Modified fracture properties of cement composites with nano/micro carbonized bagasse fibers

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ABSTRACT. A novel cost-effective alternative in the form of nano/micro carbonized particles produced from waste bagasse fibers has been explored to modify the mechanical properties and fracture pattern of the resulting cementitious composites. Carbonized bagasse particles were produced at Politecnico di Torino and characterized by Raman spectroscopy and scanning electron microscopy. When added with cement paste up to 1 wt% in six different proportions, the carbonized bagasse particles were found effective in significant enhancement of mechanical strength as well as fracture toughness. From micro-graphical observations it is evident that these heterogenic inclusions either block the propagation of micro cracks which has to deviate from its straight trajectory and has to follow the carbon nano/micro particles contour or distribute it into multiple finer cracks. Crack contouring along the carbonized particle, crack pinning, crack diversions and crack branching are the mechanisms which can explain the increase of toughness in the composite samples.

KEYWORDS. Fracture energy; Toughness; Carbonized bagasse fibers; Micro-cracking; Crack pinning.

INTRODUCTION

Cementitious materials are commonly and extensively used worldwide by construction industry for various types of infrastructures. Despite of their exceptional strength in compression they still possess limited tensile strength and tensile strain capacity. Different types of fibers have been investigated since last fifty decades to reinforce the cementitious matrix against tensile failures and to impart ductility [1–4]. The size of the reinforcing fillers has diminished from macro to micro and now even to the nano scale with recent advancements in nanotechnology. Due to exceptional intrinsic properties and large aspect ratio, carbon nanotubes have been successfully investigated as a reinforcing filler to improve the mechanical strength, fracture toughness, electrical and electromagnetic wave absorbing properties of cementitious composites [5–12]. However the problems associated with its effective dispersion, bondage with the host material as well as related expenses are the main factors that limit its widespread applications on large scale.

Recently it has been found that there is the possibility of enhancement in the fracture toughness of cement composites by inducing cost effective nano/micro carbonized bio-waste particles [13–15]. Sajjad et al. reported that the addition of micro carbonized bamboo particles contributes positively in the modification of cracking patterns and thereby enhance the overall fracture properties of cementitious composites [13]. Similar trend of increment in fracture plane and fracture toughness was observed by Ferro et al. on addition of nano/micro carbonized hemp herd and coconut shell particles [14,15]. The optimum content of addition was found similar to the one believed for the case of carbon nanotubes (CNTs) addition i-e 0.08wt% [5]. The current paper is the research continuation concerning exploration of cost effective and sustainable source to synthesize nano/micro carbonized particles that can be effectively used to modify crack path and the final fracture characteristics of cementitious matrices.

Sugarcane bagasse is a waste produced form sugar industries which is commonly used as a fuel in sugar mill boilers. Among sugarcane-producing countries, Brazil is the top producer, with 653 million tons of sugarcane in 2014, followed by India and China [16]. Generally, 280 kg of humid bagasse is generated from 1 ton of sugarcane [17]. Due to the advantages offered in term of reduced specific gravity, lower cost and acceptable mechanical properties, these fibers were investigated as a reinforcing material in cementitious composites [17–19]. Also they were successfully explored as pozzolanic material for cementitious matrices after getting burnt into fine ash powder [18]. In the recent work, these fibers have been investigated to produce nano/micro carbonized inerts that can effectively act as a sort of heterogeneity to hinder the tips of propagating cracks and thereby enhance the overall fracture properties of resultant cement composites.

MATERIALS AND METHODS

Materials and Mix Proportions

The cement used for the research work was ordinary Portland cement (Type-1, grade 52.5) confirming to the requirements of ASTM C150 [20]. The physical and chemical characteristics of cement as per the product data sheet are displayed in Table 1 & 2 respectively [21]. A high range water reducing admixture (HRWRA), based on modified acrylic polymers and confirming to the requirements of UNI EN 934-2:2012 (admixture for concrete, mortar and grout) was used to attain sufficient workability. Distilled water was used in all mix formulations. The inert nano/micro carbonized particles used for enhancing the fracture properties of cement composites were produced from bagasse fibers using the following procedure.

