important.

Several studies have been conducted to improve the physical and mechanical properties of particleboard. These studies include determining the effect of variables such as adhesive type and content (Papadopoulos et al., 2002; Hassan et al., 2009), wood species type (Zheng et al., 2006; Mendes et al., 2010), vertical density profile (Nemli Demirel 2007), cure temperature and moisture content (Adeyemi, 2002), press cycle time (Ashori & Nourbakhsh 2008), and size of raw material (Sackey et al., 2003) on the mechanical and physical properties of particleboard.

Urea formaldehyde (UF) adhesives have been used in bonding particleboards for interior use while phenol formaldehyde (PF) is more appropriate for outdoor (structural) applications (Wang and Gardner, 1999, Guru et al., 2006). When compared to PF, UF is relatively cheaper and yields adequate strength properties. However, there are concerns about formaldehyde emissions when UF is used. Replacing UF with PF could solve the problem of formaldehyde emissions; however, PF has its own disadvantages. Although PF yields better strength properties and moisture resistance, it is more brittle once cured (Mu et al., 2004).

A possible alternative to increasing composite strength will be to reinforce the adhesive with microcrystalline cellulose (MCC). Research has already found inexpensive fillers such as wood flour and wheat flour to have a positive reinforcing effect on plywood adhesive systems (So & Rudin, 1990). However, since particleboard adhesives are atomized into fine droplets (40-

60 micrometers) prior to the binding of wood particles, reinforcing elements need to be nano or micro sized. Micro scale cellulose fibers have therefore attracted attention for reinforcing different polymeric adhesives (Matthew et al., 2004; Kiziltas et al., 2010). The reinforced adhesive yields enhanced structural properties (Matthew et al., 2004; Panaitescu et al., 2007). This high reinforcing efficiency is due to the ability of the nano/microscale cellulose to integrate in the polymer matrix much because of the small size and larger aspect ratios (10-50 μ m) of the nano/microscale cellulose (Ozgur & Oksman, 2008).

Little research has been done to optimize particleboard materials cost while maintaining acceptable mechanical and physical properties. Furthermore, there is growing concern that conventionally utilized wood species will be depleted as biofuels and other biobased manufacturers will begin to compete for the same resources as wood based composites. Currently, the volume of hardwood is increasing owing to the preference of southeastern U.S. manufacturers to utilize softwoods for most structural and composite applications. The use of hardwood structural particleboard would therefore be highly desirable. Sweetgum (*liquidambar styraciflua*) hardwood offers the potential for use in particleboard manufacture against conventional softwoods like southern yellow pine. Sweetgum wood is low density, underutilized and abounds from Connecticut to Florida, ranging west all the way to Texas, Iowa and Oklahoma (Faust et al., 1991).

The objective of this paper was to manufacture a high strength particleboard from an adhesive system reinforced with microcrystalline cellulose. Liquid resol phenol formaldehyde (PF) was used as the adhesive. The effect of the cellulose reinforced adhesive system on the mechanical properties of the particleboard panels was investigated. Another aim of this project was to investigate the potential to utilize sweetgum as an alternative to southern pine.

4.2 Materials and Methods

4.2.1 Chemicals and Materials

Microcrystalline cellulose was purchased from VWR Chemical Co. (St. Louis, MO). Commercial Liquid resol Phenol formaldehyde (PF) adhesive (13BO33) for binding wood particles was provided by Louisiana-Pacific Corporation, (Hanceville, AL). Two different types of woods were used in this study: sweetgum (*Liquidambar styraciflua*) and southern yellow pine (*Pinus spp.*). Southern yellow pine wood particles were provided by Temple Inland, Monroeville, Alabama. A sweetgum tree with an average diameter at breast height (DBH) of 21 cm was harvested. After the foliage was trimmed, the tree was broken down into wood chips using a ring type flaker. The chips were conditioned at 20% moisture content and 65% relative humidity for two weeks before they were reduced to particles using a laboratory hammer mill with a 0.635 cm screen. Particles were classified into the two size categories of small and large, with oversize and undersize particles removed on a screening machine with 0.3 cm, 0.15cm, and 0.08 cm openings. The distribution of both southern yellow pine and sweetgum wood particles was evaluated using a digital image processing system (Camsizer, Retsch Technologies, Haan, Germany). The Camsizer works on the principle that bulk material (wood particles) flow falls between light source and cameras. The particles are optically recorded, digitized and processed in a computer connected to it. Results of the particle distribution test are shown in Figure 4.1. From Figure 4.1 it is seen that the distribution of both (sweetgum and southern yellow pine) larger sized wood particles were wider and tailed to the right when compared to smaller sized particles. the results also showed that the particles were similar to each other in size distributions since graphs of both larger and smaller sized particles run parallel to each other. These particles were stored at room temperature (25°C). The moisture content of the particles before use was 8%.

