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Durability of kraft pulp fiber–cement composites to wet/dry cycling

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Abstract

If pulp fiber–cement composites are to be used for exterior applications, the effect of cyclical wet/dry exposure must be known. In this research program the effects of three fiber treatments—beating, bleaching, and drying—were investigated to identify those that may minimize effects of environmental aging and degradation during wet/dry cycling. After 25 wet/dry cycles, all composites showed significant losses in first crack strength, peak strength, and post-cracking toughness. The majority of losses in mechanical properties occurred within the first 5 wet/dry cycles, though ductile fiber failure was still observed by scanning electron microscopy (SEM). A three-part progressive degradation mechanism during wet/dry cycling is proposed: (1) initial fiber–cement debonding, (2) reprecipitation of hydration products within the void space at the former fiber–cement interface, and (3) fiber embrittlement due to fiber cell wall mineralization. Unbeaten fiber–cement composites exhibited greater peak strength and post-cracking toughness, prior to cycling, while no significant differences were seen after 25 cycles. The effects of fiber beating varied prior to and after cycling. Unbleached fiber–cement composites exhibited the slowest progression of degradation during cycling. The initial drying state appeared to have no effect on composite performance after 25 wet/dry cycles.

Keywords: Fiber–cement; Durability; Wet/dry cycling; Pulp; Beating; Bleaching; Drying; Microscopy

1. Introduction

It is well known that fiber–cement composites exhibit improved toughness, ductility, flexural capacity, and crack resistance as compared to non-fiber-reinforced cement-based materials. Wood pulp fibers are a unique reinforcing material that offer numerous advantages. They are non-hazardous, renewable, and readily available at relatively low cost compared to other commercially available fibers [1]. As a result, pulp fiber–cement composites have found practical applications in recent decades in the commercial market as a replacement for hazardous asbestos fibers. Today, pulp fiber–cement composites can be found in products such as extruded non-pressure pipes and non-structural building materials, mainly thin-sheet products [2]. Fiber–cement siding has been called "tomorrow's growth product" [3] and as of the late 1990s, shares 7–10% of the North American siding market [4].

If such composites are to be used for applications where performance must be ensured after environmental exposure, the effects of cyclical wetting and drying on performance must be known. Using sisal fiber–mortar composites, Gram [5] found significant losses in post-cracking peak strength and toughness with wet/dry cycling. The majority of these losses occurred by 12 wet/dry cycles. On the other hand, Soroushian et al. [6] found that flexural strength of kraft pulp fiber–mortar composites increased with wet/dry cycling. Additionally, flexural toughness was found to significantly decrease,

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particularly by 20 wet/dry cycles. The differences between peak (flexural) strength trends with wet/dry cycling warrants further investigation of the influence of wet/dry cycling on mechanical performance, particularly flexural first crack and peak strength.

Marikunte and Soroushian [7] concluded that the mechanical properties of fiber–cement composite are adversely affected after 25 wet/dry cycles compared to control specimens (i.e., zero wet/dry cycles). However, it is unclear from the published data, if progressive damage occurs to fiber–cement composites with wet/dry cycling. That is, how do the mechanical properties, such as strength and toughness, differ after 25 wet/dry cycles as compared to a fiber–cement composite exposed to 5, 10, or 15 wet/dry cycles? It is important to examine the progression of degradation to understand and predict changes in performance with exposure.

To mitigate fiber–cement composite degradation due to wet/dry exposure, two approaches—fiber modification and matrix modification—have been investigated. Gram [5] produced encouraging results by modifying the cement matrix through the use of a high alumina cement. Prior to wet/dry cycling, high alumina cement composites exhibited lower peak strength and toughness compared to ordinary Portland cement composites. However, by 120 wet/dry cycles, the post-cracking peak strength of high alumina cement composite decreased by only 56.2% as compared to a 98.8% loss for the ordinary Portland cement composite.

The use of pozzolanic materials as a partial weight replacement of cement has also been investigated in order to reduce the alkalinity of the cement matrix as well as refining the pore structure of the matrix. Silica fume, used at relatively large amounts (i.e., 30% or greater replacement of cement by weight) appears to significantly minimize composite degradation due to wet/dry cycling [5,8,9]. Silica fume replacements of 17% and 33% of cement by weight reduced the pore water pH from 13.2 to 12.9 and 12.0, respectively [5]. Partial replacement of Portland cement with 40% slag by weight by Tolêdo Filho et al. [8] did not significantly improve the durability of sisal fiber–mortar composites after 46 wet/dry cycles. Gram [5] has also shown that replacement of cement with 70% slag by weight reduced the pore solution pH from only 13.2 to 13.0 and did not improve the durability of sisal fiber–mortar composites after 120 wet/dry cycles. Similar results were obtained using fly ash as a partial weight replacement of Portland cement. Using rice-husk ash, Ziraba et al. [10] concluded that 45% replacement of Portland cement by weight minimized composite degradation due to wet/dry cycling by reducing the pore solution pH by 15–20%.

Ziraba et al. [10] also investigated methods of sealing the matrix pore structure of sisal fiber–mortar composites by infiltrating specimens with molten asphalt or molten plasticized sulfur. Asphalt infiltration did not offer any protection against composite degradation. However, plasticized sulfur infiltration did minimize the effects of wet/dry cycling. Additional mortar matrix additives—colophony, tannin, and montan wax—were used by Canovas et al. [11] to seal the pore structure of sisal fiber–mortar composites. Though all additives significantly reduced the porosity and subsequent water adsorption of composite specimens, only colophony appeared to be effective in reducing composite degradation due to wet/dry cycling.

Another approach to reduce composite degradation due to wet/dry cycling has been to modify the fibers by coating or impregnating the fibers with water-repelling or blocking agents. By reducing the moisture movement around and within the fibers, it is presumed that the progression of fiber mineralization will be slowed or prevented. Gram [5] impregnated sisal fibers with formine and stearic acid, potassium nitrate and stearic acid, sodium chromate and fluorine–carbon–hydrogen–stearate, and borax and chromium stearate. The use of these impregnation agents slightly improved the durability of the mortar composites during wet/dry cycling, compared to unimpregnated fiber composites. However, impregnated sisal fiber composites exhibited peak strengths about half that of unimpregnated fiber composites prior to cycling. Attempts to reduce composite degradation by Ziraba et al. [10] using fiber coatings of asphalt, epoxy, and linseed oil were not effective in mitigating the effects of wet/dry exposure and decreased the strength of the composite prior to wet/dry cycling.

The main objective of this research is to investigate how variations in pulp fiber treatments influence fiber–cement composite properties prior to and after wet/dry exposure. The treatment processes investigated include refining (or beating), bleaching, and drying. Some research [7,12–15] has shown that the strength of fiber–cement composites may experience no change or actually improves with wet/dry cycling. However, in this previous research, it is difficult to separate increases in matrix strength due to continued cement hydration with time from the changes in mechanical properties of the composite due to wet/dry cycling. Therefore, in this research, to eliminate the effects of age on matrix strength, all samples are tested at the same age (i.e., 78 days), regardless of the number of wet/dry cycles. That is, all samples remained in a curing environment for at least 28 days prior to testing, with those subjected to fewer or no wet/dry cycles remaining in the curing tank for longer periods until wet/dry cycling or mechanical testing. The performance of the composites with increasing numbers of wet/dry cycles is assessed by center-point bending tests. Further characterization of the composite and the failure mode is accomplished by scanning electron microscopy (SEM) of the composite fracture surfaces.

2. Experimental study

2.1. Materials

Fiber–cement beams were made with a water-to-cement ratio of 0.60 using commercially available ASTM Type I Portland cement and deionized water. Oxide analysis and Bogue potential composition for the cement are listed in Table 1. ADVA Flow superplasticizer, obtained from Grace Construction Products, was used at a maximum dosage rate of 6.15 μL/g of cement to aid workability.

