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

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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)

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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

weight ratio of cement: sand: mineral admixture: chemical admixture would be 1: 2.9: 0.1: 0.01. The compressive and flexural strength obtained were compared.

3. Results and discussion

3.1. Characterization of mineral admixtures

The x-ray diffraction patterns of MCC, TEOS modified MCC (TMCC) and Stöber silica (SS) are shown in Fig. 1. MCC shows the typical reflections observed for cellulose such as ($1\bar{1}0$), (110), (200) and (004) corresponding to the crystalline phase. The x-ray diffraction pattern of TMCC also shows the typical reflections observed in the case of cellulose but the peaks are broader suggesting the presence of amorphous regions that arise out of the modification with TEOS. The x-ray diffraction pattern of Stöber silica suggests that it is fully amorphous. The thermogravimetric analysis of MCC, TEOS-modified MCC (TMCC) and Stöber silica (SS) are presented in Fig. 2. From this figure it can be inferred that the major weight loss (70%) peak for MCC is observed around 300 °C. In addition, MCC leaves a residue of ~10% at 900 °C under nitrogen atmosphere that could arise due to the formation of carbon suboxide. TMCC loses about 50% of its weight around 360 °C under similar conditions. The extent of weight loss (and therefore the residue content) depended on the concentration or extent of TEOS used for the modification as shown in Fig. 3. The increasing residue content with respect to MCC, its variation with the weight % of TEOS used, the shifting of the initial decomposition temperature from 300 °C for MCC to 360 °C for TMCC suggested the incorporation of TEOS to MCC through chemical reaction. This was further confirmed by simple analytical tests such as exposure to concentrated sulphuric acid and the blue flame emanating from the Bunsen burner. MCC spontaneously turned black upon exposure to dispersion in concentrated sulphuric acid while TEOS-modified MCC was unaffected. Further, upon direct exposure to the blue flame of the Bunsen burner MCC caught fire instantly while TMCC did not. Stöber silica is observed to lose about 5% of adsorbed water upon heating leaving a very high residue content of 95% at 900 °C confirming that there is no organic residue in its structure.

The SEM image of cotton fiber before and after acid treatment is shown in Fig. 4. By acid treatment most of the amorphous regions of cotton fiber was eliminated and the fiber length is reduced to below 400 μm. The image analyzed fiber size distribution pattern is shown in Fig. 5. Based on this analysis the length of the fiber is below 150 μm for about 60% of MCC. The SEM images of Stöber silica (SS) and MCC following surface modification with TEOS (TMCC) are shown in Fig. 6. The spherical morphology of SS was observed on the surface of TMCC (in independent experiments, we had observed that the shape of Stober silica particles was spherical as ascertained by AFM).

The FTIR spectra of MCC, SS and TMCC are shown in Fig. 7. The TEOS surface modification of MCC is confirmed from the Si- O- Si stretching vibration peak at 760 cm^{-1} and Si- O- Si bending vibration peak at 480 cm^{-1}.

The EDAX of MCC and TMCC are presented in Fig. 8. The EDAX of MCC shows the elemental peaks of carbon and oxygen only while that of the TMCC shows an additional peak of elemental silicon thus confirming the surface modification of MCC.

3.2. Effect of mineral admixtures on the properties of cement mortar

The workability of cement mortar having w/c ratio 0.4, 0.45 and 0.5 are shown in Fig. 9. Among the control experiments, the one with w/c ratio 0.45 gave a workability of 32% spread. Cement mortar with w/c ratio 0.4 was stiff with a workability of 14% spread. In the case of cement mortar with w/c ratio 0.5, particle segregation and bleeding appeared. The average compressive strength of mortar cubes with different w/c ratio is shown in Fig. 10. Among the control experiments, the one with w/c ratio 0.45 resulted in the highest compressive strength (35.9 ± 2.1 MPa).

The average compressive strength of cement mortar cubes with MCC, SS and TMCC as mineral admixtures and w/c ratio 0.45 is shown in Fig. 11. The cement mortar with MCC as mineral admixture, gave a compressive strength of 28.2 ± 2.1 MPa that was lower than that obtained in the control experiment. During the mixing of mortar, MCC being more hydrophilic in nature, quickly absorbs the water and as a result sufficient amount of water is not available in the initial stages for the cross linking of the inorganic frame work (C-S-H) gel growth, which results in lower compressive strength of the cement composite. The cement mortar with SS as mineral admixture, gave a 30% enhancement in compressive strength (46.9 ± 1.9 MPa) with respect to the control mortar. This enhancement can be rationalized as follows: SS consists of amorphous spherical particles of size between 50 and 500 nm, which is smaller than the pore size of cement composite. So it can successfully fill the pores in cement composite as well as it can act as a pozzolan i.e it can react with the residual calcium hydroxide in cement composite to form additional C-S-H linkage. This might be the reason for the compressive strength enhancement from 7 to 28 days of curing. Among the three mineral admixtures, TMCC exhibited 45% enhancement in compressive strength. It offered a

