

Organic fillers in phenol-formaldehyde wood adhesives

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Abstract

Veneer-based structural wood composites are typically manufactured using phenol-formaldehyde resols (PF) that are formulated with wheat flour extender and organic filler. Considering that this technology is several decades old, it is surprising to learn that many aspects of the formulation have not been the subject of detailed analysis and scientific publication. The effort described here is part of a university/industry research cooperation with a focus on how the organic fillers impact the properties of the formulated adhesives and adhesive bond performance. The fillers studied in this work are derived from walnut shell (*Juglans regia*), alder bark (*Alnus rubra*), and corn cob (furfural production) residue.

Alder bark and walnut shell exhibited chemical compositions that are typical for lignocellulosic materials, whereas corn cob residue was distinctly different owing to the high pressure steam digestion used in its preparation. Also, all fillers had low surface energies with dominant dispersive effects. Surface energy of corn cob residue was a little higher than alder bark and walnut shell, which were very similar.

All fillers reduced PF surface tension with effects greatest in alder bark and walnut shell. Surface tension reductions roughly correlated to the chemical compositions of the fillers, and probably resulted from the release of surface active compounds extracted from the fillers in the alkaline PF medium.

It was shown that viscoelastic network structures formed within the adhesive formulations as a function of shear history, filler type, and filler particle size. Relative to alder bark and walnut shell, the unique behavior of corn cob residue was discussed with respect to chemical composition.

Alder bark and walnut shell exhibited similar effects with a decrease of adhesive activation energy. However, corn cob residue caused much higher adhesive activation energy.

Alder bark exhibited significant particle size effects on fracture energy and bondline thickness, but no clear size effects on penetration. Regarding corn cob residue and walnut shell, particle size effects on fracture energy were statistically significant, but magnitude of the difference was rather small. Classified corn cob residue fillers all resulted in a similar bondline thickness (statistically no difference) that was different walnut shell.

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Chapter 1 Motivations and research outline

Phenol formaldehyde (PF) resins are outstanding wood adhesives that remain the preferred resin used to manufacture structural wood-based composites from veneer, such as plywood and laminated veneer lumber. Organic fillers based upon biomass sources such as nutshells and tree bark have been commercially formulated with phenol-formaldehyde (PF) resins for many decades. PF/filler/extender formulations are designed to meet a variety of performance criteria including bulk flow, prepress tack, precure moisture retention, gap-filling properties, post-cure strength and durability [1, 2]. In spite of their lasting commercial significance, such organic fillers have been the subject of very little detailed analysis that resulted in scientific publication. This study, representing an industry/university cooperative research effort, is intended to broaden the scientific base underlying current and future technologies by investigating filler type and particle size effects on PF adhesive performance. Three organic fillers studied here are flours of walnut shell, alder bark, and corn cob (furfural production) residue. The research is outlined as follows:

In Chapter 2, literature is reviewed about phenol formaldehyde resin, organic fillers, filler effects on adhesive bond performance as well as rheological behavior, and analytical methods.

In Chapter 3, organic filler chemistry is analyzed. Chemical compositions of fillers and filler alkaline leachates are investigated by ion chromatography (IC) and ultraviolet–visible spectroscopy (UV-Vis). Different acid groups in fillers are quantified by conductometric titration.

In Chapter 4, surface characteristics of organic fillers are investigated with the column wicking method and the Washburn equation. Rigorous criteria are developed to ensure the reliability of final filler surface energy. Filler specific surface area is derived from the wicking method and compared to Brunauer–Emmett–Teller (BET) measurements.

In Chapter 5, influence of organic fillers on adhesive surface tension is studied by using the drop weight method with the Harkins-Brown (HB) and the Lee-Chan-Pogaku (LCP) correction, and the drop shape method. Measurement procedure is optimized. Also, adhesive viscosity effect on surface tension measurements is investigated.

In Chapter 6, influence of organic filler type and particle size on adhesive rheology is studied. Rheological analysis involves a two-step acquisition of sequential, steady-state flow curves. Additionally, creep and frequency sweep testing is employed to understand structure change of the formulated adhesive system due to shearing.

In Chapter 7, influence of organic fillers on adhesive cure behavior is studied by using differential scanning calorimetry (DSC). Activation energy of the formulated adhesive is calculated with Kissinger method.

In Chapter 8, influence of organic filler type and particle size on adhesive bond performance is evaluated by double cantilever beam (mode-I) fracture testing. Moreover, adhesive bondline thickness (on un-cracked fracture specimen) and adhesive penetration (on cracked fracture specimen) are measured using reflected and transmitted microscopy techniques, respectively. Correlation between adhesive bondline thickness, fracture toughness, and penetration are statistically analyzed.

References

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Chapter 2 Literature review

Few building materials possess as long a history of applications as wood. It is not only due to its renewable characteristic, but also unique properties that make it suitable for various applications. In addition, the available wood resources nowadays have been switched to the fast-growing plantation with small diameters from the large-size lumber in the past. The operation to break down solid wood into smaller dimensions and then reform them into composites enables the increase of efficiency in the use of timber resources and the enhancement of composite performance. Adhesives are a key element in the composites such as plywood, oriented strandboard and fiberboard. Bonding wood with adhesives dates back to ancient Egypt when people used natural materials such as blood, casein, and starch as adhesives for wood furniture and tools [1, 2]. Since phenol-formaldehyde (PF) as the first synthetic polymer was developed in the early 1900s, wood adhesives shifted from natural to petroleum-based adhesives which enabled bonded composites as construction materials possessing an exterior durable bond [3, 4]. Various synthetic adhesives like resorcinol formaldehyde, melamine formaldehyde and urea formaldehyde have emerged and have been commercialized in wood composite production. Among them, PF adhesives dominate the bonding of veneer based composites such as plywood, laminated veneer lumber due to the greater water resistance and durability in the exterior environment.

PF adhesives are commonly formulated with organic fillers. The low-cost organic fillers are typically derived from lignocellulosic biomass waste streams such as nutshell flour, tree bark, and furfural-production residues. They act as a bulking agent and control the adhesive rheological behavior, fundamentally influencing wood/adhesive bond performance. Corn cob residue, walnut shell and alder bark fillers have been commercially utilized in PF resin formulations since the 1950s [5]. However, little work has been published on fundamental aspects of filler properties on adhesive performance. This study, representing an industry/university cooperative research effort, is intended to study how the organic fillers impact the properties of the formulated adhesives and adhesive bond performance.

2.1 Phenol-formaldehyde resin

Phenol-formaldehyde (PF) resin, the first synthetic polymer, has been extensively applied in wood working, molding and insulation fields since the first commercialization in the early 1900s by Dr. Leo Baekeland [3, 6].

PF resin results from the polycondensation of phenol with formaldehyde. Typically, the formaldehyde is added to phenol and then the chain-growth reaction occurs by the formation of prepolymers at temperatures less than 100 °C. The further cross-linking or hardening reaction occurs at temperatures above 100 °C. Depending on the reagent ratios and pHs, two prepolymer types are produced. Novolaks are obtained with a deficiency of formaldehyde under the acidic pH region, while resols are formulated with an excess of formaldehyde under alkaline conditions [3]. With alkaline catalysis, condensation is the predominant step because formaldehyde attack on the phenol is much faster where phenolic hydroxyl is deprotonated. Resols have been extensively used as exterior-grade wood structural adhesives. Thereby, the chemistry and properties of resols are reviewed below.

Resols are typically synthesized through adding formaldehyde to react with phenol forming hydroxymethylated phenols (HMPs). The HMPs self-condense to oligomers that are called prepolymer resins. The prepolymer resins undergo further polymerization to form a crosslinked network [7].

Hydroxymethylated phenols (HMP) are formed as phenol is added into aqueous formaldehyde under alkaline conditions. A more reactive phenoxide ion is formed by deprotonation of a phenolic hydroxyl group under the basic condition. Due to the resonance stabilization shown in Figure 2-1, the electron density at the para and ortho positions of the aromatic ring is relatively higher that results in electrophilic substitutions on these positions with formaldehyde. Besides the mono-substituted HMPs like 2-hydroxymethylphenol (2-HMP) or 4-hydroxymethylphenol (4-HMP), some di- and tri-substituted HPMPs are obtained with further substitutions shown in Figure 2-2 [7].

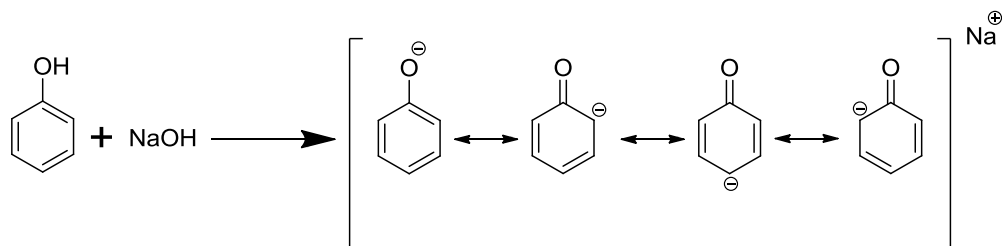


Figure 2-1 Formation of reactive phenoxide ion under alkaline conditions [7].

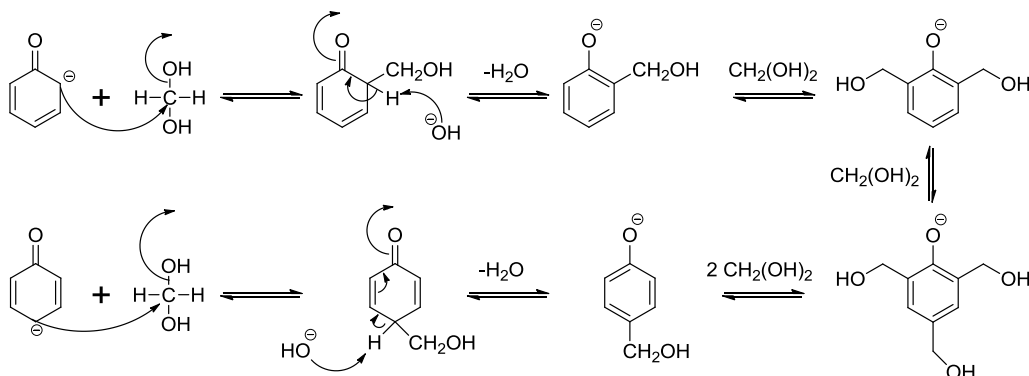


Figure 2-2 Formation of mono-, di- and tri-substituted hydroxymethylphenols (HMP) [7].

After the formation of HMPs at lower temperature typically below 60 °C, the HMPs undergo self-condensation and/or condense with phenols to form the prepolymer resins [8]. Quinone methide was proposed to be the important intermediate in HMP condensations as shown in Figure 2-3. Because quinone methides are strong electrophiles, they tend to undergo electrophilic substitutions with the nucleophilic sites on HMPs and/or phenols [9]. Generally, HMP condensations are terminated at the oligomeric resitol stage (B stage) with the exact molecular weight distributions depending on the applications of these prepolymer resins [10].

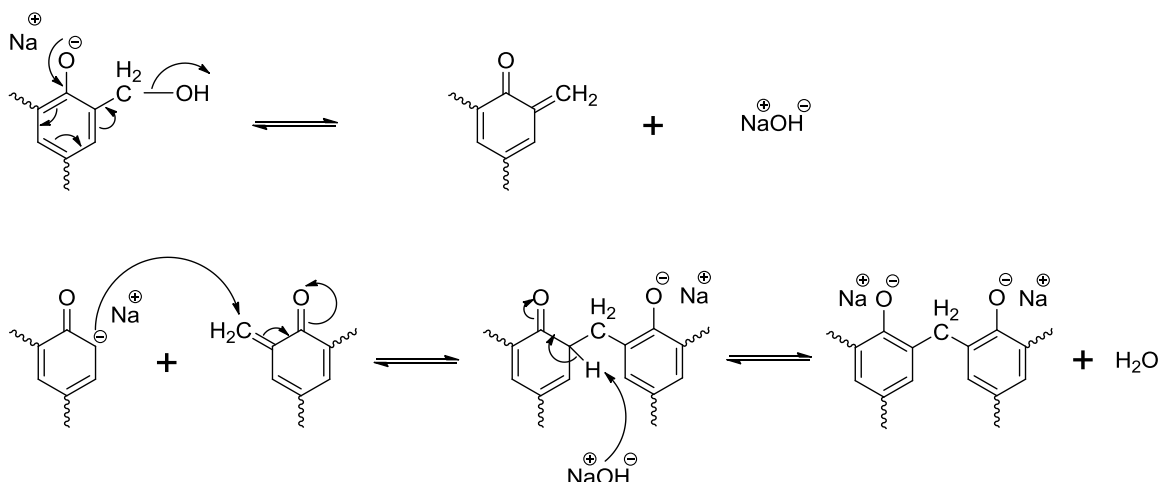


Figure 2-3 Formation of quinone methide from HMPs and condensation reactions with quinone methide.

Upon further heating as in the hot-pressing process to manufacture wood-based composites, the prepolymer resins proceed to highly crosslinked resite resins (C-stage) with the three-dimensional molecular networks that are infusible and insoluble [5, 10].

2.2 Fillers in phenol-formaldehyde adhesive

Phenol-formaldehyde (PF) resins used in structural veneer based composites such as plywood and laminated veneer lumber are typically formulated with fillers. Addition of fillers to liquid PF resins has been shown to reduce cost and improve properties of the veneer-based composites [5]. According to ASTM [11], a filler is defined as a solid material added to an adhesive to modify the strength, permanence, working properties, or other qualities, and/or to lower cost of adhesive. It is different from an extender that is defined as a substance added to an adhesive to reduce the amount of the primary binder (base resin) required per unit area. Fillers are generally non-adhesive while proteinaceous and amylaceous materials in extenders have some adhesive properties [12]. Typically, fillers act as a bulking agent and control the adhesive rheological behavior, assembly time tolerance and curing [13]. Fillers can also fill the cracks and cavities in veneer surfaces to improve the working properties of plywood products [5].

Fillers are generally categorized into inorganic and organic types. In terms of inorganic fillers, calcium carbonate, clay, talc, silica and others have been widely utilized in the plastics industry

due to the low cost, abundant supplies and availability [14]. However, the inorganic fillers because of high densities could be quite expensive with respect to volumetric basis especially considering the bulking function of fillers. Organic fillers are typically derived from biomass waste streams including wood flour, shell flour, tree bark and others. They have low densities and offer significant cost savings. The relatively high surface polarity and low aspect ratio indeed restrict the applications of organic fillers in thermoplastics. The poor compatibility between organic fillers and polymer matrix and the characteristic of water absorption result in lower performance of composites [15]. However, organic fillers have been successfully employed in phenolic resins to bond veneer based composites for several decades. Organic fillers, also called lignocellulosic fillers, can be roughly classified into nutshell flour, furfural digestion residue and bark flour regarding commercialized fillers in the wood-based composite industry [5].

2.2.1 Nutshell flour

Nutshells are one type of lignocellulosic biomass typically obtained as agriculture residues. In this category, the shells of walnuts, coconuts, almonds, and pecans are included. They were initially utilized in low-value agricultural applications such as fertilizers, insecticides, mulches, and poultry feeds [16].

Much effort has been input to improve the commercial value of nutshells by using them as abrasives for cleaning and polishing [17], additives to decrease the porosity of bricks and ceramic wares [16], non-skid media for paints [18], and the others. The application of nutshells as fillers in thermosetting resins was another important attempt. Finely grounded English walnut (*Juglans regia*) shell flours named as Glufil by Agrashell Corporation, were firstly introduced as fillers into plywood adhesives in 1942. The performance of Glufil in adhesives was found to be superior to other fillers, and thereafter was widely utilized in the plywood adhesive industry. Glufil in the application was simply mixed with liquid adhesive without any pretreating requirements. Pecan shell flour was also used as fillers in phenol-formaldehyde adhesives. Waage *et al.* [19] demonstrated that pecan shell fillers had no significant effects on cure properties and viscous behavior of phenol-formaldehyde resins. However, the utilization of pecan shell fillers was not widely extended, because the available supplies of pecan shells were limited in the Southern United States [5].

Because the unique physical characteristics and chemical properties, walnut shell has successful commercial applications. However, researches on the physical and chemical properties of walnut shell are limited. Composition Materials Company states that walnut shells they supply have a hardness of 3.5 MOH and 91 Rockwell and specific gravity of 1.2 to 1.4. Also, walnut shells can resist fermentation and are stable in the wide range of temperature and pH conditions [18].

The published chemical compositions of nutshells are summarized in Table 2-1. Since the characterization methods were not reported, the variations between different reports might be due to different compositional analysis methods.

Toles *et al.* [20] was to develop commercial adsorbents from nutshells. They reported the proximate analysis of different nutshells, but did not provide specific characterization methods. Walnut shells and almonds were found to be cellulose predominately in composition while pecans and macadamia nuts contained more lignin.

Kambarova and Sarymsakov [21] reported chemical components of walnut shells grown in Kyrgyz Republic and compared to birch wood. However, they also did not provide specific characterization methods. They reported that the chemical compositions of walnut shells and birch wood were different. The results are also different from the report from Toles *et al.* [20].

Srinivasan and Viraraghavan [22] studied walnut shell supplied by USFilter, part of the Water Technology division of Siemen's Industrial Solutions and Services (I&S) Group, USA., reported the chemical composition. They did not provide the specific characterization method. The walnut shells they studied contained 40.6 % cellulose and 20.30 % lignin that is consistent with the results from Toles *et al.* [20]. Also, walnut shells had 1.5 % ash. The hardness of walnut shells was 3 MOH and the specific gravity was in the range of 1.2 to 1.4 that is similar to the information from Composition Materials Company [18].

Preston and Sayer [23] qualitatively elucidated the chemical composition of nutshells which were composed of cellulose, hemicellulose and lignin with ^{13}C nuclear magnetic resonance spectroscopy with cross-polarization and magic angle spinning (CPMAS NMR). Zhang *et al.* [24] reported that the shell of Yangbi walnut (*Juglans sigillata*) was composed of 33.25 % cellulose, 26.72 % pentosan, 60.94 % lignin and 1.19 % ash. The characterization was based on standard

GB/T 2677.1. They also recognized that guaiacyl (G) and syringyl (S) units dominated the lignin structure where G unit was more than S unit by means of ^1H -NMR, infrared spectroscopy (IR) and ultraviolet (UV).

Table 2-1 Proximate analysis data for the nutshells.

Nutshells	Ash (%)	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Ref.
Almond shell	2.6	36.9	17.9	24.8	[20]
Pecan shell	3.1	29.8	8.6	43.3	[20]
Black walnut shell	0.6	51.9	13.9	27.4	[20]
English walnut shell	1.0	54.2	11.9	16.8	[20]
Macadamia shell	0.2	25.8	11.7	47.6	[20]
Walnut shell	-	30.47	21.25	48.28	[21]
Walnut shell	1.5	40.6	-	20.30	[22]
Walnut shell	1.19	33.25	26.72	60.94	[24]

2.2.2 Furfural digestion residue

Agriculture and forest wastes have been recognized as feedstocks for the production of furfural since 1830 when furfural was first discovered [25]. The Quaker Oats Company put much effort in the commercialized production of furfural. They set up the first factory-scale production of furfural and successfully promoted furfural into the market [26].

For the production of furfural, the pentosan contained in agricultural waste such as corn cobs, oat hulls and rice hulls was hydrolyzed to xylose, and then dehydrated to furfural. The procedure was catalyzed by dilute sulfuric acid. Steam was introduced to bring the reactor to a selected temperature and then remove the produced furfural out of the reactor for recovery [25, 27]. Although the mechanism for the transformation of furfural from xylose is still uncertain, a

mechanism proposed by Antal *et al.* [28] was shown in Figure 2-4 that was supported by the computational modeling from Nimlos *et al.* [29]. In the mechanism, an intermediate, xylose-2,5-anhydride, was formed as the C-2 hydroxyl group was displaced. Thereafter, the intermediate was dehydrated into furfural [30].

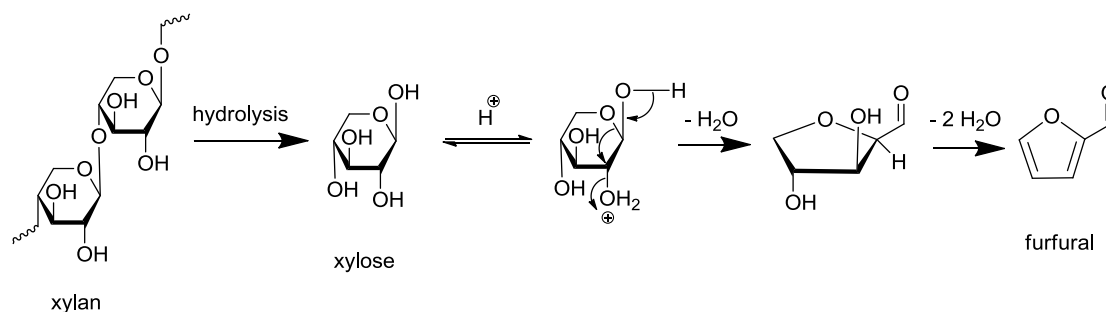


Figure 2-4 Synthesis route for furfural from xylan.

Furfural digestion residue consists of about 70 % of the original weight of raw feedstocks [25, 26]. Disposition or utilization of these residues was a big consideration from an economical aspect. One way was to burn the residue as fuels to produce the steam required for furfural production. Another way was to use the residue as soil conditioners [25, 26]. Furfural digestion residue was first introduced as exterior adhesive fillers in 1950. Theoretically, different agricultural residues have no influence on furfural production since the pentosans in these raw materials are indistinguishable. However, corn cobs were found to be an ideal furfural raw material because of the high pentosan yield and low ash content. Consequently, its residues became the preferred fillers in adhesives [5].

Understanding the chemical composition of furfural residues is beneficial to understand their effects on adhesive bond quality. Demirbas [31] demonstrated that corn cobs contained 52.33 % cellulose, 32.12 % hemicellulose, and 15.54 % lignin. Sun *et al.* [32] reported that corn cobs contain 28 % cellulose, 41.3 % xylan, and 21.4 % lignin. The xylan is a major component of corn cob. During furfural production, it has been demonstrated that xylan was almost quantitatively hydrolyzed to xylose that was further dehydrated into furfural with about 50 % yield [27, 30]. Moreover, the furfural production process did not affect the cellulose fraction of corn cobs [30]. Sun *et al.* [32] reported that corn cob residue contained 43.9 % cellulose, 3.6 % hemicellulose, and 45.1 % lignin. Xing *et al.* [33] reported that corn cob residue contained 45 %

cellulose, 3.6 % hemicellulose, and 48.4 % lignin. Bu *et al.* [34] reported that corn cob residue contained 48.10 % glucan, 41.58 % Klason lignin, 1.61 % acid soluble lignin, and 6.84 % ash.

2.2.3 Bark flour

Bark structure and cell types are more complicated than wood because bark can be roughly divided into inner bark or phloem, and dead outer bark or rhytidome [35]. Inner barks consist of sieve elements, parenchyma cells, and sclerenchymatous cells that serve for transporting liquids and nutrients, storing nutrients, and supporting tree stem. The main components of outer barks are periderms or cork layers that protects wood tissues from mechanical and environmental damage [35]. Due to the distinctive characteristics of inner and outer bark, Eberhardt and Reed [36] employed the grinding and classifications on southern yellow-pine (*Pinus palustris*) bark to generate the fraction rich in inner bark or phloem tissues and another fraction rich in outer bark or periderm tissues. They demonstrated that the fraction rich in outer bark tissues gave superior performance as fillers in plywood adhesives over the fraction rich in inner bark tissues and the unclassified barks. However, the separation typically is cumbersome and expensive, thus the whole bark is more commonly utilized.

Bark is the layer external to and surrounding the vascular cambium, amounting to about 10-15 wt% of the tree [35]. In pulp and wood industries, wood would be debarked before using. Over one million tons of bark waste are produced annually, which is mainly burned for heating. According to a 2006 report, combustion of bark for energy consumed about 83 % of softwood bark and 66-71 % of hardwood bark. In addition, about 15 % of softwood bark and about 30 % hardwood bark were utilized as compost in horticulture fields [37]. Barks have been used as absorbents for pollutants [38-40], raw materials for the production of particleboards [41, 42], raw materials for tannin-based adhesives [43], and resources for thermosetting adhesives [44]. Also, tree barks are important fillers in exterior adhesives. Douglas-fir (*Pseudotsuga menziesii*) bark as a filler entered the market in 1945. The barks typically dispersed in boiling water and sodium hydroxide solution were ready to mix with resins, which enabled the improvement of workability of adhesive mix [5]. Southern yellow-pine (*Pinus palustris*) barks were also studied as fillers for adhesives [45, 46]. Red-alder (*Alnus rubra*) bark was one of the most popular exterior adhesive fillers mentioned in many related patents [47-49].

Bark is different from wood in chemical composition. Generally, bark contains more lignin and less polysaccharide compared to wood. More ash and extractives exist in bark than in wood. The difference depends on wood types [50]. Compared to wood, the chemical composition is more complicated, depending on growth age, environmental conditions [35, 51] and storage time [52]. Apart from polysaccharides and lignin, high molecular weight tannins and cross-linked polyesters like suberin and cutin are generally present in bark. Therefore, chemical analysis by the standard methods for wood might only give approximate results for bark due to its more complicated chemical composition. The results could be valid for relative comparisons. To obtain the accurate analysis, preliminary extractions or corrections are needed, which would be cumbersome [53]. Harkin and Rowe [54] summarized the common compositional analysis procedure for barks as continuous extractions with various solvents. Generally, the extractions started with nonpolar organic solvents, and then proceed with more polar solvents, followed by polar solvents. Subsequent extraction with alkali or acid hydrolysis was utilized to analyze the residue. They also summarized the types of materials extracted by these common solvents, and generated the proximate composition of ash-free wood and bark shown in Table 2-2. Authors pointed out that the “lignin” consisted of a mixture of true lignin and suberized phlobaphene (cork). Pereira [55] reported that suberin was the main chemical component of cork from *Quercus suber* L., where it accounted for about 40 % of the cork. Gandini *et al.* [56] summarized the relative abundance of aliphatic suberin in the extractive-free outer bark of 16 wood species that ranged from 20 % to 60 %. Harkin and Rowe [54] also mentioned that polar extractives were generally three to five times as much as non-polar extractives. It was thought that the high ash content of bark was from windborne soil or sand as well as the sand and grit during debarking process, so the inorganic material content contained in barks would not be substantially different from that in wood.

Table 2-2 Proximate composition of ash-free wood and bark.

	Softwoods		Hardwoods	
	Wood	Bark	Wood	Bark
“Lignin”*	25-30	40-55	18-25	40-50
Polysaccharides*	66-72	30-48	74-80	32-45
Extractives	2-9	2-25	2-5	5-10
Ash*	0.2-0.6	Up to 20	0.2-0.6	Up to 20

*Based on extractive-free materials.

Chemical composition of bark varies by tree types. McGinnis and Parikh [57] demonstrated that the extractive-free loblolly-pine (*Pinus taeda*) bark contained 46.0 % Klason lignin. Laver *et al.* [58] reviewed the chemical constituents of Douglas-fir (*Pseudotsuga menziesii*) bark that generally included carbohydrates, tannin, wax, and cork. Labosky [59] studied chemical constituents of four southern pine barks and reported the variances in alcohol-benzene extractive content within- and among- species. Hafizoglu *et al.* [60] found that fatty acid was the major component in the lipophilic constituents of barks from black pine (*Pinus nigra*), sweet chestnut (*Castanea sativa*), and Turkish fir (*Abies bornmuelleriana*). Harun and Labosky [61] studied the chemical constituents of five northeastern barks including two softwood species of white pine (*Pinus strobus*) and red pine (*P. resinosa*) and three hardwood species of shagbark hickory (*Carya ovate*), red oak (*Quercus rubra*), and red maple (*Acer rubrum*). They found significant higher ethanol-benzene extracts and suberin in shagbark-hickory bark than those in other barks. Ash content for hardwood barks ranging from 7 % to 8 % was higher than that for softwood barks from 1 % to 2 %. While holocellulose contents for softwood barks and hardwood barks were similar from about 36 % to 47 %, Klason lignin content of hardwood barks ranging from 36 % to 38 % was lower than that of softwood barks ranging from 42 % to 50 %. Pan *et al.* [62] reported that Douglas-fir (*Pseudotsuga menziesii*) and loblolly-pine (*Pinus taeda*) barks

contained 16.5 and 23.1 % cellulose, 7.6 and 14.1 % hemicellulose, 44.2 and 43.5 % lignin, 22.5 and 13.2 % tannin, respectively.

Particle size effects on the chemical constituents of barks have been studied. Ottone and Baldwin [63] milled yellow-poplar (*Liriodendron tulipifera* L.) bark and fractionated into five sieve fractions, and found that extractive content of the bark increased with decreasing particle size, and the porosity of bark particles increased after the solvent extraction. Miranda *et al.* [64, 65] studied particle size effects on chemical composition of barks from softwood and hardwood species. They fractionated the milled Norway spruce (*Picea abies*), Scots pine (*Pinus sylvestris*) barks, silver birch (*Betula pendula*) and eucalypt (*Eucalyptus globulus*) into fine (<0.180 mm), medium (0.250-0.450 mm), and coarse (>2 mm) fractions. They reported that fine particles concentrated a high amount of ash and extractives, but no significant particle size effects on the amount of structural components. Coarse fraction of eucalypt bark contained a high amount of holocellulose but a low amount of lignin. Baptista *et al.* [66] fractionated teak (*Tectona grandis*) bark into fine (<0.180 mm), medium (0.250-0.450 mm), and coarse (>2 mm) fractions, and reported that fine particles contained more extractives and lignin, and monosaccharide contents were similar in different fractions, which is the same as Miranda *et al.* [64, 65] reported. Authors [66] also found that the medium fraction and fine fraction contained the highest and lowest content of suberin respectively. The similar composition changes with particle sizes in some agricultural crops such as switch grass, reed canary grass, corn stover, wheat, barley, oat, triticale straws and flax shives have been reported [67-69].

2.3 Wood adhesion

To fundamentally understand the influence of biomass fillers on phenol-formaldehyde adhesion to wood, the mechanisms of wood adhesion are reviewed below.

Adhesion is an attractive phenomenon between two surfaces or adherends which are held together by chemical and/or physical forces. Composite bonding is the major application of adhesive that can be found in different industries such as automobile [70], electronics [71], aerospace [72] as well as wood-based composites [73]. Various theoretical mechanisms have been proposed to explain adhesion. However, since adhesion is an interdisciplinary phenomenon, it is difficult to explain it with the aid of one specific mechanism. The various mechanisms are

typically complementary and to what extent each mechanism influences depends on the bonding system studied [74]. Among them, the theories of adsorption, mechanical interlock, covalent bonding and interpenetrating networks (IPN) have been employed in the discussion of wood adhesion [1, 75].

The adsorption theory [1, 76] was proposed by Sharpe and Schonhorn based on the thermodynamic perspective, which has been long been considered as the most dominant mechanism for wood adhesion. This theory believed that adhesion was due to the intermolecular interactions (known as Van der Waals forces) between the adhesive and the adherend. Although the individual Van der Waals force is very weak, the sum of abundant Van der Waals forces over the adhesive polymer surface is great as the chain-like adhesive polymer has the large surface area. The intermolecular forces exist only when two surfaces come into Angstrom level contact, which requires the liquid adhesive effectively wet the wood surface during bonding process. Typically, the extent of wetting is demonstrated by the contact angle that represents a balance between solid, liquid and interfacial energy. Generally, favorable wetting is achieved when contact angle is less than 90 degrees [77, 78].

The mechanical interlocking theory proposed by MacBain and Hopkins refers to the flow of the adhesive into irregularities on the surface of adherend, subsequent solidification formed strong and tough joints [74]. Wood is naturally porous where the surface contains pores as well as other irregularities from machining prior to bonding. The penetrated adhesives in these pores and irregularities reinforce the damaged wood surface that prevents wood fracture near the bondline and enhance adhesive bonding. Therefore, the mechanical interlocking is an important contributor for wood adhesion but not a dominant factor.

The covalent chemical bonding theory refers to the formation of covalent bonding between adhesive and adherend [74]. The covalent bond energy is much larger than that of the intermolecular interaction. The covalent bonding is possible formed between wood and adhesives especially such as phenol-formaldehyde, phenol-resorcinol-formaldehyde, and isocyanate adhesives because the wood surface has many functional groups [77, 79-81]. However, little conclusive evidence demonstrates this statement because the detection of the covalent bonding between wood and adhesive is difficult [82]. The accepted claim is that this

mechanism only improves durability of adhesive against the effects of weathering rather than the bonding strength [83].

The interpenetrating networks (IPN) theory refers to the adhesives containing reactive monomers that penetrate into wood cell wall on the molecular level. Upon solidification, they form a network with wood structures. Therefore, this theory only works for the adhesive system with a low molecular weight such as polymeric methylene diphenyl diisocyanate (pMDI). And this theory is considered to enhance the durability of wood bonding rather than bonding strength [84, 85].

2.4 Influence of filler on wood adhesive performance

Many research publications indicated a strong correlation between the toughness of an adhesive and the toughness of corresponding wood adhesive joints [86]. Filler is an important component in wood adhesives such as phenol-formaldehyde (PF) adhesive, phenol-resorcinol-formaldehyde (PRF) adhesive, and urea-formaldehyde (UF), where it acts as the bulking agent to adjust adhesive viscosity and reduce the cost. The influence of fillers on adhesive joint performance is crucial to adhesive applications. However, little work has been published on this subject. Ebewe [87] studied the impacts of filler types including two biomass fillers and four inorganic fillers on the joint performance of phenol-resorcinol-formaldehyde (PRF) adhesives. He reported that walnut shell fillers produced the joint with higher fracture energy than Douglas-fir (*Pseudotsuga menziesii*) bark filler and inorganic fillers. Unfilled adhesive joint was intermediate in fracture energy. Gardner *et al.* [88] reported that the flakeboard bonded by PF adhesives with pecan shell fillers or clay fillers had comparable properties to those bonded with neat PF resins. Veigel *et al.* [89] demonstrated an increase of the toughening effect up to 45 % on urea formaldehyde (UF) wood adhesive bonds when adding up to 2 % cellulose nanofibrils as fillers. Lei *et al.* [90, 91] reported that the addition of small percentages (2-10 wt%) Na⁺-montmorillonite nanoclay improved the performance of thermosetting urea formaldehyde (UF) resins for plywood and wood particleboard, but had no clear improvement on the performance of thermosetting phenol-formaldehyde (PF) and phenol-urea-formaldehyde (PUF) resins.

2.5 Factors of filler influencing adhesive steady-state viscous property

According to wood adhesion mechanisms, adhesive rheological behavior is a critical parameter to adhesive bonding. Typically, additives such as extenders and fillers are adopted to change the characteristics of phenol-formaldehyde resin. The filled adhesive belongs to a suspension system where the micro-scale particles are dispersed throughout a fluid. The suspensions basically show more complex rheological behavior when comparing to the continuous fluid [92]. In the following part, the rheological behavior of suspension impacted by filler characters (concentration, shape, dimension, size distribution) and suspending mediums are reviewed.

2.5.1 Particle concentration effect

A dilute suspension of rigid spheres without Brownian motion in a Newtonian liquid has been considered as a model suspension. The viscosity of this suspension was found to be a function of the volume fraction of particles. Einstein is the pioneer to establish the relationship between the relative viscosity of suspension and the volume fraction of particles expressed as below (equation 1) [92].

$$\eta_r = \frac{\eta}{\eta_0} = 1 + \alpha_E \phi \quad (1)$$

η_r is the relative viscosity, which is the ratio of suspension viscosity η to suspending fluid viscosity η_0 , and α_E is Einstein constant. α_E equals 2.5 for neutrally buoyant and hard spheres.

Experimental results showed that the value of α_E ranged from 1.5 to 5.5 for dilute suspension ($\phi < 0.1$) [92].

Thomas [93] proposed the expression for the suspension with $\phi < 0.15$:

$$\eta_r = \frac{\eta}{\eta_0} = 1 + 2.5\phi \left(0.1 + \frac{25\phi}{4a_1^3} \right) \quad (2)$$

a_1 is an empirical coefficient which generally lies between 1 and 2.

Ford [94] also provided a binominal expression (equation 3) that was proved to be valid for $\phi < 0.15$ by the experimental data of Cengel *et al.* [95].

$$\eta_r = \frac{\eta}{\eta_0} = \frac{1}{1 - a_E \phi} \quad (3)$$

For concentrated systems, the above equations lose their validity. Generally, the volume fraction of particles ranges between 0.15 and ϕ_m , where ϕ_m is the maximum attainable concentration. Frankel and Acrivos [96] derived the theoretical equation (equation 4) without empirical constants to depict trends in the region of high concentration levels.

$$\eta_r = \frac{\eta}{\eta_0} = \frac{9}{8} \left[\frac{\left(\frac{\phi}{\phi_m}\right)^{\frac{1}{3}}}{1 - \left(\frac{\phi}{\phi_m}\right)^{\frac{1}{3}}} \right] \quad (4)$$

Different empirical equations have been proposed which work for certain ranges of volume fractions [92]. The Maron-Pierce-Kitano equation (equation 5) with a simple form has been demonstrated to be valid for the entire range of volume fraction [97, 98].

$$\eta_r = \frac{\eta}{\eta_0} = \left(1 - \frac{\phi}{\phi_m}\right)^{-2} \quad (5)$$

2.5.2 Particle shape effect

In commercial applications, filler particles commonly have irregular shapes which would result in different rheological properties of suspensions from suspensions with sphere particles. Jeffrey [99] employed Einstein's equation to describe the viscosity of dilute ellipsoidal suspensions and found that Einstein constant depended on the axis ratio of the ellipsoid. Based on the work of Jeffrey, Guth developed the equations to express the relationship as following [92].

$$\eta_r = \frac{\eta}{\eta_0} = 1 + \alpha_{r1} \phi + \alpha_{r2} \phi^2 \quad (6)$$

$$\alpha_{r1} = \frac{r_e}{(2 \ln 2r_e - 3)} + 2 \quad (6.a)$$

$$\alpha_{r2} = \frac{0.04r_e^3}{(2 \ln 2r_e - 3)} \quad (6.b)$$

r_e is the ratio of long axis to short axis of the ellipsoid, and the value is larger than 1.