Kraft pulp softwood fibers were used as reinforcement at a 4% fiber volume fraction in the cement paste. ACI 544 recommends the use of kraft pulp fibers for use in cement-based materials because much of the lignin and hemicellulose, which are less alkali resistant than cellulose, have been removed during the pulping process [2]. The fibers were Slash pine softwoods obtained from Buckeye Technologies in Plant City, FL. With the exception of the never-dried fibers, fibers were received in dry, compacted form prior to being fluffed. The never-dried fibers were received in moist, fluffed form. The fibers were treated by a process described in [16,17] to improve dispersion. This process involves treating the fibers with cationic starch and fly ash to improve their dispersion during mixing.

Table 1
Oxide analysis and Bogue potential composition of ASTM Type I Portland cement

Oxide	Percent by mass
SiO_2	20.17
Al_2O_3	5.34
Fe_2O_3	3.85
CaO	63.93
MgO	0.91
Na_2O	0.05
K_2O	0.35
SO_3	4.00
Loss on ignition	0.80
Insoluble residue	0.05
C_3S	54.16
C_2S	7.64
C_3A	16.97
C_4AF	11.70

Four types of pulp fiber samples were used to evaluate the effect of fiber processing, i.e., beating, bleaching, and initial drying state. Table 2 lists the fiber treatments investigated for each pulp fiber sample group along with the respective ash and moisture contents, which were determined according to methods described in TAPPI T211 and T412, respectively [18,19]. Beaten pulp fibers were beaten using a laboratory Valley beater to a Canadian Standard Freeness (CSF) of 550 mL.

2.2. Sample preparation

Pastes were prepared by mixing the pulp fiber, approximately 50% of the water, and the entirety of the superplasticizer for 3 min at 60 rpm in a 1.5 L-capacity Hobart mixer to ensure separation of the fibers. Subsequently, the cement was added, followed by the remaining water. Mixing continued at 120 rpm for another 5 min to allow for uniform fiber dispersion.

It should be noted that this is a cast-in-place mix methodology as opposed to slurry-dewatering. Cement paste samples were used to isolate the effect of wet/dry cycling on composite durability, negating effects such as the presence of aggregate on composite behavior.

Flexure specimens were cast in $2.54 \times 2.54 \times 30.5$ cm ($1 \times 1 \times 12$ in.) brass molds and were placed in a curing box at 22 ± 2 °C and $90 \pm 5\%$ RH. After 24 h, the samples were demolded, cut with a masonry saw to a 10.2 cm (4 in.) length, and placed in a limewater curing tank at 18 ± 2 °C until wet/dry cycling or testing commenced.

2.3. Exposure

To determine the time to saturation and drying, a hystersis percent mass change versus time curve, similar to [20], was developed. The mass was measured to monitor mass loss and gain during wet/dry cycling. When the mass stabilized (i.e., mass change of less than 1% over a period of 3 h), the sample was assumed to be either dry or saturated, depending upon the exposure. The percent mass change over time for each fiber type when subjected to wet/dry cycling is shown in Fig. 1. Thus, it was determined that a 48-h cycle length was appropriate to allow for dry and saturated conditions in these fiber–cement beams.

Table 2
Pulp fiber treatments investigated

Fiber	Drying state	Bleaching	Beating	Ash content[a] (%)	Moisture content[b] (%)
A	Never-dried	Unbleached	Unbeaten	49.01	47.30
B	Once-dried	Bleached	Beaten	60.37	48.90
C	Once-dried	Bleached	Unbeaten	41.25	45.85
D	Never-dried	Bleached	Unbeaten	48.79	46.40

[a] Per TAPPI T211-02 [18].
[b] Per TAPPI T412-02 [19].

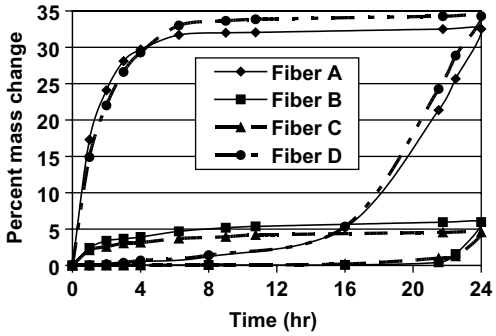

Fig. 1. Determination of wet/dry cycle length.

Therefore, a wet/dry cycle was defined for this research as 23 h and 30 min drying in an oven at 65 ± 5 °C and 20 ± 5% RH, air drying at 22 ± 5 °C and 60 ± 5% RH for 30 min, 23 h and 30 min soaking in water at 20 ± 2 °C, and air drying at 22 ± 5 °C and 60 ± 5% RH for 30 min. Air drying of samples was allowed between saturation and drying to avoid unrealistic thermal shock and subsequent microcracking. Samples were exposed to 0, 1, 2, 5, 10, 15, or 25 cycles prior to testing in order to determine how the mechanical properties of these fiber–cement composite are affected after various numbers of wet/dry cycles. Mechanical testing was performed after the 30 min at 22 ± 5 °C and 60 ± 5% RH preceded by 23 h and 30 min of soaking.

Again, it is important to note that all samples were tested at 78 days, regardless of the number of wet/dry cycles. Thus, any variations in measured properties should be attributable to exposure, rather than a combination of exposure and prolonged cement hydration.

2.4. Mechanical test methods

The 2.54 × 2.54 × 10.2 cm (1 × 1 × 4 in.) samples were tested in center-point bending with a span of 7.6 cm (3 in.). The span-to-depth ratio of 3 was chosen to comply with ASTM C 348-97 and C 293-94 [21,22]. Tests were performed in triplicate using a 98 kN (22 kip) screw driven test frame (Satec model 22EMF) with a crosshead displacement of 0.1 mm/min. The testing setup can be seen in Fig. 2. The deflection was captured using an electronic deflectometer (Epsilon model 3540-012M-ST), placed under the center point of the beam. The test was controlled using the deflection system to better capture the post-cracking behavior of the beams.

Toughness is defined here as the post-cracking toughness or the area under the load–deflection curve beyond first cracking. This definition is necessary because beams subjected to a low number of cycles exhibited load–deflection toughening after cracking, while those beams subjected to a larger number of wet/dry cycles exhibited load–deflection softening after cracking (Fig. 3(a)). In the absence of post-cracking toughening, the peak strength will be equal to the first crack strength. Peak

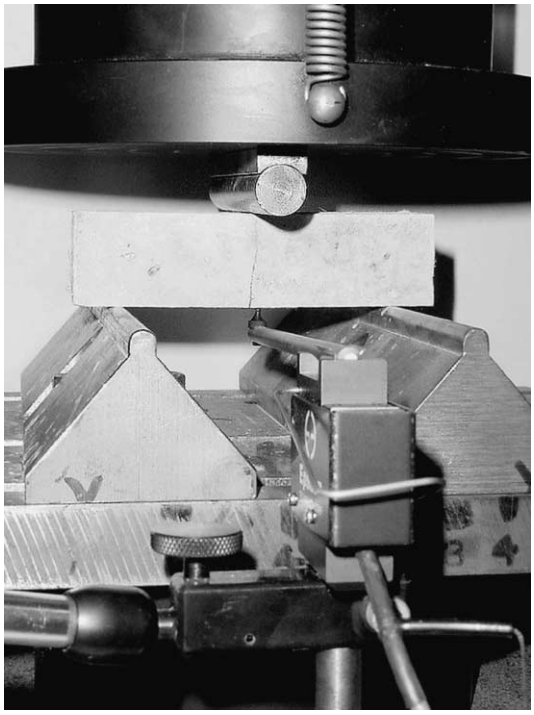

Fig. 2. Flexural testing set-up.