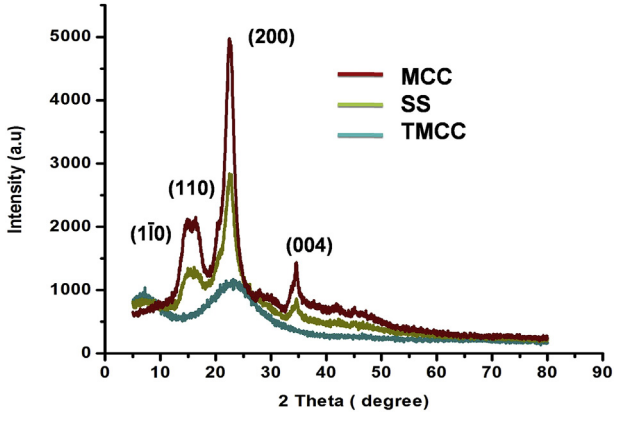

Fig. 1. X-ray diffraction patterns of MCC, TEOS modified MCC (TMCC) and Stöber silica (SS).

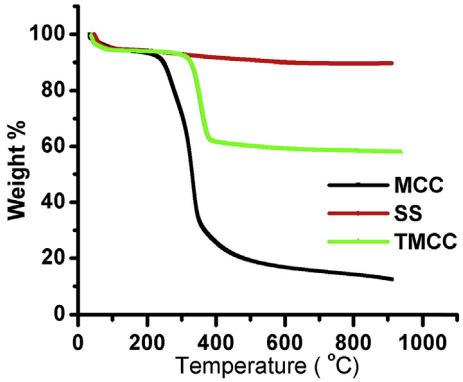

Fig. 2. Thermogravimetric analysis of MCC, SS and TMCC.

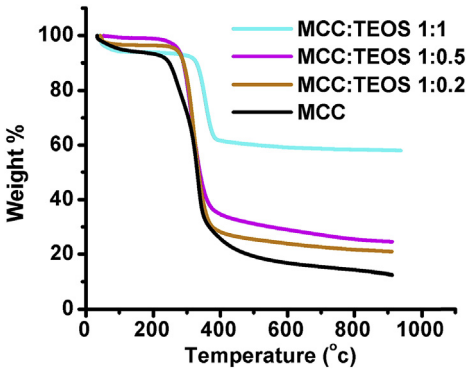

Fig. 3. Thermogravimetric analysis of TMCC with different weight % of TEOS.

propagation of micro cracks. The flexural strength enhancement was around 94% in the case of TMCC added cement composite. This is probably due to the fibrous nature of TMCC combined with its siliceous surface characteristics (due to chemical modification) that makes it more compatible with the cement matrix.

3.3. Effect of mineral and chemical admixtures on the properties of cement mortar

The workability of cement mortar with varying amount of chemical admixture polycarboxylate ether (PCE) based superplasticizer having w/c ratio 0.35 and 0.4 are shown in Fig. 13. Among these, the one with w/c ratio 0.4 and PCE dosage of 1% (by weight of cement) gives almost same workability of cement mortar without PCE and w/c ratio 0.45 (35% spread, vide Fig. 9). The PCE

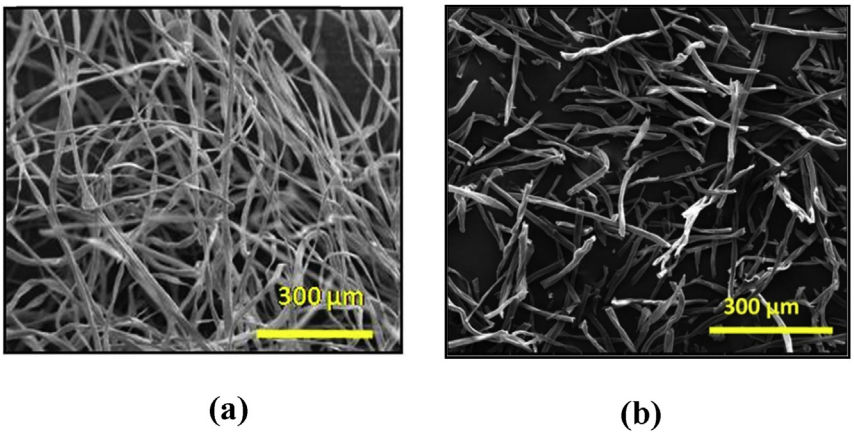

Fig. 4. SEM images of cotton fiber (a) before and (b) after acid treatment.