Since fibers as fillers are common, extensive research work has been conducted on rheological behavior of the rod-shaped particle suspensions [92]. For dilute suspensions of rod-shaped particles, Burgers [100] found that Einstein's equation could describe the relationship and established the relationship between Einstein constant and shape information of rod particles shown in equation 7.

$$\alpha_E = \frac{r_a^2}{6(\ln 2r_a - 1.8)} \sin^4 \theta \sin^2 2\psi \quad (7)$$

r_a is the aspect ratio of the rod particle, and θ and ψ are the spherical coordinates expressing the orientation of the rod.

For concentrated suspension of rod-shaped particles, Simha [101] established the following equation.

$$\eta_r = \frac{\eta}{\eta_0} = 1 + \alpha_E \phi + \bar{\alpha}(\alpha_E \phi)^2 \quad (8)$$

$\bar{\alpha}$ is the coefficient, and the value of $\bar{\alpha}$ for randomly oriented rods with purely hydrodynamic interactions is 0.73.

2.5.3 Particle size effect

Typically, the suspensions with filler particles exhibit shear-thinning behavior, where the viscosity at lower shear rates is higher and the viscosity at high shear rates is lower [102]. The higher viscosity at low shear rates is due to Brownian motion of particles. The shearing at higher shear rates overcomes Brownian motion resulting in a reduction of the viscosity [102]. Therefore, small-size particles have long-lasting Brownian motion that requires higher shear rate to produce the same degree of shear-thinning than large-size particles. This phenomenon have been found in experimental results [103, 104].

2.5.4 Particle polydispersity effect

Previous review only focused on filler particles with the same size. Actually, size distributions of filler particles have a significant impact on the rheological behavior of suspensions when

volumetric fraction of particle is above 20 % [105]. Clarke [106] found that the addition of fine particles into the suspension with mainly coarse particles decreased the suspension viscosity while the addition of coarse particles into the suspension with mainly fine particles had insignificant impact on the suspension viscosity. Experimental results [107, 108] demonstrated that the viscosity of a suspension with bimodal-size fillers showed a minimum at a relative volume fraction of the small particles around 0.2-0.25. The low percentage of small particles might act a lubricant to facilitate the rotation of large particles by blocking the interactions between larger particles, resulting in a reduction in viscosity.

2.5.5 Suspending medium effect

All of discussions above were based on Newtonian suspending medium. All of the equations showed that suspension viscosity is directly proportional to suspending medium viscosity [102]. Nicodemo *et al.* [109] studied the rheological behavior of suspensions based on Newtonian and non-Newtonian suspending mediums as a function of shear rates. The viscosity of the suspension with Newtonian liquid decreased with the increase of shear rates toward an asymptotic value. The shear-thinning behavior was explained with Krieger-Dougherty theory [110] which stated that the shear-induced doublet dissociation resulted in the decrease in viscosity. The rheological behavior of the suspension with non-Newtonian liquid at low shear rates could be explained with Krieger-Dougherty theory; however, the behavior at high shear rates could not be correlated to the theory indicating the existence of a different mechanism. Nicodemo and Nicolais [111] found that the behavior at high shear rates was due to filler effects on the flow properties of macromolecules, in particular on the relaxation time.

2.5.6 Mechanisms of suspension rheological behavior

The various interactions that interplay in suspension determine the rheological behavior, which depends on particle sizes and volume fractions. A colloid suspension is typically defined as a suspension of particles smaller than 10 microns [112]. Brownian forces, colloidal forces such as electrostatic forces and van der Waals forces, and hydrodynamic forces during settling or mixing are three basic types of forces that determine the rheological behavior of colloid suspensions [113]. In a suspension of particles larger than 10 microns, hydrodynamic forces dominate the

rheological behavior [92]. Above some volume fraction of particles, various contact forces between particles contribute to the rheological behavior remarkably [114].

At short distance, particles attract via van der Waals force. Also, the presence of adsorbed ions at particle surfaces causes the electrostatic forces that result in repulsions between particles. For the particles smaller than a few microns, Brownian forces prevent the agglomeration of particles. Rouseel *et al.* [114] carefully studied the steady-state flow of cement suspensions where particle sizes range from several *nm* to 100 μm . They found that van der Waals attractive inter-particle forces dominated the inter-particle interactions rather than Brownian effects. Polymer additives are commonly added to prevent the particle agglomeration. Polymer additives could be adsorbed at the particle surfaces to generate steric hindrance or electrostatic repulsion that increased the average inter-particle distance and therefore decreased the magnitude of the attractive van der Waal forces.

The external shear rates also impact the interplay between hydrodynamic, colloidal and contact forces, resulting in either Newtonian (constant viscosity), shear thinning (decreasing viscosity with shear rates), or shear thickening behavior (increasing viscosity with shear rates [102]).

Rouseel *et al.* [114] divided the flow curve of cement suspensions into colloidal regime, viscous regime, and particle inertial regime over a shear-rate increasing region. A shear thinning in the low shear rates represented the transition between colloidal and viscous regimes since the van der Waals forces dominated in this region. Hydrodynamic forces dominated at the intermediate shear rates, where Newtonian behavior was shown. Particle inertia dominated at high shear rates and shear thickening behavior occurred because of the transition between viscous and inertia regimes. However, in the suspension with polymer additives, the viscous dissipation in the suspension medium would dominate the inertial of particles that prevented the shear thickening.

The rheological behavior of liquid crystalline polymer (LCPs) suspension have been studied by many authors to understand the processing-structure-property relationship [115-120]. Onogi and Asada [115] first distinguished the flow behavior of LCPs suspensions into shear thinning, Newtonian plateau, and shear thinning from low shear rates to high shear rates. They also proposed domain-based model to explain the shear rate dependent flow behavior. The tactoid domains formed by crystallites began to flow over each other at low shear rates without the

destruction of the domain structures, resulting in the shear thinning region. In the intermediate shear rate range, the observed Newtonian plateau was due to the start of disruption of particle domains. At even higher shear rates, the particle domains were broken into single particles resulting in a further shear-thinning region.

Dadmun and Han [121] employed the tumbling of particles in solution to explain the flow behavior of LCPs system. In the slow regime, the shear-thinning behavior was due to an increase in speed of the tumbling of particles that caused an increase of alignments of particles. In the intermediate regime, Newtonian plateau was observed because there was slight change in alignment of the particles. The increasing shear flow inhibited the tumbling of particles in this region. In the fast regime, the flow field overcame the local dynamics of the particles and produced a narrow distribution of the alignment of particles, resulting in a shear-thinning behavior.

Li *et al.* [117] investigated the rheological properties of isotropic, biphasic and anisotropic LCPs suspensions. In the isotropic suspension, a shear thinning was observed. The rodlike particles undergoing Brownian motion and freely tumbling created a large excluded volume, resulting in a high zero shear rate viscosity. With increasing shear rates, particles were aligned producing a decrease in viscosity. For biphasic suspensions where the rodlike particles and ellipsoidal anisotropic tactoids co-existed, a two-regime flow curve was observed that was a severe shear thinning followed by a mild shear thinning. This was due to the sum of contribution of the low viscosity ordered phase and of the high viscosity disordered phase. Particles and tactoids shear oriented at the low shear rates. The increasing shear force at high shear rates partially broke the tactoids into particles that oriented further. For the anisotropic suspension, shear thinning, Newtonian and another shear thinning were observed. This behavior was attributed to tactoid orientation/deformation, rodlike particle sliding in tactoids, and completely breakup, which was proposed by Onogi and Asada [115].

Wissbrun stated that concentrated suspensions of rigid fibers might exhibit flow behavior comparable to that of LCPs suspensions [105].

Sarvestani and Picu [122] proposed the contribution of particle-matrix interactions to the filler dependent flow behavior of polymer nanocomposites with strong filler-polymer interactions.

Good affinity between particle and matrix was thought to be conducive to a better particle dispersion resulting in a decrease of the suspension viscosity. However, strong interaction between particle and matrix was in favor of forming the bead-spring structure where oligomer or polymer molecular chains acting as springs were adsorbed on the surface of particles that were viewed as beads. The increase of chain entanglements contributed to an increase of viscosity of suspension. Therefore, the final flow behavior was believed to arise from the combined effects of good particle dispersion and increased entanglements as a function of shear rates.

2.6 Analytical methods

2.6.1 Viscometric analysis

According to the mechanism of shearing generation, shear rheometer can be divided into drag flow and pressure-driven types. Shear in drag flow rheometers is generated between a moving and a fixed solid surfaces while shear in pressure-driven rheometers is generated by pressure differences over a closed channel [123]. Since they are commonly used for viscometric analysis on wood adhesive, the following review focused on drag flow rheometers with three different geometries.

2.6.1.1 Cone-and-plate viscometer

The geometric measuring system of cone-and-plate rheometer includes a flat circular plate and a linearly concentric cone which are rotated relative to each other as shown in Figure 2-5. The cone was truncated to prevent wear on the flat plate. The truncation value is the gap that should be set when using the measuring system. The sample is in the space between the cone and plate. With a specific diameter and an angle of cone, the shear stresses, shear rates and viscosity can be determined according to the following equations [124]:

$$\tau = \frac{3M_d}{2\pi R_p^3} \quad (9)$$

$$\dot{\gamma} = \omega \tan^{-1} \varphi \quad (10)$$

$$\eta = \frac{3M_d}{2\pi R_p^3 \omega \tan^{-1} \alpha} \quad (11)$$

τ is the shear stress, M_d is the torque, R_p is the radius of cone, $\dot{\gamma}$ is shear rate, ω is the angular velocity, φ is the cone angle, and η is the viscosity.

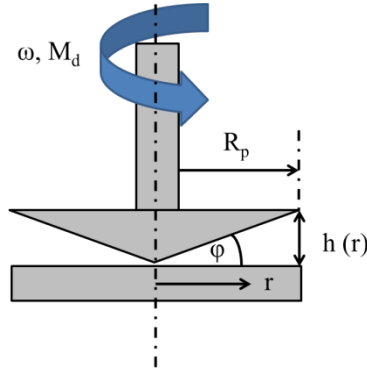


Figure 2-5 Geometric measuring system of cone-and-plate viscometer.

The major advantage of this measuring system is the constant shear rate throughout the sample. Also, the sample size is small that results in less heat generated at high shear rates. Another advantage is the ease of cleaning the system. However, it is difficult to load the optimum sample size since under or overfilling the geometry is common to occur. In addition, the maximum shear rate is restricted by inaccuracies due to the secondary flows and the sample to crawl out of the system at high shear rates. The measuring system is unsuitable for samples containing particles since the particles tend to migrate to the apex of the cone resulting in the jam in the truncation area [124].

This measuring system has been employed to study the steady-state rheological behavior of liquid phenol-formaldehyde resins (PF) [125], polymeric diphenylmethane diisocyanate resins (pMDI) [125], soy protein based adhesives [126-128], poly(vinyl acetate) (PVAc) latex adhesives [129] and polyurethane adhesives [130]. This system was also used to study the gel time of urea formaldehyde resins [131].

2.6.1.2 Parallel Plate Viscometer

Different from cone-plate viscometer, parallel plate viscometer is suitable for samples with particles. This geometric measuring system includes two identical, coaxial and parallel plates shown in Figure 2-6. The gap between two plates can be set to any distance to accommodate the sample with different sizes of particles. However, the major disadvantage is the various shear rates across the entire radius of plate which requires additional correction for shear stresses and viscosity [124]. The shear rates, shear stress and viscosity can be determined according to the following equations.

$$\dot{\gamma}(r) = \frac{\omega r}{H} \quad (0 \leq r \leq R_p) \quad (12)$$

$$\dot{\gamma}(r) = \frac{\omega r}{H} \quad (0 \leq r \leq R_p) \quad (13)$$

$$\tau = \frac{3M_d}{2\pi R_p^3} \left[1 + \frac{1}{3} \frac{d(\ln M_d)}{d(\omega)} \right] \quad (14)$$

$$\eta = \frac{3M_d H}{2\pi R_p^4 \omega} \frac{1}{\left[1 + \frac{1}{3} \frac{d(\ln M_d)}{d(\omega)} \right]} \quad (15)$$

$\dot{\gamma}$ is shear rate, r is the radius of a circle with the center of plate, R_p is radius of plate, H is the gap between two plates, τ is shear stress, M_d is torque, ω is angular velocity, and η is viscosity.

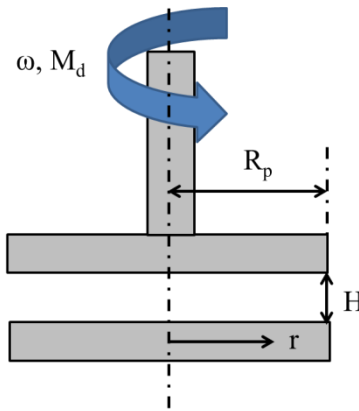


Figure 2-6 Geometric measuring system of parallel plate viscometer.

This measuring system has been employed to study the steady-state rheological behavior of starch-based wood adhesives with silica nanoparticles [132], but the similar application is not common due to the requirement of additional viscosity correction. The major application of this measuring system is to study the curing behavior of different wood adhesives [127, 133-136], because loading and cleaning sample is straightforward and the disposable plates are available.

2.6.1.3 Concentric cylinder viscometer

The geometric measuring system of concentric cylinder viscometer includes two concentric cylinders with different radii shown in Figure 2-7, which measures the rheological behavior of samples in the gap formed by two cylinders. This measuring system accommodates large sample size, gives a large shearing surface, and provides lower stress and higher sensitivity for extremely low viscosity solutions. The disadvantage of this measuring system is the requirement of water cooling jacket to release the heat generated from large volume of samples and control the testing temperature. Also, end effects are another issue for this measuring system [137]. A shear flow occurs between the end of the inner cylinder and the bottom of the outer cylinder, which is similar to the flow between parallel plates. The effects are minimized by using the conical end of the inner cylinder. The specific cone angle enables the shear rate in the trapped space between the cone and the bottom to be the same as that in the gap between two cylinders [137].

If the gap is small enough compared to the diameters of the cylinders, shear rate is approximately constant across the sample in the gap ($\frac{R_i}{R_a} > 0.97$) [137]. The shear rates, shear stress and viscosity can be determined according to the following equations.

$$\dot{\gamma} = \frac{\omega R_a}{R_a - R_i} \quad (16)$$

$$\tau = \frac{M_d}{2\pi R_a^2 L} \quad (17)$$

$$\eta = \frac{M_d(R_a - R_i)}{2\pi R_a^3 \omega L} \quad (18)$$

$\dot{\gamma}$ is the shear rate, R_a is the radius of the outer cylinder, R_i is the radius of the inner cylinder, ω is the angular velocity, L is the effective immersed length of the sample, τ is the shear stress, M_d is the torque, and η is the viscosity.

If the gap is not small enough, shear rate is dependent on the sample properties [137]. The shear rates, shear stress and viscosity can be determined according to the following equations.

$$\dot{\gamma} = \frac{2\omega}{n[1 - (\frac{R_i}{R_a})^{\frac{2}{n}}]} \quad (19)$$

$$\tau = \frac{M_d}{2\pi R_i^2 L} \quad (20)$$

$$\eta = \frac{M_d n [1 - (\frac{R_i}{R_a})^{\frac{2}{n}}]}{4\pi R_i^3 \omega L} \quad (21)$$

n is the slope of trendline in the plot of M_d vs. ω on a double-logarithmic basis.

For concentric cylinder rheometer AR G-2 with a conical end (TA instruments), $\frac{R_i}{R_a} \approx 0.93$. The shear rate, shear stress and viscosity are calculated based the following equation.

$$\dot{\gamma} = \frac{\omega(R_a^2 + R_i^2)}{R_a^2 - R_i^2} \quad (22)$$

$$\tau = \frac{M_d(R_a^2 + R_i^2)}{4\pi R_a^2 R_i^2 L} \quad (23)$$

$$\eta = \frac{M_d(R_a^2 - R_i^2)}{4\pi R_a^2 R_i^2 \omega L} \quad (24)$$

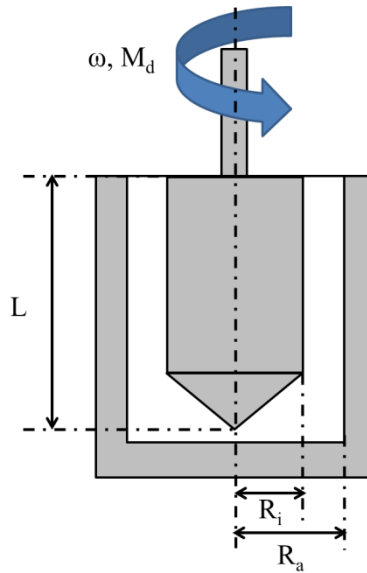


Figure 2-7 Geometric measuring system of concentric cylinder viscometer.

This measuring system has been employed to study the steady-state rheological behavior of poly (vinyl acetate) adhesives with inorganic and organic fillers [138] and urea-formaldehyde resins [139]. However, the measuring system in viscometric analysis of wood adhesives is not as common as cone-plate measuring system.

2.6.2 Mode-I fracture testing

Since the adhesive is a critical element in wood composites, testing of the mechanical performance of bonded composites is necessary when considering the safety in applications. The focus of performance evaluation is on adhesive joint rather than bulk adhesive. Many standard tests have been developed such as compression shear block (ASTM D905-08), tensile shear for veneer-based composites (ASTM D906-98) and others, which are strength-based. Bulk wood failure is inevitable in these tests because wood is weak in parallel to the grain upon shear loading. Wood failure combined with wood variables such as grain and density complicates adhesive performance assessments [140]. An alternative energy-based approach for wood adhesive testing was introduced as a complement to strength-based tests. This approach was developed based on fracture mechanics [140, 141].

The theory of fracture mechanics was pioneered by Griffith and then developed by Irwin [142]. The stress intensity factor (K) and strain energy release rate (SERR, or G) are two important concepts. Their critical values where fracture occurs characterize the fracture toughness of a material. G and K are related for a linear elastic material with elastic modulus and Poisson's ratio [142].

$$G = \frac{K^2}{E} (1 - \nu^2) \text{ (plane-strain condition)} \quad (25)$$

$$G = \frac{K^2}{E} \text{ (plane-stress condition)} \quad (26)$$

E is the elastic modulus, and ν is the Poisson's ratio.

The SERR approach is based on the energy concept that the existed crack flaw extends when the input displacement energy overcomes the resistance of the material that includes the stored elastic energy and the energy for crack propagation.

According to the approaches by which the external stress is applied, the fracture energies are classified as opening mode (mode-I), in plane shear mode (mode-II), and out-of-plane shear mode (mode-III). Among them, the mode-I fracture is most commonly in wood adhesive testing since the toughness is the lowest. The mode-I fracture energies are computed as follows [140, 142, 143]:

$$G_{Ic} = \frac{P_c^2}{2B} \frac{dC}{da} \quad (27)$$

$$G_{Ia} = \frac{P_a^2}{2B} \frac{dC}{da} \quad (28)$$

G_{Ic} and G_{Ia} are the mode-I critical and arrest fracture energy, P_c and P_a are the critical and arrest loads, C is the specimen compliance, B is the specimen width, and a is the crack length.

Although the application of this fracture testing to evaluate adhesive strength and durability is most commonly in metal and plastics, much research work have been conducted to employ the mode-I fracture method to test wood adhesive joints due to the orthotropic characteristics of

wood materials. The contoured dual cantilever beam (CDCB) was used in the early studies since the compliance changed linearly with the crack length. To exclude the influence of wood bulk properties, the beams were paired in a way that grain converged towards the bondline. This special design forced crack extensions only in the bondline. The mode-I fracture testing with the CDCB geometry was employed to study the effects of bondline thickness, wood anisotropy, grain angles, wood surface roughness, surface aging, and resin cure time on adhesive performance [141, 144, 145]. However, preparing CDCB geometry was laborious. Modification of press machine was required to accommodate the contoured shape. To obtain the constant $\left(\frac{dC}{da}\right)$, each contoured geometry was required for the calibration.

In the following years, much more efforts were put into the simplification of specimen geometry. River *et al.* [146] and Scott *et al.* [147] bonded a thin laminate to the contoured aluminum beams. This design reduced the variability from the bulk wood, improved the linear relationship between compliance and crack length, and enhanced the accuracy of fracture toughness measurement. Thin wood laminates could also be cured by conventional press machines. However, the amount of attained data was less than that from the previous geometry because the linear relationship between the compliance and the crack length was only valid for the first 90 mm of crack length. Also, fabrication of the contoured aluminum geometry was expensive, and the bonding and debonding wood laminates from the aluminum was a time-consuming task [148].

To overcome these disadvantages, wood-based composites such as oriented strand board (OSB) and laminated veneer lumber (LVL) replaced the contoured aluminum [148, 149]. Wood-based contoured composites were less expensive and easier to fabricate. A longer range for the linear $\frac{dC}{da}$ was also obtained. However, wood-based composites as the contoured beams were still laborious and demanding because the calibration of $\frac{dC}{da}$ for new beams was needed. To avoid the recalibration, the density, grain angle, and height of the test laminates should be carefully controlled.

The flat wood DCB is easy to process compared to contoured geometry; however, the nonlinear $\frac{dC}{da}$ as a major disadvantage hindered its application. This situation was changed since Gagliano and Frazier [140] developed a new procedure to monitor the real-time crack extensions with the

aid of modern digital technology. In their study, two flat beams were paired in a way that the radial grain converged to “V” shape at the bondline shown in Figure 2-8. In addition, the calculation of fracture energies for adhesively-bonded wood was based on the shear corrected compliance method that was developed by Hashemi *et al.* [150] and Blackman *et al.* [151] to correct for the fiber-reinforced polymer composites with a low shear modulus.

$$G_{Ic} = \frac{P_c^2}{B} \frac{(a+x)^2}{(EI)_{eff}} \quad (29)$$

$$G_{Ia} = \frac{P_a^2}{B} \frac{(a+x)^2}{(EI)_{eff}} \quad (30)$$

$$(EI)_{eff} = \frac{2}{3m^3}; x = \frac{b}{m} \quad (31)$$

$(EI)_{eff}$ is the effective flexural rigidity of the DCB specimen, x is the shear correction factor, or the crack length offset, m and b are the slope and the y-intercept, respectively, from the linear trendline in the plot of the cube root of compliance versus crack length shown in Figure 2-9.

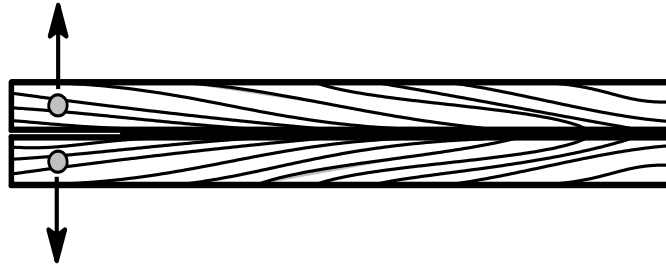


Figure 2-8 Flat DCB specimen.

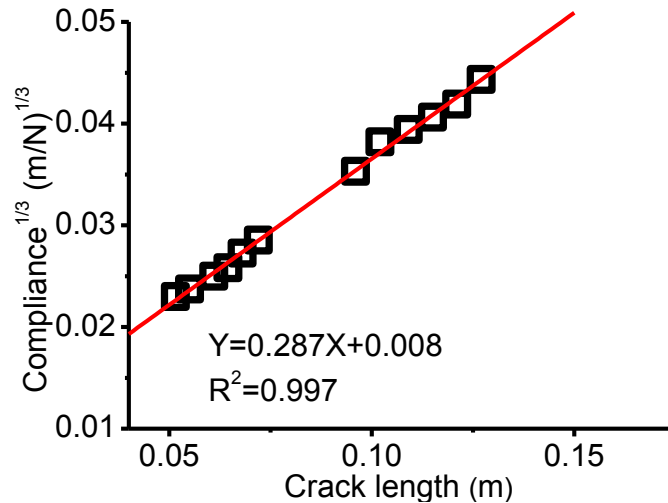


Figure 2-9 An example plot of the cube root of compliance versus crack length.

Since it is sensitive to the intrinsic adhesive performance and able to provide a great amount of data over a relatively small area for further data analysis, this simplified method for mode-I fracture testing has been employed to study various adhesively-bonded wood system. Scoville [152] compared the durability of phenolic formaldehyde (PF) and isocyanate (pMDI) adhesives based on the fracture energy. Sernek *et al.* [153] comparatively characterized the inactivated wood surfaces. Follrich *et al.* [154] evaluated the influence of thermal treatments on the adhesion between spruce wood (*Picea abies* Karst.) and polyethylene. L ópez-Suevos and Frazier [155] investigated the influence of phenolic additives on the weather durability of polyvinyl acetate (PVAc) latex adhesives. Das *et al.* [156] demonstrated the effects of wood species on the wood/polymeric isocyanate bonding. Gao [157] compared the thermal stability of polyurethane (PUR) and resorcinol-formaldehyde (RF) wood adhesives and studied the effects of wood surface thermal deactivation on wood adhesion. Paris [158] assessed the carboxymethylcellulose acetate butyrate (CMCAB) polymers as the potential wood adhesive. Nicoli [159] analyzed the factors that impacted the fracture test results in boned wood including the adhesive layer thickness and the variability of the local bending stiffness of the wood beams. Ren [160] developed the accelerated weathering procedure to evaluate commercial polyurethane (CPUR) bondline weather durability.

2.6.3 Liquid surface tension analysis

According to wood adhesion mechanism, adhesives need to develop a close contact with wood substrates, which involves wood surface energy and liquid adhesive surface tension. Since most wood adhesives are water-borne, they are similar to water with a high surface tension [82]. To achieve optimum wetting, flow and penetration of adhesives, either increasing wood surface energy or decreasing adhesive surface tension is beneficial. A lot of work has been conducted on examining the wood related factors on the wetting of adhesive including wood density, species, surface roughness, moisture content, and aging [82, 161]. Different surface preparation including physical and chemical treatments also has been well studied [82, 161]. However, little attention has been paid to liquid adhesive surface tension. To understand the influence of organic fillers on the surface tension of phenol-formaldehyde adhesives, the common techniques of liquid surface tension measurements are reviewed below.

2.6.3.1 Capillary rise method

This method is the first one for surface tension determination, which was derived from the phenomenon that the liquid level in a thin capillary tube is moving up when the tube is inserted to a container filled with the liquid [162]. When the adhesion between the liquid and the capillary wall is stronger than the cohesion between liquid molecules, the liquid rises to a defined level in the capillary tube and the meniscus is a semispherical concave. In the opposite situation, the level of the liquid like mercury in the capillary is below that in the container and the meniscus is a semispherical convex.

Based on the balance between the force resulting from the surface tension on the perimeter of meniscus and the gravity force from the liquid raised in the capillary, the equation related to the surface tension could be derived [163].

The force caused by surface tension is expressed as

$$f_1 = 2\pi R\gamma\cos\theta \quad (32)$$

R is the capillary radius, γ is the liquid surface tension, and θ is the wetting contact angle.

The gravity force is expressed as

$$f_2 = \pi R^2 \rho g h \quad (33)$$

ρ is the liquid density, g is the gravitational constant, and h is the height of liquid in the capillary above the liquid surface in the container.

Since two forces are balanced, the surface tension is expressed as

$$\gamma = \frac{R \rho g h}{2 \cos \theta} \quad (34)$$

The liquid is assumed to wet the capillary wall completely, and the contact angle is assumed to be zero. Then the surface tension equation is simplified as

$$\gamma = \frac{R \rho g h}{2} \quad (35)$$

Actually, the same equation could also be derived from Young-Laplace equation.

$$\Delta P = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (36)$$

where ΔP is the pressure difference across a curved surface, and R_1 and R_2 are the principle radii of the curvature.

Because the meniscus is semispherical, Young-Laplace equation is transformed to:

$$\Delta P = \frac{2\gamma}{R} \quad (37)$$

The pressure difference on the meniscus is balanced by the hydrostatic pressure from the raised liquid in the capillary tube.

$$\Delta P = \rho g h = \frac{2\gamma}{R} \quad (38)$$

$$\gamma = \frac{R \rho g h}{2} \quad (39)$$

In order to obtain accurate measurements, the glass capillary tube was suggested to be thoroughly clean with a uniform diameter less than 1 mm. The diameter of the container filled with the liquid should be at least 8 cm [164].

2.6.3.2 Wilhelmy plate method

This method was established by Ludwig Wilhelmy [165]. A thin and clean plate (typically platinum or glass) is suspended from a sensitive balance. As the plate bottom contacts the test liquid surface, the plate is pulled down by the surface tension force of the liquid. The force is recorded by the balance. And the surface tension is computed from the following equation:

$$\gamma = \frac{f \cos \theta}{2(w + t)} \quad (40)$$

f is the pulling force due to the surface tension of liquid, w is the width of the plate, and t is the thickness of the plate. With the assumption that the liquid wets the plate completely, the contact angle is zero.

2.6.3.3 Du Noüy ring method

The mechanism of this method is similar to Wilhelmy plate method [164]. Instead of the plate, the ring is used and submerged in the liquid. As the ring is pulled out the liquid, the maximum pulling force is recorded that typically occurs just before the ring detached from the surface.

$$\gamma = \frac{f_{max}}{4\pi R} \quad (41)$$

The correction for the buoyancy must be included to obtain accurate results. Harkins and Jordan [166] demonstrated that the correction was related to the ring radius, the radius of the ring wire and the volume raised by the ring. They also tabulated the F values.

$$\gamma = \frac{f_{max}}{4\pi R} F\left(\frac{R^3}{V}, \frac{R}{r}\right) \quad (42)$$

Compared to Wilhelmy plate method, this method requires liquid density to determine the volume raised by the ring.

2.6.3.4 Maximum bubble pressure method

This method relates the pressure difference in a bubble to surface tension [167]. The bottom of a tube is lowered to a depth h in a test liquid and gas is injected constantly to form a bubble at the bottom of the tube. The pressure difference inside the bubble is continually measured. The maximum pressure difference is reached when the bubble is semispherical. The maximum pressure difference is the sum of Laplace pressure of the bubble and the hydrostatic pressure due to the liquid layer of the thickness h .

$$\Delta P_{max} = \frac{2\gamma}{R} + \rho gh \quad (43)$$

ΔP_{max} is the maximum pressure difference inside the bubble, R is the radius of the capillary tube, ρ is the density of liquid, g is the gravitational constant, and h is the depth of the tube immersed into the liquid.

To simplify this method, two tubes with different diameters are immersed to the same depth, and the difference in the maximum bubble pressure for two tubes is measured as ΔP [168]. Then the equation is transformed to

$$\gamma = A\Delta P \left[1 + \left(\frac{0.69R_L\rho}{\Delta P} \right) \right] \quad (44)$$

R_L is the radius of the larger tube, ρ is the liquid density, and A is the constant determined by the calibration with standard liquids.

This modification avoids the knowledge of the immersing depth.

2.6.3.5 Drop weight method

The fundamental mechanism of this method is the balance of surface tension and gravitational forces. This method was firstly described in 1864 by Tate [169] who formed an equation describing the relationship between surface tension and drop weights.

$$mg = 2\pi R\gamma \quad (45)$$

m is the drop mass, g is the gravitational constant, R is the tip radius, and γ is the surface tension of the liquid.

This equation is now called Tate's law. If a liquid wets the tip, R is the outer radius of tip. If the liquid does not wet, R is the inner radius of tip.

In fact, the weight of the falling drop is lower than the drop weight in the equation 44, since some amount of liquid was retained on the tip after drop detachment. Therefore, a correction f has been introduced to the original Tate's equation.

$$mg = 2\pi R\gamma f \quad (46)$$

Harkins and Brown [170] found the correction factor f was a function of tip radius and drop volume.

$$f = f\left(\frac{R}{V^{1/3}}\right) \quad (47)$$

The f values for different $\frac{R}{V^{1/3}}$ were determined experimentally using water and benzene.

Lando and Oakley [171] employed the regression analysis on the original data including a series of drop volume, tip radius and correction factors obtained by Harkins and Brown [170], and derived a best-fit equation (equation 48).

$$F = \frac{1}{2\pi f} = 0.14782 + 0.27896\left(\frac{R}{V^{1/3}}\right) - 0.166\left(\frac{R}{V^{1/3}}\right)^2 \quad (48)$$

And Tate's equation was transformed to:

$$\gamma = \frac{mgF}{R} \quad (49)$$

However, the correction factor worked within a limited range of $\frac{R}{V^{1/3}}$ (from 0.3 to 1.2).

The Lee-Chan-Pogaku (LCP) with a wide range of $\frac{R}{V^{\frac{1}{3}}}$ (from 0 to 1.20) has been proposed as shown in equation 50 and 51 [172].

$$F = \frac{1}{2\pi f \left(\frac{R}{V^{\frac{1}{3}}} \right)} \quad (50)$$

$$\begin{aligned} f \left(\frac{R}{V^{\frac{1}{3}}} \right) = & 1.00 - 0.9121 \left(\frac{R}{V^{\frac{1}{3}}} \right) - 2.109 \left(\frac{R}{V^{\frac{1}{3}}} \right)^2 + 13.38 \left(\frac{R}{V^{\frac{1}{3}}} \right)^3 \\ & - 27.29 \left(\frac{R}{V^{\frac{1}{3}}} \right)^4 + 27.53 \left(\frac{R}{V^{\frac{1}{3}}} \right)^5 - 13.58 \left(\frac{R}{V^{\frac{1}{3}}} \right)^6 \\ & + 2.593 \left(\frac{R}{V^{\frac{1}{3}}} \right)^7 \end{aligned} \quad (51)$$

Since all these correction factors were based on the experimental data for various non-viscous liquids, the applicability of correction factors for viscous liquids is still arguable. Pu and Chen [173] reported that the correction factor was valid for surface tension measurement of viscous liquids (silicone oil) with viscosity up to 60 Pa.s and above. However, more research is needed to support their statements because of no comparison with other methods. Lee *et al.* [174] reported the calculated surface tension with the correction factor incurred more than 10 % error for silicone oil with the viscosity up to 60 Pa.s.

Lee *et al.* [174] derived a new method called LCP coefficient method for surface tension calculations that was independent of liquid properties. They found the relationship between drop mass and tip sizes by using quadratic regression as following (equation 52).

$$m = -C_1(R_o^2) + C_2(R_o) \quad (52)$$

By differentiating the above equation with respect to R and in the limit as $\Delta R \rightarrow 0$, the equation became:

$$\left(\frac{\Delta m}{\Delta R}\right)_{real} = -C_1(R) + C_2 = kC_2 \quad (53)$$

k is the correction factor.

Assuming ideal drop detachment occurred from various tip sizes, Tate's law was expressed as:

$$\gamma = \frac{g}{2\pi} \left(\frac{\Delta m}{\Delta R}\right)_{real} = 156.1kC_2 \quad (54)$$

Based on the experimental data from Wilkinson [175], Lee *et al.* [174] found that k equals to 1.097 and the above equation was described as follows:

$$\gamma = 171.2C_2 \quad (55)$$

The method was used to test silicone oil with the viscosity up to 60 Pa.s. Compared to surface tension analyses with correction factors, this method gave the lowest error.

2.6.3.6 Drop shape method

Andreas *et al.* [176] derived the equation to calculate liquid surface tension from the shape of a pendant drop. This method is based on two fundamental equations. The first is that the pressure caused by the curvature of the surface is equal to the product of the boundary tension and the mean curvature. The second is that when the drop is in equilibrium, the vertical forces acting across any horizontal plane of pendant drop are balanced. So a well-known equation was derived as

$$\gamma = \frac{\Delta\rho R_0^2 g}{\beta} \quad (56)$$

$\Delta\rho$ is the density difference between the drop and surrounding medium, g is the gravitational constant, R_0 is the curvature at drop apex, and β is the shape factor.

In the case of a pendant drop shown in Figure 2-10, the S value was defined as

$$S = \frac{d_s}{d_e} \quad (57)$$

d_e is the maximum width of the drop, and d_s is the width at the distance d_e from the drop bottom [176].

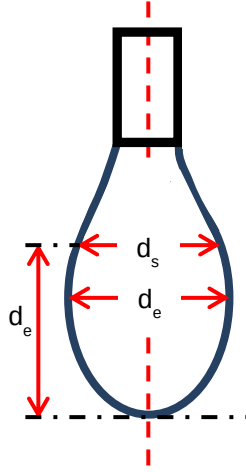


Figure 2-10 A pendant drop showing the characteristic dimensions.

The surface tension of a liquid was calculated from the equation:

$$\gamma = \frac{\Delta\rho d_e^2 g}{H} \quad (58)$$

$\Delta\rho$ is the density difference between drop and surrounding medium, g is the gravitational constant, and H is a value as a function of S .

Since the derivation of the H - S function mathematically was laborious and unsatisfactory, authors [176] employed water with known surface tension as the sample to measure various sized pendant drops and then established the H - S function in tabular form. The surface tensions of several common liquids derived from this method were in good agreement with data in literature.

Fordham [177] derived the shape factor β from the ratio S by using numerical integrations and calculated the corresponding H value according to the above two equations. Fordham also tabulated the β - S and H - S functions.

2.6.4 Solid surface energy analysis

Contact angle is commonly employed to characterize the surface energy of a solid. Different techniques for contact angle measurements have been reviewed in details by Neumann and Good [178]. Typically, the solid geometry determines the choice of methods. For example, sessile drop and captive bubble techniques are optimum for the solid with the flat surface. Wilhelmy plate method is widely used for the solid with a flat surface or fiber geometry. Wicking method is commonly used for the solid particles.