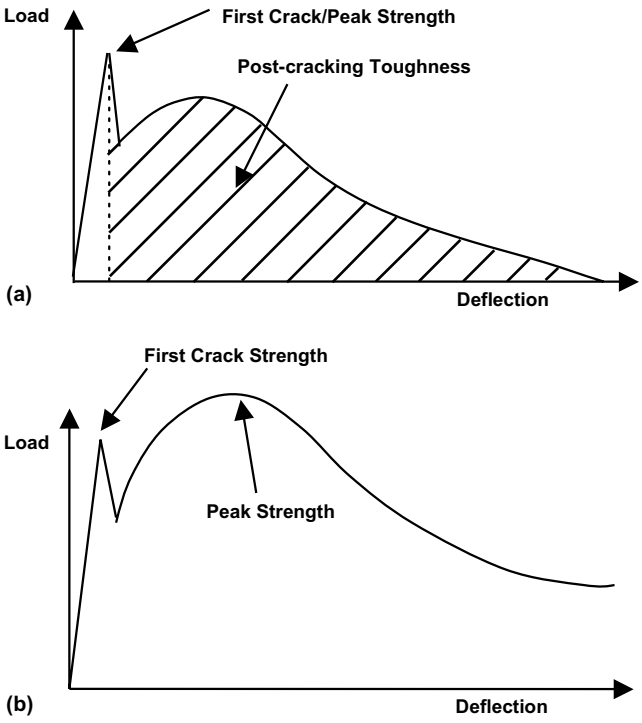

Fig. 3. Definition of first crack strength, peak strength, and post-cracking toughness. (a) Post-cracking softening where first crack strength is equal to peak strength. (b) Post-cracking toughening where first crack strength is less than the peak strength.

strength values take into consideration the toughening of the composite after cracking (Fig. 3(b)).

2.5. Microstructural characterization methods

Microstructural characterization of composite fracture surfaces was employed using a JSM 6400 scanning electron microscope in secondary electron (SE) mode. Fracture surfaces were cut from the composites, mounted on SEM stubs, and coated with osmium by the method developed by Kubotsu and Ueda [23]. Osmium coating was used to prevent charging of the sample and to improve the contrast and maximum resolution of the observed fracture surfaces, as compared to conventional gold coating.

3. Results and discussion

With the selection of the more alkali-resistant kraft pulp fibers and with the experiment designed to eliminate the effects of continued cement hydration on measured strength, the focus of this investigation was to isolate the influence of variations in fiber processing to determine if these variations affect fiber–cement composite behavior during progressive wet/dry cycling. That is, can certain processes, i.e., beating, bleaching, and initial drying state, be used to minimize degradation of fiber–cement composite strength and/or toughness due to wet/dry cycling? These fiber processes are known to change the chemical and physical structure of the fiber, as described in Sections 3.2–3.4.

3.1. Effect of wet/dry cycling

Samples were tested at 0, 1, 2, 5, 10, 15, and 25 wet/dry cycles to measure the progression of damage, if any, resulting from increasing number of cycles. Fig. 4 illustrates typical load–deflection curves after 0, 5, 10, and 25 cycles. It can be seen that there is a 43.5–52.0% loss of first crack strength, a 50.8–72.4% loss of peak strength, and a 97.5–98.8% loss of post-cracking toughness after 25 wet/dry cycles. The majority of strength and toughness loss occurs within the first two to five cycles.

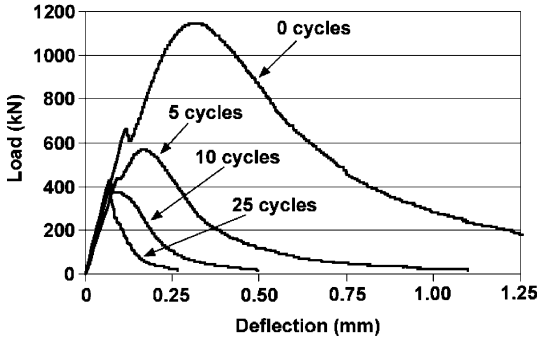

Fig. 4. Typical load–deflection curves.

With the exception of fiber A, average first crack and peak strength values were lowest between five and ten cycles. For these samples containing fibers B–D, first crack strength decreased by 53.6–60.3% and peak strength decreased by 59.2–78.2% upon reaching the minimum values as compared to samples not exposed to wet/dry cycling (i.e., zero cycles). However, after 25 cycles, values for first crack and peak strength increased relative to these minimum values by 20.6–38.8%.

Average post-cracking toughness values, with the exception of fiber A, reached minimum values after 15 cycles. These were 98.1–98.5% lower than those samples not exposed to cycling. However, after 25 cycles, post-cracking toughness increased by 2–32% relative to the minimum values after 15 cycles. In samples reinforced with fiber A, the lowest strength and toughness measured during this evaluation occurred after 25 cycles.

SEM micrographs of fracture surfaces, Fig. 5, show the progression of damage with wet/dry cycling. Without cycling, Fig. 5(a), fibers regularly extend approximately 600–1000 μm from the fracture surface. Thus, in the absence of wet/dry cycling, fiber pull-out appears to be the predominant mode of failure. Examination of fracture surfaces after 25 cycles, such as shown in Fig. 5(c), shows that the predominant mode of failure after this period of exposure is fiber fracture. This suggests that after 25 wet/dry cycles, the fiber becomes brittle, most likely due to mineralization of the fibers. Energy dispersive spectroscopy (EDS) of SEM backscattered electron imaging by Tolêdo Filho et al. [20] and Savastano and Agopyan [24] confirm the transport of cement hydration products, primarily $Ca(OH)_2$, within the lumen and voids of fibers, as well as around the fibers due to wet/dry cycling. Similar observations of cement hydration product deposits were made during this work.

Since the majority of loss in flexural performance was found by mechanical testing to occur within the first 5 wet/dry cycles, it is worthwhile to observe fracture surfaces after 5 wet/dry cycles. Examination of fracture surfaces of these samples, such as in Fig. 5(b), shows that fiber pull-out remains the predominant mode of failure, as was observed with no wet/dry exposure. However, the fiber pull-out length is significantly less (i.e., approximately 100–400 μm after 5 wet/dry cycles as compared to 600–1000 μm in the control). Even though the majority of strength and toughness losses were measured after 5 wet/dry cycles, examination of SEM micrographs, such as Fig. 5(b) and Fig. 6, of the fracture surfaces show some "necking" or a Poisson effect of the fiber near the region of fiber failure. This feature which is observed for many of the pulled-out fibers after 5 wet/dry cycles, suggests that fiber failure behavior remains ductile. Additionally, pulled-out fibers with no wet/dry