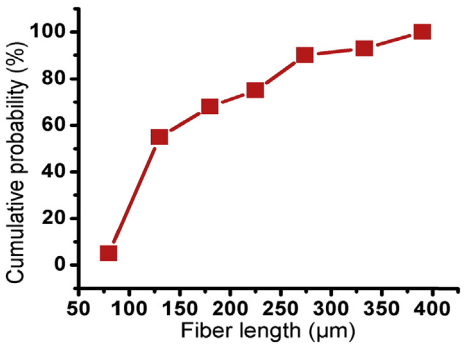

Fig. 5. Fiber size distribution pattern of MCC from the analysis of SEM image.

combined effect of cellulose (specific strength and flexibility) as well as pozzolanic and filler effect of SS. By the surface modification of MCC, the hydrophilic nature of cellulose is reduced and therefore 0.45 w/c ratio was sufficient for the hydration of inorganic frame work of TMCC modified cement mortar.

The average flexural strength of cement mortar with mineral admixtures MCC, SS and TMCC with w/c ratio 0.45 is shown in Fig. 12. By adding SS, around 40% increase in the flexural strength than the control experiment is observed. This might be due to the pozzolanic and filler effect of the admixture. Upon adding MCC the flexural strength enhancement was above 50% that could be due to the flexible fibrous admixture preventing the stress localization by dissipating the energy to the entire volume besides holding the macromolecule structure consists of two parts: the main chain, which acts as a dispersant and repels the cement grains by creating a charge separation; the side chains, which restrict the approach of water molecules towards the cement particle and thereby it can reduce the w/c ratio from 0.45 to 0.4 with the sufficient workability.

The average compressive strength of cement mortar cubes with MCC, SS and TMCC as mineral admixtures and PCE superplasticizer (1% wt of cement) as chemical admixture with w/c ratio of 0.4 is shown in Fig. 14. The compressive strength obtained for the super plasticized cement mortar [cement: sand 1: 3, w/c ratio 0.4 and PCE (1% wt of cement)] was 42.1 ± 1.2 MPa. The compressive strength enhancement by the addition of superplasticizer followed the same trend as seen earlier in its absence suggesting that the principle role of the superplasticizer is to enhance the workability. Among the cement mortar composites TMCC added superplasticized samples achieved the highest compressive strength 65.9 ± 1.7 MPa which is almost 83% enhancement, when comparing the compressive strength obtained for the control experiment (Fig. 11).

The average flexural strength of mortar cubes with PCE superplasticizer (1% wt of cement) and mineral admixtures MCC, SS and TMCC with w/c ratio 0.4 is presented in Fig. 15. The flexural strength of all PCE super plasticized cement mortar prisms increased, irrespective of the mineral admixture added. The cement mortar with PCE (1% wt of cement) exhibited flexural strength of 5.1 ± 0.4 MPa. The one with TMCC added super plasticized samples exhibited the highest flexural strength 8.1 ± 0.2 MPa.

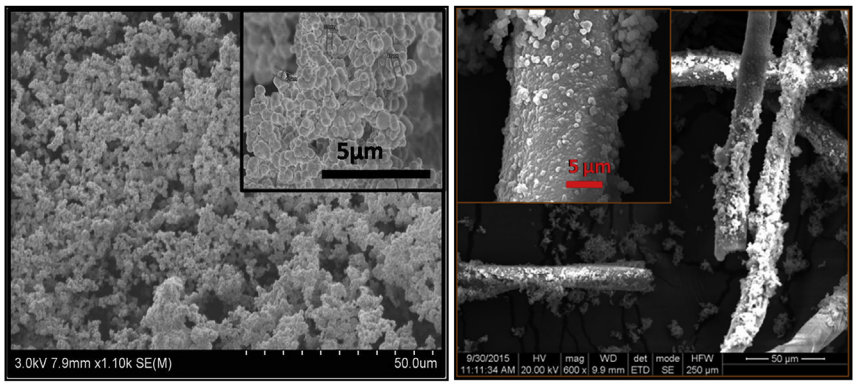

Fig. 6. The SEM images of (a) Stöber silica and (b) MCC following surface modification with TEOS (TMCC).