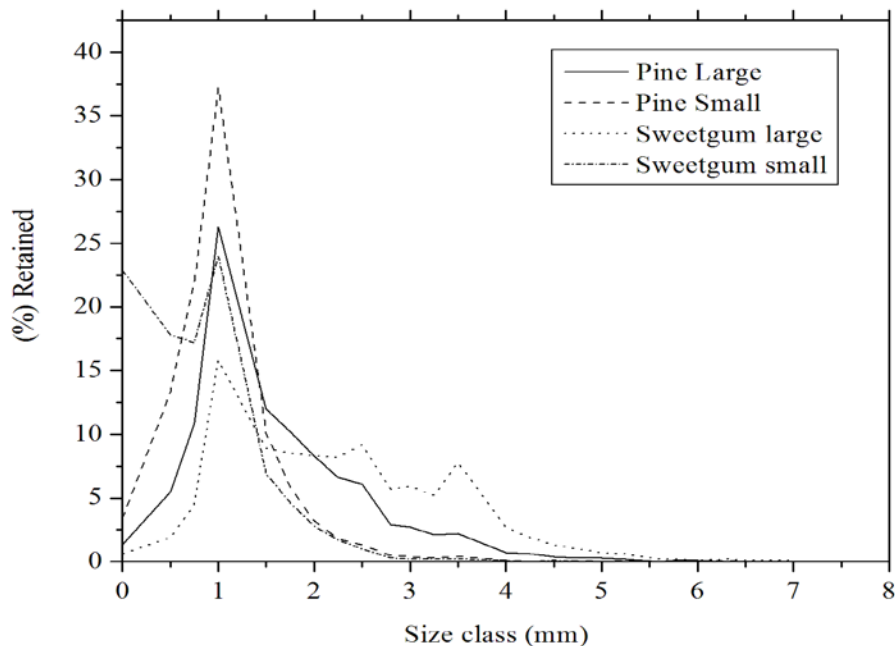


Figure 4.1 Size distributions of sweetgum and southern yellow pine Wood Particles

4.2.2 Panel Manufacture

Dried wood particles were blended with the MCC and phenol formaldehyde adhesive. The MCC loading rates were 0 and 10%. Fifteen percent adhesive was applied using an atomizing spray gun. During preliminary testing, a 12% PF loading was initially used but for some treatment combinations, a 12% PF loading was not enough due to the high surface area of MCC. All cellulose and adhesive loadings were based on dry weight of the wood particles. No wax was added. The materials were placed in a molding box (43.17 x 43.18 cm) and manually formed into homogeneous single layer board. The adhesive coated mats were then compressed on aluminum cauls in a hot press at a temperature of 200°C and a pressure of 30 kg/cm². The total pressing time was 5 minutes for all boards. A press time of 5 minutes was considered to be the time from initial contact of the press with the mat till the release of press pressure. Stops were placed in

position to produce boards of 1.27 cm target thickness. Three panels were made for each treatment at a target density of 0.70 g/cm³. A total of 24 boards were manufactured. The treatment SYSO was considered to be the control treatment based on the 0% MCC, smaller sized particles and SYP species. After pressing, the panels were trimmed to 43.18 x 43.18 x 1.27 cm. The experimental design, raw material used, forming and pressing conditions is illustrated in Table 4.1. After forming, panels were kept in a conditioning room with a relative humidity of 65% and a temperature of 20°C until their moisture contents equilibrated (23°C). These panels were then cut into test samples following protocols from ASTM D 1037 - 93.