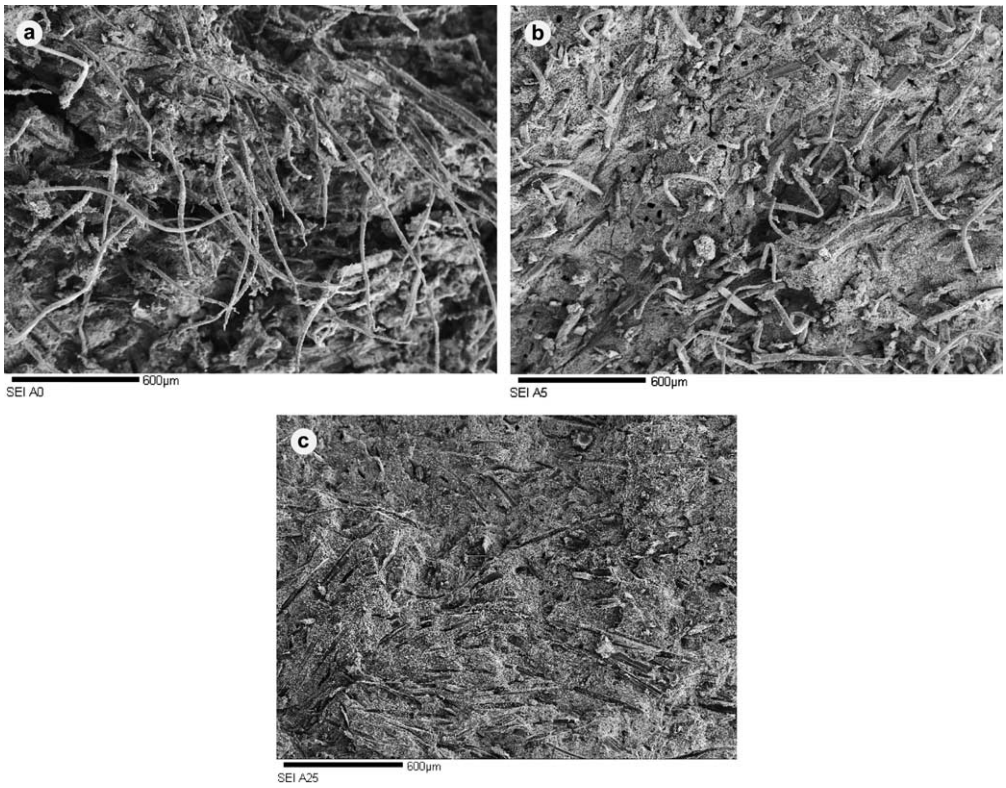

Fig. 5. Progression of fiber degradation. (a) Without cycling (50×). (b) After 5 cycles (50×). (c) After 25 cycles (50×).

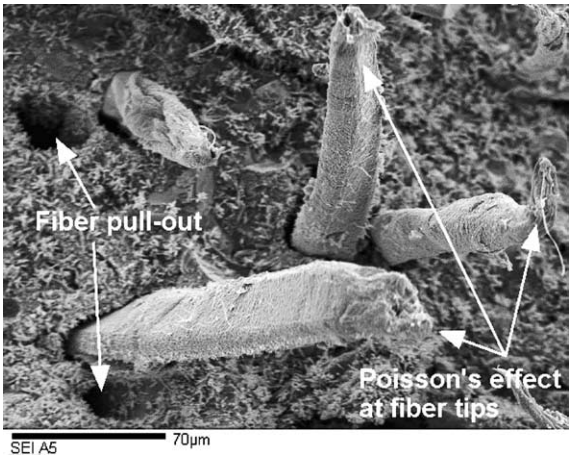

Fig. 6. Fiber ductility after 5 wet/dry cycles (450×).

exposure, Fig. 5(a), also exhibit this "necking" effect. Research, including microscopy and spectroscopy, is ongoing to determine the mechanism(s) for decreased ductile fiber pull-out lengths.

One possible explanation involves a progressive series of mechanisms: (1) initial fiber–cement debonding (due to fiber shrinkage during drying), as indicated by decreases in strength between 0 and 2 cycles, (2) reprecipitation of relatively low-strength hydration products (e.g., secondary ettringite) within this new void space, introduced at the former fiber–cement interface, minimizing fiber dimensional changes during subsequent wetting, and (3) fiber mineralization by the reprecipitation of hydration products, likely calcium hydroxide, within the fiber cell wall structure.

During the initial wet/dry cycles, prior to the reprecipitation of hydration products around the fiber, the fibers are largely free to shrink and swell without impedance. Upon drying, diametrical fiber shrinkage may create a capillary expulsive pressure on the pore solution residing within the fiber lumen. Such a pressure would cause the pore solution to be primarily expelled through the fiber ends and pits along the fiber. During this drying, reprecipitation of hydration products can occur at the former fiber–cement interface. However, the reprecipitation of hydration products such as ettringite can restrain fiber swelling upon rewetting. During subsequent drying, then, fiber shrinkage is also reduced. Thus, the driving force for pore solution expulsion is minimized. That is, the pore solution resides within the fiber for a longer period of time. Therefore, the pore solution will not only migrate from the fiber lumen to the matrix through the ends and fiber pits, but the solution can also diffuse from the lumen through the cell wall, resulting in a deposition of hydration products within the fiber cell wall. This deposition or reprecipitation decreases fiber ductility and leads to shorter fiber pull-out lengths in the composite. Complete fiber

mineralization may not take place until beyond approximately 10 wet/dry cycles in this research, as suggested by slight increases in strength. Microscopy and spectroscopy is underway to further elucidate the mechanisms for reduced strength and toughness and decreased fiber pull-out lengths.

3.2. Effect of beating

Refinement or beating of the pulp fibers fibrillates the fiber surface [25–27]. The outermost later, S1, may become damaged by beating, thereby increasing the fiber surface area. Thus, it may be proposed that beaten fibers should exhibit increased fiber–cement bonding due to this increase in fiber surface area. This increased bonding would be characterized by higher strength, but lower toughness and decreased tendency for fiber pull-out as compared to unbeaten fibers. However, beating may decrease the average fiber length. Additionally, beaten fibers tend to be more conformable. In terms of post-cracking toughness, it is possible that these changes in fiber length and conformability may present competing effects to the increased fiber surface area [17]. However, Coutts [26] has generated evidence to the contrary, showing that unbeaten fiber composites exhibit greater toughness as compared to beaten fiber composites. Thus, as the anticipated effect of beating is unclear, the goal of this part of the research was to assess how the initial mechanical behavior and behavior after wet/dry cycling is influenced by fiber beating.

Results from flexural testing of cement composites reinforced with fiber B (beaten) and C (unbeaten) are shown in Fig. 7. Prior to wet/dry cycling, the composites containing unbeaten fibers show a 61.3% greater average peak strength and a 80.3% greater average post-cracking toughness than those containing beaten fibers. Average first crack strength values were similar for both beaten (5.637 ± 0.271 MPa) and unbeaten (5.947 ± 0.323 MPa) fiber composites. SEM micrographs in Fig. 8 illustrate typical fracture surfaces of composites containing either beaten or unbeaten fibers without any wet/dry exposure. While bulk observation of fracture surfaces yields no apparent differentiation with beating, microscopy does show some variations in failure mode. Specifically, with the beaten fiber composites, it is often observed that the S1 layer separates from the fiber upon failure, remaining bonded to the matrix. Additionally, the beaten fiber pull-out length ranges from 400 to 600 μm, whereas the pull-out length of the unbeaten fibers ranges from 700 to 900 μm. Thus, the beaten fiber–cement paste bond seems to be stronger than the unbeaten fiber–cement paste bond. It is believed that the larger surface