Physical characteristics	Standard	Average values
Color	-	Light grey
Density	-	2,800 kg/m^3
Blain specific surface area	UNI EN 196-6	480 m^2/kg
Initial setting time	UNI EN 196-3	98 min
Final setting time	UNI EN 196-3	125 min

Table 1: Physical properties of cement [22]

Chemical composition	CaO	Al_2O_3	SO_3	SiO_2	Fe_3O_4	MgO	K_2O
Content (wt.%)	44	26.5	12	9.5	2.5	1.3	0.6

Table 2: Chemical composition of cement [22]

The raw bagasse fibers as shown in Figure 1 were washed with tap water and dried in oven for 48 hrs at 105±5 °C. The washed and dried fibers were then pyrolyzed in a quartz reactor at 850 °C for 1h under inert atmosphere. For the provision of inert atmosphere, constant flow of argon was maintained under 0.2 bar pressure in the reactor throughout the pyrolysis process. Carbonized bagasse fibers were ground in ethanol to sub-micron scale by ball milling for 24 hrs followed by 2 hrs of attrition milling. The physical properties of ground nano/micro carbonized bagasse fibers are given in Table 3.

Carbonized raw bagasse fibers	D_{50}	D_{90}	BET surface area (m^2/g)	Density (g/cm^3)
CRBF	600	1250	19.2	2.26

Table 3: Physical properties of carbonized raw bagasse fibers

Seven mix formulations were prepared including the reference one; detail mentioned in Table 4. Sub-micron carbonized bagasse fibers were used as an additive in six proportions i.e. 0.025%, 0.05%, 0.08%, 0.2%, 0.5% and 1.0% by weight of cement. Weight ratios of water and super plasticizer were kept constant at 35% and 1.5% by weight of cement respectively.

Denotations	Weight compositions (% mass ratio of cement wt.)			
	Cement	Water	Superplasticizer	CRBF
CEM	100	35	1.5	0.00
CRBF_0.025				0.025
CRBF_0.05				0.05
CRBF_0.08				0.08
CRBF_0.2				0.20
CRBF_0.5				0.50
CRBF_1.0				1.0

Table 4: Mix formulations

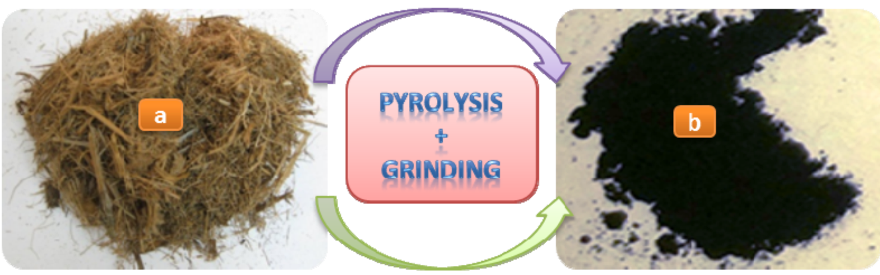

Figure 1: Synthesized nano/micro CRBF particles (b) from raw bagasse fibers (a)

Preparation Scheme

The entire preparation comprised on two major steps. In the first step, nano/micro carbonized raw bagasse fibers (CRBF) were dispersed in water with the aid of surfactant and bath sonication for 15 minutes. While in the second stage, the resultant homogeneous solution was mixed with cement using a mechanical mixer operated at 440 rpm (slow mixing) for 1.5 min and at 660 rpm (fast mixing) for 2.5 min. Mixed cement formulations were poured in associated labeled plexi-glass molds of 20 x 20 x 75 mm^3 in size. The molded specimens were kept in covered plastic box partially filled with water for initial 24 hrs. After that the specimens were demolded and immersed water curing was performed at room temperature (20±2 ^oC) for 28 days [23].