2.6.4.1 Sessile drop

This method is the most used technique for a solid with a flat surface because of its simplicity and convenience. A liquid droplet is simply placed on the flat surface of a solid and the contact angle is measured between the solid surface and the tangent of the droplet profile at the edge of the droplet. Because determination of the tangent line is subjective, the reproducibility and accuracy of this method depends on the operator's skill and experience. To ensure high accuracy, the commercial contact angle analyzers employ the Axisymmetric Drop Shape Analysis (ADSA) to determine the contact angles. This method can fit the drop profile captured during testing and derive the contact angle based on the Laplace equation [179, 180]. Also, the advanced and receding contact angle can be measure with this method when the liquid is slowly pumped out or pumped in accordingly [179, 180].

The drop profile on a solid surface results from a balance between cohesive force within the bulk liquid and adhesive force between liquid and solid. With the same probe liquid, the higher contact angle indicates the lower surface energy of the solid because the cohesive force within the liquid are stronger than the adhesive force. On the contrary, the solid with higher surface energy would give a lower contact angle, indicating that the adhesive force is stronger than the cohesive force within the liquid [181].

2.6.4.2 Wilhelmy plate method

As introduced in the above section, Wihelmy plate method relates the pulling force to the surface tension force based on the following equation.

$$\gamma = \frac{f \cos \theta}{2(w + t)} = \frac{f \cos \theta}{p} \quad (59)$$

f is the pulling force due to the surface tension of liquid, w is the width of the plate, t is the thickness of the plate and p is the perimeter of the plate.

If the solid sample is the plate with the known thickness and width, the contact angle would be obtained by the probe liquid with a known surface tension. Since the equation is related to the perimeter of the solid sample, the method is valid for the rod-like shape like fibers, wires and others. The perimeter of a sample determined by a probe liquid with the zero contact angle. Then, the contact angles can be obtained with other probe liquids same as with the plate [179].

2.6.4.3 Wicking method

This method measures contact angles on particular solids based on the capillary rise of the probe liquids. Due to the irregular shape of the particular solid, researchers tried to compress the particles to a pellet with a flat surface for contact angle measurements with the methods discussed above [182, 183]. However, the issues related the compression such as shape distortion resulted in misleading data [178]. Wicking method calculates the contact angles of liquids with particular solids by characterizing the capillary rise of the liquid through packed solids in a column. When a liquid contacts the packed particles, the liquid penetrates the pores between particles through capillary forces. This phenomenon was well described by Washburn equation [184, 185].

$$h^2 = \frac{R_e \gamma_L \cos \theta}{2\eta} t \quad (60)$$

h is the distance the liquid front travels in time t , R_e is the effective interstitial pore radius between filler particles, θ is the contact angle, γ_L is the liquid surface tension, and η is the liquid viscosity.

To obtain the contact angle, R_e is unknown. To solve this problem, n-alkanes with low surface tension are typically selected as spreading liquids which are expected to spread over the solid

surface immediately ($\theta = 0$). Then with Washburn equation, R_e can be obtained. Thereafter, the contact angles for different non-spreading liquids can be calculated through Washburn equation.

The method only provides advancing contact angles, because the liquid is actively advancing and wetting the solid particles without rest. In addition, this method is not suitable to measure the contact angles over 90° since no capillary rise happens in this case. The liquid with high viscosity like glycerol is rarely used as the probe liquid due to the tremendous time needed for the capillary rise. The uniform packing of particular solids in the column is critical to the accuracy of contact angle measurements because packing affects the smoothness of the capillary rise [186]. Shi and Gardner [187] reported that Washburn equation did not work for the swelling particles due to the interaction with the probe liquid.

2.7 References

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Chapter 3 Filler chemical analysis

3.1 Abstract

In an effort to broaden scientific understanding of the impacts of organic fillers on the performance of phenol-formaldehyde (PF) resoles, three fillers, flours of walnut shell, red alder (*Alnus rubra*) bark, and corn cob (furfural production) residue, were chemically characterized. Glucan, xylan, and acid insoluble lignin were major chemical constituents in alder bark and walnut shell. Xylan and acid insoluble lignin dominated their alkaline leachates. Corn cob residue contained a predominance of glucan and acid insoluble lignin but a small amount of xylan. Alkaline leaching resulted in the release of more lignin and much more glucan. Corn cob residue contained the extractives more than twice that found in other fillers. Additionally, the highest amount of carboxylic acid and phenolic hydroxyl groups was found in alder bark, but the lowest amount in walnut shell. Corn cob residue contained a significant amount of strong acid. Walnut shell had a lower acid buffering capacity than other fillers.

3.2 Key words

Organic fillers; Chemical composition; Conductometric titration; Acid buffering capacity

3.3 Introduction

Organic flours as fillers have been widely formulated with phenol-formaldehyde (PF) resoles that remain as the preferred resin used to manufacture structure wood-based composites from veneer, as in plywood and laminated veneer lumber. PF/filler/extender formulations are designed meet a variety of performance criteria including bulk flow, prepress tack, precure moisture retention, gap-filling properties, post-cure strength and durability [1, 2]. The fillers are typically organic flours derived from lignocellulosic biomass waste streams such as walnut nutshell, red alder (*Alnus rubra*) bark, and furfural production residues, *i.e.* corn cob residue. Considering they have held commercial significance for several decades, it is surprising to learn that fillers have been the subject of little or no detailed analysis resulting in scientific publication. In the wood products industry fillers are generally considered to be inert [3]. However, since the alkaline condition in the PF resin is comparable to that for the alkali extraction of

polysaccharides from lignocellulosic biomass [4], certain chemical components could leachate in the PF resin, which might impact the characteristics of formulated adhesives such as rheological behavior and surface tension. Therefore, the present work, as a part of university/industry research cooperation, is aimed at investigating the chemistry of three organic fillers (walnut shell, alder bark, and corn cob residue). Chemical constituents of fillers and their alkaline leachates are determined. Acid groups and acid buffering capacity of fillers are also quantified with conductometric titration.

3.4 Experimental

3.4.1 Materials

Modal™ alder bark (A) filler, walnut shell (W) filler, and corn cob residue (C) filler, were kindly provided by Willamette Valley Company (Eugene, OR, USA). The alder species was *Alnus rubra*; the walnut tree species was *Juglans regia*, English walnut, representing an unknown mixture of tree varieties characteristic of commercial production in northern California, U.S.A. The subspecies of corn (*Zea mays*) was unknown. Fillers were classified into sub-samples by sieves. The fraction retained on 200-mesh sieve (+200 mesh) was used for chemical compositional analysis. Unclassified fillers were used for charge determination. Size distributions of fillers, dispersed in isopropanol, were analyzed using a *Partica* LA-950 laser diffraction particle size distribution analyzer (HORIBA Scientific). Chemicals and reagents used in this paper were purchased from Fisher Scientific.

3.4.2 Chemical compositional analysis

Compositional analysis was conducted on size classified subsamples; fractions retained on a 200 mesh sieve were subjected to the determination of extractives, alkaline leachate, acid insoluble (Klason) and acid soluble lignin, monosaccharide content, ash content. The extractives content was determined according to ASTM D1105 using sequential ethanol/toluene extraction, ethanol extraction, and water extraction; the resulting sample was denoted as Ex-free filler.

Approximately 5 g dry Ex-free filler was alkaline extracted by stirring in 125 mL sodium hydroxide solution (4 wt%) for 24 hours. The solids were collected by centrifugation and washed with deionized water until neutral. The solids, denoted as Ex&AE-free filler, were vacuum dried

(45 °C, 5.4 mmHg, 72 hr.). Lignin and carbohydrate content in Ex-free and Ex&AE-free samples were determined respectively according to NREL/TP-510-42618 and NREL/LAP-004. Lignin and sugar contents in filler alkaline leachates were estimated by taking the differences in the chemical compositions of Ex-free and Ex&AE-free samples. Ash content was determined according to NREL/TP-510-42622 using 0.5 g of Ex-free samples that were incinerated (575 ± 25 °C for 24 hr.) and the residues weighted. The mean chemical compositions reported here are based upon duplicates.

3.4.3 Conductometric titration

Conductometric titration method was conducted according to the procedure described by Katz *et al.* [5]. Approximately 20 g dry sample was stirred magnetically in 200 mL hydrochloric acid (HCl, 0.1 M) for 4 hours and then washed with deionized water until the conductance to be constant. The solids, identified as “washing” fillers, were freeze-dried followed by vacuum dried (45 °C, 5.4 mmHg, 48 hr.). Approximately 2 g dry sample was dispersed in 450 mL sodium chloride (NaCl, 0.001 M) prepared in deionized water. The addition of NaCl was to minimize the Donnan effect of unequal ion distribution between the interior of the filler cell wall and the external solution [6]. Prior to the titration, hydrochloric acid (HCl, 0.1 M) was added to the filler suspension until pH of suspension was lower than 3.6 to achieve a clear titration curve. Titration was conducted with sodium hydroxide (NaOH, 0.1 M) or sodium bicarbonate (NaHCO₃, 0.1 M) dispersed from a digital burette while the suspension was stirred under the nitrogen atmosphere. The pH and conductivity of suspension was detected by SevenMulti™ pH/conductivity meter (Mettler Toledo).

3.5 Results and discussion

3.5.1 Particle size distribution

The size distributions of fillers are shown in Figure 3-1. The size distributions of unclassified fillers exhibited some variation, possibly indicating geometric differences that might arise from cellular anatomical differences among the three tissue types, alder bark, walnut shell, and corn cob. However, the size distributions of +200 mesh fraction of fillers were quite similar.

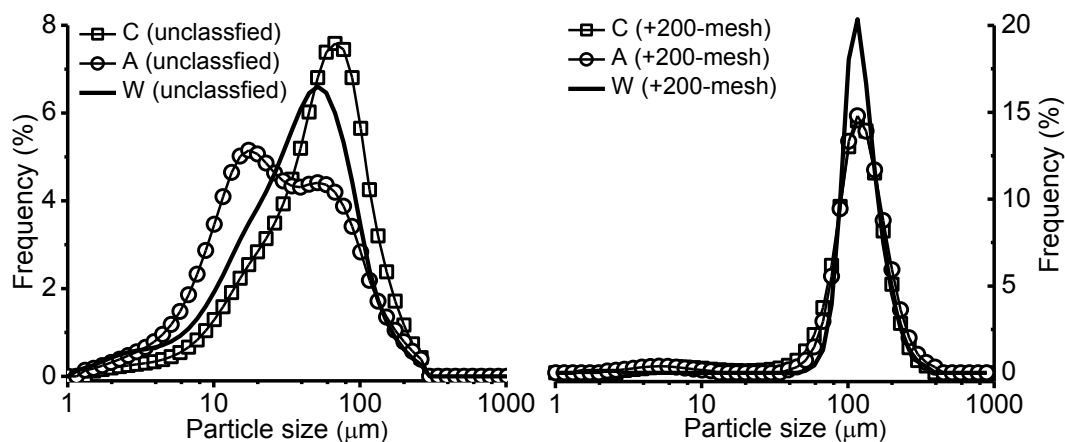


Figure 3-1 Particle size distribution of fillers.

3.5.2 Chemical compositional analysis

The chemical constituents of fillers are shown in Figure 3-2 and Table 3-1. Alder bark and walnut shell contained the similar chemical compositions, which substantially differ from corn cob residue. Glucan, xylan, and acid insoluble lignin corresponded to a significant portion of compositions of alder bark and walnut shell. Their alkaline leachates contained a similar chemical composition, where xylan and acid insoluble lignin dominated. While similar in composition, alder bark and walnut shell differed most in the quantity of extractives, xylan, and acid soluble lignin. Walnut shell also released more xylan. Alder bark contained higher extractives content. The extractives content in corn cob residue was more than twice that found in the other fillers. Corn cob residue results from the acid catalyzed, high pressure steam digestion of corn cob for the production of furfural, where most of hemicellulose has been acid hydrolyzed [7, 8]. This probably explains why corn cob residue releases more lignin, and much more glucan under alkaline leaching. Ash contents of alder bark, walnut shell, and corn cob residue are listed in Table 3-2. Three Ex-free fillers had an ash content of 2.3 %, 0.6 %, 1.7 %, respectively. Based on the percentage of extractives, the ash contents of three fillers were 2.1 %, 0.5 %, and 1.3% that is higher than that reported by Sellers *et al.* [9]. The difference could be resulted from the larger size particles in the present study, since the ash tended to accumulate in the finer fraction [10, 11].

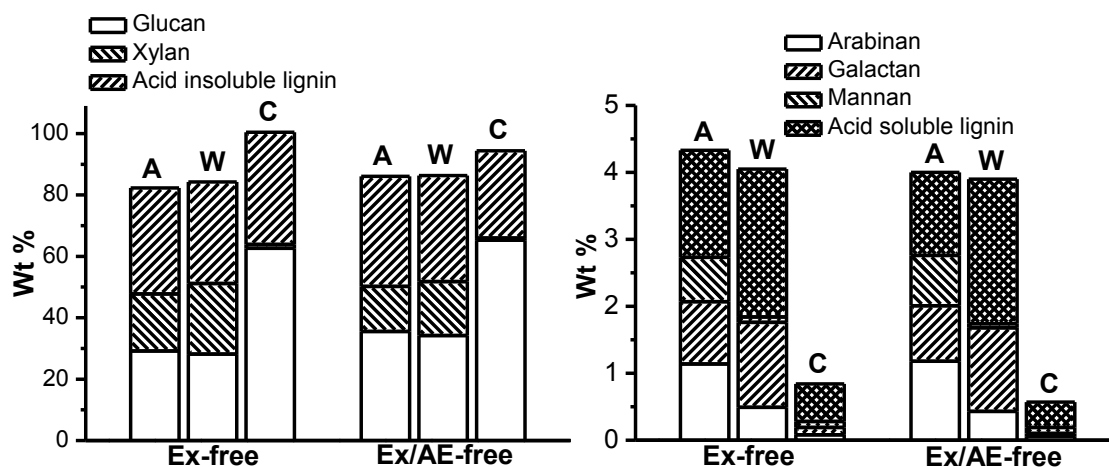


Figure 3-2 Chemical constituents of organic fillers.

Table 3-1 Chemical constituents of alder bark (A), walnut shell (W), and corn cob residue (C) (% of total dry mass).

		Soxhlet extractives	Glucan	Xylan	Acid insoluble lignin	Arabinan	Galactan	Mannan	Acid soluble lignin
	A	9.4							
	W	4.5							
	C	25.5							
Ex-free	A		26.4	16.8	31.3	1.0	0.8	0.6	1.4
	W		26.9	22.0	31.6	0.5	1.2	0.1	2.1
	C		46.7	0.9	27.2	0.1	0.1	0.1	0.4
Ex&AE-free	A		26.0	10.8	26.2	0.8	0.6	0.5	0.9
	W		25.4	13.1	25.6	0.3	0.9	0.1	1.6
	C		40.6	0.4	17.7	0.1	0.0	0.1	0.2
Alkaline leachate	A		0.4	6.0	5.1	0.2	0.2	0.1	0.5
	W		1.5	8.9	6.0	0.1	0.3	0.0	0.5
	C		6.0	0.5	9.5	0.0	0.1	0.0	0.2

Table 3-2 Ash contents of organic fillers.

Filler	Ash (%)*	Ash (%)**
Alder bark	2.3±0.1	2.1±0.1
Walnut shell	0.6±0.1	0.5±0.1
Corn cob residue	1.7±0.2	1.3±0.1

* % of total dry mass of Ex-free sample; ** % of total dry mass of raw sample

3.5.3 Conductometric titration analysis

Carboxylic acid groups associated with glucuronic acid units of xylan and phenolic hydroxyl groups associated with lignin are presented in lignocellulosic fillers [6]. The approximated pKa values were 4.5 and 10.2, respectively [6]. Thereby, sodium hydroxide (NaOH, 0.1 M) and sodium bicarbonate (NaHCO₃, 0.1 M) were used to determine the quantities of two acid group types. Figure 3-3 shows conductometric titration curves with 0.1 M NaOH and NaHCO₃ for C-washing sample after the transformation of acidic groups to a hydrogen form. An initial decrease in conductivity corresponded to the neutralization of HCl added before titration. The horizontal plateau after the first inflection point corresponded to the neutralization of weak acid groups. Beyond the second inflection point, the conductivity increased due to the excess NaOH or NaHCO₃. The acid groups were calculated on the basis of the consumed NaOH or NaHCO₃ volume in the plateau (equation 1). The curve titrated with NaOH provided the total amount of carbonic acid and phenolic hydroxyl groups, and the curve with NaHCO₃ gave the quantity of carbonic acid groups.

$$\text{Acid groups (mmol/kg)} = V_{\text{plateau}} C / m \quad (1)$$

V_{plateau} is the volume of NaOH or NaHCO₃ (0.1M) of the plateau, C is the concentration of NaOH or NaHCO₃, m is sample mass.

Mean carboxylic acid and phenolic hydroxyl group contents in three fillers are significantly different as listed in Table 3-3. Alder bark contained the largest quantity of two acid types. Corn cob residue contained a comparable amount of phenolic hydroxyl groups, but the smallest amount of carboxylic acid groups. Carboxylic acid group content is relatively low in walnut shell, and phenolic hydroxyl is the lowest.

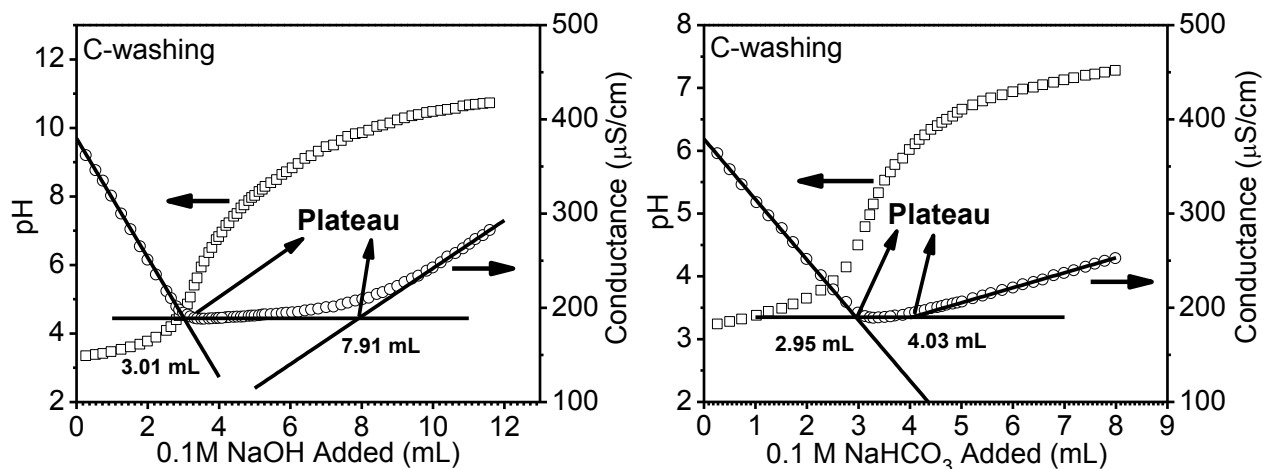


Figure 3-3 Conductometric titration curves with 0.1 M NaOH and NaHCO₃ for C-washing samples.

Table 3-3 Carboxylic acid and phenolic hydroxyl group contents (mmol/kg).

Filler	Carboxylic acid+Phenolic hydroxyl*	Carboxylic acid*	Phenolic hydroxyl
A	404±6	139±13	265
W	144±13	81±15	63
C	271±33	51±5	220

*duplicates

Additionally, C-non-washing exhibited a very low pH in 450 mL sodium chloride (NaCl, 0.001 M) solution shown in Table 3-4, indicating the existence of strong acid. After acid-washing, pH of corn cob residue increased to a similar level as other fillers. It is possible that the strong acid came from the acid catalyst residue during furfural production from corn cobs [7, 8]. To quantify the strong acid groups, C-non-washing was titrated with 0.1 M NaOH and NaHCO₃ illustrated in Figure 3-4. Since no HCl (0.1M) added before titration, the initial decrease in conductivity corresponded to the neutralization of strong acid groups in corn cob residue. With the volume of consumed alkaline solution in this region, the acid groups were quantified according to equation 1 (Table 3-5).

Table 3-4 pH of fillers in sodium chloride solution.

Filler	pH	
	non-washing	washing
A	5.3	4.6
W	5.2	4.4
C	3.2	4.3

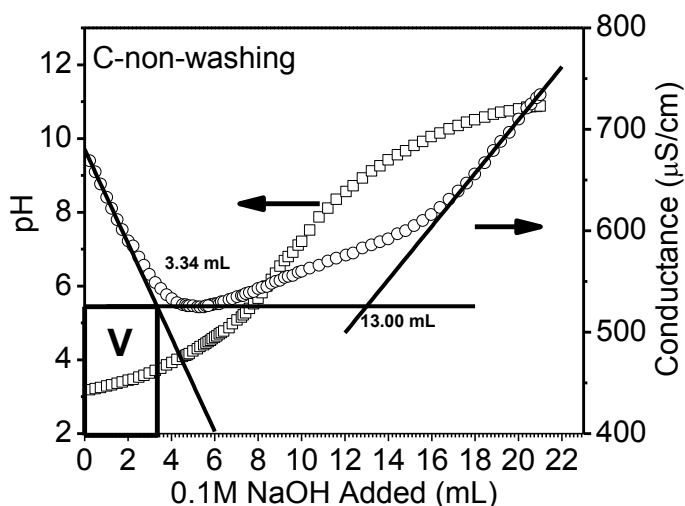


Figure 3-4 Conductometric titration curves with 0.1 M NaOH for C-non-washing sample.

Table 3-5 Strong acid group contents (mmol/kg)*.

Filler	Strong acid group	
	NaOH	NaHCO ₃
C	176±1	172±1

*duplicates

3.5.4 Acid buffering capacity

Because of different definitions, acid buffering capacity was defined here as the volume of NaOH (0.1M) added to titrate the acid-washing filler in sodium chloride (NaCl, 0.001 M) solution from pH of 7 to 10. Walnut shell exhibited the lowest acid buffering capacity among three filler types (Table 3-6), and that of alder bark is a little higher than corn cob residue.

Table 3-6 Acid buffering capacity of fillers (mL)*.

Filler	NaOH
A	6.0±0.3
W	1.4±0.1
C	4.7±0.0

*duplicates

3.6 Conclusions

Walnut shell, alder bark, and corn cob (furfural production) residue were chemically characterized with compositional analysis and conductometric titration. Alder bark and walnut shell contained similar chemical compositions, which substantially differ from corn cob residue. Glucan, xylan, and acid insoluble lignin corresponded to a significant portion of chemical compositions of alder bark and walnut shell, whereas corn cob residue only contained a small amount of xylan. Alkaline leaching resulted in a considerable amount of glucan and acid insoluble lignin in corn cob residue. Extractives in corn cob residue were more than twice that found in other fillers. Also, corn cob residue contained strong acids that were not seen in other fillers. Walnut shell was demonstrated with a lower acid buffering capacity compared to other fillers.

3.7 Acknowledgements

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Chapter 4 Filler surface analysis with the column wicking method

4.1 Abstract

Organic fillers derived from biomass waste streams are commonly formulated with phenol-formaldehyde resoles in the production of veneer-based wood composites such as plywood and laminated veneer lumber. The surface characteristics of three fillers, flours of walnut shell, red alder (*Alnus rubra*) bark, and corn cob (furfural production) residue, were investigated with the column wicking method and the Washburn equation. A series of n-alkanes (spreading liquids) provided reliable estimates of interstitial pore radii, which then enabled contact angle estimates for a variety of non-spreading liquids. Among the three fillers, only alder bark data was complicated by swelling effects, which were eliminated with strict data quality criteria. Corn cob residue exhibited the highest total surface free energy, but all fillers had low energies in comparison to what is typically published for freshly machined wood surfaces. Consistent with the wood literature, the surface free energies of all fillers were dominated by dispersive effects, and the minor polar contributions were basic in nature. Specific surface areas determined from wicking substantially disagreed with BET measurements using N₂ adsorption, where the former was considered to be more sensible and reliable.

4.2 Key words

Organic fillers; Contact angles; Wettability; Surface area

4.3 Introduction

Organic fillers based upon biomass sources such as nutshells and tree bark have been commercially formulated with phenol-formaldehyde (PF) resoles for many decades. Such formulations remain as the preferred adhesives used to manufacture structural wood-based composites from veneer, as in plywood and laminated veneer lumber. In spite of their lasting commercial significance, such organic fillers they have been the subject of very little detailed analysis resulting in scientific publication.

For instance, organic filler surface properties are expected to impact filler dispersion in the resin matrix, including filler-filler, and filler-resin interactions. However, this fundamental topic has

not been addressed in the wood adhesives literature. Stemming from an industry/university cooperative research effort, the objective of this work is to study the surface chemistry of three organic fillers that are commonly used to manufacture veneer-based composites; these are walnut shell, alder bark (*Alnus rubra*), and corn cob (furfural production) residue.

This surface analysis employs the column wicking method using the Washburn equation. This method is based on the phenomenon of favorable wetting ($\cos\theta > 0$) such that capillary forces draw probe liquids into the pores between filler particles as described by Washburn (equation 1) [1, 2].

$$h^2 = (R_e \gamma_L \cos \theta / 2\eta)t = Kt \quad (1)$$

h is the distance the liquid front travels in time t , R_e is the effective interstitial pore radius between filler particles, θ is the contact angle, γ_L is the liquid surface tension, η is the liquid viscosity.

Surface wicking has been reliably applied to a number of particulate materials [1, 3, 4]. Relatively little has been published on the wicking surface analysis of lignocellulosics. Hodgson and Berg [5] studied wicking flow in cellulose fiber networks; Walinder and Gardner studied spruce (*Picea abies* Karst.) and maple (*Acer saccharum* Marsh.) particles [6, 7], and Meijer *et al.* [8] derived the Lifshitz-van der Waals surface energy component of spruce (*Picea abies*) and meranti (*Shorea spp.*).

4.4 Experimental

4.4.1 Materials

Modal™ alder bark (A) filler, walnut shell (W) filler, and corn cob residue (C) filler were kindly provided by Willamette Valley Company (Eugene, OR, USA). The alder species was *Alnus rubra*; the walnut species was *Juglans regia*, English walnut, representing an unknown mixture of tree varieties characteristic of commercial production in northern California, U.S.A. The subspecies of corn (*Zea mays*) was unknown. Size distributions of fillers, dispersed in isopropanol, were analyzed using a *Partica* LA-950 laser diffraction particle size distribution analyzer (HORIBA Scientific). All fillers were vacuum dried (45 °C, 5.4 mmHg vacuum, 48

hours) before use. Probe liquids were obtained from Alfa Aesar, Fisher Scientific, and Sigma-Aldrich; water was HPLC grade, and the purity of perfluorohexane and 1-bromonaphthalene was 98 % and 97 %, respectively. Purity of all other liquids was 99+%; surface tension and viscosity at 20 °C (Table 4-1) were adopted from references [1, 9-12].

Table 4-1 Surface tensions (mJ/m^2), including components, and viscosities ($mPa \cdot s$) of probe liquids used in this study.

Liquid	η	γ_L	γ_L^{LW}	γ_L^{AB}	$\gamma_L^{\oplus}$	$\gamma_L^{\ominus}$
Perfluorohexane	0.69	11.9	11.9	0	0	0
Pentane	0.24	16.1	16.1	0	0	0
Hexane	0.326	18.4	18.4	0	0	0
Heptane	0.409	20.1	20.1	0	0	0
Octane	0.542	21.6	21.6	0	0	0
Dodecane	1.49	25.4	25.4	0	0	0
cis-Decalin	3.38	32.2	32.2	0	0	0
1-bromonaphthalene	4.89	44.4	44.4	0	0	0
Ethyl acetate	0.442	23.9	23.9	0	0	6.2
Formamide	3.75	58	39	19	2.28	39.6
Water	1	72.8	21.8	51	25.5	25.5

η : liquid viscosity, γ_L : liquid surface tension, γ_L^{LW} : Lifshitz-van der Waals component, γ_L^{AB} : Lewis acid-base component, $\gamma_L^{\oplus}$: Lewis acid parameter, $\gamma_L^{\ominus}$: Lewis basic parameter.

4.4.2 Filler density measurement

Filler density ρ was measured at room temperature according to ASTM D854-10 [13] by using a 50 ml water pycnometer with approximately 1 g dry sample.

4.4.3 Brunauer–Emmett–Teller (BET) surface area measurement

BET surface areas of fillers were measured using an *Autosorb-1* surface area and pore size analyzer with a 6 mm large bulb cell (Quantachrome Instruments). Samples were degassed at 45 °C until outgas pressure rise was less than 10 microns Hg per minute. The *Autosorb-1* measured the weight of the adsorbed nitrogen gas on the solid surface at different relative pressures. The specific surface areas of fillers were calculated using the BET equation for a relative pressure range p/p_0 0.05-0.35 [14-16].

4.4.4 Column wicking method

Using an electric vibrator, filler particles were packed into graduated columns (inner diameter 3 mm) the bottoms of which were plugged by glass wool, to 1 cm of column height (Figure 4-1). The top of each graduated column was fitted with an enlarging adapter (ST/NS 19/22) for connection to a powder addition funnel (50 mL). Filler particles were slowly filled into the column by turning the auger feed; filling occurred in 3 mL increments between which electric vibration was applied. Total filler-packed volume was 7-8 mL. The column loading procedure was rigorously systematic such that a uniform unit column weight (mg filler/mm column height) resulted for each filler type, but that varied naturally between filler types.

Packed columns were equilibrated (25 ± 2 °C, 30 min.) in a larger cylinder containing the probe liquid. Thereafter, the column was immersed into the probe liquid to a depth of about 10 mm above the column end (Figure 4-1). Timing began once the liquid front reached 25 mm above the column end, and times to reach subsequent 5 mm increments were recorded (12 data points per column). R_e was determined with a homologous series of n-alkanes with low surface tensions such that the contact angle θ was assumed equal to zero (*i.e.* spreading liquids). Thereafter, the contact angles for different non-spreading liquids were determined through the plot of h^2 vs. t and the Washburn equation (using R_e as determined with the n-alkanes).



Figure 4-1 Column wicking device.

4.4.5 Calculation of filler surface energy

Based on the Lewis acid-base interactions and Lifshitz-van der Waals interactions (acid-base theory), van Oss, Good and Chaudhury [9, 17] derived the van Oss-Chaudhry-Good equation (equation 2, 2a) to calculate surface free energy components of solid samples.

$$\gamma_L(1 + \cos \theta) = 2(\sqrt{\gamma_S^{LW} \gamma_L^{LW}} + \sqrt{\gamma_S^{\oplus} \gamma_L^{\ominus}} + \sqrt{\gamma_S^{\ominus} \gamma_L^{\oplus}}) \quad (2)$$

$$\gamma_S = \gamma_S^{LW} + \gamma_S^{AB} = \gamma_S^{LW} + 2\sqrt{\gamma_S^{\oplus} \gamma_S^{\ominus}} \quad (2. a)$$

γ_L is the liquid surface tension, θ is the contact angle, γ_L^{LW} and γ_S^{LW} are liquid and solid Lifshitz-van der Waals components respectively, $\gamma_L^{\oplus}$ and $\gamma_S^{\oplus}$ are liquid and solid Lewis acid parameters respectively, $\gamma_L^{\ominus}$ and $\gamma_S^{\ominus}$ are liquid and solid Lewis basic parameters respectively, γ_S is the solid surface free energy, γ_S^{AB} is the solid Lewis acid–base component. To determine the surface free energy components (γ_S^{LW} , $\gamma_S^{\oplus}$, and $\gamma_S^{\ominus}$) of a solid, at least three liquids with known surface tension components, two of which must be polar, are required [18].

Based on the concept that the surface free energy is the sum of the dispersive component (γ^d corresponding to γ^{LW}) and polar component (γ^p corresponding to γ^{AB}), the Owens [19] and Wu [20] treatments were also used to calculate solid surface free energy components (γ_S^d and γ_S^p) with the geometric mean (equation 3) and the harmonic mean (equation 4) treatments.

$$\gamma_L(1 + \cos \theta) = 2(\sqrt{\gamma_S^d \gamma_L^d} + \sqrt{\gamma_S^p \gamma_L^p}) \quad (3)$$

$$\gamma_L(1 + \cos \theta) = 4\gamma_S^d \gamma_L^d / (\gamma_S^d + \gamma_L^d) + 4\gamma_S^p \gamma_L^p / (\gamma_S^p + \gamma_L^p) \quad (4)$$

To determine the surface free energy components (γ_S^d and γ_S^p), pairs of polar and apolar liquids are required [18]. The equations were solved with a least-square approximation [21]. Two apolar liquids were first used to obtain the γ_S^{LW} and γ_S^d of fillers, since they do not swell the solid so that the contact angle does not tend to decay [9]. Then the γ_S^{AB} and γ_S^p , and/or Lewis basic/acid

parameters ($\gamma_L^\ominus/\gamma_S^\ominus$) were calculated with the other polar liquids. In the following discussion, we use the dispersive component for γ^d or γ^{LW} , and the polar component for γ^p or γ^{AB} .

4.5 Results and discussion

4.5.1 Unit column weight

The column packing procedure was carefully controlled such that the resulting unit column weights, Table 4-2, were quite uniform within fillers types. However, between filler types the unit column weights varied due to density differences, Table 4-2, differences in particle size distribution, Figure 4-2, and probably geometrical differences such as particle aspect ratio which were not determined in this study. All fillers were ground to pass through a 100 mesh sieve. The variations in particle size distribution might reflect cellular anatomical differences among the respective tissue types, alder bark, walnut shell, and corn cob.

Table 4-2 Unit column weights and densities of fillers.

Filler	UCW, mg/mm *	Density, g/cm ³ *
Corn cob residue	4.90±0.08 (32)	1.74±0.06 (3)
Alder bark	4.55±0.15 (46)	1.55±0.03 (3)
Walnut shell	5.65±0.21 (33)	1.60±0.02 (3)

* parentheses= # observations.

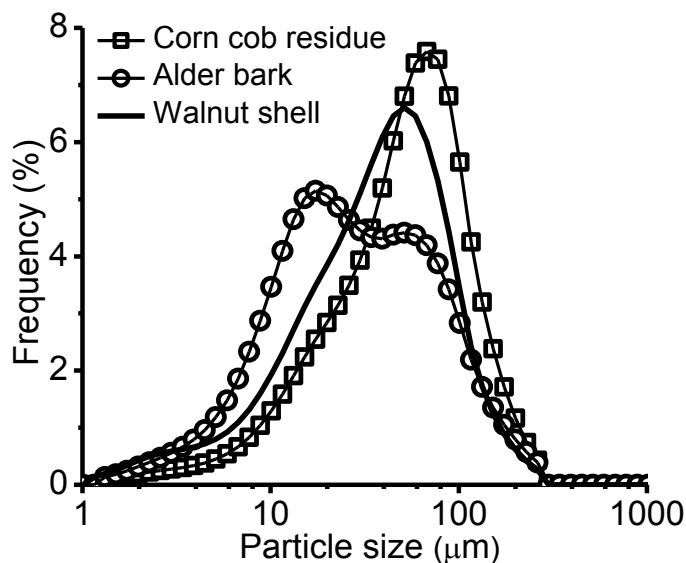


Figure 4-2 Filler particle size distributions.

4.5.2 Data quality criteria for Washburn plots

Figure 4-3 shows example Washburn plots for hexane wicking in corn cob residue (C) and alder bark (A). All wicking experiments exhibited an initial nonlinearity that has been attributed to “hydrodynamic disturbances” [1, 6]; perhaps this reflects a non-steady state mass transfer condition. Thereafter, the raw data was typically quite linear as Figure 4-3 shows for corn cob residue; not shown is that walnut shell data was similarly well behaved. In contrast, alder bark frequently exhibited evidence of particle swelling, Figure 4-3. Swelling effects must be excluded and these are observed as slope deviations indicative of reduced wicking rates at longer times. These observations lead to minimum data quality criteria required to consider any single Washburn plot as acceptable. Typically the initial four data points were excluded, and all subsequent linear fits had to exceed a correlation coefficient (R^2) of 0.998; otherwise the data was discarded as unacceptable. Furthermore, when swelling effects were apparent (only with alder bark) the long time data was excluded such that the resulting linear fit ($R^2 > 0.998$) was based upon a minimum of four data points. As these criteria were applied it was found that the resulting Washburn plot slopes were quite uniform for corn cob residue and walnut shell, but rather variable for alder bark. Consequently, a final data quality criterion was established as a minimum of four acceptable Washburn plots for each spreading liquid where for corn cob residue and walnut shell the COV (standard deviation/mean x 100) in slope did not exceed 7.0 %; and for alder bark the COV in Washburn plot slope did not exceed 19 %. Considering these data quality criteria, Table 4-3 summarizes the experimentation conducted for spreading liquids on all filler types.

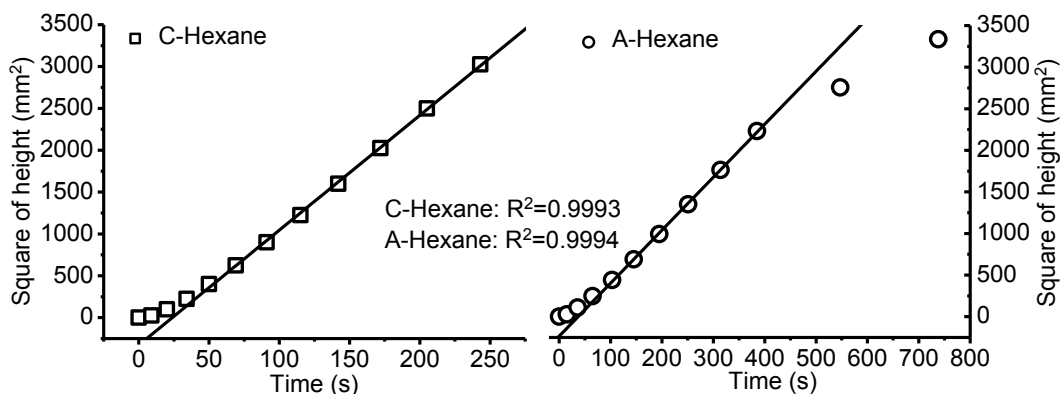


Figure 4-3 Example Washburn plots: hexane wicking in corn cob residue (C) and alder bark (A). Alder bark exhibits evidence of particle swelling during long times and any such nonlinearity was excluded.

