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

Xing Yang, Charles E. Frazier *

Sustainable Biomaterials, Virginia Tech, Cheatham Hall, RM 230, 310 West Campus Dr., Blacksburg, VA 24061, USA

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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 (*Juglans regia*), red alder (*Alnus rubra*) bark, and corn cob (*Zea mays*) 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.

1. 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 an unchanging PF base 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.

2. Experimental

2.1. 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. All fillers and wheat flour were ground and passed through a 100 mesh sieve. Size distributions of fillers and wheat flour, 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 were 5–8%, and 10%, respectively. Phenol-formaldehyde (PF) resin was a Cascophen™

* Corresponding author. Tel.: +1 540 231 8318.
E-mail address: cfrazier@vt.edu (C.E. Frazier).

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Table1
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

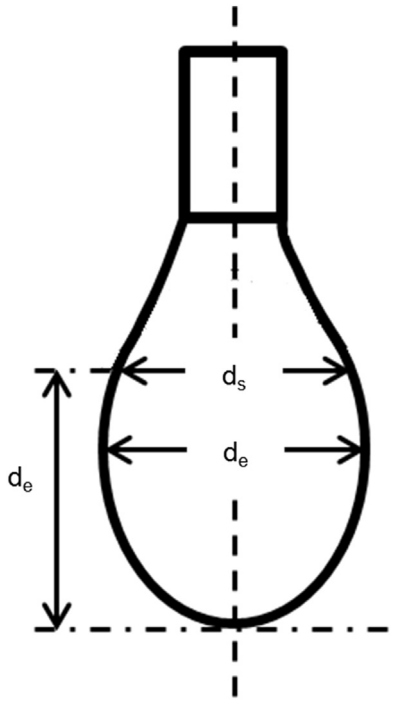

Fig. 1. A pendant drop showing the characteristic dimensions.

plywood resin, supplied by Hexion (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.

2.2. Chemical compositional analysis

Compositional analysis was conducted on the fillers using fractions retained on a 200-mesh sieve (+200 mesh) including the determination of extractives, alkaline leachates, acid insoluble and acid soluble lignin, and sugars. The extractive content was determined according to ASTM D1105 [6]. 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 h. 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

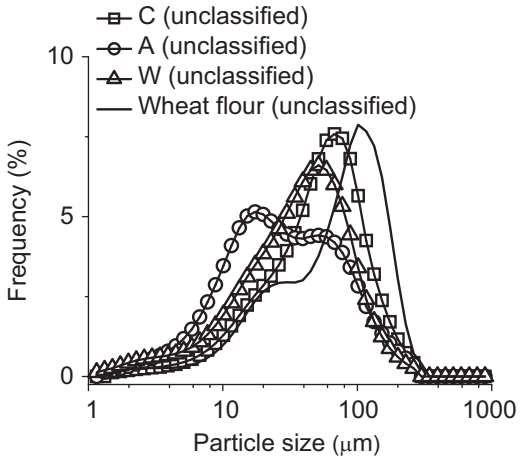

Fig. 2. Particle size distribution of fillers and wheat flour used in this study.

NREL/TP-510-42618 and NREL/LAP-004 [7,8]. 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.

2.3. Adhesive formulation

Each filler type (unclassified by size) was formulated with PF resin with the addition of Na_2CO_3, 50% NaOH, water, and wheat flour as shown in Table 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 1, but that no filler was included (PF-no filler). Regarding complete formulations, the effects of ambient (23 ± °C) storage time were studied over a 48 h. period. Samples were identified according to filler type (A, W, or C) and storage time in hr. (0 h, 8 h, 24 h, and 48 h). 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 min. The supernatants were isolated and subjected to surface tension measurement. Samples subjected to centrifugation were identified as "spun."

2.4. 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.

2.5. 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 min. All of