Characterization of Materials and Composites

To characterize the structural order of CRBF particles, Raman spectroscopy was performed by means of Renishaw micro-Raman analyzer with green laser of 514 nm wavelength. The Raman spectrum was restricted in the wavenumber range of 500-3500 cm^{-1}. To analyze morphology, microstructure, elemental composition, cracking pattern as well as the dispersion aspects of CRBF formulations, Field Emission Scanning Electron Microscopy (FE-SEM) along with Energy Dispersive X-Ray (EDX) spectroscopy was carried out.

For the evaluation of fracture properties three point bending tests were performed on 28 days moist cured (at 20^{o}C) prismatic specimens of 20*20*75 mm^3 in size according to the standard set forth in ASTM C348 [24]. The rough surfaces of specimens were smoothened with the help of rotary polishing device via #180 wx-flex paper. A standard 6mm deep notch was carefully machined in the center of each specimen using Remet type TR100S, s/n 3714 abrasive cutter with 2mm thick diamond cut-off wheel. Finally notched specimens were tested using ZwickiLine z010 single column flexural testing machine having maximum load capacity of 1kN as shown in Figure 2, under CMOD (Crack Mouth Opening Displacement) control mode with crack opening rate fixed at 0.003mm/min. Highly accurate and sensitive extensometer (clip on gauge) was employed for the measurement of crack opening and the data was digitally recorded.

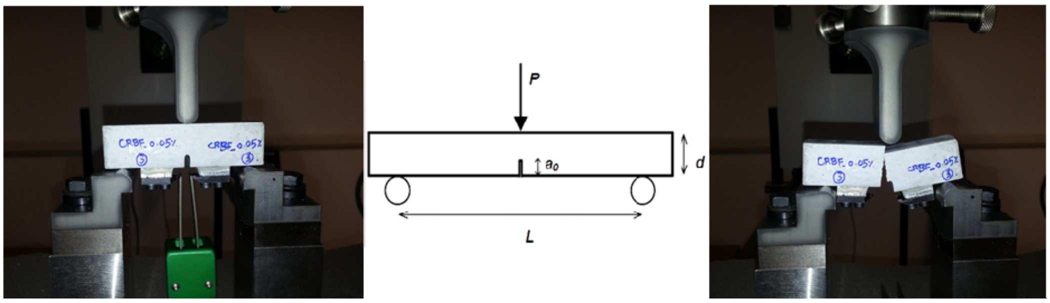

Figure 2: Experimental setup for the CMOD controlled three point bending test

RESULTS AND DISCUSSIONS

Raman Spectra Analysis

Raman spectroscopy was performed to explore the presence of structural defects on the surficial periphery of CRBF particles. The two most prominent bands in this regard are I_D and I_G commonly known as defect grade and graphitization grade respectively which usually occur in the wavenumber range of 1000-1700 cm^{-1}. The Raman spectrum of CRBF particles displayed the two distinct grades at 1346 cm^{-1} and 1592 cm^{-1} wavenumbers as given in Figure 3. The ratio of I_D to I_G band is about 0.93 which indicates that the CRBF particles contain a limited amount of amorphous carbon or of defective graphitic crystals in these materials [25].

Morphology and Composition

SEM micrographs shown in Figure 4a demonstrated that carbonized particles of bagasse fibers are in the form of plates/flakes with shape varying from angular to flat and elongated. These plates exhibit glossy and smooth texture with

average plate size restricted to less than 800 nm and thickness varying from less than 100 nm up to 300 nm. Such plates seem to be free from entanglement problem as associated with nanotubes and nanofibers, therefore it would be relatively easy to disperse them in the cement matrix
EDX spectrum of CRBF particles is shown in Figure 4b. The spectrum displayed presence of C, Si, Al, K and Mg in nano/micro carbonized inerts with detailed proportions given in Table 5.