Table 4-3 Summary of experiments conducted for spreading liquids on all filler types.

Liquid	COV (%) in Washburn plot slopes	# acceptable/ total # Washburn plots
Alder bark		
Perfluorohexane	4.6	4/5
Pentane	14.2	4/9
Hexane	11.6	4/6
Heptane	18.7	10/15
Octane	9	4/7
Dodecane	12.1	4/6
Corn cob residue		
Perfluorohexane	6.4	4/4
Hexane	6.3	4/5
Octane	6.3	4/4
Dodecane	4.9	4/6
Walnut shell		
Perfluorohexane	7	6/7
Hexane	2.5	4/5
Octane	6.3	4/6
Dodecane	6.1	5/6

4.5.3 Effective interstitial pore radius

By plotting $2\eta h^2/t$ vs. γ_L for all spreading liquids ($\cos \theta=1$), the effective interstitial pore radii (R_e) were determined as the slopes shown in Figure 4-4. Figure 4-4 includes data for perfluorohexane which had the lowest surface tension of all probes used in this study. For walnut shell, perfluorohexane fell on the same trendline as the normal alkanes, but this was not so for

the two other fillers; that data was excluded from the calculation of R_e and is presented here for general interest. Relative to normal alkanes, the suggestion is that a homologous series of perfluoro-n-alkanes might indicate significantly different values for R_e . As suggested above, corn cob residue and walnut shell data provided very reliable estimates of R_e using only hexane, octane, and dodecane. Whereas variations in alder bark data required the use of two additional spreading liquids, pentane and heptane. Figure 4-4 demonstrates that the three filler types exhibited significantly different R_e values, highest for corn cob residue and lowest for alder bark.

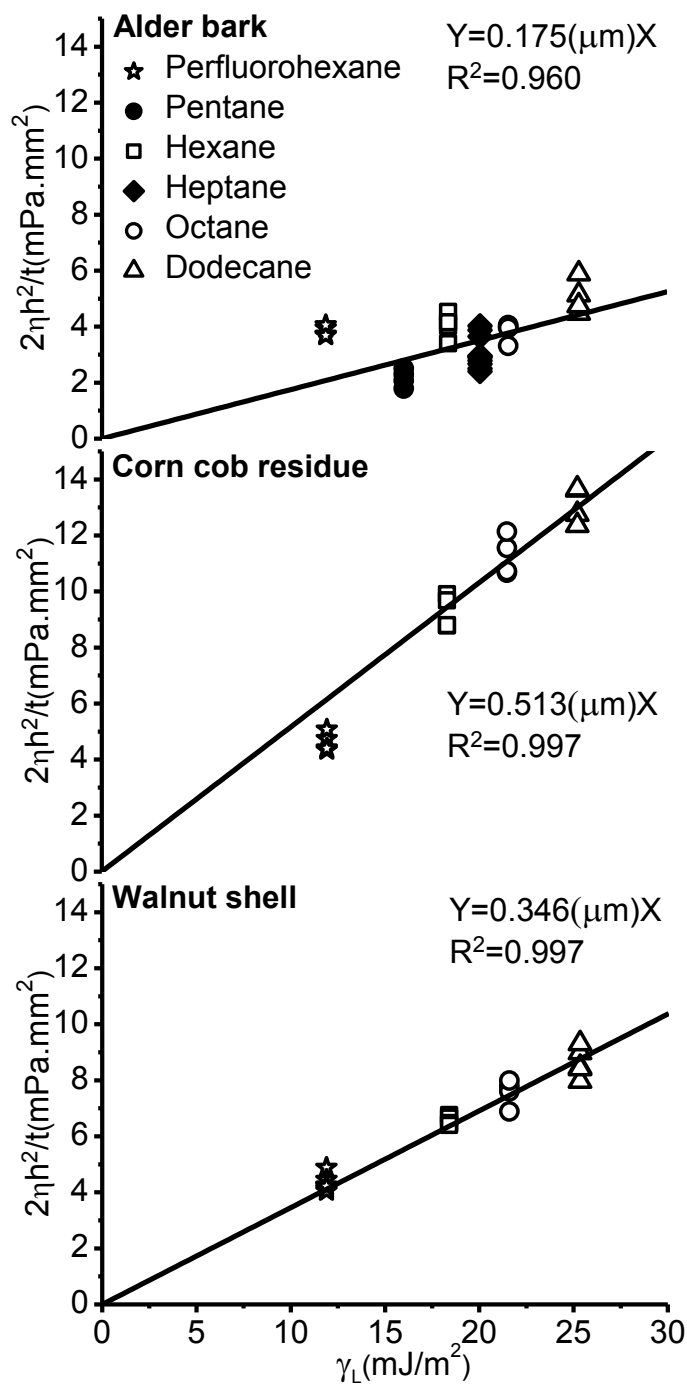


Figure 4-4 Plots of $2\eta h^2/t$ vs. γ_L for all spreading liquids used to determine R_e (slope) for each filler type; fits were forced through the origin. Note that perfluorohexane data was not used in the linear fits shown here.

4.5.4 Contact angles and surface energy components

Having established R_e for each filler type using spreading liquids, the contact angles of non-spreading liquids were determined from the corresponding raw data where all of the previously described data quality criteria were applied (except for formamide on alder bark; the first 5 data points were excluded). Figure 4-5 presents typical raw data for the non-spreading liquids on each filler type. Once again only for alder bark there were indications of particle swelling and this is why the data sets for ethyl acetate, 1-bromonaphthalene, and formamide have fewer points. Nevertheless, reliable and highly linear Washburn plots were obtained for all filler/solvent combinations.

The resulting mean contact angles for the non-spreading liquids are shown in Table 4-4. Within all filler types, the data variation was quite low for water and formamide, and it was substantially higher for the less polar probes. Likewise the variation between filler types was also much greater for the less polar liquids.

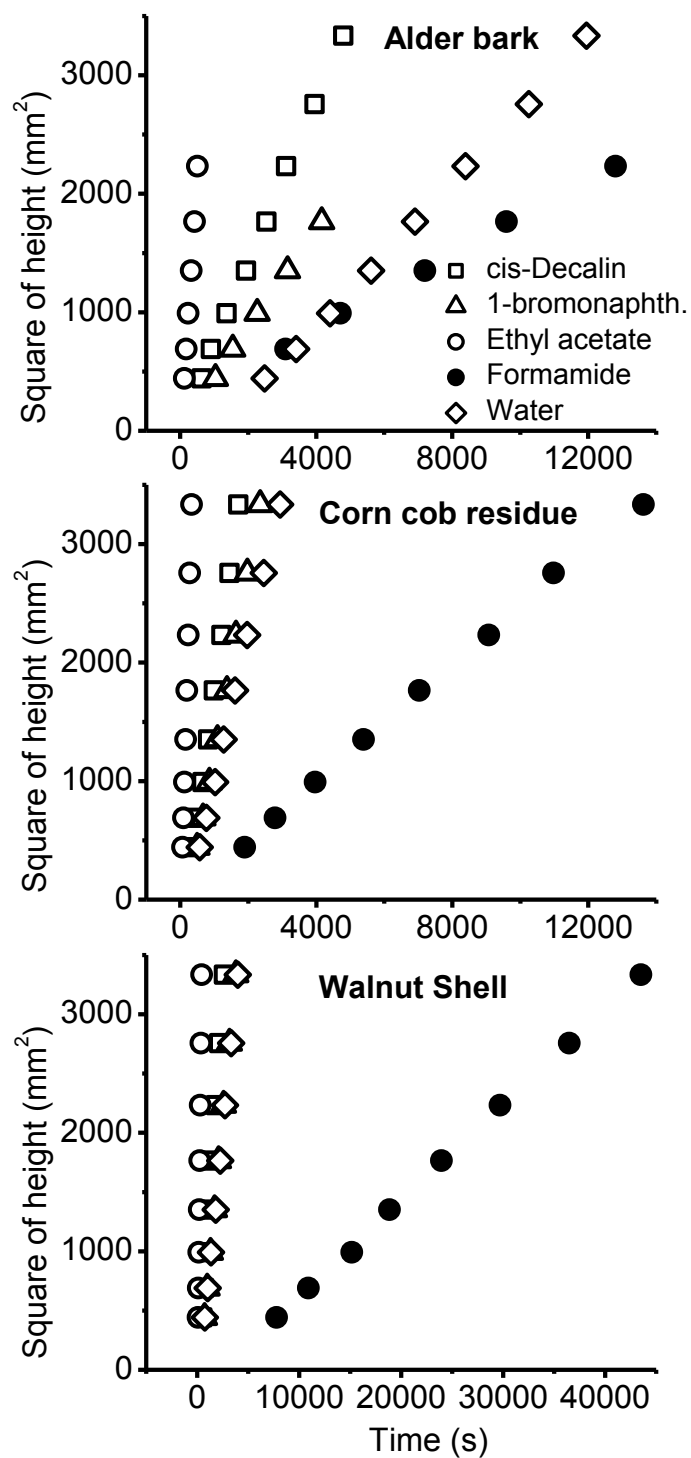


Figure 4-5 Typical raw data collected for non-spreading liquids on all filler types.

Table 4-4 Mean contact angles determined for non-spreading liquids (# observations).

Filler	Contact angle, degrees				
	cis-decalin	1-bromonaphth.	ethyl acetate	formamide	water
Alder bark	35.1±4.3 (7)	49.6±6.4 (8)	17.3±7.7 (6)	83.3±0.1 (4)	87.4±0.6 (4)
Corn cob residue	26.5±2.1 (4)	45.6±2.7 (4)	36.6±2.2 (4)	86.7±0.3 (4)	86.2±0.2 (4)
Walnut shell	30.9±4.5 (4)	51.9±1.7 (4)	31.1±2.7 (4)	88.3±0.1 (4)	86.3±0.5 (5)

The measured contact angles and published surface tension components for the non-spreading liquids were used to derive filler surface free energies, and component energies using the acid-base (AB), geometric mean (GM), and harmonic mean (HM) methods, Table 4-5. Regardless of surface models, the total surface free energies, γ_s , of all fillers were found to be significantly lower than what is generally reported for a variety of wood surfaces [8, 22-25]. However, similar to wood surfaces, the dispersive component (γ^d or γ^{LW}) dominated the surface behavior of all fillers, and the polar components were principally basic in nature [8, 22-25]. Corn cob residue exhibited a slightly higher surface energy than alder bark and walnut shell, which were effectively indistinguishable. On the other hand, the small polar components found for all fillers were consistently higher for alder bark and walnut shell in comparison to corn cob residue. Compared to AB and GM, the HM model provided consistently higher total and dispersive free energies. Among models other minor differences were observed, but no single model seemed more or less informative, excepting perhaps the AB model which specified basicity in the polar component. The relatively low filler surface energies could be related to the heat generated during their processing/grinding; it is well known that excessive heat will deactivate wood surfaces for example as in G éardin *et al* [25].

Table 4-5 Filler surface energies and component energies derived from non-spreading liquid contact angles.

Filler	Surface free energy (mJ/m^2)									
	acid-base				harmonic mean			geometric mean		
	γ_s	γ_s^{LW}	$\gamma_s^{\oplus}$	$\gamma_s^{\ominus}$	γ_s	γ_s^d	γ_s^p	γ_s	γ_s^d	γ_s^p
Corn cob residue	30.7	30.7	0	4.6	34.2	31.4	2.9	31.9	30.7	1.2
Alder bark	28.6	28.6	0	5.4	33.2	29.4	3.8	30.2	28.6	1.6
Walnut shell	28.5	28.5	0	5.4	33.1	29.8	3.3	29.9	28.5	1.4

4.5.5 Specific surface area

This work presented a good opportunity to calculate the specific surface areas of all fillers because many columns were packed and those columns exhibited highly reproducible unit column weights (Table 4-2). Consequently, related measurements were conducted using N₂ gas adsorption in the so-called BET method. With the known effective interstitial pore radius between filler particles (R_e), the specific surface areas of fillers (A_s) were determined on the basis of equation 5 derived by White [26, 27].

$$A_s = 2(1 - \Phi)/(\Phi\rho R_e) \quad (5)$$

ρ is the specific filler density, Φ is the volume fraction of solid in a packed volume of filler particles.

The volume fraction was calculated on the basis of equation 6.

$$\Phi = (m_s/\rho)/V_T \quad (6)$$

m_s is the mass of packed fillers in the column and V_T is the total volume including packed fillers and interstitial pores between fillers. Both m_s and V_T were recorded for each packing.

The specific surface areas determined by the column wicking and BET methods resulted in substantially different results, Table 4-6. Others have found that the two methods provide more similar results for inorganic particles such as talcs, montmorillonites, and kaolinites [27]. In consideration with Figure 4-2, Table 4-6 suggests that the wicking measurements are more sensible. For example alder bark exhibited the lowest average particle size, the smallest interstitial pore radius, and logically the greatest specific surface area. Furthermore, corn cob residue and walnut shell exhibited more similar, and larger, particle size distributions; and the respective specific surfaces area are correspondingly similar and much lower than for alder bark.

Table 4-6 Specific surface areas (A_s), volume fraction (Φ), effective interstitial pore radius (R_e) of fillers.

Filler	A_s (m^2/g)		Φ (%)	R_e (μm)
	Wicking	BET		
Corn cob residue	5.70 ± 0.16	2.02 ± 0.09	28.3 ± 0.6	0.513
Alder bark	17.99 ± 0.86	1.06 ± 0.03	28.5 ± 1.0	0.175
Walnut shell	6.52 ± 0.38	0.92 ± 0.05	36.4 ± 1.3	0.346

A_s (BET) is triplicates; No. of replicates of Φ and A_s (wicking) is the same as that for UCW (Table 4-1).

4.6 Conclusions

Column wicking using the Washburn equation was found effective for measuring the surface free energies of organic fillers derived from alder bark, walnut shell, and corn cob (furfural production) residue. A series of n-alkanes (spreading liquids) provided highly linear wicking data and therefore reliable estimates of the interstitial pore radii. However, perfluorohexane (the lowest surface tension spreading liquid used) deviated from the n-alkanes and was excluded from consideration. Among the three fillers, only alder bark wicking was complicated by swelling effects. Consequently, rigorous data quality criteria were imposed in the form of minimum linearity standards for Washburn plots, and minimum coefficients of variation among Washburn plots for the respective fillers. Corn cob residue exhibited the highest total surface free energy, but all fillers had low energies (ranging from 30-34 mJ/m^2) in comparison to what is typically published for freshly machined wood surfaces (~ 40 -55 mJ/m^2). Consistent with the wood literature, the surface free energies of all fillers were dominated by dispersive effects, and the minor polar contributions were basic in nature. The many filler-packed columns used here also allowed for measurement of filler specific surface areas, and so the BET method using N_2 adsorption was conducted for comparison. Specific surface areas resulting from the wicking and BET methods were in disagreement, where the former was considered to be more sensible and reliable.

4.7 Acknowledgements

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4.8 References

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Chapter 5 Influence of organic fillers on surface tension of phenol-formaldehyde adhesives

5.1 Abstract

Organic fillers derived from biomass waste streams are commonly formulated with phenol-formaldehyde resoles (PF) in the production of veneer-based wood composites such as plywood and laminated veneer lumber. The surface tensions of PF/filler formulations were studied as a function of filler types: flours of walnut shell, red alder (*Alnus rubra*) bark, and corn cob (furfural production) residue. Surface tensions were measured using the drop weight method (with the Harkins-Brown and the Lee-Chan-Pogaku corrections), and also the drop shape method. In these non-Newtonian liquids, viscosity effects on surface tension were determined over a 10-fold range in shear rate. Viscosity effects were minor or negligible, but measurements at the lowest shear rates were considered most reliable. All fillers reduced PF surface tension by 17-25 % with effects greatest in alder bark and walnut shell. For all fillers, room temperature aging resulted in further reductions in surface tension. Surface tension reductions roughly correlated to the chemical compositions of the fillers, and probably resulted from the release of surface active compounds extracted from the fillers in the alkaline PF medium.

5.2 Key words

Adhesives for wood; Phenolic; Wettability; Organic filler; Surface tension

5.3 Introduction

Veneer-based structural wood composites such as plywood and laminated veneer lumber are typically manufactured using phenol-formaldehyde resoles (PF) that are formulated with wheat flour extender plus organic filler. The most common fillers are ground from biomass waste streams such as tree bark, nut shell, or corn cob (furfural production) residue. Considering that this technology is several decades old, it is surprising to learn that many aspects of the formulation have not been the subject of detailed analysis and scientific publication. The effort described here is part of a university/industry research cooperation with a focus on how organic fillers impact the surface tension of the formulated adhesive. The surface tension of these

formulations will not only impact wetting and penetration, but also bondline water retention, green strength (prepress tack), and final bond quality [1]. Hse [2] has demonstrated how PF synthesis variables impact the surface tension of the base resin, and that these effects translate into bondline performance. However, given a fixed PF resin no one has investigated if and how the organic fillers alter surface tension in this formulation. The objective of this work is to study the influence of organic fillers (walnut shell, alder bark, and corn cob residue) on adhesive surface tension using the drop weight method with the Harkins-Brown [3] and the Lee-Chan-Pogaku corrections [4], and also the drop shape method [5]. Since these methods were derived using non-viscous Newtonian liquids, the complications associated with non-Newtonian flow must be carefully considered because the adhesives studied are complex suspensions.

5.4 Experimental

5.4.1 Materials

Modal™ alder bark (A) filler, walnut shell (W) filler, corn cob residue (C) filler, and wheat flour (WF) extender were kindly provided by Willamette Valley Company (Eugene, OR, USA). The alder species was *Alnus rubra*; the walnut species was *Juglans regia*, English walnut, representing an unknown mixture of tree varieties characteristic of commercial production in northern California, U.S.A. The subspecies of corn (*Zea mays*) was unknown. Fillers were classified into sub-samples by sieves. The fraction retained on 200-mesh sieve (+200 mesh) was used for chemical compositional analysis. Size distributions of fillers, dispersed in isopropanol, were analyzed using a *Partica* LA-950 laser diffraction particle size distribution analyzer (HORIBA Scientific). Moisture contents of fillers and wheat flour, measured with an Ohaus moisture analyzer, were 5-8 %, and 10 %, respectively. Phenol-formaldehyde (PF) resin was a Cascophen™ plywood resin, supplied by Momentive Specialty Chemicals (pH = 11~12, solids content = 43 %). Sodium carbonate (powder) and 50 % sodium hydroxide (liquid) were obtained from Willamette Valley Company (Eugene, OR, USA) and Fisher Scientific, respectively.

5.4.2 Chemical compositional analysis

Compositional analysis was conducted on size classified subsamples; fractions retained on a 200 mesh sieve were subjected to the determination of extractives, alkaline leachate, acid insoluble

(Klason) and acid soluble lignin, and monosaccharide content. The extractives content was determined according to ASTM D1105 using sequential ethanol/toluene extraction, ethanol extraction, and water extraction; the resulting sample was denoted as Ex-free filler.

Approximately 5 g dry Ex-free filler was alkaline extracted by stirring in 125 mL sodium hydroxide solution (4 wt%) for 24 hours. The solids were collected by centrifugation and washed with deionized water until neutral. The solids, denoted as Ex&AE-free filler, were vacuum dried (45 °C, 5.4 mmHg, 72 hr.). Lignin and carbohydrate content in Ex-free and Ex&AE-free samples were determined respectively according to NREL/TP-510-42618 and NREL/LAP-004. Lignin and sugar contents in filler alkaline leachates were estimated by taking the differences in the chemical compositions of Ex-free and Ex&AE-free samples.

5.4.3 Adhesive formulation

Each filler type (unclassified by size) was formulated with PF resin with the addition of Na₂CO₃, 50 % NaOH, water, and wheat flour as shown in Table 5-1 (Willamette Valley Company, Eugene, OR, USA). Each formulation (800 g) was prepared in a mixer (5 quart bowl-lift stand mixer, KitchenAid®) with a speed of 75 rpm (“stir” speed level) at room temperature. Within complete adhesive formulations the wheat flour volume fraction was 3.6 % and filler volume fractions were 4-6 %. Additionally, the influence of the wheat flour extender was observed by preparing a formulation as in Table 5-1, but that no filler was included (PF-no filler). Regarding complete formulations, the effects of ambient (23±1 °C) storage time were studied over a 48 hr. period. Samples were identified according to filler type (A, W, or C) and storage time in hr. (0h, 8h, 24h, and 48h). After mixing, a portion of each formulation was frozen at -13 °C for 2 months. Afterwards these samples were thawed and centrifuged at 5000 rpm for 30 minutes. The supernatants were isolated and subjected to surface tension measurement. Samples subjected to centrifugation were identified as “spun.”

Table 5-1 PF adhesive formulation (and mixing procedure).

Formulation contents	weight %
Water	18.4
Filler (Mix 2 min.)	7.5
PF resin (Mix 2 min.)	22.8
Extender (wheat flour) (Mix 8 min.)	5.5
Sodium hydroxide, 50 % (Mix 10 min.)	3.0
Sodium carbonate (Mix 1 min.)	0.5
PF resin (Mix 2 min.)	42.3
Total mixture	100

5.4.4 Adhesive density

The density of each liquid sample was measured using a 10 mL volumetric cylinder where the cylinder was carefully filled in increments ($n = 10$). Sample density was obtained from the linear slope of the mass/volume plot; the corresponding correlation coefficients (R^2) were always above 0.999.

5.4.5 Rheological analysis

Rheological flow-curves were obtained for all adhesive formulations, and also for the base resin (neat PF), and the adhesive formulation without added filler (PF-no filler). A concentric cylinder geometry (conical rotor: 14 mm radius, 42 mm height; cup: 15 mm radius; gap: 1 mm; 25 °C) was employed on a *TA instruments* AR G2 rheometer. The rheological analysis involved a steady-state flow curve with increasing shear rate from 0.05 to 4000 s^{-1} without specimen pre-shear. The steady-state criterion was defined as less than 5% change in shear stress among three consecutive data points over a period not longer than 1 minute. All of the data met the criterion except those at shear rate of 0.05 s^{-1} , which have been excluded from this discussion.

5.4.6 Drop weight method

The surface tensions of all samples were measured using a First Ten Angstroms (FTA) 200 dynamic contact angle analyzer (Figure 5-1).

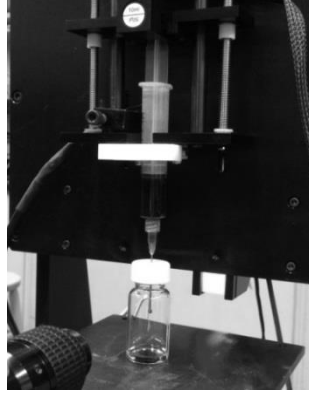


Figure 5-1 Set-up of the FTA 200 dynamic contact angle analyzer.

A 10 mL disposable syringe with stainless steel needle was mounted onto the FTA 200 syringe pump. The needle was inserted through a small hole machined into the screw-cap that covered a 20 mL glass vial. Silicone oil (~ 2 g) was added to the vial in order to minimize evaporative loss from the aqueous adhesives deposited into the vial. Samples were equilibrated at ambient condition (23 ± 1 °C). For each sample a total of 15 drops was continuously pumped into the vial, whereafter the resulting total mass was measured using an analytical balance. The mean surface tensions reported here are based upon 2-4 observations using the drop weight method, and as many as 60 observations using the drop shape method, as specified in the data below. Viscosity effects were studied using various pump rates and syringe needle diameters as will be described. The drop weight results were analyzed to determine the adhesive surface tensions by using the Harkins-Brown (HB) correction and the Lee-Chan-Pogaku (LCP) coefficient method [3, 4].

5.4.6.1 HB correction factors method

Since a small amount of liquid is retained on the syringe tip after each drop detachment, Harkins and Brown [3] modified Tate equation with the HB correction factor, which is a function of the needle tip radius (R) and the drop volume (V). Subsequently Lando and Oakley conveniently summarized the data from Harkins and Brown in the form of equation 1, which is used to calculate the correction factor, F [6].

$$F = 1/2\pi f = 0.14782 + 0.27896 \left(R/V^{1/3} \right) - 0.166(R/V^{1/3})^2 \quad (1)$$

Then surface tensions (γ) of the samples were calculated from the corrected Tate equation:

$$\gamma = mgF/R \quad (2)$$

γ is the liquid surface tension, m is the drop mass, g is the gravitational constant, and R is the outer radius of the tip (assuming the liquid wets the tip).

This method was denoted as drop weight HB.

5.4.6.2 LCP coefficient method

Using four different syringe needle sizes, the sample drop weights were plotted against the outer radii of the corresponding tips (R_o). The data ($n=8$, 2/tip) were fitted by a quadratic equation (equation 3) passing through the origin, where C_1 and C_2 are fitting parameters. Then the surface tension was calculated through a linear semi-empirical equation (equation 4) using C_2 obtained from fitting equation 3.

$$m = -C_1(R_o^2) + C_2(R_o) \quad (3)$$

$$\gamma = 171.2C_2 \quad (4)$$

This method was denoted as drop weight LCP.

5.4.7 **Drop shape method**

The drop shape method is based on equations 5, 5a derived by Andreas *et al.* who related the liquid surface tension to the shape parameters of a pendent drop (Figure 5-2) [5].

$$\gamma = \Delta\rho d_e^2 g / H \quad (5)$$

$$S = d_s / d_e \quad (5a)$$

$\Delta\rho$ is the density difference between the drop and surrounding medium (assumed as sample density), g is the gravitational constant, d_e is the maximum width of the drop, d_s is the drop width at distance d_e from the drop bottom, and H and S are shape parameters. Andreas *et al.* [5] found parameter H was a function of parameter S and tabulated the function.

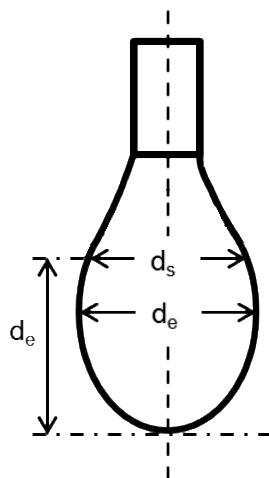


Figure 5-2 A pendant drop showing the characteristic dimensions.

During the drop weight method, described above, the FTA 200 video system recorded the process of drop detachment. The characteristic dimensions of the pendent drop (just before the detachment) were measured, and the surface tension was calculated by using Fta32 software (First Ten Angstroms).

5.5 Results and discussion

5.5.1 Filler size distribution

All fillers and wheat flour were ground and passed through a 100 mesh sieve. The size distributions of fillers and wheat flour are shown in Figure 5-3. The size distributions of unclassified fillers exhibited some variation, possibly indicating geometric differences that might arise from cellular anatomical differences among the tissue types, alder bark, walnut shell, corn cob, and wheat flour.

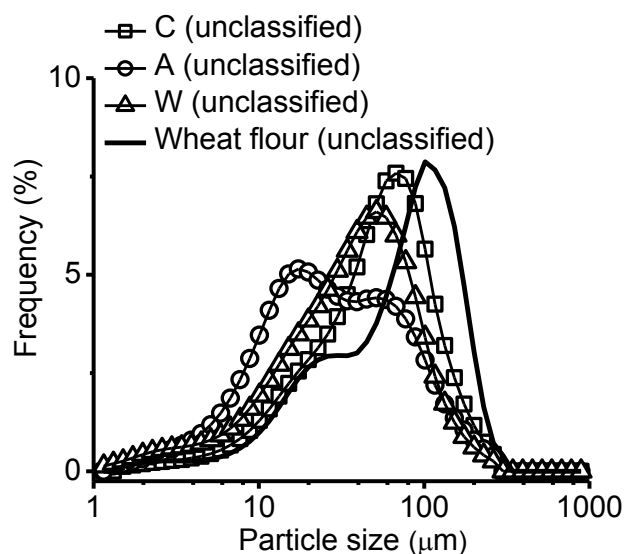


Figure 5-3 Particle size distribution of fillers and wheat flour used in this study.

5.5.2 Adhesive rheology

Characteristic flow curves are presented in Figure 5-4. The neat PF resin exhibited essentially Newtonian flow with shear thinning at the highest shear rates. When fillers were excluded from the formulation it was seen that wheat flour caused non-Newtonian flow and shear thinning behavior over most of the flow curve (PF-no filler). In contrast, the complete formulations exhibited two shear thinning zones separated by a plateau at intermediate shear rates. Figure 5-4 also shows that the complete formulations underwent viscosity increases (most evident in the plateau region) during room temperature storage, and most change occurred within the first 8 hr.

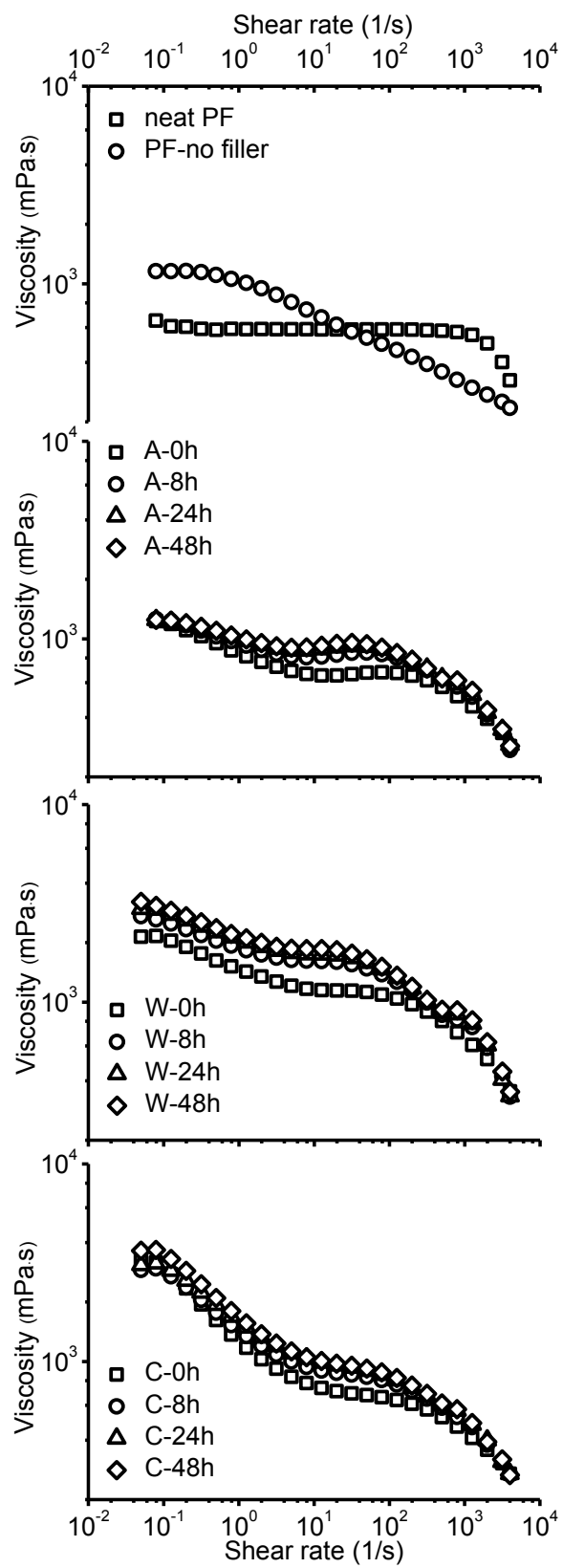


Figure 5-4 Rheological behavior of the adhesives.

5.5.3 Influence of adhesive viscosity on surface tension analysis

To determine the influence of viscosity (*i.e.* shear rate) on surface tension measurement, shear rates occurring within the syringe needles were calculated using equation 6 (Table 5-2)

$$\dot{\gamma} = 4Q/\pi R_i^3 \quad (6)$$

Q is the pump rate, and R_i is the inner radius of the syringe tip. The syringe pump flow rate was fixed at the lowest possible setting (0.5 $\mu\text{L/s}$) in order to avoid disrupting the tails of falling drops [7]. The corresponding viscosities (taken from the flow curves) are shown in Figure 5-5. During surface tension measurement, it is seen that neat PF exhibited a fixed viscosity and most other systems exhibited more substantial viscosity differences during surface tension measurement. Surface tensions from the drop weight HB and drop shape methods are plotted against the inner radii of the syringe tips used, Figure 5-6. Viscosity effects on surface tension were observed, and while often statistically significant the magnitudes were not dramatic. For instance, neat PF exhibited a fixed viscosity and yet minor (sometimes statistically significant) differences in surface tension were observed as a function of tip radius for both methods. In contrast, PF-no filler exhibited highly uniform surface tensions (within the respective methods) despite the fact that viscosity varied substantially within the tips used. When comparing analytical methods, viscosity (*i.e.* shear rate) effects on surface tension were generally more systematic under the drop shape method, where tip radius and surface tension trended in a direct fashion (when shear rate effects were observed). The drop weight HB method showed a tendency to trend in either direction (when shear rate effects were observed). Shear rate effects were generally most evident among formulations that were aged for 48 hr., corresponding to viscosity changes mentioned above. Shear rates varied by an order of magnitude across the syringe tips used, and the smallest tip (R_o : 0.455 mm; highest shear rate) naturally produced the smallest drops. It was observed that the smallest drops tended to climb the syringe needle, and so the corresponding error might be obscuring the viscosity effects discussed here. Considering these observations, the data obtained from the two largest tips (R_o : 0.915 mm, 0.825 mm) was considered most reliable, and was pooled for subsequent reports of mean surface tension using the drop weight HB and the drop shape methods. Since the drop weight LCP method relies on

curve fitting as a function of tip radius, all data (all tip sizes) were necessarily included in that case.

Table 5-2 Calculated shear rates based on selected syringe tip size and pump rate.

R_o (mm)	R_i (mm)	Q (μL/s)	$\dot{\gamma}$ (1/s)
0.915	0.685	0.5	2.0
0.825	0.600		2.9
0.635	0.420		8.6
0.455	0.305		22.4

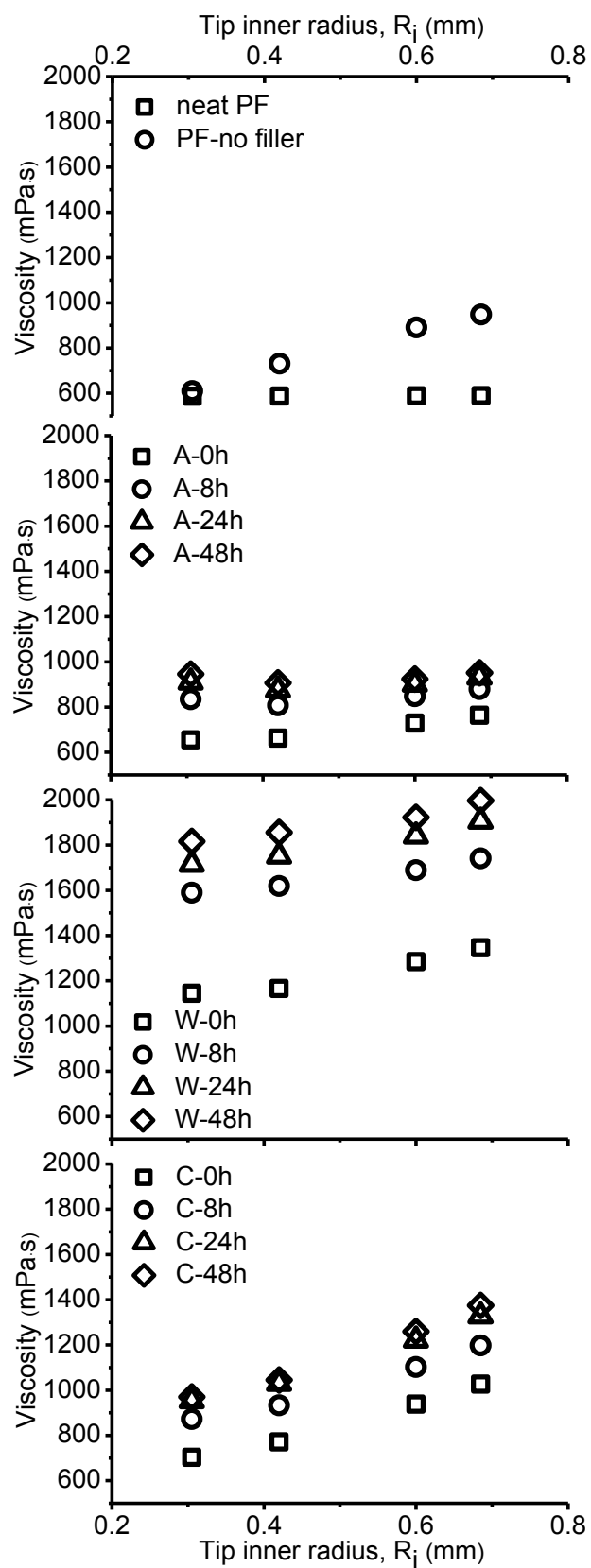


Figure 5-5 Viscosities of adhesives at different inner radii of syringe needles.