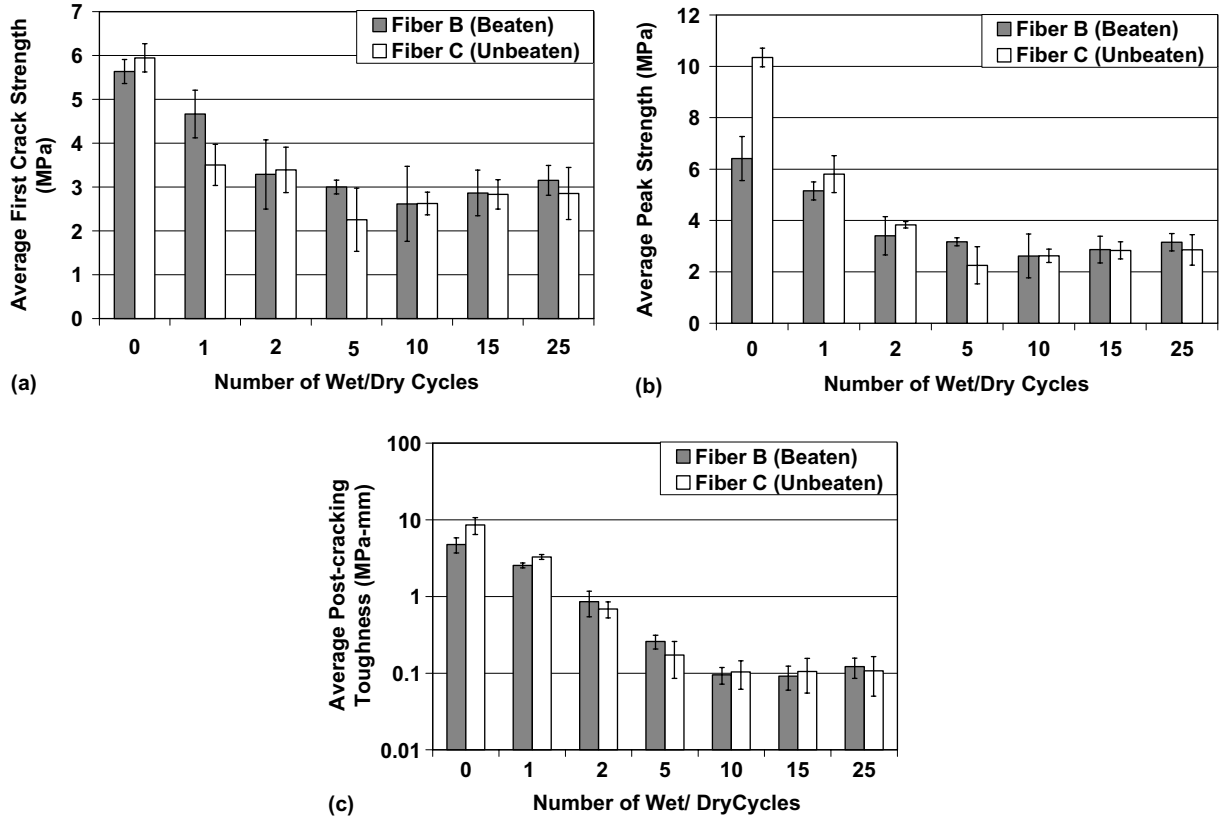

Fig. 7. Flexure test results for fiber B (beaten) and fiber C (unbeaten). (a) Average first crack strength (MPa) versus number of wet/dry cycles. (b) Average peak strength (MPa) versus number of wet/dry cycles. (c) Average post-cracking toughness (MPa mm) versus number of wet/dry cycles.

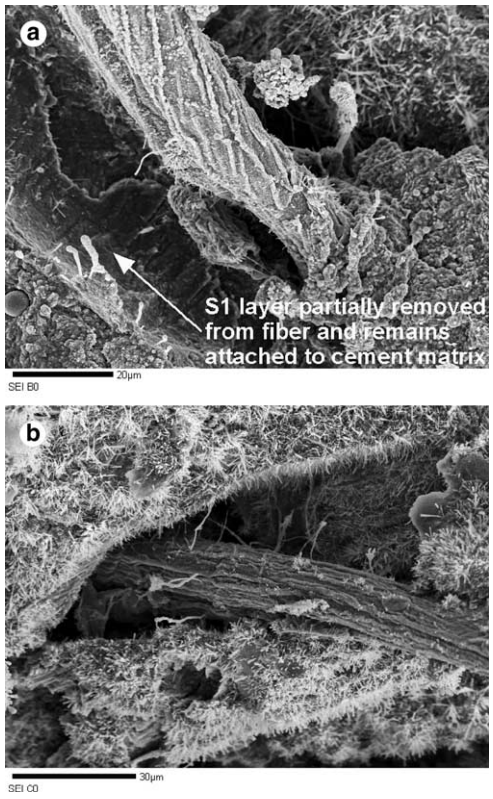

Fig. 8. SEM micrographs after 0 wet/dry cycles. (a) Beaten fiber (1200×). (b) Unbeaten fiber (1000×).

area of the beaten fiber is the primary contributing factor to this observed behavior.

Fig. 7 also shows data describing the progressive effect of wet/dry cycling on mechanical behavior. After 5 wet/dry cycles, the composites containing beaten fibers generally show increased strength and toughness values as compared to those of the unbeaten fiber composites. Beyond 10 wet/dry cycles, no appreciable difference between the beaten and unbeaten fiber composites is apparent from this data. It is worth noting, however, that the beaten fiber composites exhibit a 10.5% increase in peak/first crack strength and a 12.9% increase in post-cracking toughness after 25 wet/dry cycles, as compared to the unbeaten fiber composites.

Micrographs of typical fracture surfaces for each of these samples after 25 wet/dry cycles are shown in Fig. 9. For the beaten fibers, it is commonly observed that the S1 and S2 layers are partially removed from the fiber during composite failure, while such observations are not made for unbeaten fibers. Similar observations were made without wet/dry cycling (Fig. 8). Thus, the fiber–cement paste bond appears to be stronger for the beaten fiber–cement composite prior to and after cycling. The mechanical testing data collected supports this supposition. That is, the beaten fiber composites exhibited greater peak/first crack strength and toughness in flexure after 25 wet/dry cycles. The increased fiber/matrix bond-

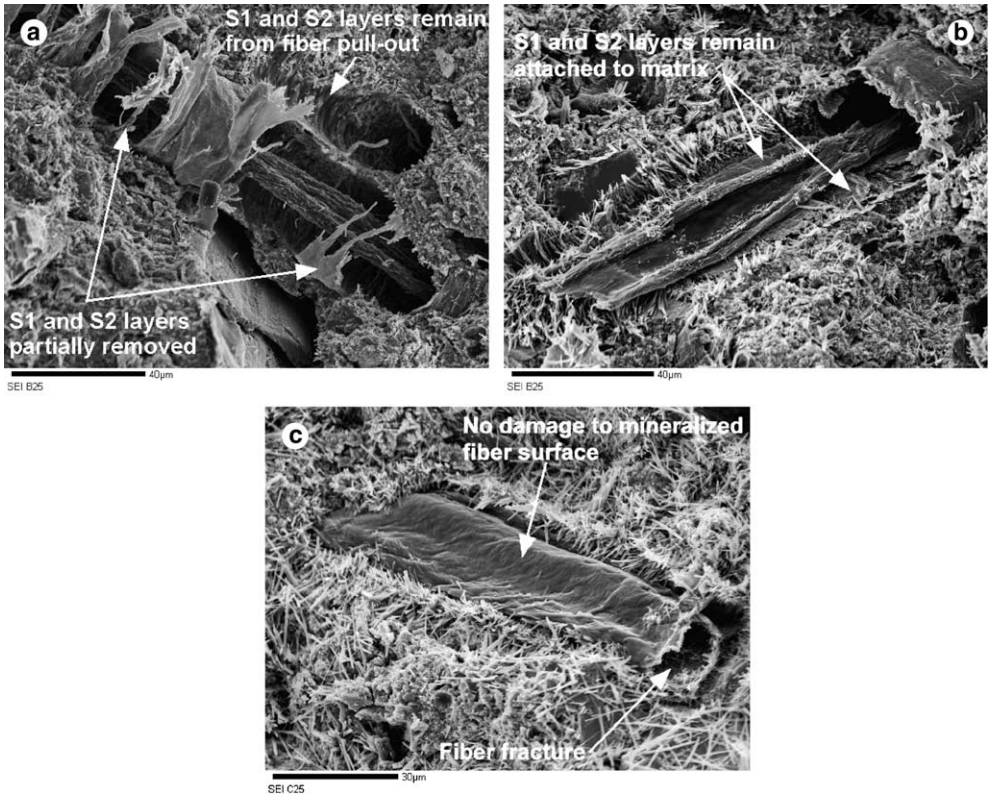

Fig. 9. SEM micrographs after 25 wet/dry cycles. (a) Beaten fiber (800×). (b) Beaten fiber (850×). (c) Unbeaten fiber (1000×).

ing with beaten fibers could result in a larger fiber failure surface area and greater energy dissipation during composite failure, given that both the beaten and unbeaten fibers fail by brittle fracture.