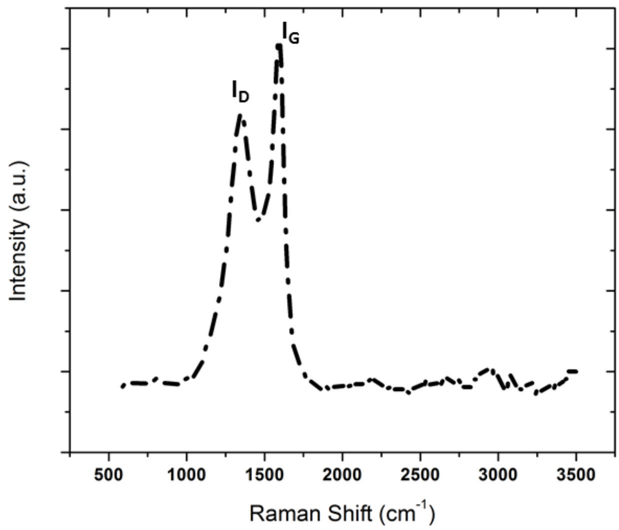

Figure 3: Raman spectrum of pyrolyzed bagasse fibers

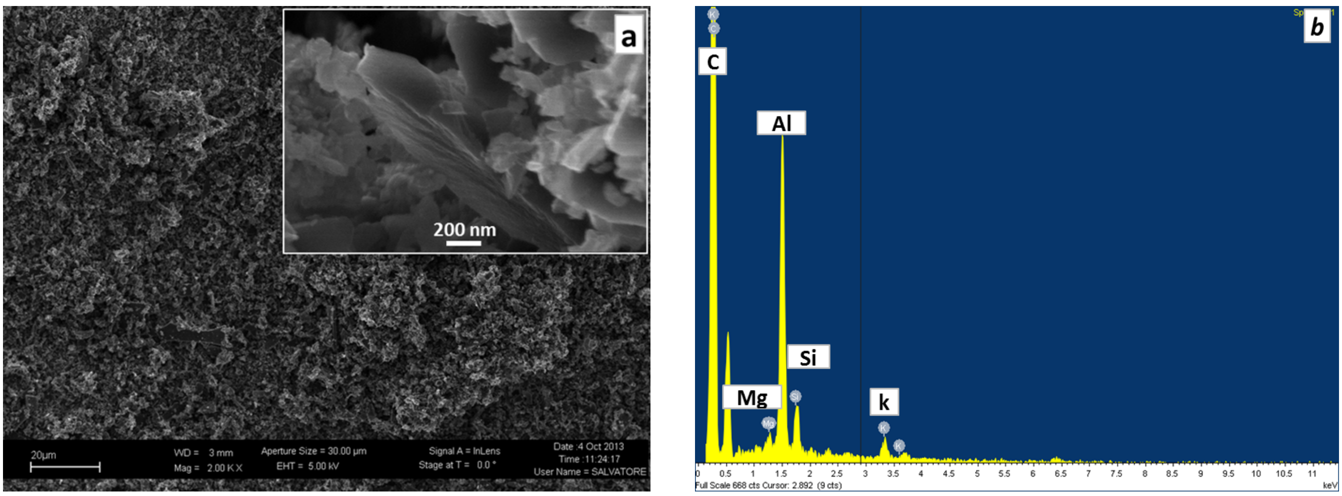

Figure 4: FESEM micrograph (a) and EDX spectrum (b) of CRBF particles

Elements	C	Al	Si	K	Mg
Content (wt.%)	44	26.5	9.5	2.5	1.3

Table 5: Elemental analysis of CRBF particles

Mechanical Characterization
Load-CMOD curves from three point bending tests on cement formulations with and without CRBF reinforcements are displayed in Figure 5. The comparison load-CMOD curves comprise on the typical specimen's curve randomly selected from each formulation to have the idea concerning modification in the cracking behaviour of cementitious matrices on

addition of reinforcing CRBF particles. Both the flexural strength as well as fracture toughness have been observed to increase due to nano/micro modifications as revealed form the curves given in Figure 5. Most of the formulations offering maximum resistance in flexure contain CRBF particles in the content of 0.2 to 0.5 wt% of cement.

