International Journal of Adhesion & Adhesives 66 (2016) 93–98

Contents lists available at ScienceDirect

International Journal of Adhesion & Adhesives

journal homepage: www.elsevier.com/locate/ijadhadh

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

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ARTICLE INFO

Article history:
Accepted 16 December 2015
Available online 31 December 2015

Keywords:
Adhesives for wood
Phenolic
Rheology
Organic filler

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 (*Zea mays*) 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.

1. 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 to 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 (*Juglans regia*), 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.

2. Experimental

2.1. 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.

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http://dx.doi.org/10.1016/j.ijadhadh.2015.12.035
0143-7496/

2.2. Filler size classification

The fillers were classified into sub-samples by sieves. The classified filler 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).

2.3. 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, 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 extracted with 125 mL sodium hydroxide solution (4 wt%) for 24 h. The solid fraction of the mixture was collected by centrifugation and washed with 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 [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.

2.4. Adhesive formulation

Sub-samples were formulated with PF resins with the addition of Na_2CO_3, 50% NaOH, water, and wheat flour as shown in Table 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 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 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

2.5. 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 complete adhesive formulation minus the 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 min. 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 using the two-step procedure described above, but with additional segments (X, Y, and Z) to create the following sequence: 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).

3. Results and discussion

3.1. Filler size distribution

The size distributions of unclassified fillers and wheat flour are shown Fig. 1. Three fillers were classified into three size ranges using the same sieves for each filler-type. Fig. 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.

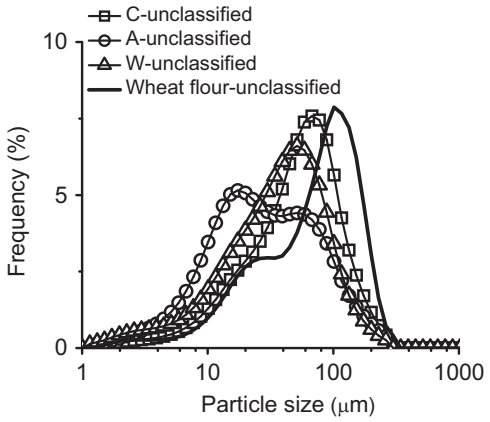

Fig. 1. Particle size distribution of unclassified fillers and wheat flour.