

Degradation behavior and kinetics of sisal fiber in pore solutions of sustainable cementitious composite containing metakaolin



Jianqiang Wei

Sonny Astani Department of Civil and Environmental Engineering, University of Southern California, 3620 S. Vermont Avenue, KAP 210, Los Angeles, CA 90089-2531, USA

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ABSTRACT

Degradation of cellulose is the primary cause for the premature failure of natural fibers in the alkaline environment of cementitious systems. However, the degradation behavior and kinetics of cellulosic fibers in cementitious composites have not been thoroughly understood. In this study, the aging kinetic of cellulose exposing to pore solutions of cementitious materials is experimentally investigated and a model for service-life prediction of cellulose in cement is developed. To assess the impact of cement hydration on degradation behavior of cellulosic fibers and understand the correlations between fiber degradation and alkaline environment of cement, an approach to directly assess degradation rate of the embedded fibers was developed by determining fiber's tensile properties, thermal decompositions, crystallinity, and microstructures. The results indicate a strong dependence of degradation of sisal fiber on alkalinity of cement pore solutions. By incorporating 30 wt% metakaolin clay, the hydration of cement was modified and a mild environment was generated. Concentration of OH^- was reduced and the pore solution becomes from oversaturated to unsaturated for calcium hydroxide after 7 days. As a result, tensile strength loss of the aged fiber was mitigated and the service life of cellulose was extended by 13.7 times.

1. Introduction

In the quest for green and energy-efficient infrastructure, the requirement of renewable, lightweight, low-cost and high-performance construction materials with exceptional durability was proposed. Unfortunately, renewability and durability tend to be mutually exclusive, and the application of natural materials is always a compromise between environmental sustainability and long-term service. A typical representative of this is the application of cellulosic fibers as reinforcement for cement based construction materials to improve their ductility and crack resistance. Since the 1970s [1], following the banned use of asbestos, cellulosic fibers reawakened interests of researchers in the field of infrastructure engineering due to their readily availability and renewability. From then on, a systematic evaluation of engineering properties of composites containing these biomass reinforcements was performed.

As shown in Fig. 1, the cell wall of cellulosic fibers is primarily consisted of three components: lignin, hemicellulose and cellulose. As a linear polymer made of glucose subunits linked by β -1,4 bonds, cellulose has a basic repeating unit cellobiose [2]. Cellulose's rigid and insoluble micro-fibrils chains enable it to have high stiffness and to serve as structural component of cellulosic fibers. The individual cellulose

fiber-cells are linked together by means of the middle lamella [3]. The polymerization degree of cellulose in sisal fiber is around 25,000, which means its crystalline arrangement may be disrupted by the chain-ends [3,4]. Hemicellulose, which emerges as an immense renewable biopolymer resource, represents about 25–35% of lignocellulose biomass [5–7], only less than cellulose. In contrast to cellulose, hemicellulose represents a type of hetero-polysaccharides with complex structures containing mannose, glucose, galactose, fucose, xylose, arabinose, galacturonic acid, and glucuronic acid [8]. Its main chain is characterized by a β -1,4-linked-D-xylopyranosyl [9]. As the most abundant natural aromatic polymer [10], the role of lignin is to bind cellulose microfibrils together in plants. This heteropolymer binding phase has a complex three-dimensional structure with aliphatic and aromatic constituents [11]. The most common linkages formed during lignin biosynthesis are the β -O-4 ether linkages, followed by other types of ether and C-C linkages such as α -O-4, β - β , β -5, and 5-5 [12–14]. These three main components assemble together forming a distinct cell wall structure, with excellent mechanical properties and ultra-low density. This endows cellulosic fibers outstanding reinforcing effect in the matrix of cement, however, their long-term service life is confined due to the easily degradation behavior of amorphous phases and premature damage of cellulose chains. Gram [15] and Tolêdo Filho [16] investigated

E-mail addresses: jw2938@columbia.edu, jw2938@yahoo.com.

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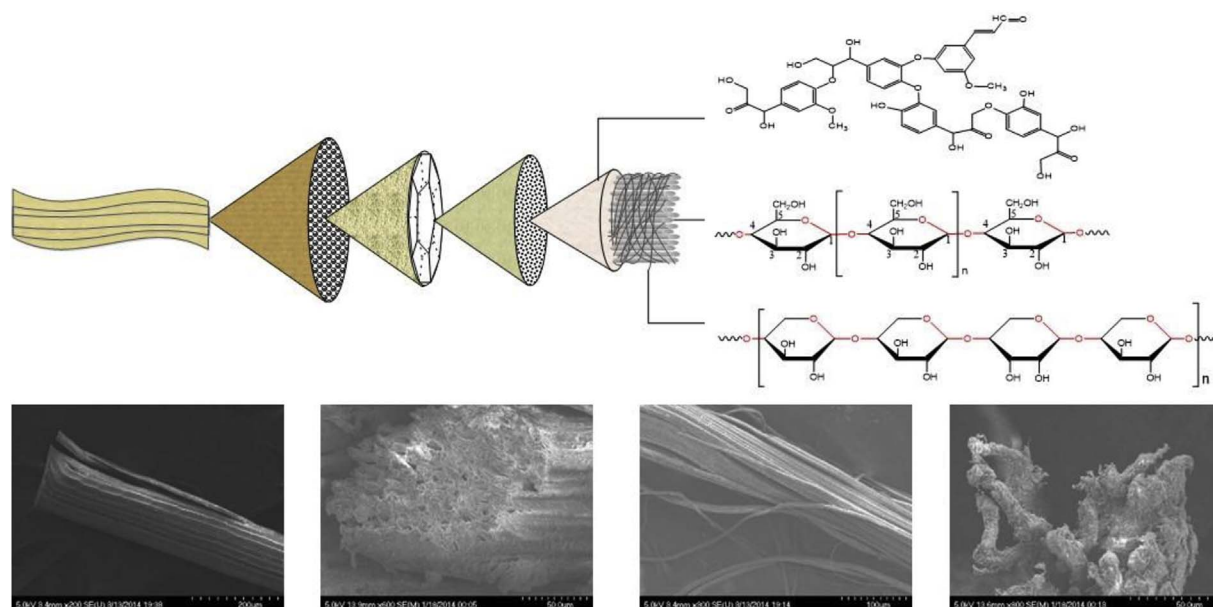