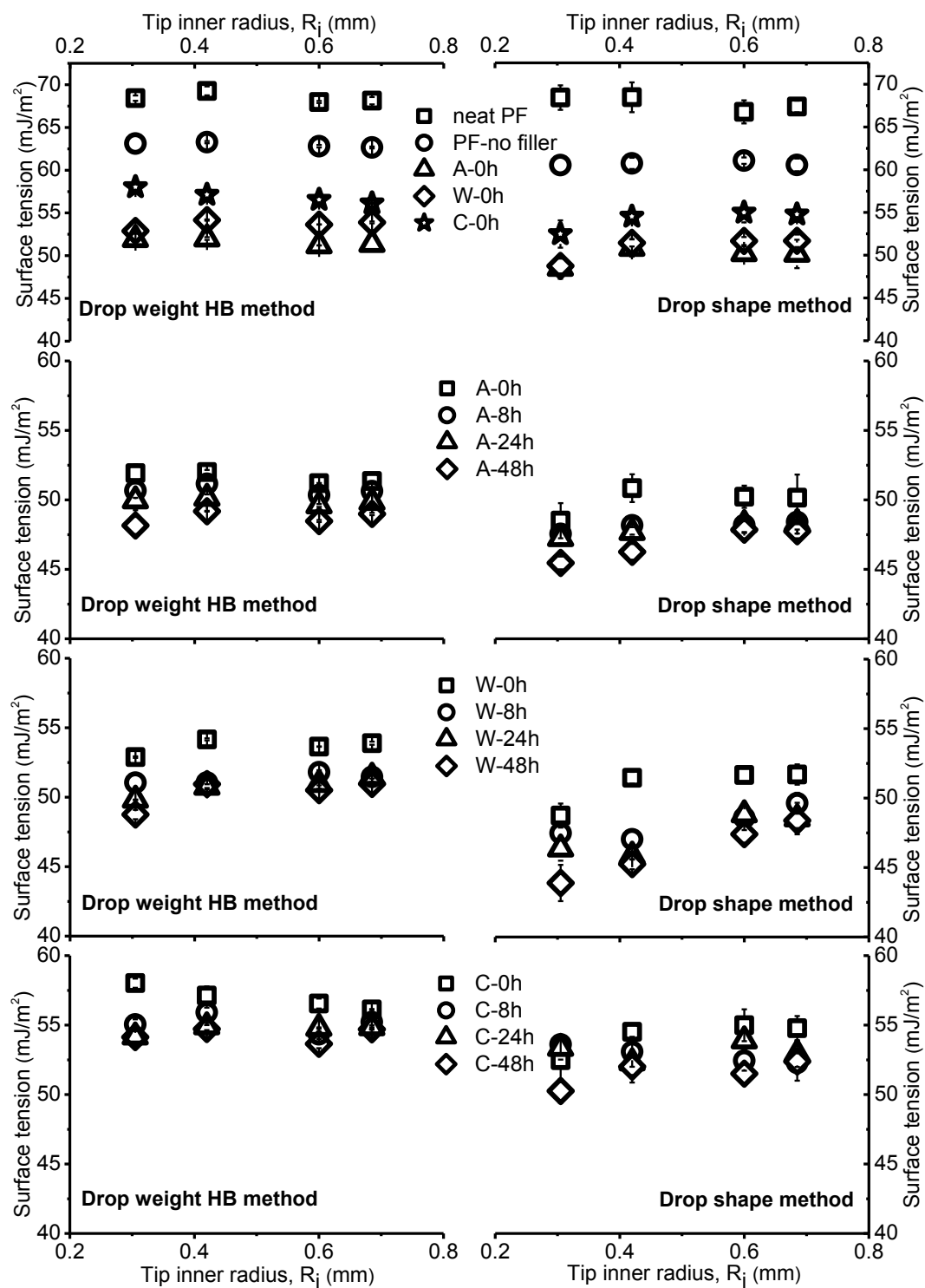


Figure 5-6 Mean surface tensions of adhesives at different inner radii of syringe needles (2 observations for drop weight HB method; 30 observations for drop shape method).

5.5.4 Influence of fillers on adhesive surface tension

Mean surface tensions from the drop weight LCP, drop weight HB, and drop shape methods are listed in Table 5-3. The drop weight HB method generally provided slightly higher surface tensions, but all methods were in reasonable agreement. Surface tensions measured for neat PF were within previously published ranges [2]. It is seen that wheat flour, with no added filler (PF-no filler), caused a substantial reduction in PF surface tension. Wheat flour is known to release lipid, polysaccharide, and protein under alkaline conditions [8, 9], as occurring in the PF resin. Such alkaline leaching is the probable cause for surface tension reduction [8]. Similarly the organic fillers are expected to release surface active compounds, and all three fillers caused a further reduction in adhesive surface tension. Among the fillers, alder bark caused the greatest surface tension reduction, which was similar to walnut shell; corn cob residue caused the lowest change. The similar effects of alder bark and walnut shell are probably related to the similarities in chemical compositions, which substantially differ from corn cob residue, Table 5-4. While similar in composition, alder bark and walnut shell differed most in the quantity of extractives, xylan, and acid soluble lignin. Of the latter two components, walnut shell released more xylan (according to the estimated alkaline leachates, Table 5-4). This suggests that the higher extractives content in alder bark may correlate to the lower adhesive surface tension relative to walnut shell. However, the extractives content in corn cob residue was not associated with surface activity; corn cob residue caused the lowest decrease in adhesive surface tension even though the extractives content was more than twice that found in the other fillers. The extractives in corn cob residue must be substantially different from the lipids expected in alder bark and walnut shell. Most of such lipids are probably removed from corn cob during the production of furfural; corn cob residue results from the acid catalyzed, high pressure steam digestion of corn cob for the production of furfural [10, 11]. This probably explains why corn cob residue releases more lignin, and much more glucan under alkaline leaching, Table 5-4. Furthermore, it is seen that all PF/filler formulations experience comparable reductions in surface tension while aging at room temperature for 48 hr., Table 5-4; this is perhaps related to the corresponding viscosity reductions, Figure 5-4. Regarding the proceeding hypotheses, more insight would be gained from a careful characterization of the extractive and alkaline leachate fractions.

Table 5-3 Mean surface tensions from drop weight LCP (observations, n=8 for fitting; 2/tip), drop weight HB (n = 4) and drop shape methods (n = 60).

Sample	Density (g/mL)	Drop weight LCP			Drop weight HB	Drop shape
		R^2	C_2	γ (mJ/m ²)	γ (mJ/m ²)	γ (mJ/m ²)
neat PF	1.160	0.999	0.403	69.0	68.1±0.3	67.1±1.1
PF-no filler	1.152	0.999	0.367	62.8	62.7±0.1	60.8±0.6
A-0h	1.178	0.999	0.298	51.1	51.3±0.1	50.2±1.3
A-8h	1.166	0.997	0.290	49.6	50.5±0.2	48.3±0.7
A-24h	1.178	0.999	0.284	48.6	49.7±0.2	48.3±0.5
A-48h	1.174	0.997	0.272	46.5	48.7±0.3	47.8±0.6
W-0h	1.178	0.999	0.301	51.4	53.8±0.2	51.7±0.6
W-8h	1.167	0.999	0.285	48.8	51.6±0.2	49.1±1.0
W-24h	1.167	0.999	0.275	47.1	51.2±0.4	48.7±1.0
W-48h	1.164	0.998	0.273	46.7	50.7±0.3	47.9±0.8
C-0h	1.172	0.999	0.339	58.0	56.3±0.3	54.9±1.0
C-8h	1.163	0.997	0.318	54.4	54.8±0.6	52.4±1.0
C-24h	1.180	0.999	0.307	52.6	54.8±0.1	53.4±0.9
C-48h	1.167	0.997	0.307	52.6	54.2±0.6	51.9±0.8

Table 5-4 Chemical constituents of alder bark (A), walnut shell (W), and corn cob residue (C) (% of total dry mass).

		Soxhlet extractives	Glucan	Xylan	Acid insoluble lignin	Arabinan	Galactan	Mannan	Acid soluble lignin
A		9.4							
W		4.5							
C		25.5							
Ex-free	A		26.4	16.8	31.3	1.0	0.8	0.6	1.4
	W		26.9	22.0	31.6	0.5	1.2	0.1	2.1
	C		46.7	0.9	27.2	0.1	0.1	0.1	0.4
Ex&AE-free	A		26.0	10.8	26.2	0.8	0.6	0.5	0.9
	W		25.4	13.1	25.6	0.3	0.9	0.1	1.6
	C		40.6	0.4	17.7	0.1	0.0	0.1	0.2
Alkaline leachate	A		0.4	6.0	5.1	0.2	0.2	0.1	0.5
	W		1.5	8.9	6.0	0.1	0.3	0.0	0.5
	C		6.0	0.5	9.5	0.0	0.1	0.0	0.2

While leachates from the fillers are the likely cause of reduced surface tension in the adhesives, the filler particles themselves might have surface activity. For instance it was reported that when suspended in water, nano- and micro-scale polystyrene particles reduced water surface tension, presumably absent from the effects extraneous contaminants [12, 13]. In fact surface energies of the organic fillers (28-31 mJ/m^2 ; Chapter 4) are comparable to or lower than that published for polystyrene [14, 15]. This scenario was probed by measuring the surface tension of samples subjected to centrifugation.

Table 5-5 indicates that filler removal resulted in little or no change in surface tension. While it is possible that the smallest filler particles were not completely removed by centrifugation, it seems likely that the fillers reduce PF surface tension principally through the effects of surface active compounds that leach from the fillers.

Table 5-5 Mean surface tensions of PF/filler formulations as in Table 5-3, and of formulations where filler was removed by centrifugation; spun (n=2, drop weight HB; n=30, drop shape).

Sample	Density (g/mL)	Drop weight HB	Drop shape
		γ (mJ/m^2)	γ (mJ/m^2)
PF-no filler	1.158	63.8 $\pm$ 0.3	61.4 $\pm$ 0.5
PF-no filler-spun	1.153	62.3 $\pm$ 0.1	62.5 $\pm$ 0.8
A	1.178	50.5 $\pm$ 0.0	47.8 $\pm$ 0.5
A-spun	1.161	49.3 $\pm$ 0.1	49.3 $\pm$ 0.4
W	1.175	52.3 $\pm$ 0.3	50.0 $\pm$ 1.8
W-spun	1.144	50.7 $\pm$ 0.2	49.0 $\pm$ 0.4
C	1.172	54.8 $\pm$ 0.2	52.9 $\pm$ 0.7
C-spun	1.160	53.0 $\pm$ 0.2	52.4 $\pm$ 0.5

5.6 Conclusions

The drop weight method (with HB correction and LCP corrections) and the drop shape method were found effective for measuring the surface tensions of PF resins formulated with organic fillers. In these non-Newtonian liquids, viscosity effects (over a 10-fold range in shear rate) on surface tension were sometimes statistically significant, but the relative magnitudes were not dramatic. However, measurements at the lowest shear rates were considered most reliable. Wheat flour decreased PF surface tension by 8-10 %; all fillers caused a further reduction of 7-

18 % with effects greatest in alder bark and walnut shell. Room temperature aging resulted in surface tension reduction. A correlation appeared between the surface tension reductions and the chemical compositions of the fillers. The alkaline leachates are the probable cause for surface tension reduction, but confirmation requires a careful characterization of the extractive and alkaline leachate fractions.

5.7 Acknowledgements

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Chapter 6 Influence of organic fillers on rheological behavior in phenol-formaldehyde adhesives

6.1 Abstract

Phenol-formaldehyde resoles (PF) formulated with wheat flour and organic fillers have long been established for the manufacture of veneer-based wood-composites, and yet much remains unknown about these complex fluids. The rheology of PF/filler formulations was studied as a function of filler type and particle size. Corn cob residue fillers behaved differently from those made from alder bark (*Alnus rubra*) and walnut shell (*Juglans regia*). It was shown that viscoelastic network structures formed within the liquid formulations as a function of shear history, filler type, and filler particle size. The precise nature and origin of these effects is unknown but could involve disintegration of filler particle aggregates on a non-colloidal scale, and/or colloidal effects within the liquid PF medium. In the latter case colloidal structures could form among associated PF chains and also from proteins, polysaccharides, and lignins that leach from wheat flour and filler particles. Relative to alder bark and walnut shell, the unique behavior of corn cob residue was discussed with respect to chemical composition. Many implications for impact on industrial practice are feasible and should be the subject of future research.

6.2 Key words

Adhesives for wood; Phenolic; Rheology; Organic filler

6.3 Introduction

Phenol-formaldehyde (PF) resoles are outstanding wood adhesives that remain as the preferred resin used to manufacture structural wood-based composites from veneer, as in plywood and laminated veneer lumber. In such veneer applications PF resoles are commonly formulated with fillers and extenders [1]. Definition of the terms “filler” and “extender” vary [2], but in the wood products industry fillers are considered to be generally inert, while extenders are proteinaceous and amylaceous materials that exhibit some intrinsic adhesive properties. [3]. Contemporary PF/filler/extender formulations are designed meet a variety of performance criteria including

bulk flow, prepress tack, precure moisture retention, gap-filling properties, not to mention post-cure strength and durability [1, 4].

For the applications described here, the fillers are typically organic flours derived from lignocellulosic biomass waste streams such as walnut nutshell, red alder (*Alnus rubra*) bark, and furfural production residues, i.e. corn cob residue [1]. While these fillers have held commercial significance for several decades, they have been the subject of little or no detailed analysis resulting in scientific publication. Only Ebewele *et al.* [5] reported the impact that walnut shell fillers had on adhesive performance. This publication represents an industry/university cooperative research effort intended to broaden the scientific base underlying current and future technologies. The organic fillers studied here, flours of walnut shell, alder bark, and corn cob (furfural production) residue impact the flow properties of PF adhesives. Accordingly, this is a report of how liquid PF adhesive rheology is impacted by the type and particle size of organic filler.

6.4 Experimental

6.4.1 Materials

Modal™ alder bark (A) filler, walnut shell (W) filler, corn cob residue (C) filler, and wheat flour extender were kindly provided by Willamette Valley Company (Eugene, OR, USA). The walnut tree species was *Juglans regia*, English walnut, representing an unknown mixture of tree varieties characteristic of commercial production in northern California, U.S.A. The subspecies of corn (*Zea mays*) was unknown. Phenol-formaldehyde (PF) resin was a Cascophen™ plywood resin, supplied by Momentive Specialty Chemicals (pH = 11~12, solids content = 43 %). Sodium carbonate (powder) and 50 % sodium hydroxide (liquid), used for adhesive formulation, were obtained from Willamette Valley Company (Eugene, OR, USA) and Fisher Scientific, respectively.

6.4.2 Filler size classification

The fillers were classified into sub-samples by sieves. The classified fillers samples (A, W, or C) were numerically coded as 1, 2, or 3: 1, small size range (passing through 325 mesh); 2, medium (passing through 200 mesh but retained on 325 mesh); 3, large size range (passing through 100

mesh but retained on 200 mesh). Size distributions of the classified fillers, dispersed in isopropanol, were analyzed using a *Partica* LA-950 laser diffraction particle size distribution analyzer (HORIBA Scientific).

6.4.3 Chemical compositional analysis

Large size (3) fillers were used for chemical compositional analyses including the determination of extractives, alkaline leachates, acid insoluble (Klason) and acid soluble lignin, carbohydrates. The extractive content was determined according to ASTM D1105. The extractive-free sample was denoted as Ex-free filler. Approximately 5 g dry Ex-free filler was alkaline extracted by 125 mL sodium hydroxide solution (4 wt%) for 24 hours. The solid fraction of the mixture was collected by centrifugation and washed by deionized water until neutral. The residue, denoted as Ex&AE-free filler, was vacuum dried (45 °C, 5.4 mmHg). Lignin and carbohydrate content in Ex-free and Ex&AE-free samples were determined respectively according to NREL/TP-510-42618 and NREL/LAP-004 [6, 7]. Lignin and sugar contents in filler alkaline leachates were estimated by taking the differences in the chemical compositions of Ex-free and Ex&AE-free samples.

6.4.4 Adhesive formulation

Sub-samples were formulated with PF resins with the addition of Na₂CO₃, 50 % NaOH, water, and wheat flour as shown in Table 6-1 (Willamette Valley Company, Eugene, OR, USA). The moisture contents of fillers and wheat flour in the formulation, measured with an Ohaus moisture analyzer, were 5-8 %, and 10 %, respectively. Each formulation (800 g) was prepared in a mixer (5 quart bowl-lift stand mixer, KitchenAid®) with a speed of 75 rpm (“stir” speed level) at room temperature. The formulated adhesives were denoted as A-1, A-2, A-3, W-1, W-2, W-3, C-1, C-2, and C-3 respectively. Additionally, the influence of the wheat flour extender was observed by preparing a formulation as in Table 6-1, but that no fillers were included (PF-no filler). Within complete adhesive formulations, the wheat flour volume fraction was 3.6 % and filler volume fractions were 4-6 %.

Table 6-1 PF adhesive formulation (and mixing procedure).

Formulation contents	weight %
Water	18.4
Filler (Mix 2 min.)	7.5
PF resin (Mix 2 min.)	22.8
Extender (wheat flour) (Mix 8 min.)	5.5
Sodium hydroxide, 50 % (Mix 10 min.)	3.0
Sodium carbonate (Mix 1 min.)	0.5
PF resin (Mix 2 min.)	42.3
Total mixture	100

6.4.5 Rheological analysis

Rheological flow-curves were obtained for all adhesive formulations (as a function of filler type and particle size), and flow-curves were also obtained for the base resin (neat PF), and the adhesive formulation without added filler (PF-no filler). A concentric cylinder geometry (conical rotor: 14 mm radius, 42 mm height; cup: 15 mm radius; gap: 1 mm; 25 °C) was employed on a *TA instruments* AR G2 rheometer. For all adhesive formulations, the flow-curves were obtained immediately after formulation mixing. The rheological analysis involved a two-step acquisition of sequential, steady-state flow curves as follows: Step 1) using no specimen pre-shear, steady-state flow analysis with increasing shear rate from 0.05 to 4000 s⁻¹, and Step 2) steady-state flow analysis under decreasing shear rate from 4000 to 0.05 s⁻¹; the transition between steps 1 and 2 was immediate with no intervening equilibration time. The steady-state criterion was defined as less than 5% change in shear stress among three consecutive data points over a period not longer than 1 minute. All data met the criterion except those at shear rates less than 0.08 s⁻¹, which has been excluded.

Additional experiments were conducted on specimens A-1 and C-3. The same two-step flow curve analysis was applied; however, creep/recovery and frequency sweep segments were included in the following order: Segment X; Step 1 (ramp-up) flow curve; Segment Y; Step 2 (ramp-down) flow curve; Segment Z. The segments X, Y, and Z contained a creep/recovery

(0.05 Pa, 60 s.; 0.0 Pa, 60 s.), followed by a frequency sweep (0.01 – 0.5 Hz; 0.05 Pa). The 0.05 Pa stress applied in segments X, Y, and Z was well within the linear response (as determined from an oscillatory, 1 Hz, stress sweep).

6.5 Results and discussion

6.5.1 Filler size distribution

The size distributions of unclassified fillers and wheat flour are shown Figure 6-1. Three fillers were classified into three size ranges using the same sieves for each filler-type. Figure 6-2 demonstrates that the large and medium size fractions were very comparable among filler types. Whereas the small size fraction exhibited some variation among filler types, possibly indicating geometric differences that might arise from cellular anatomical differences among the three tissue types, alder bark, walnut shell, and corn cob.

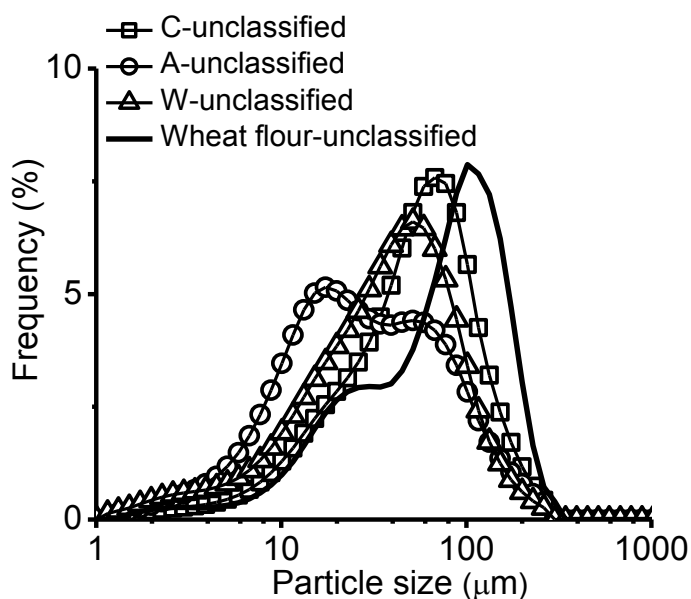


Figure 6-1 Particle size distribution of unclassified fillers and wheat flour.

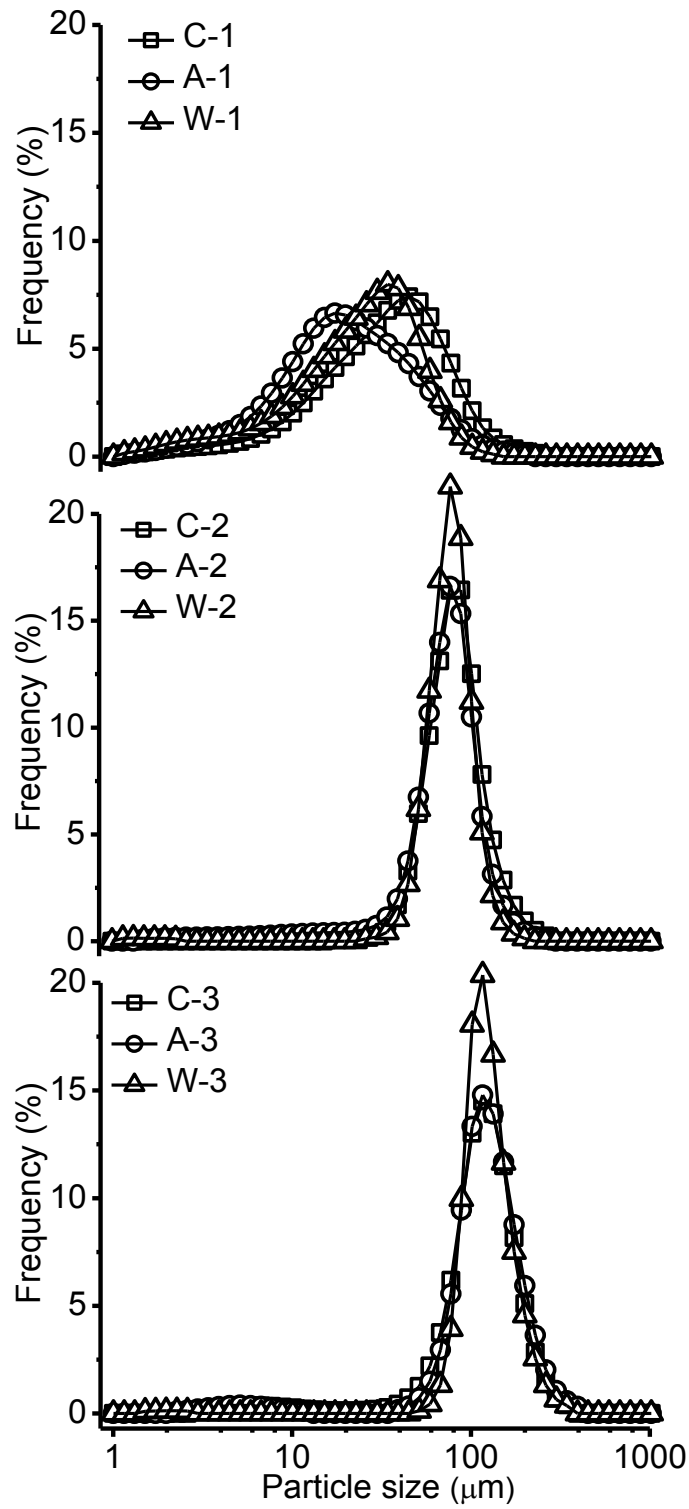


Figure 6-2 Particle size distributions of classified fillers.

6.5.2 Rheology of neat PF resin and PF-no filler under increasing shear rate

Flow curves (increasing shear rate) of the base resin (neat PF) and of the adhesive formulation without filler (PF-no filler) are shown in Figure 6-3. The neat PF resin was principally Newtonian, but shear-thinning was observed at shear rates above 1250 s^{-1} . According to its viscosity and polymer concentration, the neat PF resin probably exhibited chain entanglement [8]; however, this topic was not studied. Consequently, the shear-thinning could reflect chain disentanglement and/or the dissociation of phenolic interactions [1, 8]. In contrast, PF-no filler exhibited a Newtonian plateau but with more gradual shear thinning over a broader shear rate range. The wheat flour particles ($\sim 3\%$ volume fraction in this specimen) are known to release proteins and polysaccharides under the highly alkaline conditions in the PF resin [9-11].

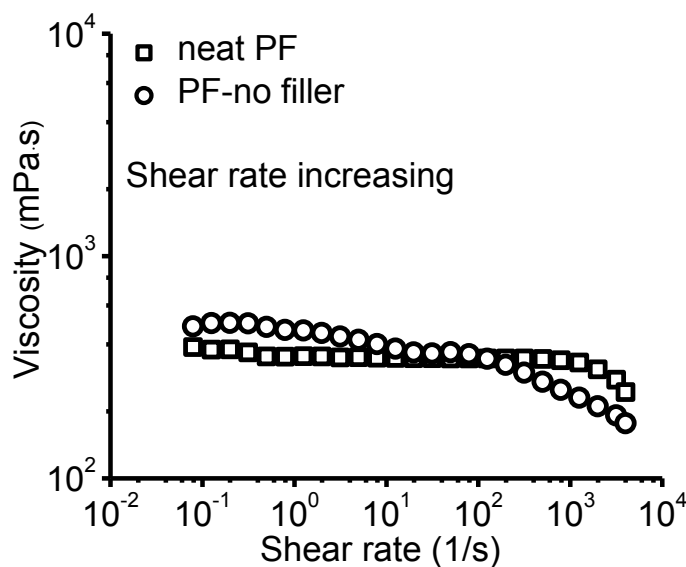


Figure 6-3 Flow curves (increasing shear rate) of neat PF and PF-no filler.

6.5.3 Rheology of PF with classified fillers

Complete adhesive formulations (varying by filler type and particle size) were subjected to a two-step rheological analysis. Without pre-shear, analysis began by ramping-up the shear rate (Step 1), immediately followed by ramping-down the shear rate (Step 2) with no intervening equilibration or delay, Figure 6-4. Comparison of Figure 6-3 and Figure 6-4 (shear rate increasing) reveals that all fillers produced more complex flow behavior as compared both to the base resin and the formulation without fillers (PF-no filler). Under increasing shear rate, all three filler types exhibited a generally similar behavior: shear thinning at low shear rates, followed by

an intermediate plateau, and shear thinning at the highest shear rates. As the shear rate was ramped-down (Step 2), all formulations regained viscosity in a recovery that was principally monotonic (*i.e.* W-2), or that exhibited two distinct regions with remarkably rapid recovery at lower shear rates (*i.e.* A-1). Three of the corresponding hysteresis curves are shown in Figure 6-5, which crudely indicate the presence or absence of structural reorganization [12, 13]. In Figure 6-5 no significant reorganization is seen in C-3 and W-2; the hysteresis curves generally formed closed loops where the initial pre-shear structure appeared to reform (thixotropy is not implied, nor of concern here). In contrast, A-1 exhibited cross-over behavior in the low shear region which is suggestive of structural reorganization [12, 13]. Among the particle size effects observed in Figure 6-4, the most dramatic were seen for the large corn cob residue particles (C-3) in Step 1 (ramping-up), and for the small alder bark and walnut shell particles (A-1, W-1) in Step 2 (ramping-down). All three specimens exhibited a similar Step 2 recovery process, but C-3 does not restructure whereas A-1 (and perhaps W-1) do.

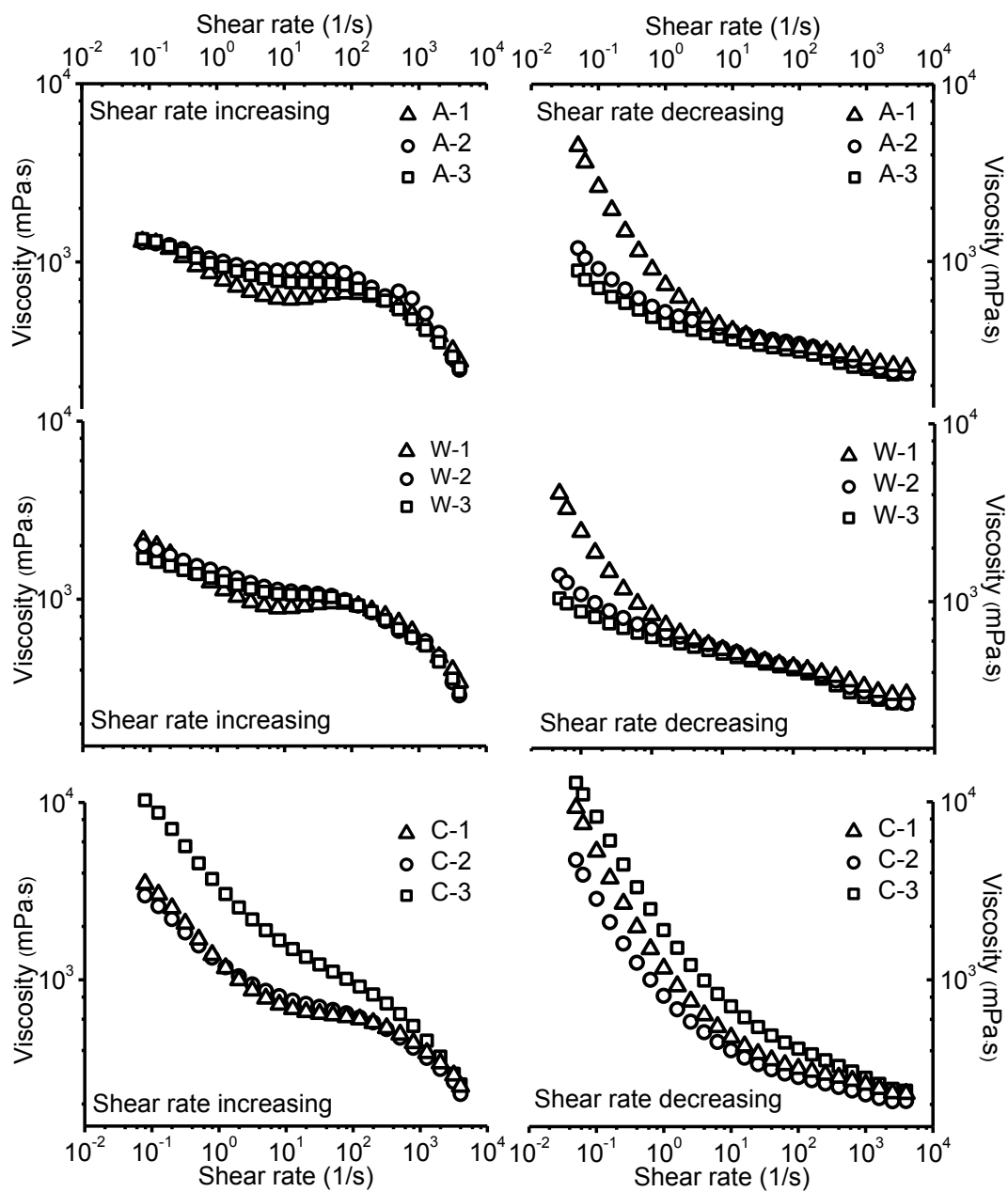


Figure 6-4 Rheological behaviors of PF with classified fillers under a two-step acquisition.

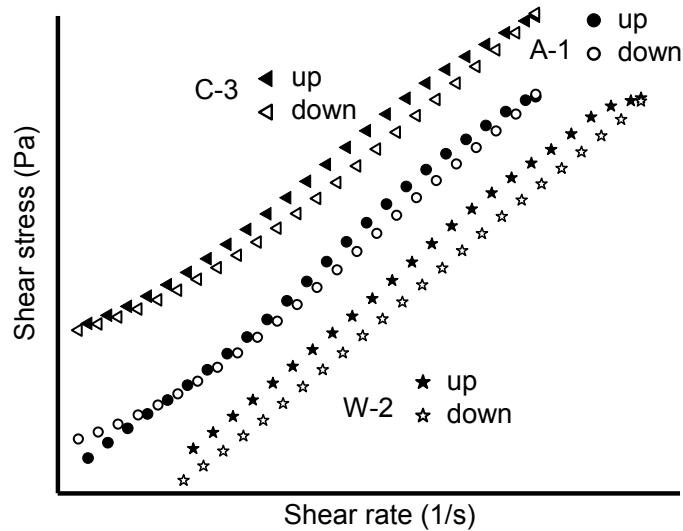


Figure 6-5 Hysteresis curves for select PF/filler formulations, all scaled identically but shifted for clarity.

Formulations A-1 and C-3 were subjected to more detailed analysis. In this case the same two-step flow was imposed, however three additional segments were added (named X, Y, and Z). Segment X occurred just prior to Step 1 (ramping-up); segments Y and Z respectively occurred immediately before and after Step 2 (ramping-down). Segments X, Y, and Z contained a 120 second creep/recovery followed by a frequency sweep; the applied stresses (0.05 Pa) were well within the linear response (determined separately using a 1 Hz stress sweep). Figure 6-6 indicates that the pre-shear character of formulation A-1 was principally viscous (segment X); the creep response was nearly linear and very little creep recovery occurred. Subsequent shearing during Step 1 flow caused increased elasticity (segment Y), which developed further as the viscosity recovered during Step 2 decreasing shear flow (segment Z). The restructuring in formulation A-1 apparently involved a transformation from mostly viscous to remarkably viscoelastic behavior, suggesting the development of some type of network structure. In contrast to A-1, the pre-shear nature of formulation C-3 was viscoelastic. Subsequent shearing during Step 1 flow caused decreased elasticity (segment Y), which is similar in magnitude as A-1 (segment Y). However, a great elasticity developed dramatically (segment Z) as the viscosity recovered during Step 2 decreasing shear flow (note scale difference in Figure 6-6).

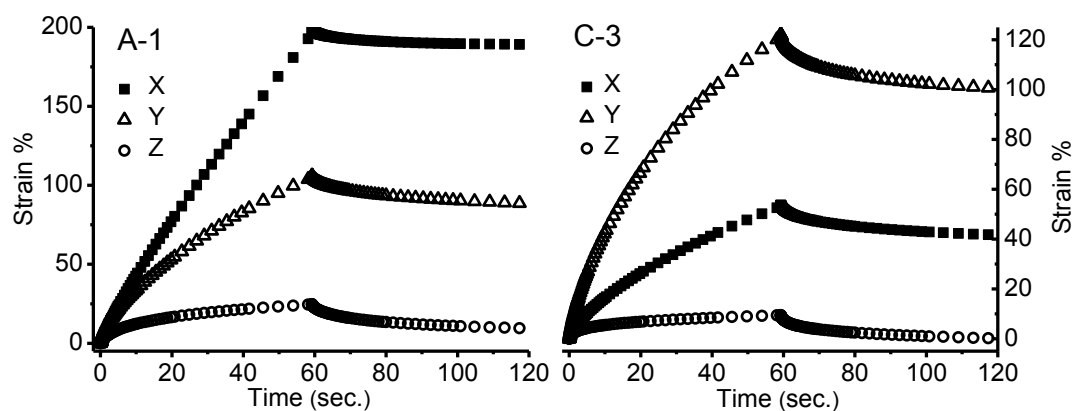


Figure 6-6 Creep/recovery responses, respectively X and Y, occurring before and after Step 1 ramping-up flow; Z occurred after Step 2 ramping-down flow. Note the different scales for samples A-1 (left) and C-3 (right).

Figure 6-7 shows the corresponding frequency sweeps occurring after the creep/recovery tests. As above, the pre-shear nature of A-1 was mostly viscous where in segment X the loss modulus was greater than the storage modulus across the frequency range employed. Attending the transformation in A-1 was an increase in the storage and loss moduli; and the storage and loss were effectively equal over the lowest frequencies (segments Y and Z). The very low moduli observed in A-1 (segment Z) are indicative of high fluidity, but the equivalence of the storage and loss moduli are also suggestive of network structure in this viscoelastic fluid. Regarding formulation C-3, careful inspection of Figure 6-7 reveals that the frequency sweeps in segments X and Y were essentially identical; the loss moduli always remained above the storage moduli, but the loss and storage very nearly converged at about 0.1 Hz (in Figure 6-6, the greater elasticity of C-3 compared to A-1 is explained by comparing the ordinate scales in Figure 6-7). However, segment Z shows a cross-over, also near 0.1 Hz, where below that frequency the storage exceeds the loss. Note for formulation C-3 that all moduli in segments X and Y fall off (trend towards increasing slope) over the low frequency range; whereas in segment Z the moduli trend towards plateau behavior. The tendency towards a low frequency plateau indicates greater network development in C-3 as compared to formulation A-1.

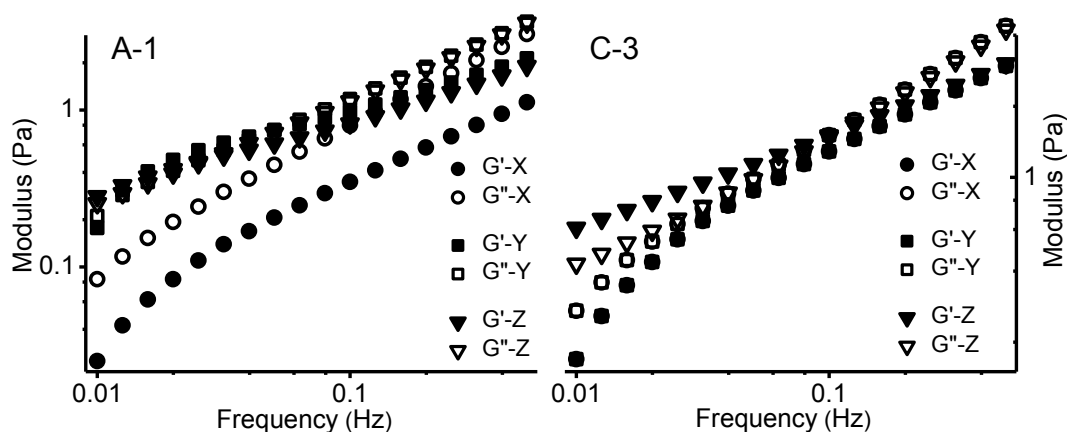


Figure 6-7 Storage (G') and loss (G'') moduli from frequency sweeps, respectively X and Y, occurring before and after Step 1 flow; Z occurred after Step 2 decreasing flow (All applied after creep/recovery, Figure 6-6). Note different ordinate scales in formulations A-1 (left) and C-3 (right).