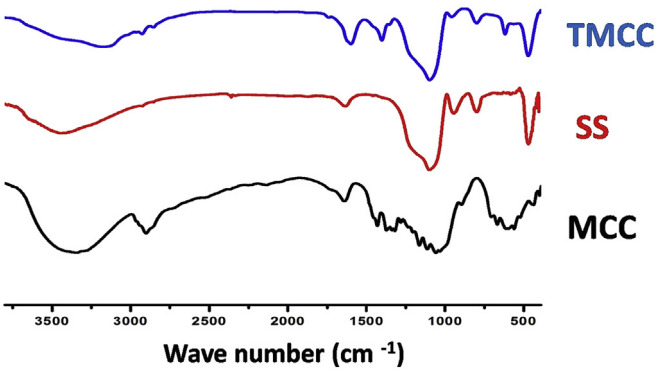

Fig. 7. FTIR spectra of MCC, SS and TMCC.

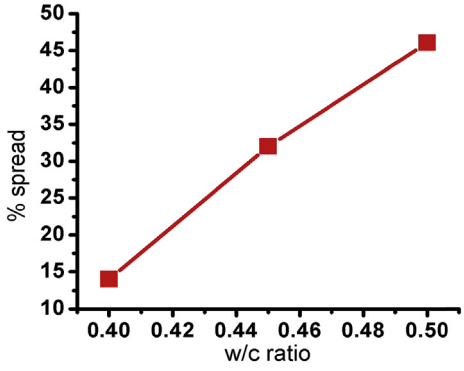

Fig. 9. Workability of mortar with different w/c ratio.

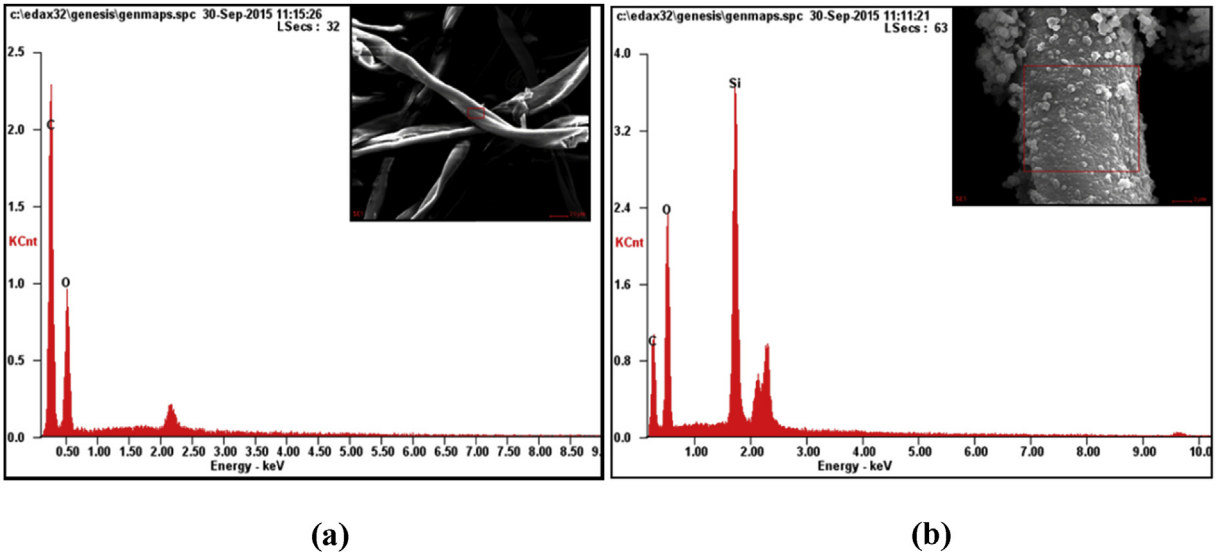

Fig. 8. EDAX of (a) MCC and (b) TMCC.