Table 4.1 Properties of sweetgum and southern yellow pine Particleboards

Panel Type	Species	Particle Size (cm)	Adhesive loading (%)	MCC loading (%)	Avg. board density (g/cm ³)	Avg. board thickness (cm)	Panel replications
SGS0	Sweetgum	0.083	15	0	0.64 (0.005)	1.28 (.0046)	3
SGS10	Sweetgum	0.083	15	10	0.64 (0.011)	1.25 (0.0016)	3
SGB0	Sweetgum	0.230	15	0	0.66 (0.009)	1.29 (0.0054)	3
SGB10	Sweetgum	0.230	15	10	0.64 (0.014)	1.28 (0.0013)	3
SYS0	Southern Yellow Pine	0.113	15	0	0.67 (0.017)	0.503 (0.0052)	3
SYS10	Southern Yellow Pine	0.113	15	10	0.65 (0.004)	1.25 (0.0031)	3
SYB0	Southern Yellow Pine	0.162	15	0	0.68 (0.007)	1.28 (0.0037)	3
SYB10	Southern Yellow Pine	0.162	15	10	0.67 (0.006)	1.28 (0.0042)	3

Numbers in parenthesis are standard errors.

4.2.3 Water Resistance

The effect of the cellulose reinforced adhesive on thickness swell and linear expansion, were determined using protocols from ASTM D 1037 (2003). Sample particleboards were cut into squares measuring 30.48 x 30.48 cm. Three specimens of each treatment were soaked in tap water for 2 and 24 hours. To prevent them from floating, weights were used to fully submerge the samples in water. The thickness at the middle of the test sample was measured with a digital thickness gauge (C1050EB, Mitutoyo Co., Japan). Thickness and length measurements were taken before and after soaking. From these, thickness swell and linear expansion were calculated. Thickness swell percentage was determined from the formulae:

$$TS_{2h} (\%) = \frac{t_2 - t_1}{t_1} \times 100$$

$$TS_{24} (\%) = \frac{t_{24} - t_1}{t_1} \times 100$$

where t_1 is the thickness at the middle of the specimen before soaking, t_2 and t_{24} are the thicknesses of the test specimens after soaking for 2 and 24 h, respectively.

4.2.4 Density Determination

The density of the particleboard is an important variable that influences the mechanical properties of the board such as modulus of elasticity (MOE) and modulus of rupture (MOR). The density of the board can also be controlled to meet specific application requirements. American National Standard Institute (ANSI) has designated boards with target densities above 0.80 g/cm³ as high-density, between 0.64-0.80 g/cm³ as medium density and less than 0.64 g/cm³ as low density. The density of each test sample was measured before testing. The volume of the samples was calculated from length, width and thickness measurements taken from a digital caliper (CD-800 C, Mitutoyo Co., Japan). The bulk density was determined by dividing the particleboard mass (g) by its volume (cm³).

4.2.5 Mechanical Properties

All test samples were conditioned at 65% relative humidity to a constant temperature of 23°C for at least a week before testing. ASTM D 1037-99 standard was followed for tests of mechanical properties. Modulus of elasticity (MOE) and modulus of rupture (MOR) measurements were obtained from three-point bending tests. MOE is a ratio of the stress to strain curve that describes the potential ability of the board to sustain deformation. MOR, on the other hand, describes the stress to failure.

Samples for three point bending (evaluation of MOE and MOR) measured 22.86 x 7.62 x 1.27 cm. A span of 17.78 cm for bending at loading rate of 10KN/min was used. Tests were carried out on a Zwick/Roell Universal Testing machine (Z010, Zwick Roell Testing systems; Germany). Six replicates were evaluated for each treatment. MOE and MOR of the sample specimen were calculated based on the formulae:

$$\text{MOR (MPa)} = \frac{3PL}{2bd^2}$$

$$\text{MOE (GPa)} = \frac{P_1 l^3}{4bd^3} Y_1$$

where P is maximum load (N), P₁ is the load at proportional limit (N), b is the width of the specimen (mm), d is the thickness of the specimen (mm), Y₁ is the deflection corresponding to P₁ (mm), and L is the span (mm).