Figure 6-4 to Figure 6-7 indicate that the PF/filler formulations exhibit complex behavior with the ability to form, or not form, viscoelastic fluids that exhibit some type of network structure. The formation of network structures correlated to the occurrence of the distinct viscosity recovery observed under decreasing shear (Step 2 flow). Figure 6-4 demonstrates that this occurred for all corn cob formulations, regardless of particle size, but only for alder bark and walnut shell formulations containing the smallest particle size. The great challenge, not addressed here, is to determine the origin of this network behavior. Perhaps some of these observations could be explained by high shear disintegration of filler aggregates, remembering that all filler (and wheat flour) particles exceed 1 micron in size. So while soluble polymer in the liquid medium could interact with filler and flour particle surfaces, these particles are not expected to exhibit Brownian, or colloidal, interactions. Nevertheless, these various formulations clearly exhibit filler-specific effects where corn cob residue is distinct, and alder bark and walnut shell behave quite similarly, Figure 6-4. Filler-specific effects could influence colloidal behavior in the liquid medium, discussed below.

As mentioned previously, PF chains in these formulations likely form entanglements and they are known to develop associations via hydrogen bonding among phenolic hydroxyls [8]. Phenolic associations among PF chains occur as a function of NaOH levels used in the highly

alkaline resin. It is this high alkalinity that could create colloidal effects that are specific to the fillers used here. Aqueous alkali is known to promote the release of xylan and lignin fragments from within lignocellulose [14], not to mention gluten proteins and polysaccharides (amylose, amylopectin, and xylan) from wheat flour [9-11]. Under this scenario one could envision highly complex colloidal interactions mediated by soluble lignin, polysaccharides, and proteins, all among associating PF chains. Such colloidal phenomena would occur within the liquid medium that surrounds the massive, non-colloidal filler and wheat flour particles.

Insight on potential colloidal effects is available from the chemical compositions of the respective fillers, Table 6-2. Relative to alder bark and walnut shell, the distinct character of corn cob residue is seen in the xylan contents. Corn cob residue is produced from the acid catalyzed, steam digestion of corn cob where xylose is converted to the industrial monomer furfural. As a result of alkaline extraction (comparing Ex-free to Ex&AE-free), it is seen that alder bark and walnut shell would likely release xylans into the PF medium, whereas corn cob residue would release very little. Likewise, the estimated alkaline leachates suggest that corn cob residue would release substantially more lignin (see acid insoluble lignin). Furthermore, corn cob residue contains much more solvent extractables (see soxhlet extractives). Due to the prior steam digestion of corn cob residue, these extractives are not expected to resemble the lipophilic compounds typical for materials such as alder bark and walnut shell. For example, the glucan content in the estimated alkaline leachate suggests that corn cob residue might release significant quantities of glucose during solvent extraction. These same compositional effects were suggested to explain why PF/corn cob residue formulations exhibit significantly higher surface tensions in comparison to alder bark and walnut shell formulations (Chapter 5).

Table 6-2 Chemical constituents of alder bark (A), walnut shell (W), and corn cob residue (C).

		Soxhlet extractives	Glucan	Xylan	Acid insoluble lignin	Arabinan	Galactan	Mannan	Acid soluble lignin
	A	9.4							
	W	4.5							
	C	25.5							
Ex-free	A		26.4	16.8	31.3	1.0	0.8	0.6	1.4
	W		26.9	22.0	31.6	0.5	1.2	0.1	2.1
	C		46.7	0.9	27.2	0.1	0.1	0.1	0.4
Ex&AE-free	A		26.0	10.8	26.2	0.8	0.6	0.5	0.9
	W		25.4	13.1	25.6	0.3	0.9	0.1	1.6
	C		40.6	0.4	17.7	0.1	0.0	0.1	0.2
Alkaline leachate	A		0.4	6.0	5.1	0.2	0.2	0.1	0.5
	W		1.5	8.9	6.0	0.1	0.3	0.0	0.5
	C		6.0	0.5	9.5	0.0	0.1	0.0	0.2

Considering that the fillers and wheat flour will release polymeric and monomeric compounds under alkaline conditions, the formation of colloidal particles within the PF medium seems quite plausible. Complex rheological behavior within these adhesive formulations could arise from colloidal effects within the PF medium and also from polymeric adsorption onto filler particle surfaces. In the latter case, it is known that PF chains adsorb onto cellulosic/lignocellulosic surfaces as a strong function of pH and ionic strength [15, 16]. Furthermore, complexes between PF and non-ionic water soluble polymers are known to hinder PF adsorption [16].

The rheological complexity of these PF/filler formulations is apparent and this work demonstrated that shearing stimulates the formation of viscoelastic network structure within the fluids. And the shear rate range in the present work includes those in the adhesive application such as mixing and stirring (10^1 - 10^3 s⁻¹), pipe flow (10^0 - 10^3 s⁻¹), spraying and brushing (10^3 - 10^4 s⁻¹). Not determined here are the minimum shear rates required to stimulate the transformations, and how these relate to the shear rates employed during industrial manufacture. Also unknown is the stability of these structures and the time periods over which they may evolve. Finally, perhaps the most important question is if and how these structures impact adhesive performance, with possible effects ranging from adhesive tack, to bondline moisture retention, and ultimately into the morphology and toughness of the cured bondlines.

6.6 Conclusions

PF/wheat flour/organic filler formulations are well established technologies for the commercial manufacture of veneer-based wood composites, and yet much remains unknown about structure within these fluids and the corresponding impact on adhesive performance. It was shown that viscoelastic network structures form within the liquid formulations as a function of shear history, organic filler type, and filler particle size. The precise nature and origin of these effects is unknown but could involve disintegration of filler particle aggregates on a non-colloidal scale, and/or colloidal effects within the liquid PF medium. In the latter case colloidal structures could form from the proteins, polysaccharides, and lignins that emanate from wheat flour and filler particles under the alkaline conditions within the PF resin. These natural polymers will likely interact with individual PF chains, and among clusters of PF chains associating by phenolic secondary interactions. Many implications for impact on industrial practice are feasible and should be the subject of future research efforts.

6.7 Acknowledgements

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Chapter 7 Influence of organic fillers on phenol-formaldehyde adhesive cure

7.1 Abstract

Organic fillers derived from biomass waste streams are commonly formulated with phenol-formaldehyde (PF) resols in the production of veneer-based wood composites such as plywood and laminated veneer lumber. The effects of three filler types, flours of walnut shell, red alder (*Alnus rubra*) bark, and corn cob (furfural production) residue, on PF adhesive cure were investigated with differential scanning calorimetry (DSC). Alder bark and walnut shell exhibited the similar effects with a decrease of peak temperature and activation energy. However, corn cob residue exhibited much lower peak temperature and much higher activation energy as neat PF. Additionally, it was found that the variation between peak temperatures of samples was opposite to that between activation energies.

7.2 Key words

Adhesives for wood; Phenolic; Organic filler; Cure

7.3 Introduction

Organic fillers based upon biomass sources such as nutshells and tree bark have been commercially formulated with phenol-formaldehyde (PF) resols for many decades [1]. Such formulations remain as the preferred adhesives used to manufacture structural wood-based composites from veneer, as in plywood and laminated veneer lumber. In spite of their lasting commercial significance, such organic fillers they have been the subject of very little detailed analysis resulting in scientific publication. Cure behavior of resin is known to affect hot pressing procedure and performance of structural wood-based composites [2]. Ebewele *et al.* [3] reported that walnut shell and Douglas fir (*Pseudotsuga menziesii*) bark flours had no effect on phenol-resorcinol-formaldehyde adhesive cure; Waage *et al.* [4] demonstrated that the cure of phenol-formaldehyde resol was not influenced by pecan shell and wheat flour; Miyazaki and Hirabayashi [5] found that *Acacia mangium* bark powder influenced reaction enthalpy of PF resol. Many research showed that wood particles impacted phenolic resin cure which depended on wood specie, resin property, experimental methods [2, 6-9]. Stemming from an

industry/university cooperative research effort, the objective of this work is to investigate the effect of three organic fillers on PF adhesive cure using differential scanning calorimetry (DSC); these are walnut shell, alder bark (*Alnus rubra*), and corn cob (furfural production) residue that are commonly used to manufacture veneer-based composites.

7.4 Experimental

7.4.1 Materials

Modal™ alder bark (A) filler, walnut shell (W) filler, corn cob residue (C) filler, and wheat flour (WF) extender were kindly provided by Willamette Valley Company (Eugene, OR, USA). The alder species was *Alnus rubra*; the walnut tree species was *Juglans regia*, English walnut, representing an unknown mixture of tree varieties characteristic of commercial production in northern California, U.S.A. The subspecies of corn (*Zea mays*) was unknown. Size distributions of fillers, dispersed in isopropanol, were analyzed using a *Partica* LA-950 laser diffraction particle size distribution analyzer (HORIBA Scientific). Moisture contents of fillers and wheat flour, measured with an Ohaus moisture analyzer, were 5-8 %, and 10 %, respectively. Phenol-formaldehyde (PF) resin was a Cascophen™ plywood resin, supplied by Momentive Specialty Chemicals (pH = 11~12, solids content = 43 %). Sodium carbonate (powder) and 50 % sodium hydroxide (liquid) were obtained from Willamette Valley Company (Eugene, OR, USA) and Fisher Scientific, respectively.

7.4.2 Adhesive formulation

Each filler type was formulated with PF resins with the addition of Na₂CO₃, 50 % NaOH, water, and wheat flour as shown in Table 7-1 (Willamette Valley Company, Eugene, OR, USA). Each formulation (800 g) was prepared in a mixer (5 quart bowl-lift stand mixer, KitchenAid®) with a speed of 75 rpm (“stir” speed level) at room temperature. Within complete adhesive formulations the wheat flour volume fraction was 3.6 % and filler volume fractions were 4-6 %. Additionally, the influence of the wheat flour extender was observed by preparing a formulation as in Table 7-1, but that no fillers were included (PF-no filler). Formulated adhesives were stored in the freezer (-13 °C) until use.

Table 7-1 PF adhesive formulation (and mixing procedure).

Formulation contents	weight %
Water	18.4
Filler (Mix 2 min.)	7.5
PF resin (Mix 2 min.)	22.8
Extender (wheat flour) (Mix 8 min.)	5.5
Sodium hydroxide, 50 % (Mix 10 min.)	3.0
Sodium carbonate (Mix 1 min.)	0.5
PF resin (Mix 2 min.)	42.3
Total mixture	100

7.4.3 Differential scanning calorimetry (DSC)

All measurements were conducted on a TA Instruments Q100 DSC equipped with a refrigerated cooling system. Indium was used for the calibration. Nitrogen was used as the purge gas (50 mL/min). Samples were thawed immediately prior to analysis. Resin samples (approximately 40-60 mg) were analyzed in sealed, stainless steel high-volume DSC pans (TA Instruments).

Dynamic temperature scans were conducted from 40 to 170 °C at 5 heating rates: 2, 5, 8, 10, and 12 °C/min. Experiments were run in triplicate at 2 and 12 °C/min, and in duplicate at 5 °C/min for the sample with corn cob residue. Other samples were randomly selected for duplicate. Peak temperatures were determined with Universal Analysis 2000 software (TA instrument).

Values for the activation energy (E_a) and the frequency factor (Z), were determined using the Kissinger method [10], which is based on the equation 1.

$$\frac{\beta}{T_p^2} = \frac{ZR}{E_a} \exp\left(-\frac{E_a}{RT_p}\right) \quad (1)$$

β is the heating rate (K/min), R is the universal gas constant (8.314 J/mol.K), and T_p is the peak temperature (K). By taking the logarithm of equation 1, the equation 1 was transformed to:

$$-\ln\left(\frac{\beta}{T_p^2}\right) = \frac{E_a}{RT_p} - \ln\left(\frac{ZR}{E_a}\right) \quad (2)$$

The activation energy (E_a) and the frequency factor (Z) were obtained from the plotting of $-\ln\left(\frac{\beta}{T_p^2}\right)$ against $\frac{1000}{T_p}$.

7.5 Results and discussion

7.5.1 Filler size distribution

All of fillers and wheat flour were ground and passed through 100 mesh sieve. The size distributions of fillers and wheat flour are shown in Figure 7-1. The size distributions of fillers and wheat flour exhibited some variation, possibly indicating geometric differences that might arise from cellular anatomical differences among the tissue types, alder bark, walnut shell, corn cob, and wheat flour.

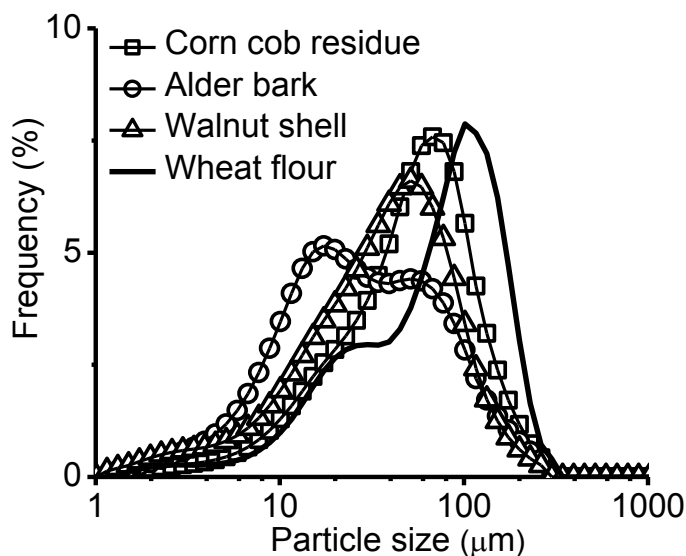


Figure 7-1 Particle size distribution of fillers and wheat flour.

7.5.2 Differential scanning calorimetry (DSC)

All DSC curves of the samples (Figure 7-2) showed a well-defined exothermic peak that shifted to higher temperature as the increase of heating rate. Exotherms in this temperature region have been generally attributed to the condensation involving the methylol groups [11-13]. Figure

7-3 shows the DSC curing curves of samples at a heating rate of 10 °C/min. The peak temperature (T_p) of PF-no filler was the largest. Considering all additives in PF-no filler could contribute to the overall curing response, PF-no filler was used as control sample to analyze the influence of fillers on adhesive curing. Fillers decreased T_p of PF-no filler such that corn cob residue produced the lowest T_p close to neat PF.

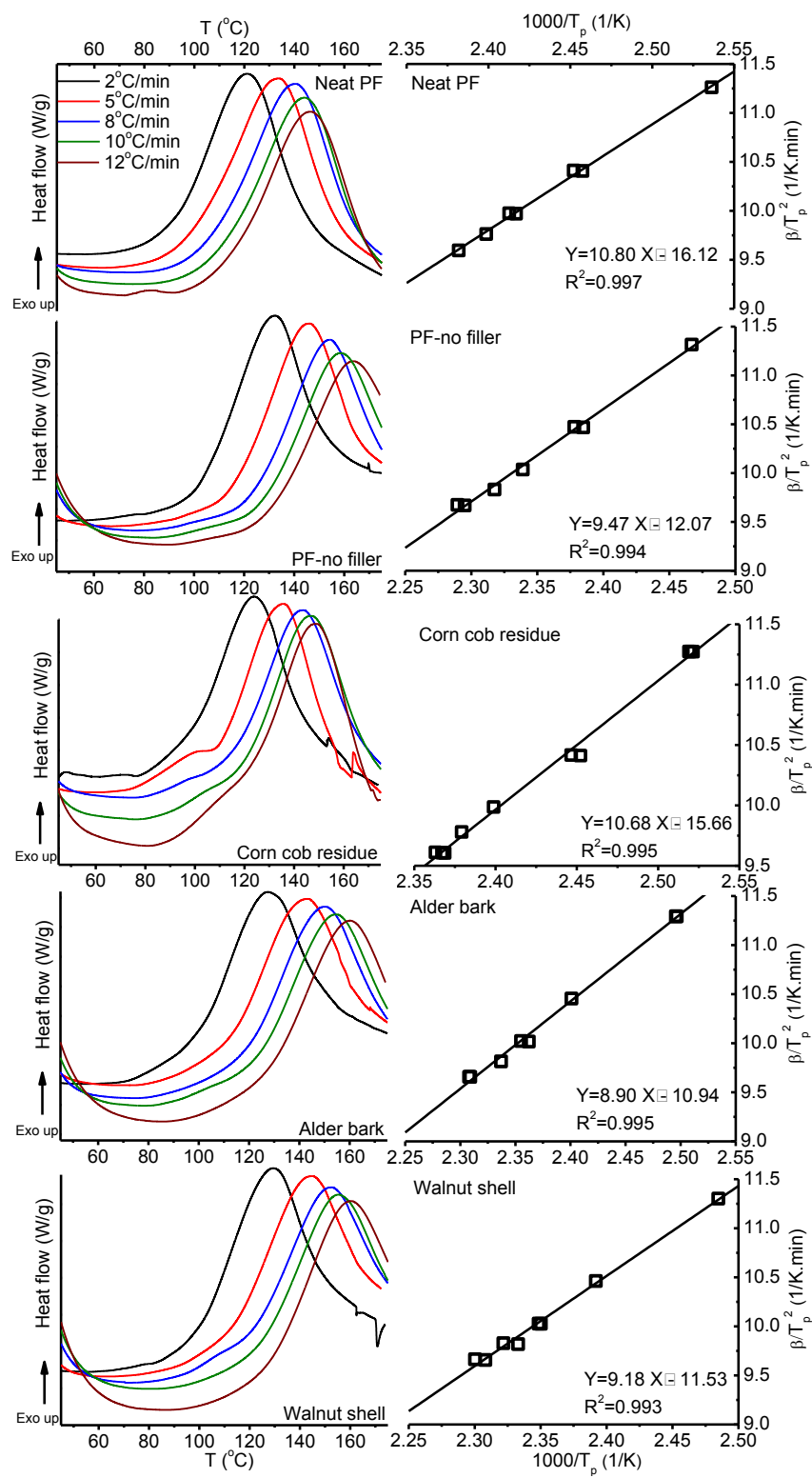


Figure 7-2 DSC curves at different heating rates (left) and Kissinger plots (right).

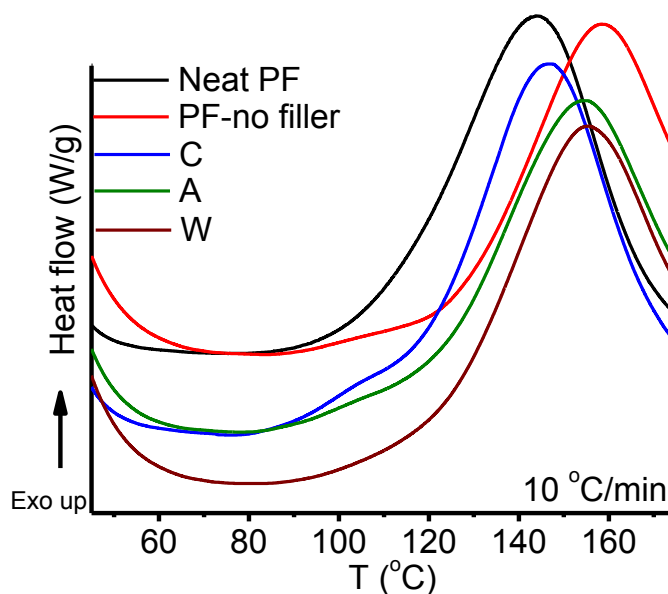


Figure 7-3 DSC curves at a heat rate of 10 °C/min.

The peak temperature at different heating rates could be used to determine the activation energy that is useful to compare the curing reactivity between samples. Based on the Kissinger method, the plots of $-\ln(\frac{\beta}{T_p^2})$ against $\frac{1000}{T_p}$, Figure 7-2, provided the activation energy of samples as shown in Table 7-2. PF-no filler provided lower activation energy than neat PF that indicates the curing initiation of PF-no filler was easier than neat PF. Compared to the neat PF, PF-no filler contained wheat flour, sodium hydroxide, sodium carbonate. Waage *et al.* [4] reported that wheat flour had no effect on the curing of PF resol. Pizzi and Stephanou [14] reported that under very alkaline condition the increase of pH of PF resin inhibited the curing that is contrary to the results in the present work. Therefore, sodium carbonate, a common curing accelerator in PF resin, might result in the lower activation energy. Regarding filler effects on adhesive curing, alder bark and walnut shell decreased adhesive activation energy, as found in some wood/PF systems [15, 16]. Pizzi *et al.* [16] reported that the decrease of activation energy in wood/PF system might be attributed to the catalytic activation of carbohydrates in wood. However, corn cob residue resulted in a higher activation energy that was also found in some reports related to wood/PF system [2, 6]. It was believed that acidity of wood species might reduce the reactivity of functional groups for the condensation reaction resulting in higher activity energy [2]. Our previous chemical analysis (Chapter 3) demonstrated that corn cob residue, different from the other two types, contained little hemicellulose but a large amount of strong acid groups. Perhaps

these chemical differences between fillers resulted in the different influences on adhesive curing. Additionally, peak temperature and activation energy generally varied in the same trend [2, 5, 17]. It is interesting to find that the variation between peak temperatures of samples in the present work was opposite to that between activation energies. This perhaps indicates a complicated curing mechanism in our adhesive systems.

Table 7-2 Peak temperature and activation energy of samples (# observations).

Sample	β , °C/min	T_p , °C	E_a , kJ/mol
Neat PF	2	121.1 (1)	89.8
	5	134.2 $\pm$ 0.6 (2)	
	8	141.0 $\pm$ 0.5 (2)	
	10	143.8 (1)	
	12	146.7 (1)	
PF-no filler	2	132.2 (1)	78.7
	5	146.8 $\pm$ 0.8 (2)	
	8	154.4 (1)	
	10	158.3 (1)	
	12	163.1 $\pm$ 0.7 (2)	
Corn cob residue	2	123.7 $\pm$ 0.2 (3)	88.8
	5	135.1 $\pm$ 0.7 (2)	
	8	143.7 (1)	
	10	147.2 (1)	
	12	149.5 $\pm$ 0.5 (3)	
Alder bark	2	127.5 $\pm$ 0.1 (2)	74.0
	5	143.4 (1)	
	8	150.8 $\pm$ 0.9 (2)	
	10	154.7 (1)	
	12	160.0 $\pm$ 0.1 (2)	
Walnut shell	2	129.3 (1)	76.3
	5	144.9 (1)	
	8	152.5 $\pm$ 0.2 (2)	
	10	156.5 $\pm$ 1.4 (2)	
	12	160.8 $\pm$ 1.0 (2)	

7.6 Conclusions

Differential Scanning Calorimetry (DSC) analysis demonstrated the filler impacts on PF adhesive cure. PF-no filler provided a higher peak temperature but lower activation energy

compared to neat PF. This might be resulted from the additives such as sodium carbonate. Considering PF-no filler as a control sample, the influences of alder bark and walnut shell were similar with a little lower peak temperature and activation energy. However, corn cob residue exhibited much lower peak temperature but much higher activation energy as neat PF. This might relate to different chemical characteristics of fillers such as acidity and chemical constituents. It is also interesting to find that the variation between peak temperatures of samples was opposite to that between activation energies. This is different from that found in literatures.

7.7 Acknowledgements

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Chapter 8 Influence of organic fillers on bond performance of phenol-formaldehyde adhesive

8.1 Abstract

In an effort to broaden the scientific understanding on the impacts of organic fillers, mode-I fracture testing was used to evaluate bond performance as a function of filler particle size, with the hope of correlating aspects of bondline thickness and adhesive penetration. The organic fillers studied here, flours of walnut shell, red alder (*Alnus rubra*) bark, and corn cob (furfural production) residue, were classified into sub-samples having the reduced particle sizes and particle size distributions (small, medium, large). A large amount of bondline thickness measurements were collected from the un-cracked fracture specimens. Adhesive penetration along the selected cracked fracture specimen formulated and bonded with alder bark was measured with maximum penetration (MP), effective penetration (EP), and weighted penetration (WP) methods. Alder bark exhibited significant particle size effects on fracture energy and bondline thickness, but no clear size effects on penetration. Regarding corn cob residue and walnut shell, particle size effects on fracture energy were statistically significant, but the magnitude difference was rather small. The similar bondline thickness (statistically no difference) was observed for classified corn cob residue fillers which was different from the significant particle size effects of other fillers.

8.2 Key words

Adhesives for wood; Phenolic; Fracture toughness; Bondline thickness; Adhesive penetration

8.3 Introduction

Bondline thickness and adhesive penetration have a significant impact on wood/adhesive bonding [1, 2]. Regarding bondline thickness, no general agreement was achieved, although numerous authors have studied this parameter. River *et al.* [1] reported that a thin bondline (75-150 μm thick) provided the greatest bond performance. In contrast, the bonding performance of phenol-formaldehyde/wood [3], epoxy/wood [4], phenolic-resorcinol-formaldehyde/wood [5], and polyurethane/wood [5], has been reported to increase as the increase of bondline thickness.

Additionally, Ebewele *et al.* [6] reported that the optimum bondline thickness for the greatest fracture energy of phenolic-resorcinol wood joints was between 80-90 μm . Therefore, the optimum thickness perhaps depends on the wood-adhesive combination used.

Moreover, wood bonding requires adequate penetration of liquid resin into wood structure since adhesive penetration enables adhesive to reinforce the damaged cells and achieved a maximum amount of surface contact [2, 7]. Thereby, under-penetration is not able to move adequate adhesive into wood to form a strong wood-adhesive interaction. Beside a lack of penetration, excessive adhesive penetration could result in a starved bondline. Hse [3] found adhesive bondline thickness negatively correlated with bonding performance of southern pine (*Pinus*) plywood bonded with phenol-formaldehyde resin. On the other hand, White [8] reported that the adhesive penetration had a positive effect on fracture energy of loblolly pine (*Pinus taeda*) bonded with resorcinol formaldehyde. Therefore, an optimum amount of adhesive penetration could achieve the greatest bonding performance of wood-based composites.

Fillers are known to adjust adhesive viscosities and possibly impact adhesive bondline thickness and penetration. Organic fillers based upon biomass sources such as nutshells and tree bark have been commercially formulated with phenol-formaldehyde (PF) resoles for many decades [9]. In spite of their lasting commercial significance, such organic fillers have been the subject of very little detailed analysis resulting in scientific publication. Only Ebewele *et al.* [10] reported the impact that that walnut shell fillers had adhesive performance. Therefore, stemming from an industry/university cooperative research effort, the objective of this work is to study how adhesive bondline thickness, adhesive fracture toughness, and adhesive penetration are impacted by the type and particle size of three organic fillers; these are walnut shell, alder bark (*Alnus rubra*), and corn cob (furfural production) residue that commonly used to manufacture veneer-based composites.

8.4 Experimental

8.4.1 Materials

Modal™ alder bark (A) filler, walnut shell (W) filler, corn cob residue (C) filler, and wheat flour extender were kindly provided by Willamette Valley Company (Eugene, OR, USA). The alder

species was *Alnus rubra*; the walnut species was *Juglans regia*, English walnut, representing an unknown mixture of tree varieties characteristic of commercial production in northern California, U.S.A. The subspecies of corn (*Zea mays*) was unknown. Phenol-formaldehyde (PF) resin was a CascophenTM plywood resin, supplied by Momentive Specialty Chemicals (pH = 11~12, solids content = 43 %). Sodium carbonate (powder) and 50 % sodium hydroxide (liquid) were obtained from Willamette Valley Company (Eugene, OR, USA) and Fisher Scientific, respectively.

8.4.2 Filler size classification

The fillers were classified into sub-samples by sieves. The classified fillers samples (A, W, or C) were numerically coded as 1, 2, or 3: 1, small size range (passing through 325 mesh); 2, medium (passing through 200 mesh but retained on 325 mesh); 3, large size range (passing through 100 mesh but retained on 200 mesh). Size distributions of the classified fillers, dispersed in isopropanol, were analyzed using a *Partica* LA-950 laser diffraction particle size distribution analyzer (HORIBA Scientific). All of fillers were imaged by scanning electron microscopy (SEM). The vacuum dried samples (45 °C, 5.4 mmHg vacuum, 48 hours) were pre-coated with 3.5-4.0 nm gold-palladium sputter prior to imaging in a NeoScope JCM-5000 benchtop Scanning Electron Microscope.

8.4.3 Adhesive formulation

Sub-samples were formulated with PF resins with the addition of Na₂CO₃, 50 % NaOH, water, and wheat flour as shown in Table 8-1 (Willamette Valley Company, Eugene, OR, USA). Moisture contents of fillers and wheat flour, measured with an Ohaus moisture analyzer, were 5-8 %, and 10 %, respectively. The filler volume fractions were 4-6 %. Each formulation (800 g) was prepared in a mixer (5 quart bowl-lift stand mixer, KitchenAid[®]) with a speed of 75 rpm (“stir” speed level) at room temperature. Samples were identified according to filler types (A, W or C) and particle size (1, 2 or 3).

Table 8-1 PF adhesive formulation (and mixing procedure).

Formulation contents	weight %
Water	18.4
Filler	7.5
(Mix 2 min.)	
PF resin	22.8
(Mix 2 min.)	
Extender (wheat flour)	5.5
(Mix 8 min.)	
Sodium hydroxide, 50 %	3.0
(Mix 10 min.)	
Sodium carbonate	0.5
(Mix 1 min.)	
PF resin	42.3
(Mix 2 min.)	
Total mixture	100

8.4.4 Fracture specimen preparation

Two defect-free pieces of southern yellow pine (*Pinus spp.*) lumber (flat-sawn) were used such that each piece respectively formed the top and bottom of every bonded assembly. From the lumber were machined flat-sawn planks (longitudinal x tangential x radial = 249 x 152 x 11 mm) with a 3-5° grain angle between the tangential bonding surface and the longitudinal axis. The planks were equilibrated at 27 °C and 22 % relative humidity (RH) (final moisture content: ~ 6 %), and then paired for subsequent bonding into fracture specimens as described in Gagliano and Frazier. Immediately prior to bonding, the paired plants were planed to a final thickness of 10 mm. Subsequently, a thermocouple-slot was machined into the crack initiation end of one of the paired planks, and using a paraffin marker the same region was marked with a 38 mm long debond area (Figure 8-1.a). Adhesive (269 g/m²) was applied to the bottom plank whereafter the top plank was closed upon it. A thermocouple was inserted into the slot and the bondline temperature was monitored during hotpressing: platen temperature 160 °C; initial pressure 1.31 N/mm² (190 lb/in²). Curing was complete 2 min. after the bondline temperature reached 104 °C, when the final pressure dropped to about 0.62 N/mm² (90 lb/in²). After 24 hr. cooling, each composite sample was ripped into five double cantilever beams (DCBs) (Figure 8-1.b) and equilibrated (RH 22 %, 27 °C, ~6 % moisture content). For each filled adhesive, two bonded assemblies were prepared which supplied 10 DCBs.

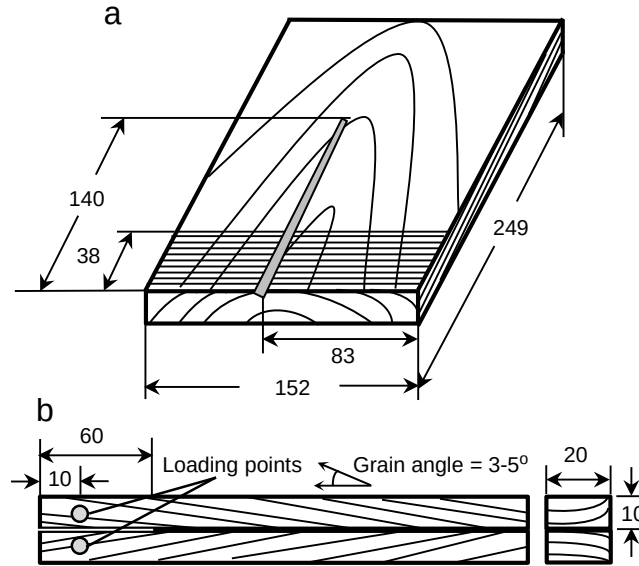


Figure 8-1 Details of materials (a) Top plank with a slot and 38mm debond area. (b) Double cantilever beam (DCB) specimen (unit: mm).

8.4.5 Adhesive bondline thickness measurement

The adhesive bondline was defined as the adhesive layer not including adhesive-penetrated wood. Bondline thickness was measured with 100 X magnification by a Nikon SMZ1500 stereoscope equipped with a Nikon DS-Fi1 digital camera. The images were collected on both specimen sides in 10 mm increments between 60 mm to 140 mm from the loading hole centers. Within the magnified field of view, seven equally spaced measurements were taken (NIS-Elements BR 3.1 image analysis software) totaling 126 measurements per specimen.

8.4.6 Mode-I fracture test

Adhesive performance was measured by cyclic mode-I fracture cleavage testing using a crack length correction as per Gagliano and Frazier [11]. A chisel and vise were used to initiate a 50 mm pre-crack, as measured from the center of the loading-pin holes. Testing was conducted with TestWorks 4.0 and a screw-driven MTS (Model GL-10) with a 1000 N load cell. Valid data were defined as crack lengths between 50 mm and 150 mm from the loading pins. The cyclic nature of the test produces about 10 crack extensions per specimen, thereby providing ample statistical power from a modest bond area. A corrected beam theory method was used to obtain critical fracture energy (G_{Ic}) and arrest fracture energy (G_{Ia}).

$$G_{Ic} = \frac{P_c^2}{B} \frac{(a+x)^2}{(EI)_{eff}} \quad (1.a)$$

$$G_{Ia} = \frac{P_a^2}{B} \frac{(a+x)^2}{(EI)_{eff}} \quad (1.b)$$

$$(EI)_{eff} = \frac{2}{3m^3}; x = \frac{b}{m} \quad (1.c)$$

P_c is the critical load, P_a is the arrest load, a is the crack length (distance from crack tip to pin hole centers, x the crack length offset, and $(EI)_{eff}$ is the effective flexural rigidity of the DCB specimen. m and b are the slope and the y-intercept, respectively, from the linear trendline in the plot of the cube root of compliance versus crack length described in the literature [11].

8.4.7 Adhesive penetration measurement

After fracture testing, adhesive penetration was measured at locations along the DCB length corresponding to sites of crack initiation. Of course among different specimens these crack locations were not evenly distributed along the bondline; therefore additional penetration measurement locations were added to ensure having more than 3 measurement locations in 10 mm intervals. Tested DCB specimens were cut into small blocks that were water saturated. Accordingly, the cross-sectional slices ($\sim 25 \mu m$ thick) were cut using a sledge Lab-microtome “G.S.L. 1” (Schenkung Dapples, Zürich, Switzerland); the sections were mounted on glass slides and covered by glycerol and then fixed with cover slips. More than 3 sections were prepared at each cutting location. Since the DCB specimens had been fracture tested, sections were prepared from the separated DCB beams. Adhesive penetration was observed with 100 X magnification using a Nikon Eclipse LV100 POL stereoscope equipped with a Nikon DS-Fi1 digital camera. Using NIS-Elements BR 3.1 image analysis software, individual images (field of view = $870 \mu m$) were digitally combined or stitched to provide complete bondline sections with an approximate width of $20,00 \mu m$ (using 24 horizontal images x 3 vertical images with 5 % overlap). Adhesive penetration was measured using three different calculations referred to as maximum penetration, effective penetration, and weighted penetration.

Maximum penetration (MP) along the complete bondline was measured with a simple average representing a modified maximum penetration equation [12]:

$$MP = (\sum_{i=1}^n y_i)/n \quad (2)$$

y_i is the distance from the baseline to the farthest edge of adhesive object i along the direction of the ray cells, and n is the total number of measurements. The baseline was defined as wood surface directly adjacent to the adhesive layer, and maximum penetration was measured in 400 μm intervals (NIS-Elements BR 3.1 image analysis software). On occasion the sectioning process damaged baseline regions and so some intervals were skipped when the baseline was absent from the field of view.

Effective penetration (EP) and weighted penetration (WP) were calculated with equation 3 and 4 respectively [12, 13].

$$EP = (\sum_{i=1}^n A_i)/FOV \quad (3)$$

$$WP = \sqrt{(\sum_{i=1}^n A_i y_i^2) / \sum_{i=1}^n A_i} \quad (4)$$

Each section image was divided into about 5 sub-images. The maximum field of view (FOV) of the sub-image was 4000 μm . Discrete adhesive objects having area A_i were located at a distance y_i away/perpendicular from the baseline to the center of A_i . If the baseline was flawed, the FOV was adjusted to approximate 4000 μm . EP and WP measurements were obtained using Fiji Is Just ImageJ software, in which case greyscale thresholds were set to distinguish adhesive (white color) from wood. To remove the noise, each pixel was replaced with the median value in the 3x3 neighborhood (median filter function) and only penetrated adhesives with the size between 150-infiinte μm^2 were measured.

All statistical analyses in this study were operated on JMP 10 software with the confidence level of 95 %.

