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Surface modified microcrystalline cellulose from cotton as a potential mineral admixture in cement mortar composite

T.R. Anju [b], K. Ramamurthy [a, *], R. Dhamodharan [b]

[a] Department of Civil Engineering, IIT Madras, Chennai 600 036, India
[b] Department of Chemistry, IIT Madras, Chennai 600 036, India

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ABSTRACT

The objective of the work is to examine the performance of tetraethyl orthosilicate (TEOS) modified microcrystalline cellulose (MCC) fiber, derived from cotton, as a mineral admixture that could be compatible in cement mortar composites. The effectiveness of surface modification of MCC is characterized by powder X-ray diffraction, FTIR, TGA and SEM techniques. The present silane based surface modifier (TEOS) minimizes the water uptake and acts as a pozzolan, that could result in additional calcium silicate hydrates (C-S-H) linkages. This is reflected by the enhancement in the mechanical properties of the cement mortar composite. A dramatic two fold enhancement of flexural strength and almost 45% increase of compressive strength are observed in the case of TEOS-MCC when compared with the cement mortar composites without any mineral admixture there by validating the method chosen. The enhancement of compressive and flexural strength could be due to proper dispersion of smaller size MCC fibers within the pores of the cement mortar composite. When an optimized amount of chemical admixture (polycarboxylate ether (PCE) superplasticizer) is used along with TEOS- MCC a greater enhancement in flexural strength and compressive strength is observed with good workability, at a lower water/cement ratio.

1. Introduction

The development of durable cement mortar composites reinforced with fibers and especially natural fibers is an interesting option available for the construction industry in the areas of thin walls/thin-sheet partitions, building envelope/ceilings flat sheets, roofing tiles and pre-manufactured components. Cellulosic fibers offer a variety of advantages such as wide availability, renewable resource, relatively low cost, no known health hazards, low density, adequate stiffness and strength, variety of morphologies, controllable aspect ratio and surface roughness as well as interfacial compatibility through appropriate chemical modification of the fiber surface. In this context, it is relevant to point out that the use of fique fiber as mineral admixture in cementitious roofing tiles and the effects of natural weathering on the microstructure of the composite was reported [1]. Cement mortar as well as concrete possess enough specific strength, but are brittle in nature. The incorporation of different type and size of fibers into cementitous composite reduces the matrix brittleness and increases the durability, which is proportional to the resistance to crack propagation offered by the fibers that bridge the matrix, thereby effectively transferring the load. Substantial increase in flexural strength, toughness and impact resistance post-reinforcement with cellulosic fibers has been reported [2–4]. Cellulosic fibers are also known to reduce plastic shrinkage [5], decrease the thermal conductivity [6] and improve the acoustic performance by increasing the sound absorption [7]. The use of cellulose nanocrystals to enhance the flexural strength of cementitious materials is also known [8].

Cellulosic fibers typically consist of micro fibrils of macromolecules, which in turn consist of two parts: the amorphous regions characterized by flexibility and crystalline regions that contribute to the specific strength. By the chemical treatment of cellulose fiber, especially acid treatment, most of the amorphous part of the long fiber can be reduced or eliminated. The resultant short fiber that is micrometer in size mostly consists of crystalline regions and is known as microcrystalline cellulose (MCC). It has an elastic modulus of about 150 GPa, which is superior to glass fibers (85 GPa)

* Corresponding author.
E-mail addresses: vivek@iitm.ac.in (K. Ramamurthy), damo@iitm.ac.in (R. Dhamodharan).

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and aramid fibers (65 GPa) [9,10]. The use of MCC as a mineral admixture in mortar offers better distribution, greater surface area and reactivity and enhanced mechanical performance [11–14]. But the industrial production of natural fiber based cementitious composites is limited due to certain disadvantages such as long-term durability that is caused by alkali attack. The high alkalinity in the cementitious matrix degrades the cellulose fibers besides mineralization resulting in the loss of long term tenacity. In addition, fiber fracture, volume (density) variation due to reversible water absorption (due to continuous variation in the weather conditions) is also observed [15–18]. The key to overcoming these disadvantages is to decrease the water uptake of the cellulose fiber through suitable modification and in this process ensure that the fiber is untouched by the matrix while its surface is still amenable for good interfacial bonding with cement. In this context, hornification of fibers [19], immersion in slurried silica fumes prior to incorporation in the matrix and surface modification are well known [20]. The durability of silane treated eucalyptus kraft pulp cellulose on the durability of fiber-cement composited was reported [21].

In the present work, the surface of microcrystalline cellulose (MCC), prepared by the acid catalyzed hydrolysis of cotton fibers, is modified with tetraethyl orthosilicate (TEOS) for the purpose of enhancing the mechanical properties through improved compatibility with the siliceous cement based mortar besides reducing the water uptake by the fiber. The role of surface modified MCC on the compressive and flexural strength of cement based mortar is investigated. In addition, Stöber silica prepared by the self-condensation of TEOS is used as a control to delineate the role of siliceous moieties on the mechanical properties of the cement mortar composites. A superplasticizer of polycarboxylate ether (PCE) type (copolymers of methylpolyethyleneglycol methacrylate and methacrylic acid) is also used as a chemical admixture along with the cement mortar as a water reducer. The addition of superplasticizer, without disturbing the workability [22], and the concomitant enhancement of the mechanical property is known. As the adsorbed dispersant on the cement particle, the superplasticizer minimizes the friction between the particles [23]. The resulting compressive and flexural strength enhancements of the cement mortar are also compared.