3.3. Effect of bleaching

Bleaching, commonly used to increase the brightness of pulp, largely removes lignin from wood fibers. Lignin is a highly crosslinked polymer that binds the fibers together. Typically, unbleached fibers consist of 65–75% cellulose, 17–32% hemicellulose, and 3–8% lignin, while bleached kraft fibers contain 70–80% cellulose and 20–30% hemicellulose, by mass [28]. Lignin-containing by-products of paper pulping, such as lignosulfonates, are commonly used as chemical admixtures in concrete to retard cement hydration.

The effect of fiber bleaching on initial fiber–cement composite performance and performance after wet/dry cycling is difficult to anticipate. First, the removal of lignin from the fiber is suspected to increase fiber/matrix bonding. It is possible that the removal of lignin results in both a physical and chemical mechanism of increased fiber–cement bonding. Physically, the loss of lignin may result in a more open or rougher fiber surface, allowing for increased physical bonding with the cement paste. Also, chemically, due to the retarding effect of lignin on cement hydration, it is anticipated that the presence of lignin in an unbleached fiber may slow or prevent localized cement hydration and subsequent embrittlement of the fiber. However, bleached fibers have been shown to be stronger but less ductile than unbleached fibers [29]. Furthermore, bleached fibers tend to be more collapsible due to the removal of lignin. Also, lignin has been found to be more susceptible to alkali attack than cellulose, which may present a competing effect in terms of long-term performance [2].

Without wet/dry cycling, it seems that the flexural behavior for composites reinforced with bleached or unbleached fibers is largely indistinguishable (Fig. 10), while some variations in microstructure are apparent. Characterization of bleached and unbleached fiber–cement composite fracture surfaces without wet/dry cycling was performed by SEM (Fig. 11). With the bleached fibers, Fig. 11(b), microfibrils in the S1 layer are clearly visible as striations on the fiber surface. However, with the unbleached fibers (Fig. 11(a)), cement hydration products—rather than cellulosic microstructure—are apparent on the surface of the pulled-out unbleached fibers. Flexural test data, Fig. 10, without wet/dry cycling, shows that the peak strength, first cracking strength, and post-cracking toughness are each slightly (13.3%, 2.3%, and 26.0%, respectively) greater for the composites containing unbleached fibers (fiber

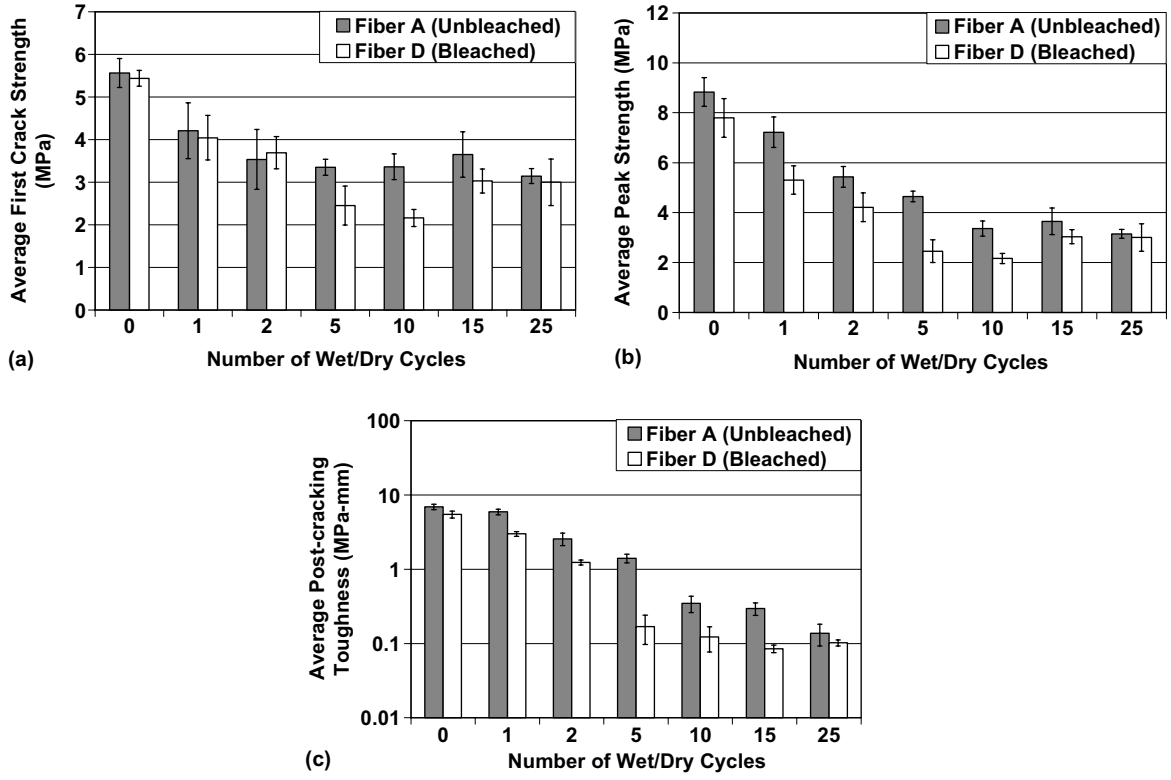

Fig. 10. Flexure test results for fiber A (unbleached) and fiber D (bleached). (a) First crack strength (MPa) versus number of wet/dry cycles. (b) Peak strength (MPa) versus number of wet/dry cycles. (c) Post-cracking toughness (MPa mm) versus number of wet/dry cycles.

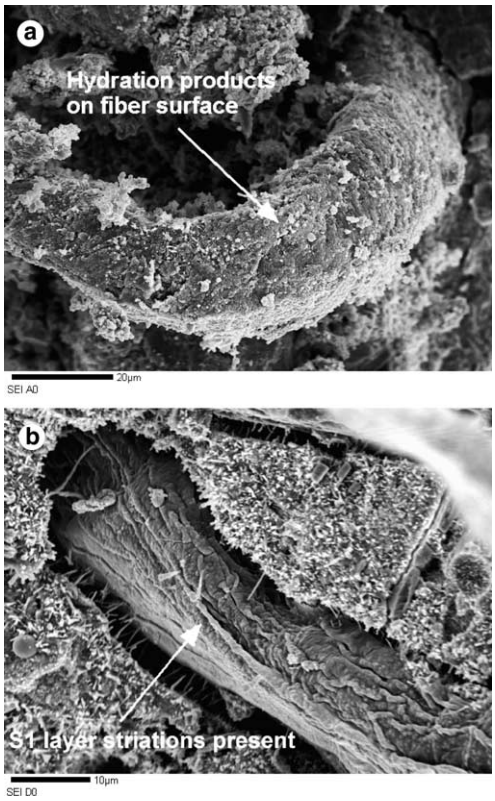

Fig. 11. SEM micrographs after 0 wet/dry cycles. (a) Unbleached fiber (1200×). (b) Bleached fiber (1900×).

A) as compared to bleached fibers (fiber D). Therefore, this data does support the concept that lignin impedes fiber–cement bonding or cement hydration near the fiber–cement interface, in the absence of wet/dry cycling. The presence of lignin leads to slightly longer unbleached fiber pull-out lengths (approximately 600–800 μm) as compared to pull-out lengths of 500–700 μm for bleached fibers.