Based on experimental load-CMOD curves, modulus of rupture as well fracture toughness were evaluated. Modulus of rupture is defined as maximum surface stress at the failure of specimen in three point bending test given by $\sigma=(3P_mL)/(2wh^2)$ where 'P_m' is the maximum applied force on the prism at the instant of failure, 'L' is the effective span, "w" is the prism width while "h" is considered as the height of specimen under the point of load application. Fracture toughness has been divided into two classes' first crack toughness and ultimate toughness. First crack toughness corresponds to area under load-CMOD curve till the onset of first crack in vicinity of 6mm deep notch while the ultimate toughness corresponds to area under the load-CMOD curve till the extent of complete failure in accordance with the Rilem Recommendations and ASTM C 1018 [26].

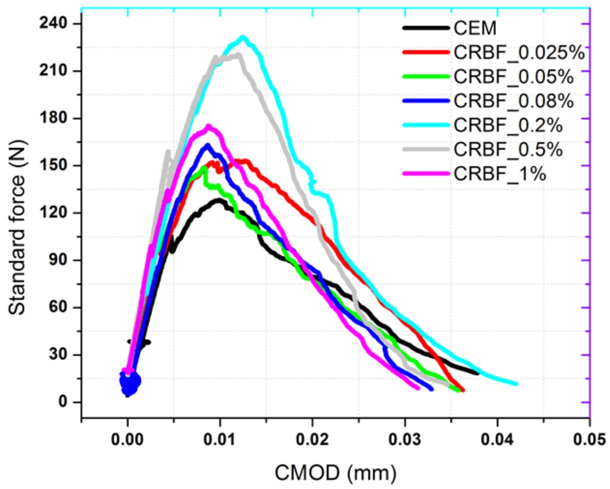

Figure 5: Typical load-CMOD curves for cement composites with and without CRBF particles additions

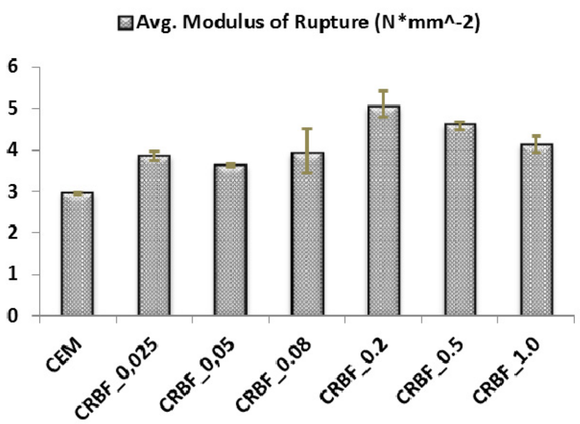

Figure 6: Modulus of rupture of the cement composites with CRBF particles inclusions.

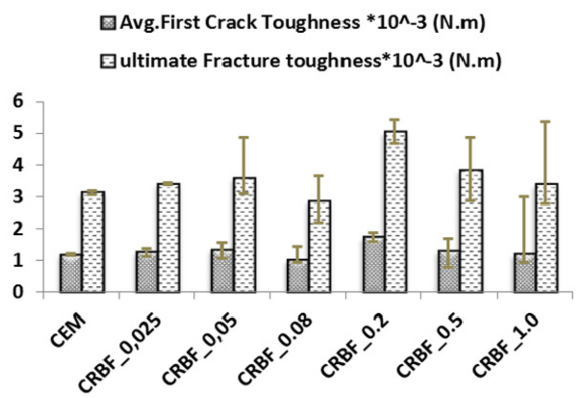

Figure 7: Fracture toughness of the cement composites with CRBF particles inclusions.

The average modulus of rupture of cement composite samples along with fracture toughness are reported in Figures 6 & 7 respectively. The results demonstrated significant increase in the flexural strength as well as the fracture toughness of cement composites with CRBF addition. The trend of increment is ascending till the percentage addition of 0.2 wt% but beyond this content it has been shifted to the descending order. The optimum content of addition is revealed to be 0.2 wt% as observed from the plotted bar charts which is slightly more than 0.08 wt% commonly believed as an optimum level of CNTs induction [5]. The results demonstrated that an addition of CRBF particles by 0.2wt% improved the flexural resistance measured in terms of MOR by 69.9% while an increment of 46.4% and 61.2% was achieved in first crack and ultimate fracture toughness respectively. On further addition of CRBF particles, the values tend to decrease due to relatively high proportion of inerts inclusion as observed by Konsta et al. while dealing with the case of CNTs additions [5]. The value of optimum content varies with the type of carbonized additive.