4.2.6 Experimental design and data analysis

To study the effects of cellulose loading and particle size on the physical and mechanical properties of the particleboards, a preliminary 3 x 2 factorial experiment was conducted. MCC loading was set at three levels: 0, 5 and 10%. Two levels of particle size were used. A 10% adhesive content (10%) was used for all treatments. Results of the initial experiment showed that

mechanical properties decreased with addition of MCC. Based on the results of the preliminary experiment, a 2 x 2 x 2 factorial design was conducted for the main experiment. Two levels of particle size were used (i.e. sweetgum: 0.08 and 0.23cm and southern yellow pine: 0.10 and 0.16 inches and two levels of cellulose loading (0 and 10%) were used. Adhesive content was increased to 15% after it was found that a 10% loading was not enough to support the high surface area MCC as indicated by visual inspection. Triplicates for each treatment were analyzed. Analysis of variance (ANOVA) and calculation of least significant differences (LSD) were carried out with Statistical Analysis System software (SAS Institute Inc., Cary, NC). Correlation between board mechanical properties and density was also investigated. Achieving a uniform density along the length of the boards was quite difficult since boards were hand formed. An adjustment using analysis of covariance (ANCOVA) was performed to correct for any variation in density that may have occurred between samples. Density was chosen as a covariate variable and adjusted means were separated using Least Significance Different (LSD) method.

4.3 Results and discussion

4.3.1 Effect of microcrystalline reinforced PF adhesive on mechanical and physical properties of particleboards

Analysis of variance (ANOVA) results of the effect of microcrystalline cellulose loading (0 and 10%) and the other factors (particle size and species type) on the mechanical and physical properties of particleboard are summarized in Table 4.2. Detailed analysis of the effect MCC loading, wood particle size and species type on mechanical and physical properties of the particleboards are presented in the following sections.

Table 4.2 Results of Analysis of Variance of Contrasts with MCC Loading on Mechanical and Physical Properties of Particleboards.

Panel properties	Source of variation	F-Ratio	Significance level
MOE	Particle size	18.82	0.0001
	MCC loading	55.12	< .0001
	Species	19.16	0.0001
	Species*Particle size	4.13	0.0497
	Species*MCC	3.59	0.0665
	Particle size*MCC	0.87	0.3561
	Species*Particle size*MCC	0.21	0.6506
MOR	Particle size	0.30	0.5848
	MCC loading	34.68	< .0001
	Species	16.93	0.0002
	Species*Particle size	22.80	< .0001
	Species*MCC	0.40	0.5328
	Particle size*MCC	2.45	0.1266
	Species*Particle size*MCC	1.07	0.3086
WFmax	Particle size	23.36	< .0001
	MCC loading	8.45	0.0063
	Species	61.50	< .0001
	Species*Particle size	52.36	<.0001
	Species*MCC	0.68	0.4153
	Particle size*MCC	2.86	0.0996
	Species*Particle size*MCC	1.18	0.2845
24- Hr Thickness swelling	Particle size	134.61	<0.0001
	MCC loading	88.53	<0.0001
	Species	0.87	0.3657
	Species*Particle size	12.78	0.0028
	Species*MCC	33.23	<0.0001
	Particle size*MCC	22.92	0.002
	Species*Particle size*MCC	30.25	<0.0001

4.3.2 Bending Strength

Table 4.2 shows a significant effect of MCC loading as well as species type used on the bending properties (both MOE and MOR) of particleboards manufactured, at a 0.05 probability

level. In addition, there was also a significant effect of the interaction between type of species used and particle size on the MOE and MOR of the particleboards made. This suggests that the

Table 4.3 Results of Mechanical Properties of Particleboards;

Panel type	MOE (GPa)	MOR (MPa)	WFmax
SGS0	1.6002 (0.0833)	11.027 (0.5128)	1249.50 (72.49)
SGS10	1.1019 (0.0885)	8.8138 (0.5442)	1035.75 (74.03)
SGB0	1.7043 (0.0673)	9.1757 (0.4139)	587.57 (58.29)
SGB10	1.2565 (0.0678)	7.3156 (0.4167)	618.35 (58.65)
SYS0	1.6571 (0.0679)	8.3137 (0.4176)	566.64 (58.75)
SYS10	1.3041 (0.0677)	5.8497 (0.4162)	375.31 (58.83)
SYB0	1.9216 (0.06865)	8.8054 (0.4225)	636.16 (59.33)
SYB10	1.7115 (0.06795)	7.9795 (0.4179)	499.28 (58.58)