Fig. 1. Schematic diagram and microstructure of cellulosic fiber.

the aging behavior of the three main components of cellulosic fibers (lignin, hemicellulose and cellulose) in cement, and reductions of fiber strength and degree of polymerization were observed. B.J. Mohr et al. [17] reported a three-step aging progress of cellulosic fibers: (1) initial fiber debonding from cement, (2) precipitation of hydration products within the interfacial transition zone between cellulosic fiber and cement and (3) mineralization of fiber revealed by the increased embrittlement. Almeida Melo Filho et al. [18] proposed two aging mechanisms for cellulosic fibers in cement: mineralization of fiber cell walls and degradation of lignin and holocellulose. In the author's previous work [19], both of the two degradation mechanisms, alkaline hydrolysis and mineralization, were quantified by directly investigating the fiber's component change, degradation of tensile strength and crystallization indices.

The degradation of sisal fibers in cement pore solutions proceeds gradually from fiber surface to inside of cell walls. In other words, the amorphous protective layers, lignin and hemicellulose, suffer deterioration first resulting in the infiltration of alkaline pore solutions in fibers. Then the exposed cellulose fibrils deteriorate leading to premature failure of the fibers.

Lignin functions as cuticle or glue in the cell wall of natural fiber giving it structure and protecting the fiber against microbial or chemical degradation of the polysaccharides. Unlike cellulose and hemicellulose, lignin is a non-carbohydrate aromatic heteropolymer or phenolic polymer that is derived from the oxidative coupling of three different phenylpropane building blocks (monolignols): p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol [20,21]. Lignin and hemicellulose have one characteristic in common: they are both amorphous, which means lignin is also easy to undergo alkaline hydrolysis. The alkaline hydrolysis of α -O-4 bonds and free phenolic hydroxyls results in the formation of α -alcohols (1-guaiacyl ethanol, 1-guaiacylpropanol) [22]. The cleavage of β -O-4 ether bond is one of the most important reactions of alkaline delignification [23]. When free hydroxyls are present on neighboring α - or γ -carbon atoms or if there is a CO group in the α -position, structural units of lignin of the non-phenolic β -ether type are capable of undergoing alkaline hydrolysis, and lead to the formation of guaiacol, guaiacylpropane, 3-guaiacylpropanol, and p-hydroxyphenylpropane [24–26]. The alkaline degradation products of lignin are mainly protocatechuic acid, vanillic acid catechol, oxalic, and other simple aliphatic acids [27], as well as a dark, amorphous, humin-like “lignic acid”, which is the cause of the

darkening effect of alkaline treated fiber, especially under high temperature. The degradation of lignin results in an exposure of hemicellulose and cellulose to the alkaline environment of the cement matrix. Even though a partial degradation of lignin might provide an express path for pore solution of cement to penetrate into fiber's cell walls. This leads to an enhanced alkali aging and mineralization of the embedded fibers.

Different from the highly uniform polyglucan structure of cellulose, hemicelluloses represent a type of hetero-polysaccharide with complex structures containing glucose, xylose, mannose, galactose, arabinose, fucose, glucuronic acid, and galacturonic acid in various amounts, depending on the source [8]. As shown in Fig. 1, hemicelluloses do not serve as load-bearing component in cell walls of natural fiber, but they bind and fix cellulose micro-fibrils to make the fiber more stable. Probably no chemical bonds exist between cellulose and hemicellulose, and the mutual adhesion is provided by hydrogen bonds and van der Waals forces [28]. In other words, the content of holocellulose (including hemicellulose and cellulose) determines rigidity and strength of natural fiber. Hemicelluloses are usually divided into four general groups of structurally different polysaccharide types: (1) xyloglycans (xylans); (2) manno glycans (mannans); (3) xyloglycans (XG); and (4) mixed-linkage β -glucans [29]. All hemicelluloses are amorphous and lack the crystalline regions that can be found in cellulose, thus making them less mechanically protected against degradation reactions during chemical pulping [30]. Therefore, hemicellulose is much easier degraded in the alkaline environment of a cement matrix. The deterioration of this binding phase might lead to an enhanced stripping and peeling of cellulose micro-fibrils.

Cellulose molecular chains are ordered into strands of approximately 40 cellulose microfibrils, which have a diameter of 35 Å, through inter- and intra-molecular hydrogen bonding [31]. These microfibrils are not homogeneous, consisting of crystalline and amorphous regions. As the vulnerable spots, the amorphous regions are most prone to degradation in the alkaline environment [32,33]. Fig. 2 shows the microfibrillar structure of cellulose, from which it can be seen that, in amorphous regions, cellulose molecules have a non-reducing end and a reducing one, along with repeating glucose units. The reducing and non-reducing ends feature original C4-OH and C1-OH groups, respectively. The reducing end is a latent aldehyde, like an aldehyde function, responding to both reduction and oxidation processes and it plays a key role in the alkaline degradation [34]. Therefore, the alkali degradation

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