Micro-Cracking Patterns

The FESEM micrographs of fractured high performance cementitious matrices displayed in Figure 8 revealed that the induction of nano/micro carbonaceous inerts remarkably interrupted the straight and smooth trajectory of crack as attained in case of pristine cement matrix. The plain cement paste (Figure 8a) showed major cracks usually pass through dense hydration products in a relative straight direction. The cement composites with nano/micro heterogenic particles showed a number of fine cracks with occasional branch and considerable discontinuity. The entire phases of crack arresting phenomena were successfully observed through microscopic visuals.

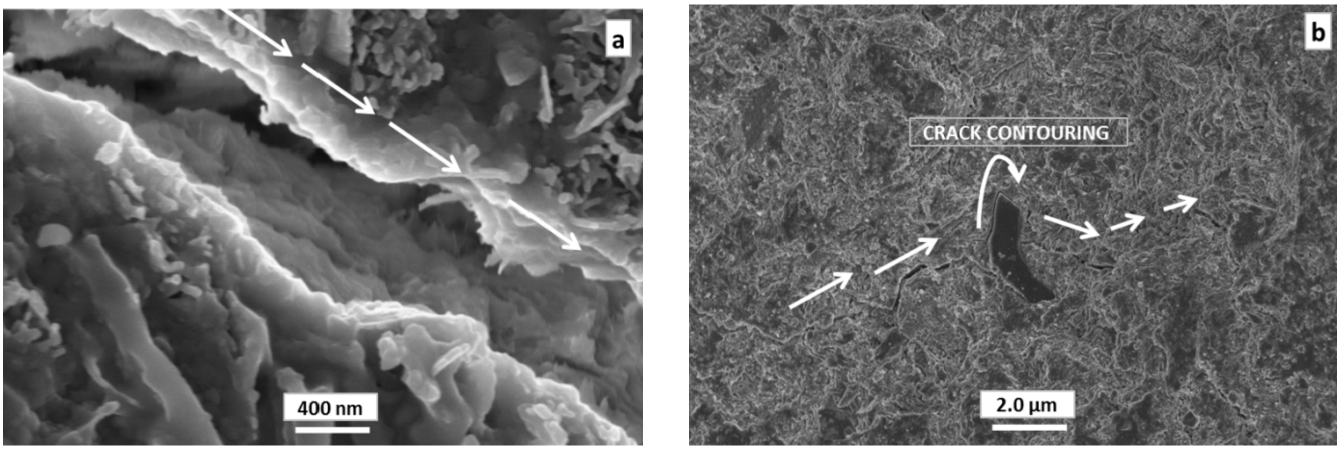

Figure 8: Micro-cracking pattern in plain (a) and CRBF reinforced (b) cementitious composites.

On addition of CRBF particles, major signs of crack pinning and crack deflection were observed in complicating the straight crack paths. Due to the angular shape of CRBF particles, the crack gets diverted from its original trajectory in case of encounter. Such crack deflections or crack contouring result in the requirement of an extra energy input to further propagate the crack along a different path and consequently enhanced fracture toughness of the reinforced cementitious matrix is attained.

Conclusions

It is concluded that we can synthesize carbonized particles from agricultural residue and they can be effectively used in cement matrix to enhance the fracture properties and to refine microstructure. The dependence of the particle shape on toughening is critical and angular grains are needed to produce effective crack-bridging. In our case, from what observed by means of micro-graphical obervations, we believe that carbonized bagasse particles contouring by the crack, crack pinning and crack diversions are the mechanisms which can explain the increase of toughness in the composite samples.

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