Numbers in parenthesis are standard errors.

effect of particle size on mechanical properties depends on species type. Figures 4.2 and 4.3 show that static bending properties (MOE and MOR) of boards manufactured from the untreated PF adhesives are higher than those made from the MCC reinforced PF adhesive for both species types. The MOE of all boards varied from 1.3 – 1.9 GPa while MOR values ranged from 5.8 – 11 MPa. The MOE of boards made of small and large sized sweetgum wood particles decreased by 31 and 26% respectively with the addition of 10% MCC. The addition of 10% MCC to small and large sized southern yellow pine particles also decreased their MOE by 21 and 11% respectively.

For breaking strength, the addition of 10% MCC resulted in a decrease in MOR by 20% for both small and large particle treatments (sweetgum), whereas there was a decrease of 30 and 9% in MOR values of small and larger sized particle treatments for boards made from southern pine. ANSI A208.1-1999 standards states that the minimum values of MOE and MOR required for M-1 grade particleboard is 1.725 GPa and 11 MPa respectively. Boards produced from larger

sized sweetgum and southern yellow pine particles met the MOE requirement. However, almost all boards produced had MOR close to ANSI A208.1 requirement but slightly lower, including

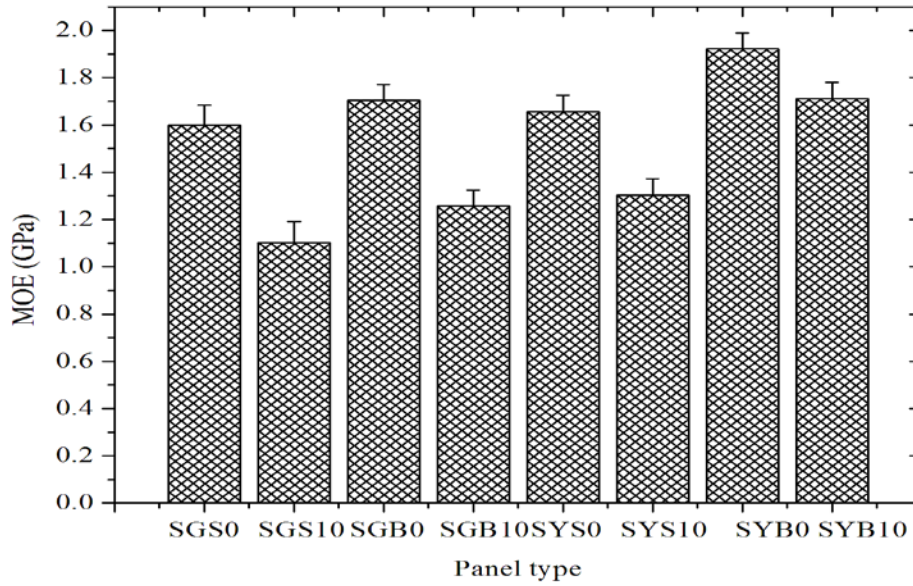


Figure 4.2 Effect of Reinforcing PF with MCC on the MOE of sweetgum and southern yellow pine Particleboards.