4. Conclusions

Microcrystalline cellulose (MCC) was prepared from surgical cotton using acid hydrolysis. The hydrophilic nature of MCC is reduced through surface modification reaction involving the hydrolysis of TMCC followed by condensation to enable better interfacial energetic compatibility with the cementitious matrix. Three mineral admixtures viz: MCC, surface modified MCC (TMCC) and Stober silica (SS) are prepared and characterized by PXRD, TGA, SEM, EDAX and FTIR. The performance of these three mineral

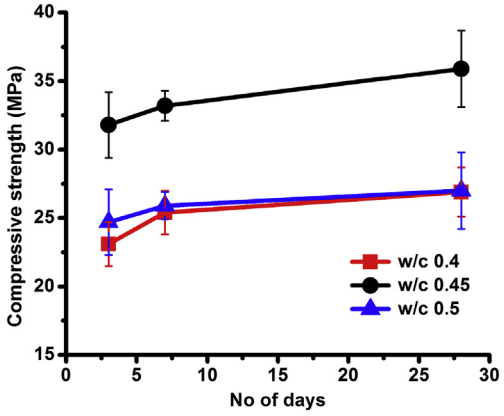

Fig. 10. Average compressive strength of mortar cubes with different w/c ratios.

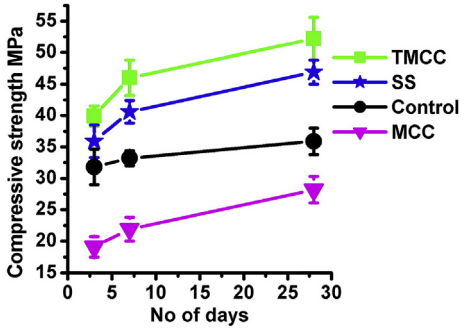

Fig. 11. Average compressive strength of cement mortar cubes with various mineral admixtures having w/c ratio 0.45.

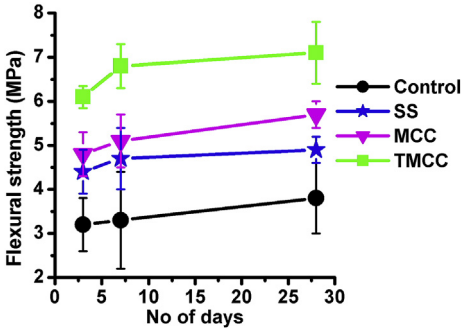

Fig. 12. Average flexural strength of cement mortar with mineral admixtures and w/c ratio as 0.45.

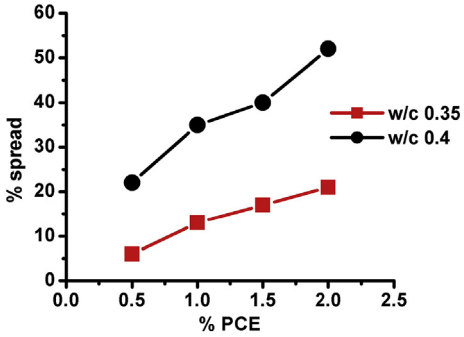

Fig. 13. Workability of cement mortar with PCE superplasticizer having w/c ratio 0.35 and 0.4.

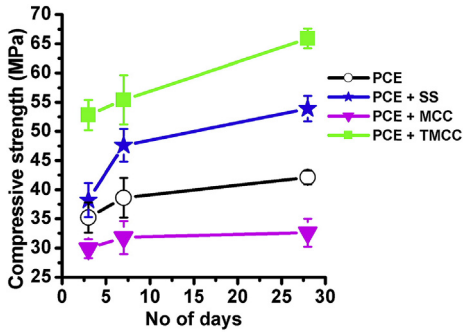

Fig. 14. Average compressive strength of mortar with PCE superplasticizer and various mineral admixtures.

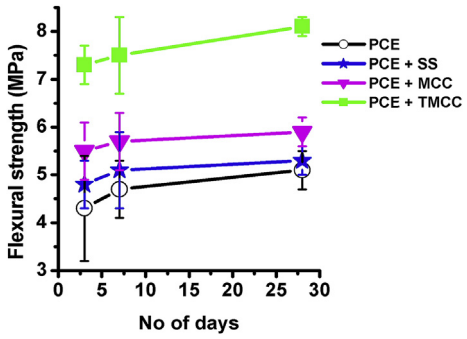

Fig. 15. Average flexural strength of mortar cubes with PCE superplasticizer and various mineral admixtures.

admixtures in cement mortar (w/c 0.45) was studied by analyzing the compressive and flexural strengths of the cured composites. Further compressive and flexural strength with the above mineral admixtures and PCE super plasticized cement mortar (w/c 0.4) was also studied. It is observed that surface modified MCC, with or without superplasticizer exhibited the highest compressive and flexural strengths. TMCC added superplasticized cement mortar achieved the highest compressive strength (65.9 ± 1.7 MPa) and flexural strength (8.1 ± 0.2 MPa) with an enhancement of 50–80% compared to the control without TMCC.

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