8.5 Results and discussion

8.5.1 Filler size distribution

The size distributions of unclassified fillers and wheat flour are shown Figure 8-2. Three fillers were classified into three size ranges using the same sieves for each filler type. Figure 8-3 demonstrates that the large and medium size fractions were very comparable among filler types. Whereas the small size fraction exhibited some variation, possibly indicating cellular anatomical differences among the respective tissue types, alder bark, walnut shell, and corn cob. SEM images of classified and unclassified filler particles are shown in Figure 8-4. It was noted that among the large-size particles, corn cob residue particles seem to have a greater aspect ratio. However aspect ratio measurements were not made.

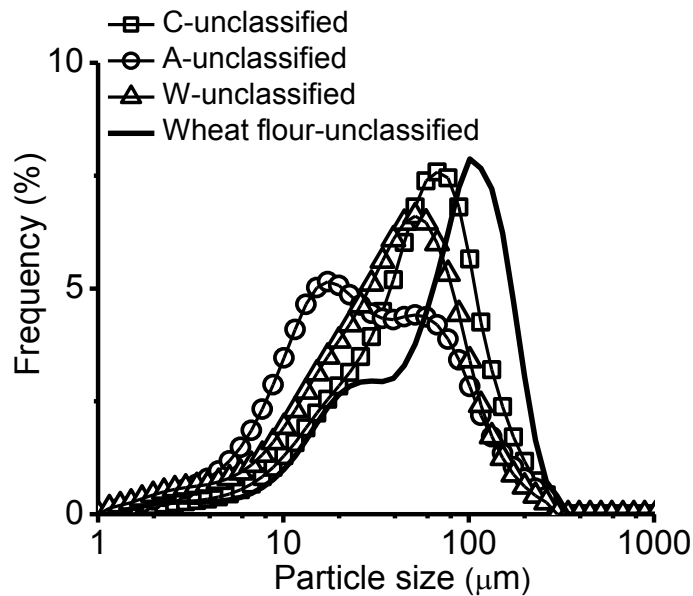


Figure 8-2 Particle size distribution of unclassified fillers and wheat flour.

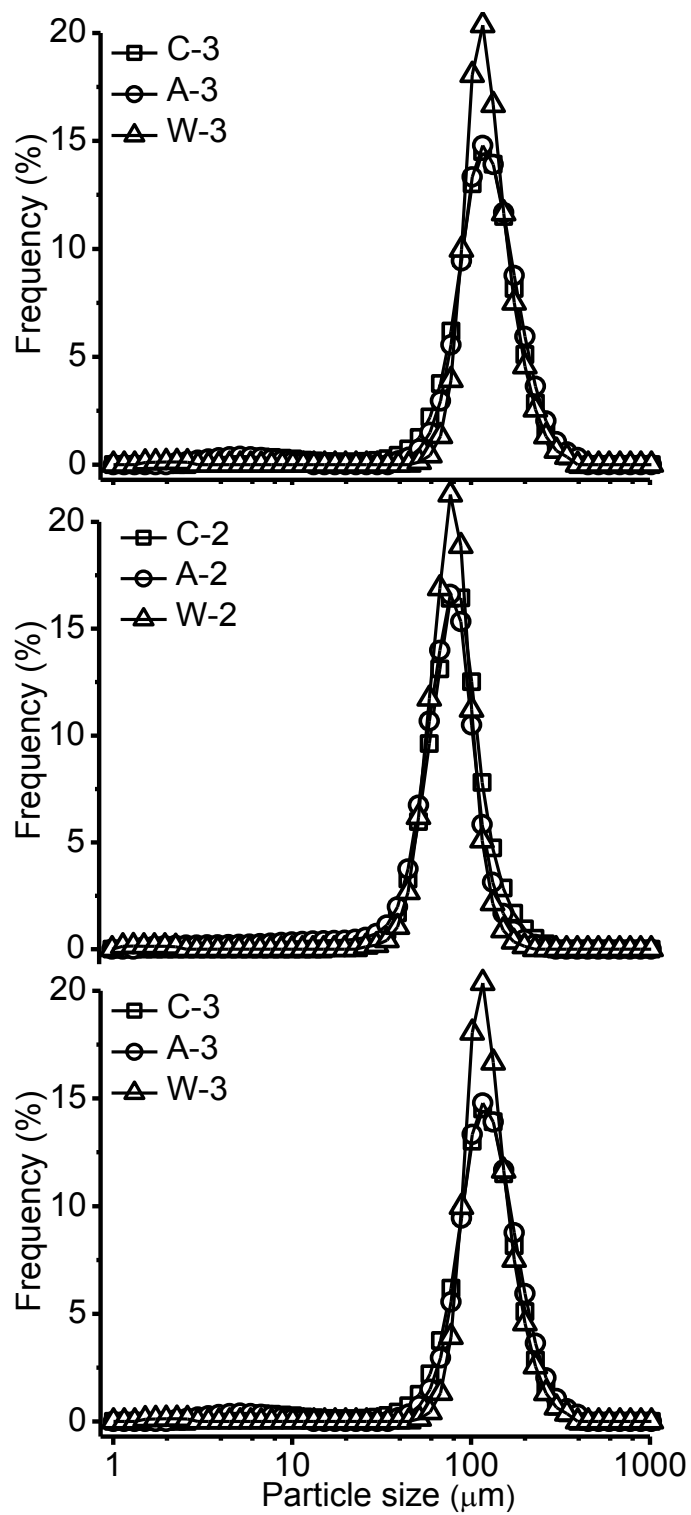


Figure 8-3 Classified filler particle size distributions.

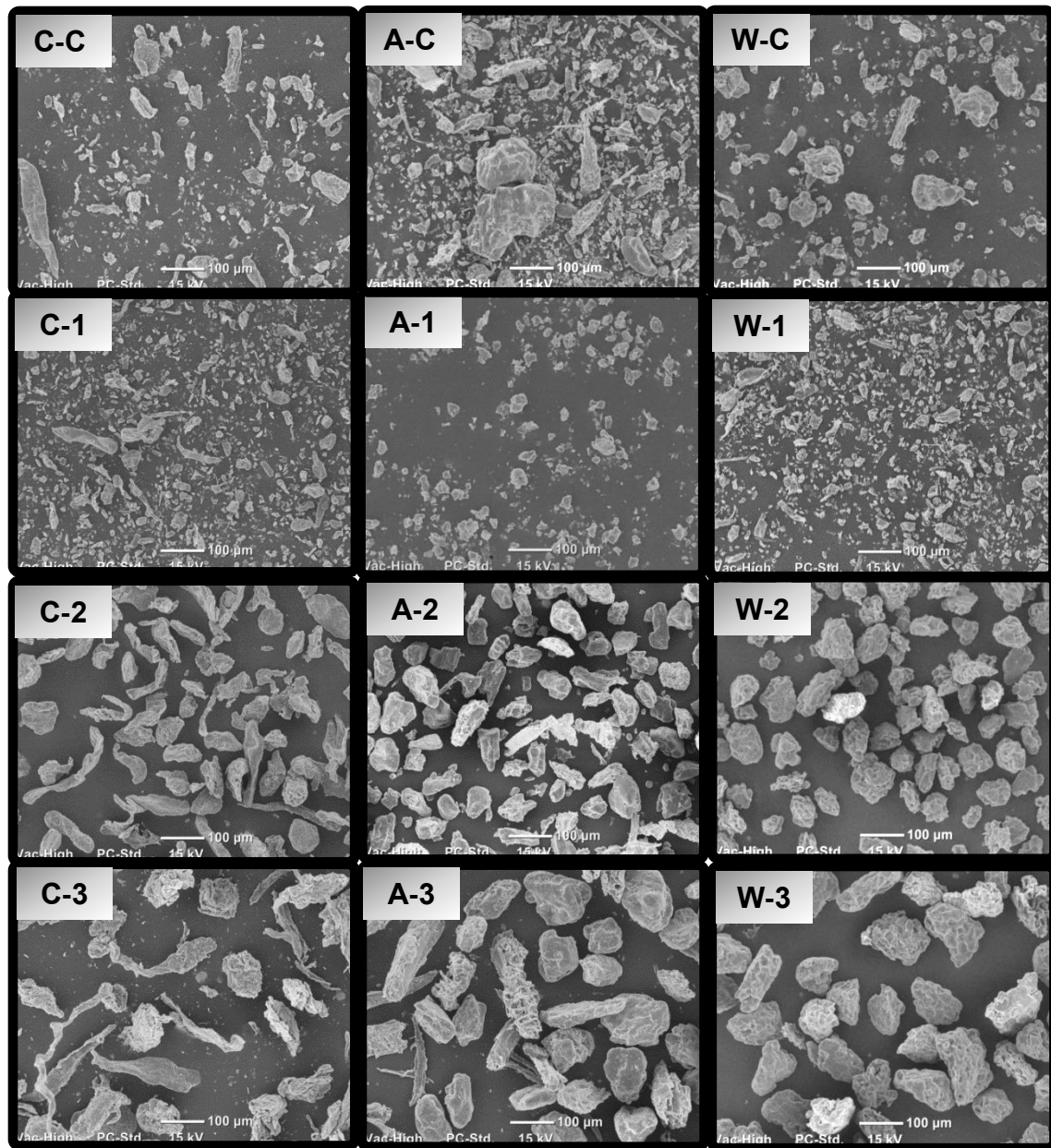


Figure 8-4 SEM images of unclassified and classified fillers.

8.5.2 Bondline thickness measurement

Adhesive bondline thickness in bonded wood is generally believed to impact adhesive bond performance [3-6]. Average bondline thickness measurements exhibited substantial variation as expected from the abrupt growth ring transitions in southern pine (Figure 8-5). In most cases the average bondline thickness was independent of location within the DCB; exceptions were alder bark and walnut shell. Even when bondline thickness was dependent upon measurement location,

the magnitude of the difference was considered acceptably low such that all measurements were pooled among sample types to provide the overall average bondline thickness in Figure 1-6. The bondline thickness data had a non-normal distribution and so non-parametric methods were used for analysis; Table 8-2 lists results from the Kruskal-Wallis (KW) test, and the Steel-Dwass (SD) method for pairwise comparisons [14]. It is interesting to note that all bondlines are quite thin, ranging from 30-50 μm , which is comparable to the diameters of southern pine tracheids (~ 35 -60 μm). Comparison of Figure 8-3 and Figure 8-6 reveal that bondline thickness is not simply related to filler particle size. For instance even though alder bark and walnut shell bondline thicknesses correlate positively to trends in particle size, the filler particles are generally much larger than the average bondline thicknesses. This might suggest that the wood substrate deforms around isolated filler particles, because most filler particles are too large to penetrate into southern pine tracheid lumens (only the small-size range fillers are capable of substantial penetration). It is also possible that isolated filler particles deform during pressing. Finally, corn con residue stands out because the corresponding bondline thicknesses have no dependence on particle size.

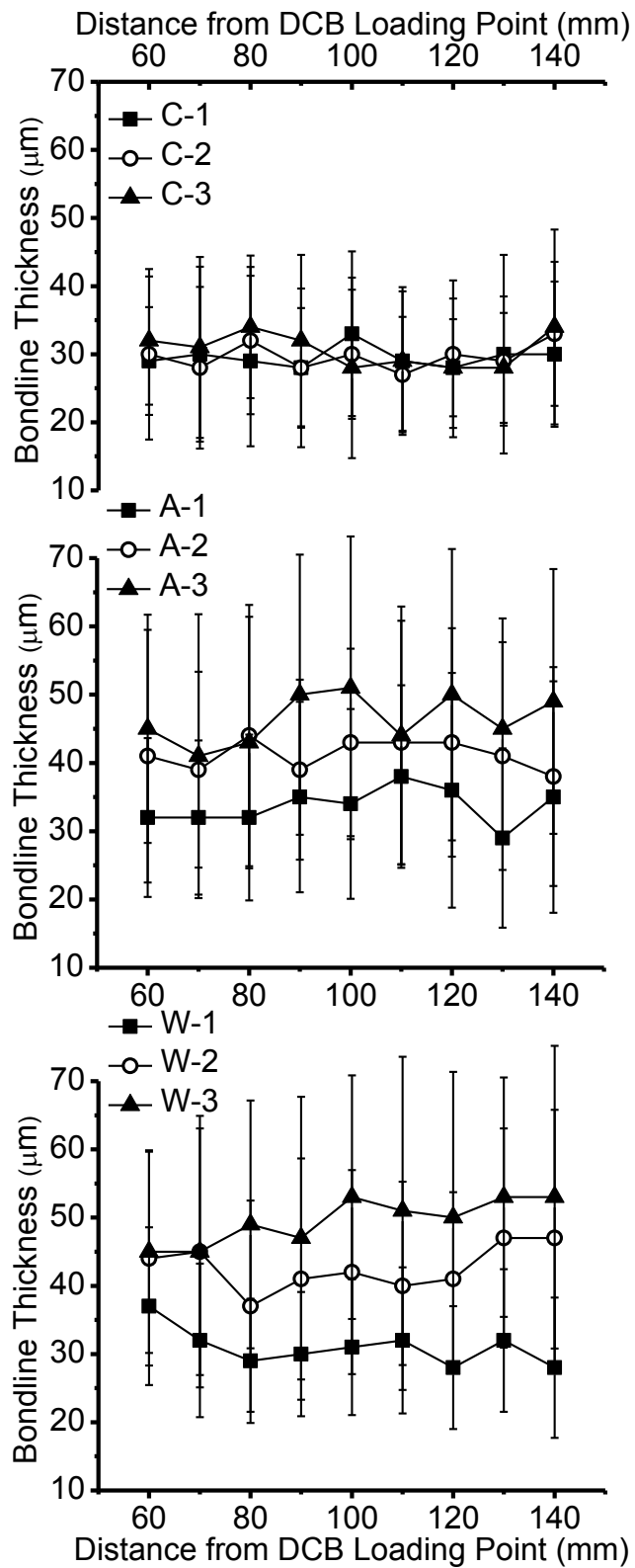


Figure 8-5 Average bondline thickness along the length of DCB specimens; each datum represents 140 observations.

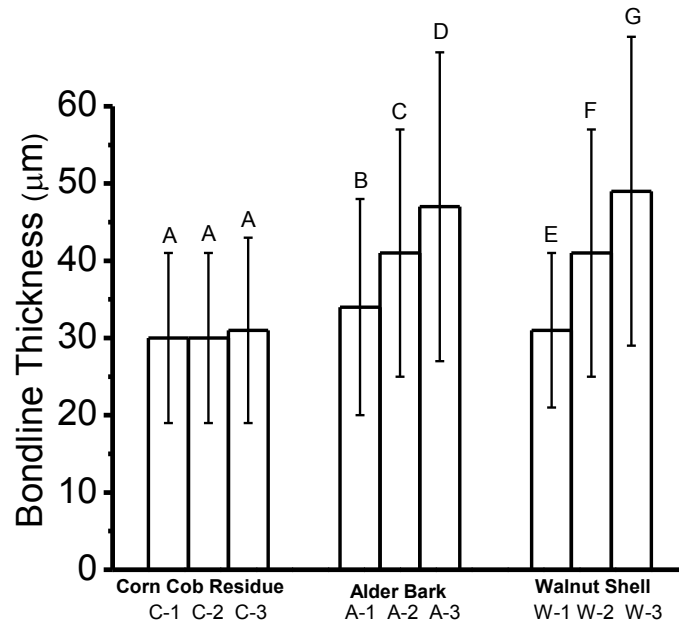


Figure 8-6. Average bondline thickness for specimens bonded with formulations prepared as a function of filler particle size. Each datum represents 1,260 observations taken over 10 DCB specimens; different letters indicate significant differences with a confidence exceeding 99 %.

Table 8-2 Statistical analysis of adhesive bondline thickness.

Filler	KW test	SD Method		
Corn cob residue	p=0.1007	C-3	C-1	p=0.0848
		C-3	C-2	p=0.3426
		C-2	C-1	p=0.7927
Alder bark	p<0.0001	A-3	A-1	p<0.0001
		A-3	A-2	p<0.0001
		A-2	A-1	p<0.0001
Walnut shell	p<0.0001	W-3	W-1	p<0.0001
		W-3	W-2	p<0.0001
		W-2	W-1	p<0.0001

8.5.3 Mode-I fracture test

In wood adhesion research one common advantage of mode-I fracture testing can be the generation of very much test data from a modest bond area [11]. In this case 10 DCBs were prepared for each sample type (2 bonded assemblies each producing 5 DCBs) and among the 90 DCBs tested only one could not be analyzed (it catastrophically delaminated upon the first crack initiation). The average number of fracture cycles per DCB was 11 (coefficient of variation = 27 %, min/max = 4/17) and crack propagation produced smooth failure surfaces, or surfaces with varied degrees of surface fiber pullout only in early wood regions. Fiber bridging across the crack plane was rarely observed in this work and so complications such as the fracture-resistance curve (R curve) were of no concern here [15]. Fracture energies were calculated using the crack length offset correction [11, 16, 17], where for each DCB the plot of compliance^{1/3} versus crack length provides the crack length correction and the DCB effective flexural rigidity; two typical examples are shown in Figure 8-7. In this work all such plots were highly linear; the average correlation coefficient, R^2 , was 0.994 with a coefficient of variation equal to 0.4 %. The detailed

results for each DCB are provided in Appendix A. Figure 8-8 shows the final compilation of fracture results where critical and arrest fracture energies were simply averaged across all fracture cycles among all like specimens. Such simple averages equally represent all sources of natural variation expected from bonded wood (however the wood used here was defect free, excepting minor localized grain variations). Within sample types the typical coefficient of variation was about 15-20 % and sometimes as high as 40 %. This scatter in fracture energy is typical and results from the intrinsic variability that includes annual growth ring transitions, variations in flexural modulus variation along the DCB length, and mixed mode-I/II effects because a wooden DCB is rarely symmetrical [5, 11, 18]. The variation in fracture energy found here is comparable to that found in previous efforts [11, 18, 19]. However, those previous efforts did not attempt to minimize wood variation as was attempted here. Recall from the experimental section that the top and bottom pieces of all 90 DCBs were machined respectively from two defect free pieces of lumber. In other words, substrate variation among the 90 DCBs was carefully minimized, but the resulting fracture energies nevertheless varied substantially within sample types.

Average critical (G_{Ic}) and arrest (G_{Ia}) fracture energies of specimens bonded with formulations prepared as a function of filler particle size are shown in Figure 8-8. Average critical fracture energies varied between 200 and 400 J/m², where A-1 and A-2 were on the lower end, and most other systems were above 300 J/m². Here again the data was not normally distributed and so non-parametric testing was conducted as before, KW and SD pairwise comparison, Table 8-3. All filler types exhibited particle size effects; however the magnitude of this effect was substantial in alder bark, and relatively minor in corn con residue and walnut shell. In alder bark fillers each particle size range caused a significant difference in critical energy; and these energies positively correlated with particle size. Whereas critical energies for the small and medium size filler particles were indistinguishable within corn cob residue and walnut shell fillers. Among corn cob residue and alder bark, critical energies tended to increase with increasing filler particle size; but the opposite was true for walnut shell fillers.

Filler particle size effects on arrest (G_{Ia}) fracture energy were similar to those discussed for critical energies. The difference between G_{Ic} and G_{Ia} indicates the unstable crack propagation during fracture testing. This is similar to the wood bonding with phenol-resorcinol-

formaldehyde/walnut shell or Douglas fir (*Pseudotsuga menziesii*) bark studied by Elbewele [10]. They reported that fillers as crack stoppers could introduce the discontinuities and alter the stress distribution of the joint to increase the strength properties of adhesive joint. And the performance of joints from different filled adhesives depended on the size and amount of discontinuities, and the filler/adhesive interactions. Our formulations are more complicated filler/resin systems. Corn con residue released different chemical components in PF medium from alder bark and walnut shell, which have been found to impact PF properties such as rheology, surface tension and cure. It is possible that the moduli of cured PF adhesives are different with three filler types. This complicates the analysis of filler/adhesive interactions, although the surface energies of all three fillers are quite similar. Therefore, it is necessary to image the fracture surface to observe the actual cracks that could happened in bulk adhesive, filler/adhesive interface, or bulk filler particle. This will give more information to analyze the filler (types and particle sizes) effects on PF adhesive fracture toughness.

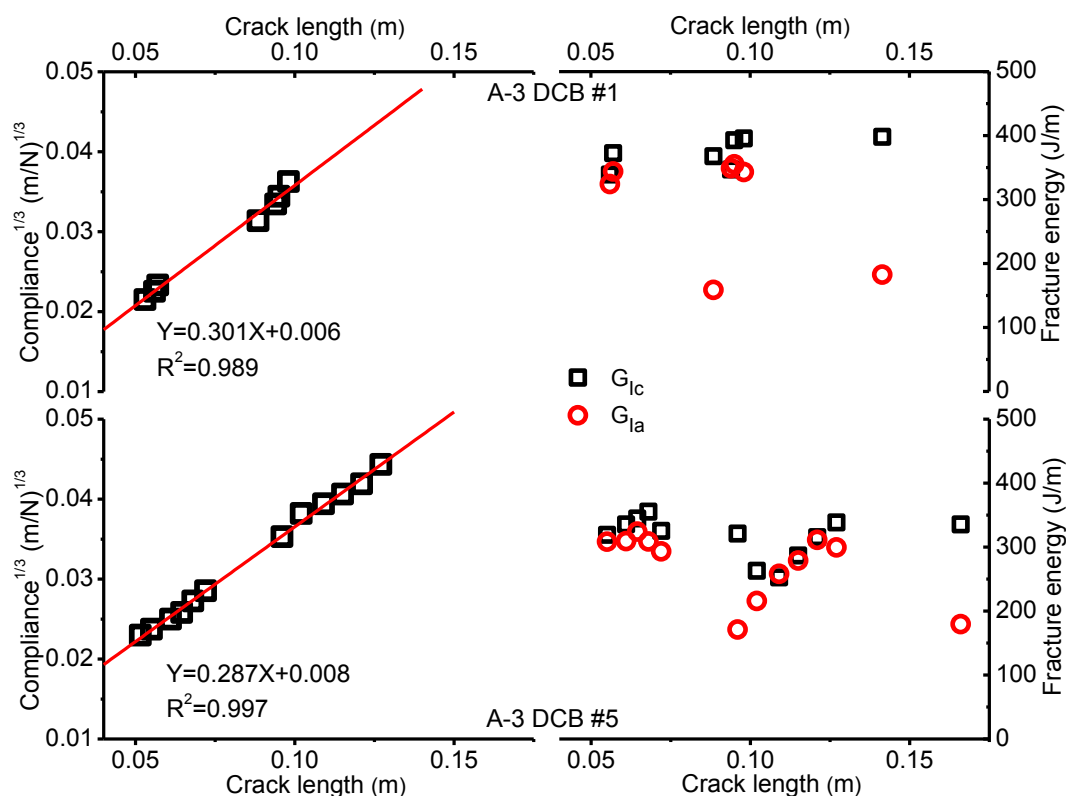


Figure 8-7 Representative cubed-root compliance vs. crack length plots and the corresponding fracture energies.

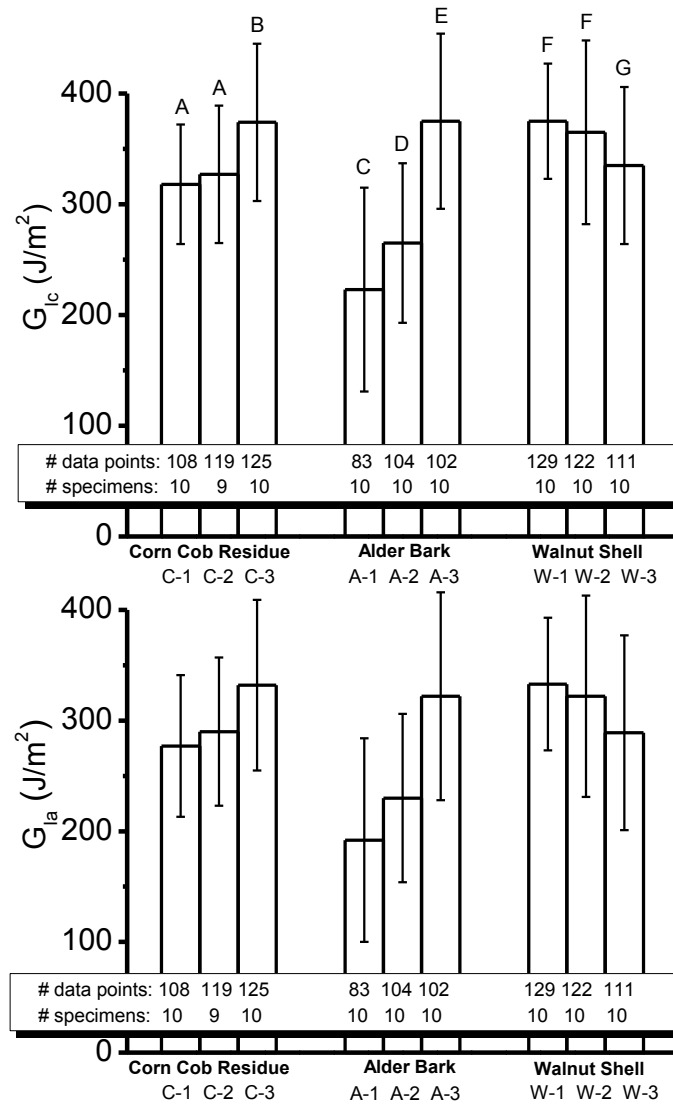


Figure 8-8 Average critical (G_{Ic}) and arrest (G_{Ia}) fracture energies of specimens bonded with formulations prepared as a function of filler particle size bonded with fillers; different letters indicate significant differences with a confidence exceeding 98 %.

Table 8-3 Statistical analysis of adhesive critical fracture energies.

Filler	KW test	SD Method		
Corn cob residue	p<0.0001	C-3	C-1	p<0.0001
		C-3	C-2	p<0.0001
		C-2	C-1	p=0.1736
Alder bark	p<0.0001	A-3	A-1	p<0.0001
		A-3	A-2	p<0.0001
		A-2	A-1	p=0.0012
Walnut shell	p<0.0001	W-3	W-1	p<0.0001
		W-3	W-2	p=0.0153
		W-2	W-1	p=0.1192

8.5.4 Adhesive penetration

It is generally believed that an optimum amount of adhesive penetration could achieve the greatest bonding performance of wood-based composite [2, 7]. Figure 8-9 shows the complete cross-sectional bondline of DCB formulated and bonded with unclassified alder bark. The variation of penetration was obvious that depended on wood anatomy. Latewood region and earlywood region showed small and large penetration, respectively. This study was to collect a large amount of penetration measurements and then pool all measurements for statistical analysis to see filler particle size effects on adhesive penetration. Since alder bark fillers were clear different as having the most dramatic particle size effects on fracture energy, penetration measurements were conducted on A-1 and A-3, of which two DCB specimens with the largest G_{Ic} and the smallest G_{Ic} respectively were selected. Mean adhesive penetration for specimens with alder bark (A-1 and A-3) is shown in Figure 8-10. Within each method, the data exhibited a great statistical variation that was expected when considering the complicated porous structure of southern yellow pine wood. Interestingly, all three methods indicate no statistically significant

particle size effects on adhesive penetration for fracture specimens with alder bark, although significant particle size effects indeed existed on adhesive bondline thickness (Figure 8-6) and performance (Figure 8-8).

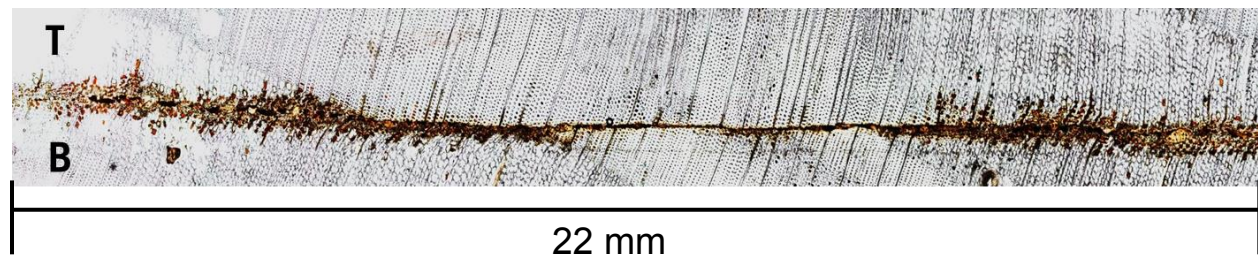


Figure 8-9 Complete cross-sectional bondline of DCB formulated and bonded with unclassified alder bark; T is the top substrate and B is the bottom substrate.

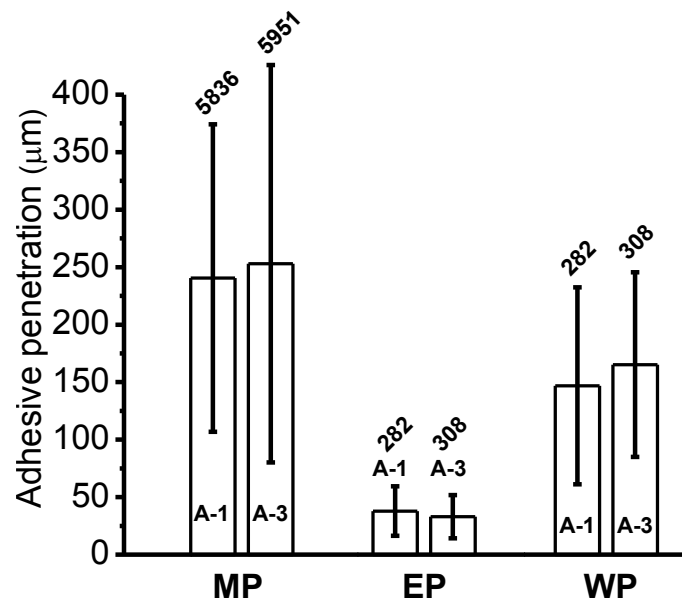


Figure 8-10 Average adhesive penetration for specimens formulated and bonded with alder bark (A-1 and A-3); Numbers above the bars represent no. of measurements.

8.6 Conclusions

Mode-I fracture testing was used to evaluate bond performance as a function of filler particle size, with the hope of correlating aspects of bondline thickness and adhesive penetration. Significant particle size effects were found with respect to fracture energy and bondline thickness of alder bark. However, no clear particle size effects on penetration were observed. A positive correlation between bondline thickness and critical energy existed for alder bark. In the

case of corn cob residue and walnut shell, while statistically significant, the magnitude of fracture energy differences was rather small. Regarding bondline thickness, classified corn cob residue fillers all resulted in the similar bondline thickness (statistically no difference) that was different from the significant particle size effects of walnut shell. Therefore, the final fracture energies might be related to different characteristics of filler types that could be as a function of particle size.

8.7 Acknowledgements

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Chapter 9 Conclusions

9.1 Research summary

The impacts of walnut shell (*Juglans regia*), alder bark (*Alnus rubra*), and corn cob (furfural production) residue on the properties of the formulated adhesives and adhesive performance were investigated with different techniques. Some aspects of this research considered filler particle size effects. In other cases unclassified fillers were studied.

The compositional analyses showed that alder bark and walnut shell had the similar chemical constituents, which substantially differ from corn cob residue. Alkaline leaching resulted in a considerable amount of glucan and acid insoluble lignin in corn cob residue that also differ from other fillers. The extractives in corn cob residue were more than twice that found in other fillers. Also, conductometric titration revealed that corn cob residue contained strong acids that were not seen in other fillers. The distinct characteristics of corn cob residue were owing to the high pressure steam digestion used in its preparation.

The column wicking method with the Washburn equation demonstrated that corn cob residue exhibited the highest total surface free energy, but all fillers had low energies (ranging from 30-34 mJ/m²) dominated by dispersive effects that are consistent with the wood literature. Specific surface areas resulting from the wicking and BET methods were in disagreement, where the former was considered to be more sensible and reliable.

The drop weight method (with the Harkins-Brown and the Lee-Chan-Pogaku corrections), and also the drop shape method showed that all fillers reduced PF surface tension with effects greatest in alder bark and walnut shell. Room temperature aging resulted in further reductions in surface tension. Surface tension reductions roughly correlated to the chemical compositions of the fillers, and probably resulted from the release of surface active compounds extracted from the fillers in the alkaline PF medium, but confirmation requires a careful characterization of the extractive and alkaline leachate fractions.

Corn cob residue fillers behaved differently from the other fillers regarding the rheology of PF/filler formulations. It was found that viscoelastic network structures form within the liquid

formulations as a function of shear history, organic filler type, and filler particle size. The origin of these effects could involve disintegration of filler particle aggregates on a non-colloidal scale, and/or colloidal effects within the liquid PF medium. Differential scanning calorimetry (DSC) analyses showed that alder bark and walnut shell exhibited the similar effects with a decrease of peak temperature and activation energy of PF adhesive cure. However, corn cob residue exhibited much lower peak temperature and much higher activation energy as neat PF. This might relate to different chemical characteristics of fillers such as acidity and chemical constituents.

It was demonstrated that filler effects on adhesive bondline thickness, fracture toughness, and adhesive penetration were dependent on organic filler type, and filler particle size. Alder bark exhibited significant particle size effects on fracture energy and bondline thickness, but no clear size effects on penetration. Regarding corn cob residue and walnut shell, particle size effects on fracture energy were statistically significant, but the magnitude difference was rather small. Classified corn cob residue fillers all resulted in the similar bondline thickness (statistically no difference) that was different from walnut shell.

9.2 Recommendations for future research

9.2.1 Filler chemical analysis

Filler chemical compositions have been roughly correlated to the properties of the formulated adhesives. However, the present work characterized the large-size fillers. Also, it has been reported that bark particle sizes impacted the chemical compositions [1-3]. Future work should include the particle size effects on filler chemical analysis. In addition, prior to the application fillers are typically subjected to different processing from the living plants to various aging stages. It is necessary to analyze the variations in filler chemical compositions through the whole process. Moreover, since the filler alkaline leachates are the probable cause of surface tension reduction, more detailed chemical analysis of filler extractives and alkaline leachates are necessary.

9.2.2 Filler geometrical analysis

The present work roughly demonstrated the geometrical differences among three filler types. Also, corn cob residue exhibited insignificant particle size effects on adhesive bondline thickness.

This differs from alder bark and walnut shell with significant particle size effects. Future work should quantitate the geometrical information (*i.e.* aspect ratio) with microscopy techniques. This also should involve raw fillers, fillers in the formulated adhesive medium, and fillers on the fracture surface.

9.2.3 Rheological analysis

This work demonstrated that shearing stimulates the formation of viscoelastic network structure within the fluids. However, the stability of these structures and the time periods over which they may evolve are unknown; the minimum shear rates required to stimulate the transformations was not determined; and how these relate to the shear rates employed during industrial manufacture is another question. Also, how these structures impact adhesive performance was not addressed. Future work should resolve these questions. In addition, it is known that PF chains adsorb on to cellulosic/lignocellulosic surfaces as a function of pH and ion strength [4, 5]. This could contribute the complex rheological behavior within adhesive formulations. It is necessary to study the adsorption PF chains adsorption on filler surfaces in the alkaline condition of formulated adhesive.

9.3 References

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- [4] Johansson K., Larsson A., Ström G., Stenius P., Adsorption of phenol-formaldehyde resin onto cellulose, *Colloids and Surfaces*, 25 (1987) 341-56.
- [5] Stack K., Dunn L., Roberts N., Adsorption studies of phenolformaldehyde resin onto cellulose fibres, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 70 (1993) 23-31.

Appendix A Fracture testing results

A.1 Summary of fracture testing results

The fracture testing results discussed in Chapter 8 are summarized in Table A-1. The neat PF resin for adhesive formulation was denoted as 1st batch.

Table A-1 Summary of critical energy (G_{Ic}), arrest energy (G_{Ia}), crack-growth-rate stability ($SI = G_{Ia}/G_{Ic}$, crack length offset (x), and effective flexural rigidity (EI_{eff}).