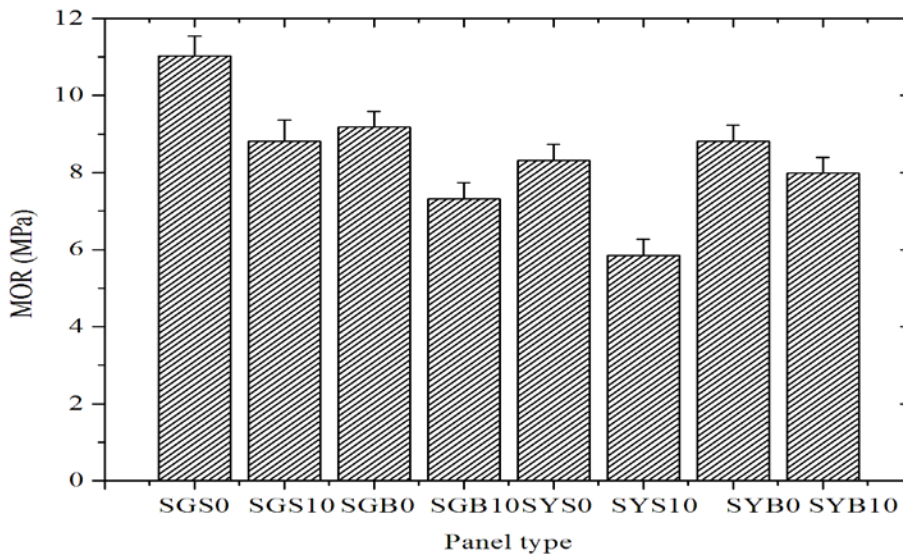


Figure 4.3 Effect of Reinforcing PF with MCC on the MOR of sweetgum and southern yellow pine Particleboards

the control. This result indicates that particleboard can be produced with either larger particles or sweetgum (or both) while maintaining acceptable mechanical properties.

4.3.3 Thickness Swell

Table 4.2 shows a significant effect of MCC loading as well as particle size used on the thickness swell properties (24-hour) of particleboards manufactured, at a 0.05 probability level. In addition, there was also a significant effect of the interaction between type of species used, MCC loading and particle size on the thickness swell property of the particleboards made and thus not all pairwise comparisons in Figure 4.4 and 4.5 can be made due to confounding. Figures 4.4 and 4.5 shows that using 10% MCC reinforced PF adhesive system increased the thickness swell properties (both 2 and 24 hour) of the boards irrespective of the particle size or species used. 24-hour thickness swell values ranged from 15 to 38%.

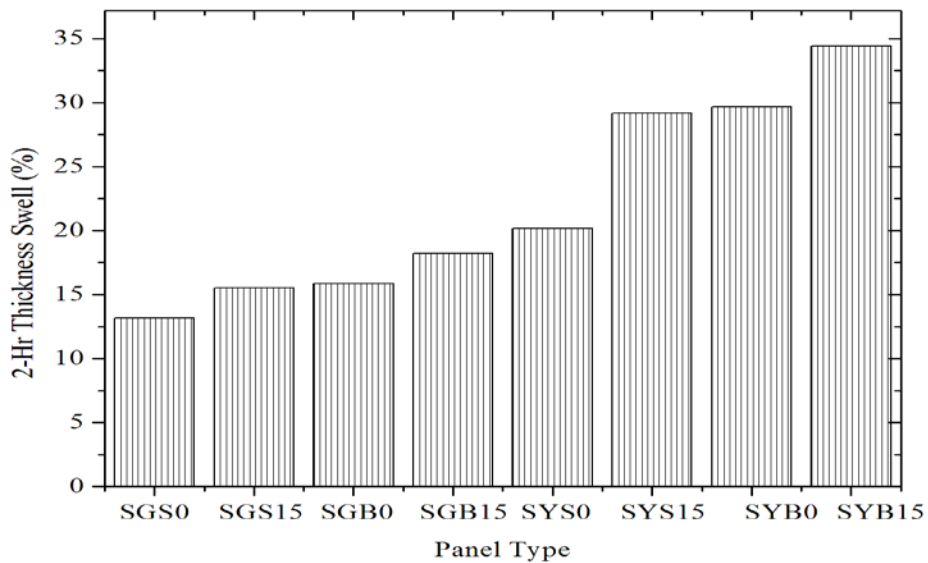


Figure 4.4 Effect of Reinforcing PF with MCC on 2-hour Thickness Swell Properties of sweetgum and southern yellow pine Particleboards