2. Experimental

2.1. Materials and instrumentation

Conventional surgical cotton was used to prepare microcrystalline cellulose (MCC). All the chemicals were supplied by Sigma Aldrich and used as received. For preparing cement mortar, river sand of particle size <2.36 mm and ordinary Portland cement conforming to 53 grade (IS 12269) were used. Scanning electron microscopy (SEM) images were obtained by using a FEI Quanta FEG 200 microscope operating between 200 V and 30 kV. The size of MCC was determined by analyzing the corresponding SEM images using digital micrograph software. FTIR spectra were obtained using JASCO 4100 FTIR spectrometer (JASCO, Japan). The solid pellet samples were prepared by mixing 2–3 mg of sample in 100 mg of KBr. The thermogravimetric analysis was carried out using Q500 Hi-Res TGA. The samples were heated at 10 °C min^{-1} under nitrogen atmosphere. Powder X-ray diffraction patterns were recorded with Bruker D8 Advanced diffractometer equipped with Cu-Kα source of wavelength 1.5406 A°. The compressive strength and three point bending flexural strength tests of cement mortar specimens were determined by using Universal Testing Machine as per IS: 516–1959 after 3, 7, and 28 days of sample curing. For each parameter three samples were tested.

2.2. Methods

2.2.1. Acid hydrolysis of cotton to microcrystalline cellulose (MCC)

Surgical cotton (15 g) was added to 30% v/v (5.52 M) sulphuric acid solution (1: 20 w/w). It was heated to boil and maintained at 100 °C for 10 min. After the acid treatment, the whole solution was transferred to a vessel containing tenfold excess volume of cold water. This solution was centrifuged at 4000 rpm to separate cellulose as sediment from the liquid phase. The collected sample was rinsed with water multiple times, 5 (w/w) sodium bicarbonate solution until the pH of the rinsed water was about 6. It was finally rinsed with distilled water, ethanol and acetone, in that order. The wet samples were placed in a hot air oven maintained at 60 °C for ~12 h (overnight) and then at 105 °C for 1 h.

2.2.2. Preparation of TMCC by the surface treatment of MCC with TEOS

The procedure used for the surface modification of MCC was based on the method proposed by Abdeimouleh et al., [24]. In this work, tetraethyl orthosilicate (TEOS) was used as the silane coupling agent. 5 w/w % TEOS was added to a suspension of cotton powder in 80/20 (v/v) ethanol/water mixture. Liquid ammonia was added to the above mixture until the pH was around 12. It was then maintained at room temperature for 2 h, with constant stirring. The mixture was then centrifuged for 20 min to collect the sediment. The wet sample was subjected to heat curing at 120 °C for 2 h. This experiment was repeated for other MCC: TEOS mixtures of weight ratio 1: 1, 1: 0.5 and 1: 0.2.

2.2.3. Synthesis of Stöber silica (SS)

Stöber process for the preparation of spherical nanosilica particles from TEOS is well known [25]. TEOS was added to a mixture of ethanol/water (80/20 v/v) and liquid ammonia was added until the pH was around 12. This mixture was maintained at room temperature for 2 h with constant stirring and then centrifuged to remove the liquid phase. The wet sample was cured at 120 °C for 2 h.

2.2.4. Cement mortar composite preparation

TEOS surface modified MCC (TMCC), unmodified microcrystalline cellulose (MCC) and Stöber silica synthesized from TEOS (SS) were used in the cement based mortar as mineral admixture and their behavior studied. The workability of cement mortar (cement: sand 1: 3) with water/cement (w/c) ratio as 0.4, 0.45 and 0.5 were tested by flow table method (ASTM C1437) [26]. The % spread was calculated as the percentage of the increase in the average base diameter of the mortar mass (average of four readings taken in four directions) to the original base diameter. For example if the average of the increase in base diameter was 13.2 with respect to the original base diameter of 10, then % spread = (132−100)/100 × 100 = 32%. For compressive strength determination (ASTM C109) [27], 50 mm cubes, with and without mineral admixtures, were cast using thoroughly fitted and oiled standard molds. For flexural strength determination (ASTM C348) [28] prism specimens with size 40 × 40 × 160 mm^3 were cast using standard molds. After 24 h, the mold was dismantled and the samples were set for water curing. The compressive and flexural strength of samples were determined after 3, 7 and 28 days.

In order to enhance the workability at a lower w/c ratio, one set of cement mortar was prepared by adding superplasticizer of polycarboxylate ether (PCE) as chemical admixture. Different amount of PCE viz. 0.5, 1.0, 1.5, 2.0 (% weight of cement) added to the cement mortar having w/c ratio both 0.35 and 0.4. By flow table test, the optimum workability was obtained for cement mortar with PCE 1% (by weight of cement) and w/c ratio as 0.4. The corresponding