Filler	DCB	G_{Ic} , J/m ² (Crack #)	G_{Ia} , J/m ²	SI	x (m)	EI_{eff} , Pa.m ⁴	R ²
C-1	1	300±35 (9)	243±69	0.810	0.030	36.4	0.998
	2	286±31 (16)	262±37	0.916	0.028	31.8	0.993
	3	362±34 (9)	280±88	0.773	0.034	36.5	0.993
	4	294±34 (7)	249±73	0.847	0.064	75.9	0.982
	5	341±27 (14)	313±29	0.918	0.040	40.3	0.984
	6	263±17 (13)	238±31	0.905	0.024	27.7	0.994
	7	346±35 (10)	312±31	0.902	0.036	35.3	0.997
	8	341±113 (10)	299±104	0.877	0.025	28.4	0.997
	9	341±27 (14)	297±57	0.871	0.025	28.0	0.988
	10	323±42 (6)	250±69	0.774	0.022	23.8	0.995
C-2	1	349±44 (12)	310±49	0.888	0.023	29.1	0.995
	2	285±62 (10)	239±77	0.839	0.028	36.5	0.996
	3	Failed	N/A	N/A			
	4	335±41 (12)	291±67	0.869	0.040	43.2	0.995
	5	340±19 (17)	314±16	0.924	0.038	42.7	0.999
	6	299±22	257±37	0.860	0.033	42.6	0.995

		(13)							
	7	288±62 (14)		253±54		0.878	0.031	38.5	0.997
	8	396±29 (12)		348±47		0.879	0.021	27.1	0.999
	9	387±23 (13)		344±63		0.889	0.025	28.3	0.994
	10	294±43 (16)		270±40		0.918	0.030	30.8	0.994
C-3	1	294±52 (14)	374±71 (125)	267±53	332±77	0.908	0.026	27.5	0.998
	2	407±83 (17)		368±84		0.904	0.024	26.9	0.998
	3	346±43 (10)		293±62		0.847	0.026	28.9	0.986
	4	468±36 (12)		406±86		0.868	0.028	30.6	0.999
	5	318±38 (11)		277±54		0.871	0.042	41.6	0.997
	6	377±33 (16)		339±42		0.899	0.022	27.0	0.994
	7	403±47 (12)		354±72		0.878	0.023	25.8	0.996
	8	452±56 (9)		388±105		0.858	0.026	26.8	0.999
	9	325±20 (9)		305±18		0.938	0.034	43.1	0.990
	10	355±35 (15)		319±44		0.899	0.025	28.1	0.997
A-1	1	306±45 (15)	223±92 (83)	280±39	192±92	0.915	0.023	30.9	0.991
	2	126±29 (4)		87±21		0.690	0.075	92.5	0.998
	3	154±39 (9)		133±37		0.864	0.032	37.2	0.998
	4	303±107 (13)		279±96		0.921	0.031	35.9	0.994
	5	233±45 (10)		203±55		0.871	0.023	30.1	0.999
	6	170±15 (6)		138±29		0.812	0.038	42.6	0.988
	7	310±40 (6)		231±100		0.745	0.019	27.7	0.989
	8	169±40		127±50		0.751	0.031	31.4	0.995

		(6)							
	9	123±37 (7)		109±41		0.886	0.050	50.2	0.981
	10	137±29 (7)		113±30		0.825	0.020	23.9	0.997
A-2	1	253±36 (10)	265±72 (104)	209±56	230±76	0.826	0.035	42.5	0.989
	2	296±85 (12)		263±84		0.889	0.028	35.1	0.996
	3	138±48 (9)		125±57		0.906	0.035	42.1	0.992
	4	309±34 (8)		247±67		0.799	0.030	32.5	0.997
	5	246±21 (11)		219±31		0.890	0.032	41.3	0.998
	6	279±55 (10)		252±59		0.903	0.025	31.4	0.996
	7	213±30 (9)		178±48		0.836	0.034	47.2	0.992
	8	335±80 (12)		300±94		0.896	0.027	33.2	0.998
	9	308±44 (10)		272±53		0.883	0.025	34.7	0.993
	10	246±22 (13)		211±34		0.858	0.035	40.5	0.997
A-3	1	373±24 (7)	375±79 (65)	294±85	322±94	0.788	0.019	24.5	0.989
	2	390±67 (9)		338±90		0.867	0.029	36.3	0.999
	3	398±118 (12)		355±113		0.892	0.017	22.1	0.994
	4	467±30 (14)		419±59		0.897	0.020	24.3	0.997
	5	316±32 (12)		271±54		0.858	0.027	28.1	0.997
	6	329±32 (10)		272±74		0.827	0.022	27.4	0.996
	7	414±47 (12)		364±73		0.879	0.017	23.9	0.994
	8	356±81 (7)		293±104		0.823	0.016	22.3	0.992
	9	380±52 (11)		325±61		0.855	0.016	23.7	0.998
	10	263±27		209±59		0.795	0.034	39.1	0.999

		(8)							
W-1	1	414±38 (17)	375±52 (129)	388±36	333±60	0.937	0.028	36.8	0.988
	2	357±42 (11)		322±65		0.902	0.037	48.1	0.986
	3	329±29 (14)		303±21		0.921	0.033	40.8	0.989
	4	403±42 (15)		358±54		0.888	0.024	32.6	0.990
	5	363±26 (15)		327±22		0.901	0.030	36.3	0.989
	6	411±57 (11)		359±75		0.873	0.018	29.0	0.997
	7	391±74 (13)		349±82		0.893	0.024	33.7	0.989
	8	400±56 (8)		302±84		0.755	0.018	25.0	0.996
	9	350±19 (13)		309±45		0.883	0.024	31.6	0.998
	10	326±18 (12)		288±26		0.883	0.028	30.8	0.995
W-2	1	341±43 (13)	365±83 (122)	295±47	322±91	0.865	0.023	27.6	0.998
	2	347±82 (13)		315±87		0.908	0.027	29.6	0.995
	3	345±108 (15)		310±105		0.899	0.020	27.1	0.994
	4	492±65 (17)		452±73		0.919	0.029	31.9	0.995
	5	359±28 (15)		328±28		0.914	0.036	39.0	0.996
	6	314±38 (9)		252±62		0.803	0.024	34.6	0.999
	7	347±61 (9)		285±90		0.821	0.022	30.7	0.992
	8	439±26 (7)		346±112		0.788	0.020	26.3	0.996
	9	344±47 (9)		291±81		0.846	0.029	35.3	0.998
	10	305±35 (15)		282±42		0.925	0.026	31.8	0.991
W-3	1	311±39 (15)	335±71 (111)	271±54	289±88	0.871	0.023	31.7	0.997
	2	310±60		275±69		0.887	0.026	33.7	0.995

	(13)								
3	338±52 (12)		287±73		0.849	0.032	38.0	0.993	
4	393±59 (15)		365±68		0.929	0.015	23.3	0.993	
5	301±14 (10)		248±50		0.824	0.028	29.9	0.999	
6	285±32 (8)		228±60		0.800	0.030	40.0	0.998	
7	242±20 (6)		169±54		0.698	0.028	35.6	0.995	
8	453±36 (13)		409±63		0.903	0.022	24.3	0.998	
9	318±39 (11)		272±58		0.855	0.028	33.1	0.997	
10	283±39 (10)		232±50		0.820	0.030	31.2	0.999	

A.2 Bond performance of adhesives with unclassified fillers

This part is aimed at testing the fracture toughness of adhesives with unclassified fillers. Since alder bark exhibited significant particle size effects on adhesive fracture toughness and the neat PF (1st batch) has been frozen at -13 °C for 2 years, not only adhesive with unclassified alder bark (A-C) were selected for fracture testing, the fracture testing of adhesives with A-1 and A-3 was replicated. Neat PF resin used here was denoted as 1st batch frozen. Steady-state flow curves (shear rate increasing) of formulated adhesives were also collected according to the procedure described in Chapter 6. The adhesive formulation, fracture specimen preparation, and fracture testing were the same as described in Chapter 8. Fracture testing results are summarized in Table A-2 and Figure A-1. Unclassified alder bark (A-C) provided lower critical energy than small size alder bark. However, it is clear that fracture toughness of A-3 (frozen) was lower than A-3 (1st batch). The similar inconsistency occurred in flow behavior of adhesive with A-3 (Figure A-2). Considering the neat PF was frozen for 2 years, the possible property change like aging might be the reason.

A new batch neat PF (CascophenTM plywood resin) was synthesized and supplied by Momentive Specialty Chemicals. Rheological analysis and fracture testing were replicated for adhesives with A-1, A-3, and A-C. Fracture testing results are summarized in Table A-3 and Figure A-1, and

flow curves were presented in Figure A-2. Same as before, only A-3 exhibited the unusual particle size effects on adhesive flow behavior and fracture toughness. The specific reason for this finding is not clear yet, which requires more research in the future.

Table A-2 Summary of critical energy (G_{Ic}), arrest energy (G_{Ia}), crack-growth-rate stability ($SI = G_{Ia}/G_{Ic}$, crack length offset (x), and effective flexural rigidity (EI_{eff}); 1st batch neat PF frozen for 2 years.

Filler	DCB	G_{Ic} , J/m ² (Crack #)		G_{Ia} , J/m ²		SI	x (m)	EI_{eff} , Pa.m ⁴	R ²
A-1	1	207±16 (15)	228±40 (126)	183±24	201±44	0.884	0.028	39.8	0.997
	2	288±34 (16)		259±41		0.899	0.025	33.1	0.996
	3	220±43 (10)		186±45		0.845	0.029	32.3	0.989
	4	206±40 (10)		170±42		0.825	0.036	35.5	0.996
	5	235±43 (10)		205±47		0.872	0.026	30.4	0.997
	6	232±15 (13)		202±29		0.871	0.031	44.7	0.993
	7	206±22 (10)		188±22		0.913	0.021	30.2	0.996
	8	253±36 (10)		225±55		0.889	0.025	26.4	0.997
	9	199±36 (10)		171±34		0.859	0.031	33.9	0.995
	10	225±23 (16)		205±27		0.911	0.032	32.1	0.993
A-3	1	204±16 (19)	276±70 (133)	185±18	243±72	0.907	0.028	35.2	0.997
	2	207±24 (13)		182±37		0.879	0.022	28.0	0.999
	3	314±41 (10)		275±75		0.876	0.018	21.1	0.991
	4	278±59 (12)		242±62		0.871	0.017	22.7	0.997
	5	305±51 (13)		269±57		0.882	0.030	35.0	0.998
	6	263±31 (13)		230±38		0.875	0.028	36.7	0.999

	7	263±42 (12)		226±55		0.859	0.017	25.7	0.998
	8	265±63 (13)		234±65		0.883	0.029	37.4	0.994
	9	393±47 (17)		360±43		0.916	0.020	27.9	0.997
	10	268±34 (11)		222±50		0.828	0.028	30.3	0.996
A-C	1	153±37 (15)	196±57 (130)	139±32	171±54	0.908	0.036	44.7	0.996
	2	188±29 (16)		174±31		0.926	0.038	39.8	0.994
	3	315±46 (7)		263±94		0.835	0.029	28.4	0.999
	4	176±30 (18)		158±31		0.898	0.026	27.5	0.995
	5	200±16 (12)		171±23		0.855	0.025	27.1	0.998
	6	130±46 (15)		115±39		0.885	0.042	51.3	0.996
	7	226±63 (14)		198±64		0.876	0.033	43.4	0.991
	8	199±59 (9)		150±54		0.754	0.019	25.2	0.997
	9	219±16 (13)		187±24		0.854	0.023	24.4	0.998
	10	238±26 (11)		212±36		0.891	0.036	40.7	0.992

Table A-3 Summary of critical energy (G_{Ic}), arrest energy (G_{Ia}), crack-growth-rate stability ($SI = G_{Ia}/G_{Ic}$), crack length offset (x), and effective flexural rigidity (EI_{eff}); 2rd batch neat PF.

Filler	DCB	G_{Ic} , J/m ² (Crack #)		G_{Ia} , J/m ²		SI	x (m)	EI_{eff} , Pa.m ⁴	R ²
A-1	1	223±40 (11)	204±44 (58)	189±48	176±45	0.850	0.025	34.0	0.999
	2	163±37 (12)		153±36		0.937	0.045	41.5	0.995
	3	236±34 (11)		196±43		0.829	0.025	35.9	0.997
	4	203±74 (7)		157±83		0.774	0.025	23.3	0.998
	5	200±11 (17)		180±13		0.904	0.027	31.2	0.998

A-3	1	163±23 (11)	215±57 (60)	136±37	185±55	0.833	0.043	45.7	0.997
	2	300±50 (8)		245±65		0.818	0.022	30.5	0.998
	3	270±17 (12)		237±34		0.878	0.029	34.8	0.998
	4	178±16 (17)		157±23		0.885	0.031	42.0	0.997
	5	203±31 (12)		177±36		0.874	0.021	23.7	0.999
A-C	1	169±49 (9)	164±36 (58)	142±44	142±33	0.841	0.025	27.9	0.997
	2	169±23 (16)		149±25		0.881	0.019	31.4	0.997
	3	170±32 (9)		147±28		0.863	0.031	36.9	0.998
	4	149±32 (15)		134±28		0.899	0.029	27.8	0.997
	5	166±52 (9)		142±46		0.859	0.021	29.1	0.996

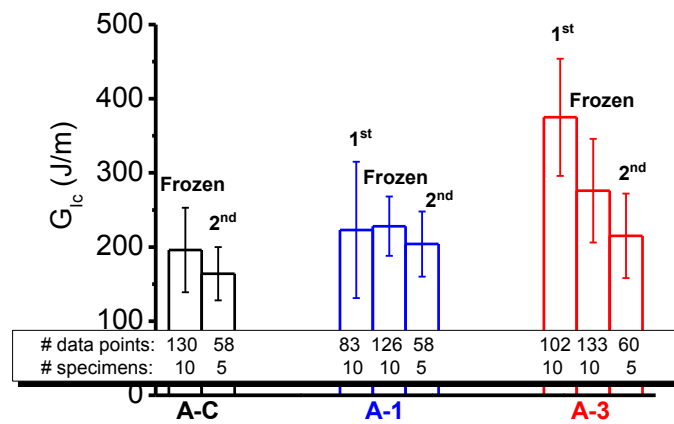


Figure A-1 Summary of fracture testing (1st: 1st batch neat PF; Frozen: 1st batch neat PF frozen for 2 years; 2nd: 2nd neat PF).

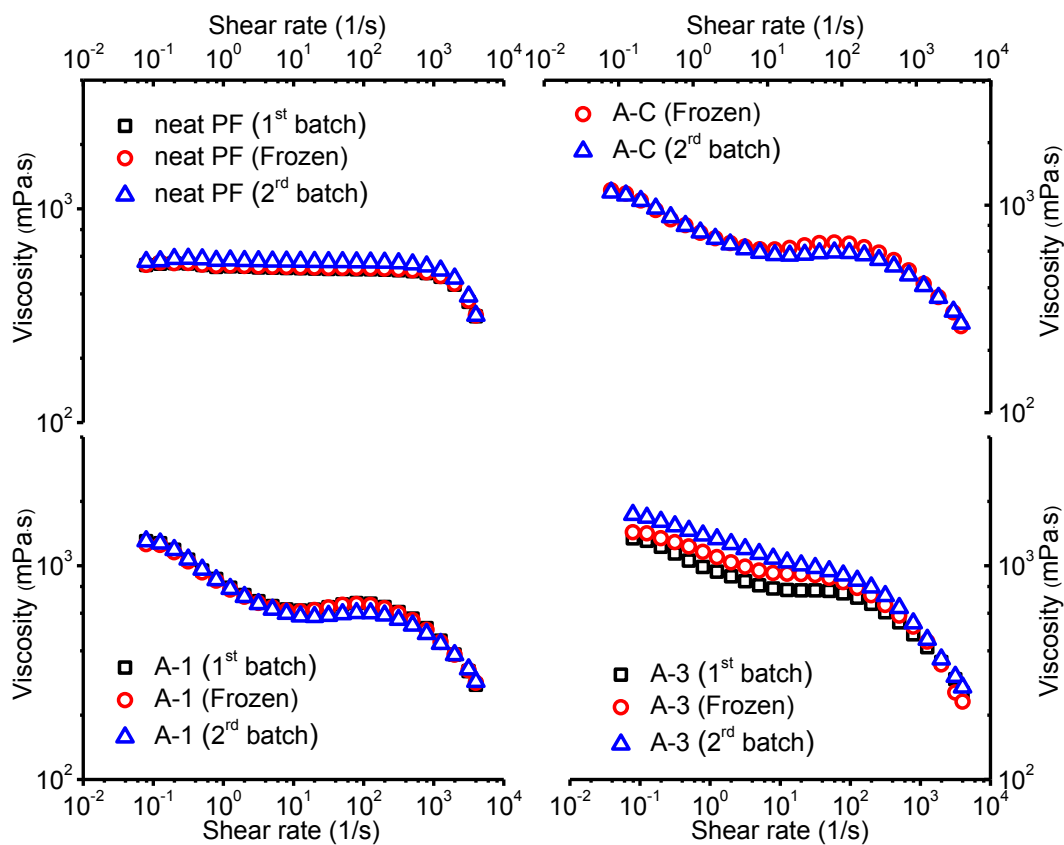


Figure A-2 Summary of shear rate increasing flow curves (1st: 1st batch neat PF; Frozen: 1st batch neat PF frozen for 2 years; 2rd: 2rd neat PF).

Appendix B Rheological model fitting of adhesive flow curves

B.1 Introduction

To quantitatively compare the rheological behavior with different filler types and particle sizes (Chapter 6), the flow curves were fitted by the proper mathematical models.

B.2 Experimental

Power Law model (equation 1) is the most widely used model to describe shear-thinning behavior [1].

$$\eta = K\dot{\gamma}^{n-1} \quad (1)$$

where η is the viscosity term, $\dot{\gamma}$ is the shear rate, K is the fluid consistency coefficient, and n is the flow behavior index indicating the closeness to Newtonian flow. That n equals to 1 indicates the Newtonian behavior of fluid and the value of the parameter K equals to the viscosity of the fluid. When $n < 1$, the fluid shows shear-thinning behavior. The more deviation from 1 the index n has, the more obvious shear-thinning behavior the fluid exhibits [2].

However, Power Law model cannot predict the transition between a shear-thinning behavior and a Newtonian behavior. Also, the shear rate range the model could be applied in is limited. Despite these limitations, it has been frequently used because of its simplicity.

Sisko model (equation 2) is a three parameter model, which typically describes the shear-thinning behavior and the following Newtonian region [3]. Compared to Power Law model, Sisko model contains an extra parameter η_{∞} , which is expressed as the infinite viscosity. The model can fit the flow curve over a broader shear-rate region than Power Law model.

$$\eta = \eta_{\infty} + K\dot{\gamma}^{(n-1)} \quad (2)$$

Their best-fit parameters in two models were obtained by using the solver function of Microsoft Excel software [4, 5].

B.3 Results and discussion

The power law model was fitted to experimental flow curves of adhesives with different fillers including both increasing shear-rate and decreasing shear-rate steps. The increasing shear-rate flow curves with different fillers were divided into three regions for fitting, while the decreasing shear-rate flow curves were separated into two regions for fitting, displayed in Figure B-1. The calculated parameters are listed in Table B-1 and Table B-2. The square of correlation coefficient (R^2) indicates that the estimated η fitted the experimental data well. The more deviation from 1 the index n had, the more obvious shear-thinning behavior the fluid exhibited.

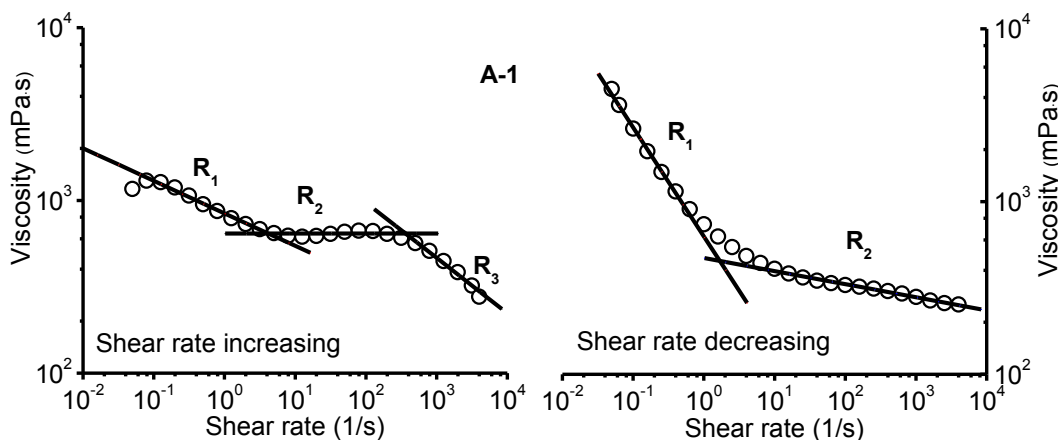


Figure B-1 Flow curve with small-size alder bark (A-1) fitted by Power Law model.

Table B-1 Calculated parameters of Power Law model for increasing shear-rate step.

Shear-rate range (s^{-1})	R_1	R_2	R_3	R_1	R_2	R_3	R_1	R_2	R_3
Filler	$K (\text{mPa} \cdot \text{s}^n)$			n			R^2		
A-1	8.42	6.42	4.23	8.12	1.00	6.80	9.83	0.00	9.82
	E+02	E+02	E+03	E-01	E+00	E-01	E-01	E+00	E-01
A-2	8.99	7.50	5.90	8.40	1.00	6.39	9.95	0.00	9.84
	E+02	E+02	E+03	E-01	E+00	E-01	E-01	E+00	E-01
A-3	9.74	7.65	3.85	8.66	1.00	6.83	9.89	0.00	9.87
	E+02	E+02	E+03	E-01	E+00	E-01	E-01	E+00	E-01
W-1	1.20	9.22	6.67	7.64	1.00	6.50	9.95	0.00	9.88
	E+03	E+02	E+03	E-01	E+00	E-01	E-01	E+00	E-01
W-2	1.43	1.10	1.12	8.70	1.00	5.73	9.97	0.00	9.14
	E+03	E+03	E+04	E-01	E+00	E-01	E-01	E+00	E-01
W-3	1.29	1.05	6.52	8.93	1.00	6.42	9.99	0.00	9.98
	E+03	E+03	E+03	E-01	E+00	E-01	E-01	E+00	E-01
C-1	1.31	8.32	3.28	6.05	9.28	6.98	9.97	9.71	9.87
	E+03	E+02	E+03	E-01	E-01	E-01	E-01	E-01	E-01
C-2	1.25	1.04	3.13	6.52	8.88	6.94	9.99	9.85	9.89
	E+03	E+03	E+03	E-01	E-01	E-01	E-01	E-01	E-01
C-3	3.40	2.79	1.16	5.57	7.64	5.44	9.97	9.96	9.98
	E+03	E+03	E+04	E-01	E-01	E-01	E-01	E-01	E-01

Table B-2 Calculated parameters of Power Law model for decreasing shear-rate step.

Shear-rate range (s^{-1})	R_1	R_2	R_1	R_2	R_1	R_2
Filler	$K (\text{mPa} \cdot \text{s}^n)$		n		R^2	
A-1	6.29	4.72	3.69	9.24	9.98	9.87
	E+02	E+02	E-01	E-01	E-01	E-01
A-2	5.45	5.56	7.17	9.07	9.92	9.93
	E+02	E+02	E-01	E-01	E-01	E-01
A-3	4.40	4.44	8.00	9.18	9.86	9.96
	E+02	E+02	E-01	E-01	E-01	E-01
W-1	6.88	7.06	4.34	8.92	9.96	9.89
	E+02	E+02	E-01	E-01	E-01	E-01
W-2	6.47	7.12	7.61	8.85	9.87	9.96
	E+02	E+02	E-01	E-01	E-01	E-01
W-3	6.09	6.52	8.34	8.92	9.89	9.89
	E+02	E+02	E-01	E-01	E-01	E-01
C-1	1.01	4.09	2.78	9.07	9.98	9.96
	E+03	E+02	E-01	E-01	E-01	E-01
C-2	6.91	4.37	3.77	9.07	9.97	9.92
	E+02	E+02	E-01	E-01	E-01	E-01
C-3	1.87	8.55	3.57	8.41	9.99	9.97
	E+03	E+02	E-01	E-01	E-01	E-01

Compared to Power law model, Sisko model includes an extra parameter of the infinite viscosity η_∞ . The decreasing shear-rate flow curves were fitted by Sisko demonstrated in Figure B-2. The calculated parameters are listed in Table B-3. The fittings cover the entire shear-rate range. The values of fluid index n , were similar to those in the first region modeled by Power law. Therefore, the Sisko model provided the similar conclusion as Power law model. Additionally, the fitting at high shear rates was not perfect. Because of the limited capacity of the instrument, there were limited available data to derive the infinite viscosity more accurately.

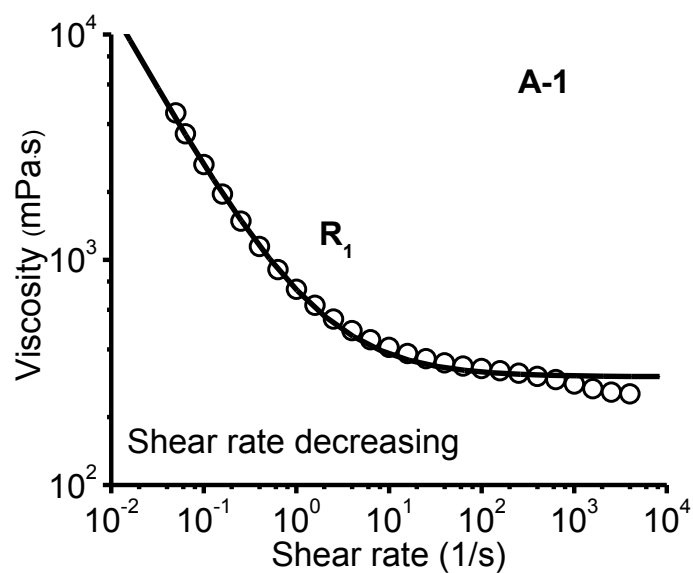


Figure B-2 Flow curve with small-size alder bark (A-1) in decreasing shear rate fitted by Sisko model.

Table B-3 Calculated parameters of Sisko model for decreasing shear-rate step.

Shear-rate range (s^{-1})		R_1		
Filler	$K (mPa \cdot s^n)$	n	$\eta_{\infty} (mPa \cdot s)$	R^2
A-1	4.34E+02	2.64E-01	3.03E+02	9.99E-01
A-2	3.16E+02	6.26E-01	2.87E+02	9.92E-01
A-3	2.47E+02	7.14E-01	2.25E+02	9.91E-01
W-1	4.42E+02	3.19E-01	3.87E+02	9.96E-01
W-2	4.95E+02	7.59E-01	2.38E+02	9.85E-01
W-3	5.41E+02	8.52E-01	1.16E+02	9.90E-01
C-1	8.30E+02	2.19E-01	2.95E+02	9.99E-01
C-2	5.38E+02	3.12E-01	2.56E+02	9.99E-01
C-3	1.64E+03	3.19E-01	3.12E+02	9.99E-01

B.4 References

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Appendix C Characterization of cured adhesive by solvent-submersion dynamic mechanical analysis

C.1 Introduction

A novel solvent-submersion method has been successfully employed to probe the lignin glass/rubber transition in lignocellulosic materials [1]. In addition, Schmidt and Frazier [2] demonstrated that dimethyl sulfoxide (DMSO) was a good swelling agent for cured PF. Therefore, this present work is to optimize the DMSO-submersion procedure to determine the different cure degree of PF adhesives and investigate if filler chemistry and/or particle size impact PF curing. Also, this work is to demonstrate this method is promising to analyze actual adhesive bondline.

C.2 Experimental

C.2.1 Materials

Modal™ alder bark (A) filler, corn cob residue (C) filler, and wheat flour (WF) extender were kindly provided by Willamette Valley Company (Eugene, OR, USA). The subspecies of corn (*Zea mays*) was unknown. The fillers were classified into sub-samples having reduced particle sizes by air swept particle analyzer (Reynolds Engineering& Equipment). The classified fillers samples (C, M, or W) are numerically coded: 1 represents small size range (-325 mesh); 2 represents medium (-200/+325 mesh); 3 represents large size range (+200 mesh). Adhesives with A-1, C-1 and C-2 were studied. The moisture contents of fillers and wheat flour in the formulation, measured with moisture analyzer (OHAUS Corporation), were 5-8 %, and 10 %, respectively. Phenol-formaldehyde (PF) resin was a Cascophen™ plywood resin, supplied by Momentive Specialty Chemicals (pH = 11~12, solids content = 43 %). Sodium carbonate (powder) and 50 % sodium hydroxide (liquid), used for adhesive formulation, were obtained from Willamette Valley Company (Eugene, OR, USA) and Fisher Scientific, respectively. HPLC grade dimethyl sulfoxide (DMSO) was purchased from Sigma Aldrich.

C.2.2 Adhesive formulation

Each type of fillers was formulated with PF resins with the addition of Na_2CO_3 , 50 % NaOH, water, and wheat flour as shown in Table C-1 (Willamette Valley Company, Eugene, OR, USA). Each formulation (800 g) was prepared in a mixer (5 quart bowl-lift stand mixer, KitchenAid®) with a speed of 75 rpm (“stir” speed level) at room temperature. Formulated adhesives were stored in the freezer until use (stored over 8 months). Within complete adhesive formulations the wheat flour volume fraction was 3.6 % and filler volume fractions were 4-6 %.

Table C-1 PF adhesive formulation (and mixing procedure).

Formulation contents	weight %
Water	18.4
Filler	7.5
(Mix 2 min.)	
PF resin	22.8
(Mix 2 min.)	
Extender (wheat flour)	5.5
(Mix 8 min.)	
Sodium hydroxide, 50 %	3.0
(Mix 10 min.)	
Sodium carbonate	0.5
(Mix 1 min.)	
PF resin	42.3
(Mix 2 min.)	
Total mixture	100

C.2.3 Solvent-submersion dynamic mechanical analysis (DMA)

Samples were thawed. Approximately 2.8 g sample was poured into a glass vial (diameter: 10 mm) and cured at 70 °C (42 hr. for A-1; 24 hr. for C-1 and C-2) followed by 120 °C (1 hr.) or 90 °C (2 hr.). The first cure procedure was denoted as cure-1, and the other was cure-2. Disk DMA specimens (diameter x thickness = 8 mm x 3 mm) were prepared from cured adhesives. Dry specimens were prepared under vacuum (0.5 mmHg, room temperature, 48 hr.) and then stored over anhydrous P_2O_5 and dry N_2 . Specimens were saturated with dimethyl sulfoxide (DMSO) using vacuum/pressure treatment at room temperature (0.75 mmHg for 2 hours, then atmosphere pressure for different time).

Solvent-submersion analysis was conducted on Rheometer AR2000 (TA instruments) with modified 8 mm diameter parallel-plates such that the bottom plate was surrounded by a stainless steel cup that maintained specimen immersion. A thin silicon oil layer was covered on solvent surface and an aluminum cover was put on the steel up to reduce solvent evaporation.

All analyses were rigorously conducted within the linear viscoelastic response (LVR) region. This was determined from stress sweep experiments at the temperature extremes. LVR limit was defined as the highest stress level that maintained the plot's correlation coefficient (R^2) above or equal to 0.9995. During analysis, a single specimen was held (normal force 15 N) between two plates under DMSO and heated from 25-150 °C (3 °C/min, 1 Hz). A-1 (no solvent), denoted as no solvent involved during sample preparation and testing, was heated from -20-180 °C (3 °C/min, 1 Hz). The peak of $\tan \delta$ was used to determine glass transition temperature (T_g).

C.3 Results and discussion

C.3.1 Solvent effect

Although the softening in modulus plot was obvious for adhesive with C-1 (cure-1, no solvent), it was difficult to determine glass transition temperature (T_g) from $\tan \delta$ plot (Figure C-1). Since it has been demonstrated as a good swelling agent for cured PF, dimethyl sulfoxide (DMSO) was used as plasticizer in solvent-submersion DMA to determine T_g of cured adhesives. For C-1 (cure-1) with DMSO, a clear peak of $\tan \delta$ was observed (Figure C-1). Additionally, the peak of $\tan \delta$ of C-1 (cure-2) with DMSO was shifted to a lower temperature in comparison to C-1 (cure-1), which demonstrated that DMSO-submersion DMA could detect the relative cure degree of PF adhesives. Therefore, it is promising to analyze the actual bondline excised from fracture specimens.

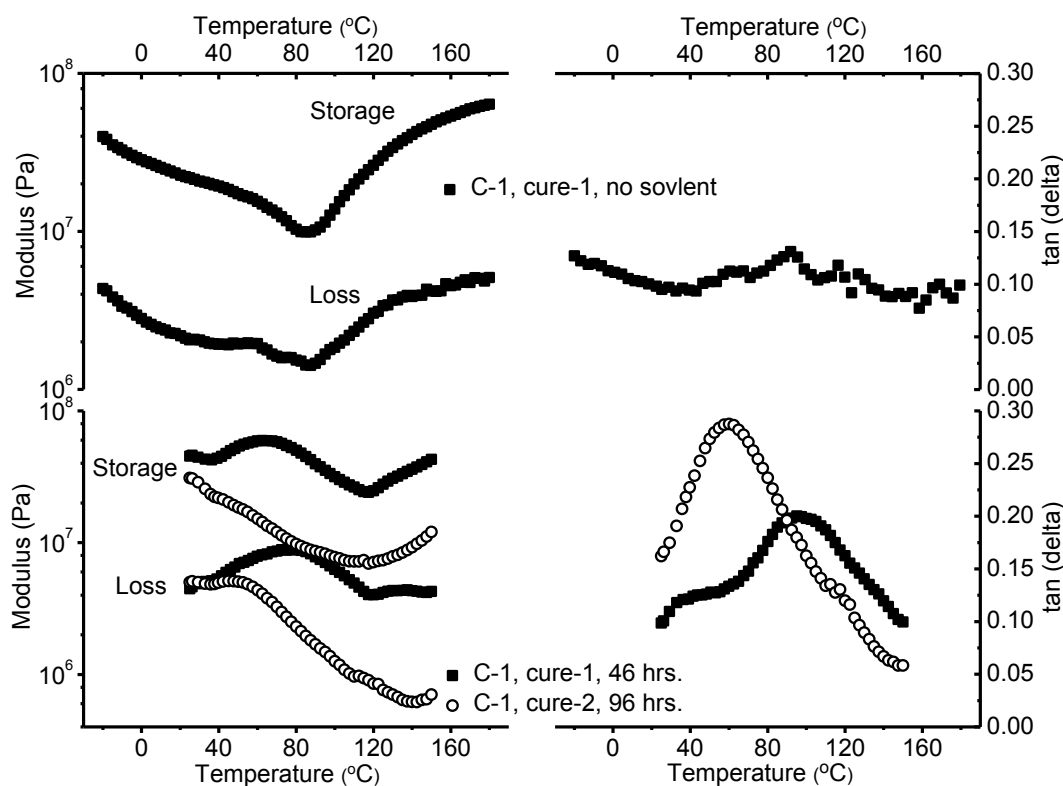


Figure C-1 Heating scans of C-1 with/without DMSO.

C.3.2 Solvent saturation time effect

Specimens, after vacuum/pressure treatment at room temperature (0.75 mmHg for 2 hours), was saturated under atmosphere pressure for different time. Figure C-2 shows that regarding A-1 and C-2, the T_g was shifted to a higher temperature as the increase of solvent saturation time except for 84 hr. and 132 hr. of A-1. This suggested that the saturation time should be similar for relative comparison of T_g .

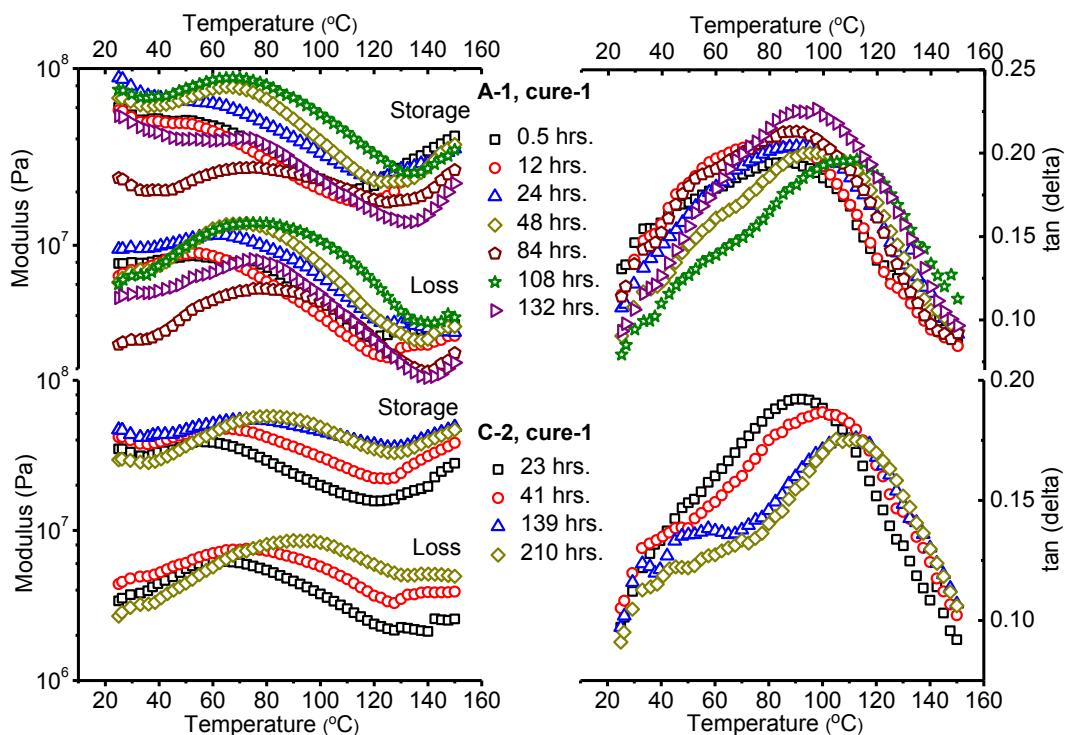


Figure C-2 Heating scans of A-1 and C-2 with different saturation time.

C.3.3 Filler type effect

Figure C-3 shows the heating scans of A-1, C-1, C-2 under the similar saturation time. Filler type and filler particle size has insignificant effects on the glass transition temperature of adhesive.

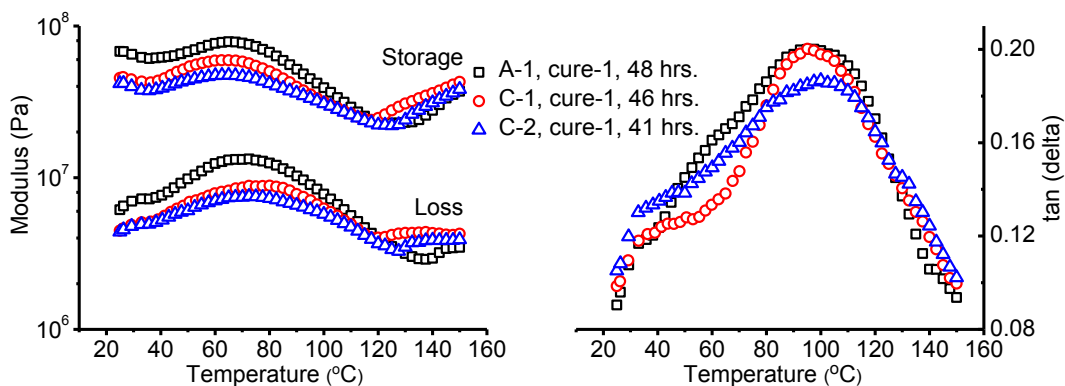


Figure C-3 Heating scans of A-1, C-1, C-2 under the similar saturation time.

C.4 References

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