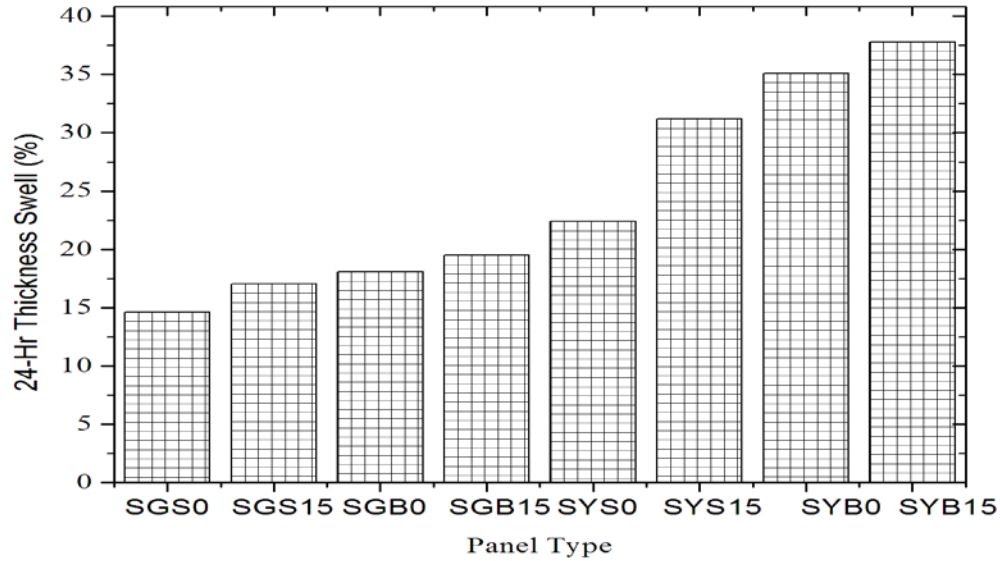


Figure 4.5 Effect of Reinforcing PF with MCC on 24-hour Thickness Swell Properties of sweetgum and southern yellow pine Particleboards

The mechanical properties (MOE and MOR) boards made from the untreated PF adhesive system was better than the MCC/PF adhesive boards. Irrespective of the wood species or particle size used, the addition of MCC to PF used in manufacturing the particleboards decreased their mechanical properties (Tables 4.2 and 4.3). A preliminary experiment was set up based on a 10% adhesive system. Visual inspection of wood particles blended with a 10% adhesive system showed that there was not enough adhesive coated on the wood particles as such its resultant lower mechanical properties. Based on this, a 15% adhesive loading rate was used for the main experiment and was necessary for all treatments such that comparisons between all treatments could be made. However, such an adhesive loading is normally not used in industry and may not be cost effective for industrial purposes due to the high cost of PF. In order to better fine tune the mechanical and physical properties of the particleboard to changes in length and species, it may

be desirable for industrial research and development to redo the experiment at resin levels normal to their manufacturing process.

An analysis of board thickness out of the press with a t-test revealed a statistical difference between panels with 10% MCC and no MCC. Panels with no MCC exhibited higher levels of springback. Springback is an irreversible thickness swell caused by the release of compression stress imparted to the board when the furnish is pressed in the hot-press (Geimer and Price, 1978; Palardy et al., 1989, Mohebbi et al., 2009). During springback there is debonding of the adhesion between the wood elements and the adhesive. Debonding results in lowering of mechanical strength such as shear strength, modulus of elasticity, and modulus of rupture. This is because these strength values are developed by the mechanical interlocking of the compressed particles in the composites (Nemli and Demirel, 2007). Natural wood is heterogeneous, consisting of hemicelluloses, cellulose and lignins. Within a furnish (wood particles blended with MCC/PF adhesive), it was found that the wood component would spring back more than the more refined and particulate microcrystalline cellulose. In a similar study, Yang and Gardner (2011) reported a decline in tensile strength of MCC-Polypropylene composites. The decline in strength values was attributed to the fact that the MCC acting as a stress concentrator within the more homogeneous PP matrix.

The size of the wood particles used affects the results of the bending strength properties (Kelemwork et al., 2009; Hashim et al., 2010). From Figures 4.2 and 4.3, it was shown that increasing the particle size in both species resulted in an increase in board MOE. A similar trend was observed for MOR values of southern yellow pine boards. The increased strength values of boards made from larger particles can be attributed to the increased thickness and length of the particles. This is explained by the fact that larger particles have less surface area compared to

smaller particles for a given volume of wood particles. When larger particles are used, resin is effectively applied because a greater percentage of the area of the wood particle is covered since they are thicker. This results in better bond and subsequently higher strength values.