Fig. 10 shows the progression of degradation with wet/dry cycling for unbleached and bleached fiber composites. The trend in loss of strength and toughness with increasing numbers of cycles is slower for unbleached fiber–cement composites as compared to bleached fiber composites. Like the data without wet/dry cycling (presented previously), this data also supports the notion that cement hydration and fiber–cement bonding is impeded in the presence of lignin. It is important to note, however, that the progressive decrease in these properties is indeed slowed, but not prevented. The mechanism for this slower degradation trend has not been definitely established. However, it may be related to lignin present on the fiber surface and in the fiber cell wall acting as a physical and/or chemical barrier to hydration product formation, or it may be related to local retardation of cement hydration in the fiber by lignin. Generally, over the range of wet/dry cycles examined here, the unbleached fiber composite exhibited greater strength and toughness. The relatively greater strength and toughness with unbleached fibers is particularly apparent between 2 and 15 wet/dry cycles. After 25 cycles, the unbleached fiber composites exhibit 4.8% greater peak/first crack strength and 34.9% greater toughness, as compared to the bleached fiber composite. The unbleached fiber–cement composite exhibited minimum flexural property values after 25 cycles, whereas, the bleached fiber–cement composites reached minimum values between 10 and 15 cycles and increased moderately with additional cycling.

Fig. 12 shows typical fiber–cement composite fracture surfaces after 25 wet/dry cycles. Images of unbleached fiber–cement composite fracture surfaces show significant damage to the fiber. In Fig. 12(a) and (b), specifically, the removal of the S1 layer from the fiber, separation of S1 and S2 layers, and the formation of hydration products within the fiber are apparent. However, fracture surfaces for bleached fiber–cement composites exhibit similar forms of damage. For example, Fig. 12(c) shows that separation of S1 and S2 layers as well as interior fiber mineralization. However, from observation of a range of fracture surfaces for bleached and unbleached fiber reinforced composites, it appears that significantly more bleached fibers exhibit interior mineralization after 25 cycles, as compared to unbleached fibers.

3.4. Effect of initial drying state

The potential for fiber/matrix debonding and microcracking at the interface during wet/dry cycling of composites is dependent upon (among other factors) the dimensional stability of the fiber reinforcement in response to moisture fluctuations. Wood fibers are hygroscopic, taking up moisture from a wet environment and giving up moisture to a drier environment. As a result, wood fibers swell with increasing moisture content and shrink upon its loss, below the fiber saturation point. Swelling/shrinking occurs primarily diametrically, with little dimensional change in the longitudinal direction. That is, 2–3% longitudinal expansion with swelling is typical, while the fiber cross section may change by 40–60%, depending on species, pulp type, and moisture content, among other factors. The initial drying state of a fiber, too, affects its dimensional stability during subsequent wetting and drying. Fibers which have been dried once (market pulp) prior to introduction to a matrix material are expected to swell less upon re-wetting, as compared to fibers which have not been previously dried (mill pulp). This improved dimensional stability is due to increased S1–S2 interlayer bonding in once-dried fibers compared to never-dried fibers. As a result, once-dried fibers tend to show a degree of concavity in their cross-section (prior to re-wetting), while never-dried fibers tend to be cylindrical or elliptical. Thus,

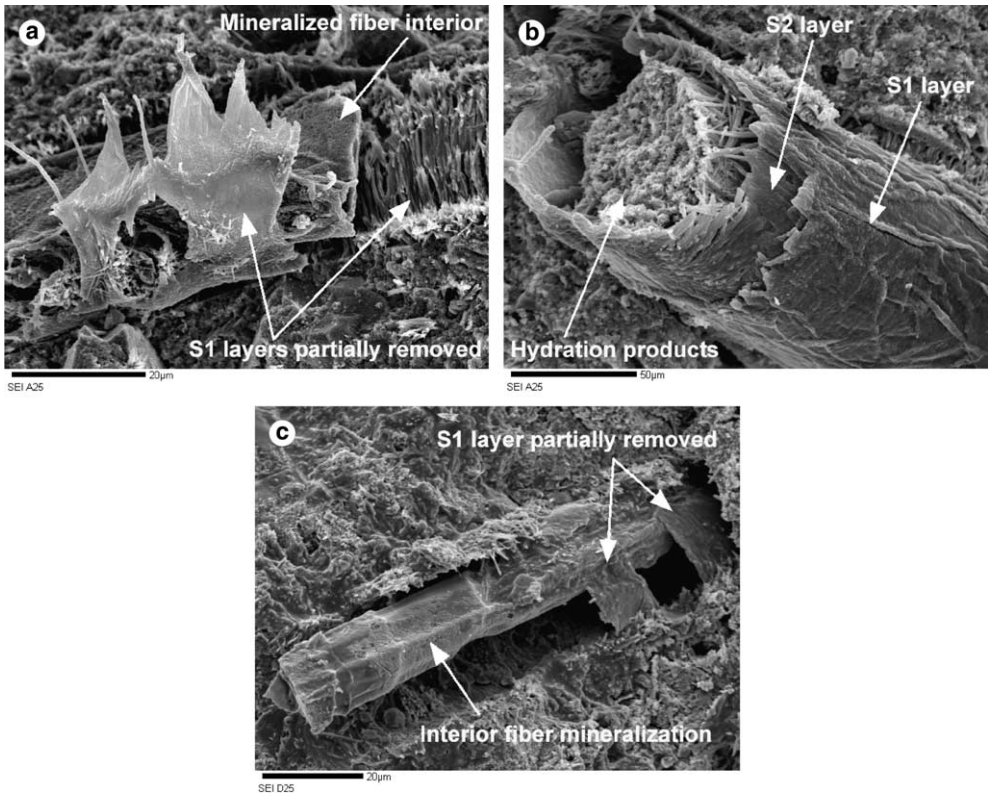

Fig. 12. SEM micrographs after 25 wet/dry cycles. (a) Unbleached fiber (1600×). (b) Unbleached fiber (2000×). (c) Bleached fiber (1200×).

never-dried fibers may hasten the formation of hydration products within the cell wall and lumen during wetting and drying due to their larger swelling capacity, larger fiber diameter, and smaller cell wall thickness.

Savastano and Agopyan [24] have shown that the transition zone around vegetable fibers was significantly larger than that of hygrophobic polypropylene fibers. Due to vegetable fibers releasing water into the surrounding matrix, it is assumed that an area of increased water-to-cement ratio forms. This may lead to a localized increase in transition zone porosity around hygroscopic fibers, as compared to polypropylene fibers. Thus, it is possible that the larger swelling capacity of never-dried pulp fibers may cause a larger and less dense transition zone, as compared to once-dried pulp fibers. Mechanical testing and microstructural characterization was performed to determine if once-dried fibers would impart improved performance as compared to never-dried fibers when used to reinforce cement paste.

First, the characteristics of the different fiber types were examined indirectly while determining an appropriate wet/dry cycle length for the composites. In a plot of percent mass change with time over the course of wetting and subsequent drying, Fig. 1, composites containing never-dried fibers (fibers A and D), increase approximately 32–35% in mass during soaking, while composites containing once-dried fibers (fibers B and C) increase approximately 4–6% in mass. This data agrees with the supposition that once-dried fibers are more dimensionally stable, gaining less water (mass) over the exposure period.

Bending test results comparing fiber C (once-dried) and fiber D (never-dried) are shown in Fig. 13. Without any wet/dry cycling, the once-dried fiber composites exhibited a 9.3%, 32.7%, and 56.3% greater first cracking strength, peak strength, and post-cracking toughness, respectively, compared to the never-dried fiber composites. No apparent differences were observed by SEM, except for the fiber morphology as mentioned previously. These results appear to indicate that the larger swelling capacity of never-dried fibers tends to weaken the transition zone around these fibers. This weak interface may impart less friction during ductile never-dried fiber pull-out, as suggested by Savastano and Agopyan [24], leading to greater strength and toughness of once-dried fiber composites prior to wet/dry cycling.