Research has shown that an increase in the overall panel density has a positive influence on the bonding strength of composites (He et al., 2007; Nirdosha et al., 2009). Variation in the vertical density profile can also influence mechanical properties with higher densities in the surface being desirable. For instance, it has been shown that increasing the density of the face material in a three layered board resulted in improvements in bending strength (MOE and MOR) of boards (Wong et al., 1999; Nemli and Demirel, 2007). Table 4.1 describes the average densities of each of the panel types used in this experiment. The result show that the density of the boards varied from 0.64 0.68 g/cm³. This differed from the target panel density which was 0.70 g/cm³. The reason for the slightly lower densities than targeted was due to the evaporation of water during pressing. The weight of the particles during forming was measured on an air dry basis. The slightly lower strength values reported for the control resulted in some treatments not reaching the ANSI A208.1-1999 standard and were attributable to the fact that board densities were slightly below target. Since particle size increases were better than the control for mechanical properties and sweetgum was better in dimensional stability and indifferent in mechanical properties when compared to the control, it can be concluded that increasing particle size, changing species or both can yield acceptable panels that meet industry standards.

It is noteworthy to point out that a higher than desired resin loading was necessary to accommodate a 10% MCC loading. This likely resulted in better distribution and higher strength properties than conventional particleboard. A uniform distribution results in more efficient bonding of all flakes in the composite. The bonding strength also increases with adhesive content

(Ashori & Nourbakhsh, 2008) due to the removal of weak spots attributable to localized under application of resin. Increasing adhesive loading is always costly, but this was necessary due to the high surface area of MCC.

Dispersion of MCC in the blender to achieve a uniform resin distribution was also a challenge. Wood particles blended with the MCC looked dried compared to that of those with no MCC. Also there were noticeable amounts of MCC which settled on the bottom of the mat during forming and was another indication that there was not enough PF adhesive in the matrix the furnish dried out too quickly. The decrease in bending strength (MOE and MOR) of particleboards made with MCC can be attributed to the fact that, there wasn't enough bonding strength generated to hold particles together. This therefore had a negative effect on the board mechanical properties.

Results of the 2 and 24 hour tests are detailed in Figures 4.4 and 4.5. Thickness swell was higher in MCC/PF boards than those made from untreated PF. The type of species used as well as particle size influenced the results of the thickness swell test. After 24 hours, thickness swell was higher in southern yellow pine particleboards than their sweetgum counterparts. It was also obvious that thickness swell increased with increased particle size. The increased particle size resulted in more void space during consolidation resulting in higher porosity and easier diffusion of water through the boards during soaking.

4.3.4 Conclusions

The results obtained from this experiment led to the following conclusions:

1. Adding microcrystalline cellulose to phenol formaldehyde adhesive led to a decline in board mechanical properties. Results from static bending tests revealed a decrease in both

MOE and MOR values. This was explained by a springback effect which occurs more in MCC/PF bonded particleboards.

2. Particle size and species type had a significant effect on mechanical properties. MOE and MOR increased with increasing particle size. This was perhaps so because increasing the size of the particles lowered the overall surface area resulting in better adhesive coverage.
3. The addition of MCC resulted in higher thickness swell properties.
4. Conventionally particleboards have been made from southern yellow pine. Results of this study showed that the bending strength values of sweetgum boards compared favorably with that of southern yellow pine. Sweetgum boards also had better and improved swell properties than southern yellow pine. Sweetgum is thus a viable alternative to southern yellow pine and will lead to an efficient utilization of our forest resource since sweetgum is currently underutilized.

In summary, due to springback, the addition of MCC was not successful in improving the mechanical properties while increasing the particle length did have a positive influence on both strength and stiffness. Because the addition of MCC may be more costly than increasing particle length, manufacturers may wish to increase particle length for strength improvement if surface smoothness is not a concern. Additionally, sweetgum particleboards were at least equivalent to southern pine boards in mechanical and physical properties. Since sweetgum is widely available in the southeastern United States, but is currently underutilized, it may be a viable alternative to southern pine in the production of particleboard.

4.3.5 References

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