The data in Fig. 13 shows that with exposure to wet/dry cycling, the strength and post-cracking toughness of the two fiber types are virtually indistinguishable. SEM micrographs of fracture surfaces of never-dried and once-dried fiber composites after 25 wet/dry cycles are found in Fig. 14. Images like the one in Fig. 14(a) verify that once-dried fibers tend to exhibit concavity in their cross-section. No separation between fiber layers was observed to occur during failure of once-dried fiber composites. This suggests that the strengthening of the

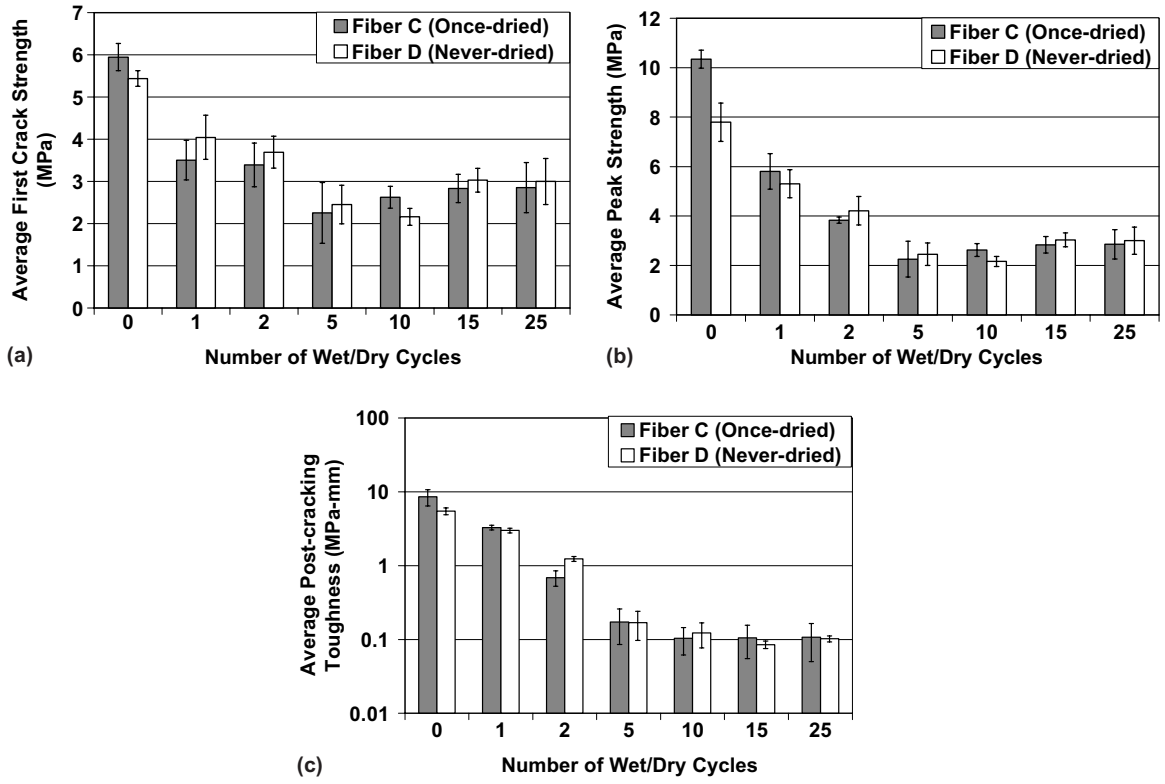

Fig. 13. Flexure test results for fiber C (once-dried) and fiber D (never-dried). (a) First crack strength (MPa) versus number of wet/dry cycles. (b) Peak strength (MPa) versus number of wet/dry cycles. (c) Post-cracking toughness (MPa mm) versus number of wet/dry cycles.

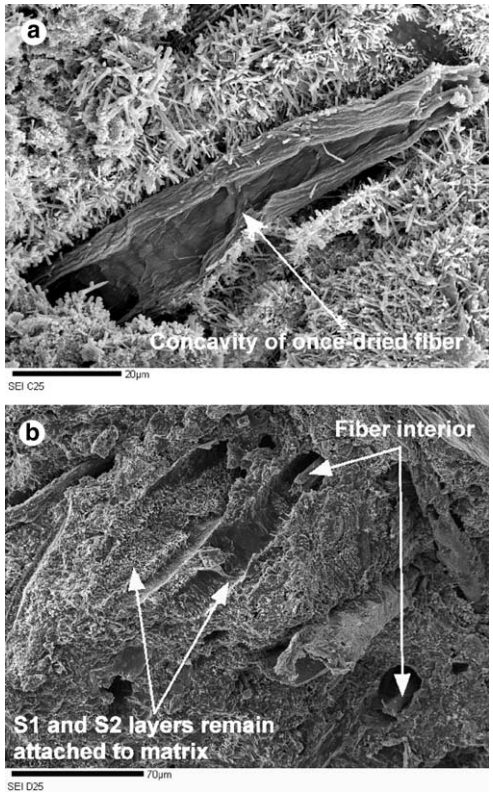

Fig. 14. SEM micrographs after 25 wet/dry cycles. (a) Once-dried fiber (1500×). (b) Never-dried fiber (450×).

interlayer bonding during the initial drying does influence the mode of failure. However, the effect of this interlayer bonding within the fibers is not directly observed in the flexural test data, suggesting that other factors overshadow this effect. In contrast, damage to and separation between the S1 and S2 layers is observed in the never-dried fiber samples (Fig. 14(b)). This seems to indicate that the fiber–cement bonding is stronger for the never-dried fibers after cycling. This should manifest itself in lower toughness of the never-dried fiber–cement composite relative to the once-dried fiber–cement composite, but the toughness values are so similar in these samples after 10, 15, and 25 cycles that no conclusive determination can be made about the role drying on performance.

4. Conclusions

Three pulp fiber treatments were evaluated to identify those treatments that may minimize composite degradation due to wet/dry cycling. Mechanical testing of specimens was conducted after 0, 1, 2, 5, 10, 15, and 25 wet/dry cycles. SEM observation of fracture surfaces was done to verify the mechanical testing results. From testing and microstructural characterization, these conclusions may be drawn:

- With the exception of fiber A (unbleached), the majority of first crack and peak strength loss and decrease in post-cracking toughness occurred within a low number of wet/dry cycles (typically less than 5 cycles).
- Beating did not appear to significantly affect mechanical behavior of the composite after exposure, although variations in fiber damage (including separation of S1 from S2 layer) were observed by SEM. Prior to wet/dry cycling, unbeaten fiber composites exhibited greater peak strength and post-cracking toughness.
- Bleached (i.e. low-lignin) fibers exhibited accelerated progression of fiber mineralization as compared to unbleached fibers. Unbleached fiber–cement composites exhibited greater toughness, particularly for low numbers of wet/dry cycles. Without exposure, unbleached fiber composites exhibit greater flexural properties than bleached fiber composites.
- Once-dried fiber composites exhibited superior dimensional stability compared to never-dried fiber composites. However, the drying state of the fibers did not appear to have any significant effect composite performance during wet/dry exposure. Thus, initial fiber swelling/shrinking does not seem to play any role in composite degradation.
- It is proposed that a three-part progressive series of degradation mechanisms exists for these fiber–cement composites: (1) fiber–cement debonding up to 2 cycles, (2) subsequent reprecipitation of hydration products within the void space at the former fiber–cement interface, prior to 10 wet/dry cycles, as evidenced by observations of ductile fiber failure at the same time as significant decreases in strength and toughness, and (3) fiber embrittlement due to mineralization, which appears to occur beyond 10 cycles as indicated by relatively small increases in strength and no recovered toughness.

Acknowledgments

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