



Improvements in self-consolidating cementitious composites by using micro carbonized aggregates

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ABSTRACT. There is growing interest in the use of self-consolidating cementitious systems in construction industry. The present research was conducted to enhance the mechanical performance of cement composites by the utilization of micro-sized inert particles. This paper deals with the synthesis of micro-sized inert carbonized particles from hemp hurds. The synthesized carbonized particles were characterized by field emission scanning electron microscope (FESEM). These particles were further used as additive in self-consolidating cement composites. Total of four different wt% additions (i.e. 0.08, 0.20, 1.00 and 3.00 by wt% of cement) were investigated. The cement composites containing carbonized particles inclusions were characterized by three point bending and compression tests. The results indicate that the carbonized particles additions enhanced the flexural and compressive strengths of the cement composites. It was also observed that the fracture properties and the energy absorption capability of the cement composites were enhanced substantially.

KEYWORDS. Self-consolidating cement composites; Pyrolysis; Hemp hurds; Fracture energy; Toughness indices.

INTRODUCTION

Concrete is the most produced and utilized manmade composite in the world. It is majorly composed of cement, aggregate and sand [1]. In recent years, production of cement has reached to 4.0 billion metric ton [2]. The production of ordinary Portland cement (OPC) is an energy intensive process and a major cause of anthropogenic production of CO₂ in the atmosphere [3]. For the standpoint of eco-efficiency and sustainability, it is highly desirable to improve the mechanical performance of the cement composites. High performance of cement composites can be achieved by good proportioning of the mix quantities i.e. cement, sand, water and mineral or chemical additives. Various types of powders/fillers such as fly ash, silica fume, metakaolin, limestone, glass, ground granulated blast furnace slag, bentonite, rice husk ash, coconut shell ash have already been investigated by the researchers for the production of high performance cement composites [4–12]. The utilization of the nano/micro-sized fillers improves the mechanical performance due to the secondary hydration, heterogeneous nucleation and/or due to the filling effect of small particles

[13]. In the present research, a novel micro-sized material has been synthesized by the pyrolysis of hemp hurds and afterwards has been utilized in the production of cement composites.

History of hemp cultivation and use dates back to twelve thousands years. In the 16th century hemp was considered as a necessary crop for the production of cloth, food, oil and ropes [14]. In the beginning of nineteenth century its importance was reduced due to the development of cotton and synthetic fibers; however the interest of farmers has been revived by the use of hemp as insulation material, energy recovery and feedstock for paper [15]. Currently hemp is cultivated over an area of 41,246 hectare around the world producing 53,495 metric ton of hemp tow waste [16].

Hemp belongs to the cannabis family of plants. It is a fast growing plant with a maturity age of 3 to 4 months. The plant usually grows in a single and slender stem of around 20 mm thickness and height can range up to 5 meters at maturity [17]. The stem tissues inside the bark are referred as hemp or bast fiber. The fibers are composed of disordered arrangement of cellulose fibrils that are held together by the complex organic matrix of hemicellulose, lignin and proteins [18]. The inner woody portion that is surrounded by the hemp fibers contains the pith and xylem vessels and is referred as hurd or hemp hurd (Fig. 1) [17]. The hemp hurds (HH) have wood like structure and makes about 70% of the mass of stem [19].

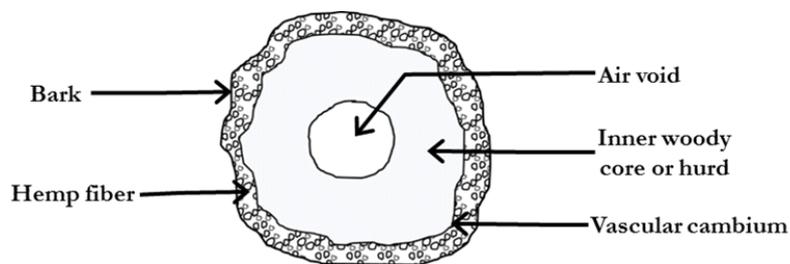


Figure 1: Transverse section of hemp stem

Major portion of hemp hurd (HH) is generally used for inferior applications such as animal bedding etc. Being economically available, hemp hurds have been successfully tried with cement composites for producing light weight concrete or hempcrete, in epoxy composites and in magnesium oxide composites for producing thermal insulation panels [20]. There is nothing in the literature so far concerning its use in carbonized form in self-compacting cementitious systems. In the current study, hemp hurds have been investigated in a novel way to enhance the mechanical performance and fracture properties of self-compacting cementitious composites.

MATERIALS AND METHODS

Materials

Cement composite samples were prepared with general purposes ordinary Portland cement type-1 (Buzzi Unicem 52.5R). High range water reducer Mapei Dynamon SP-1 was used to provide fluidity or workability to the cement composites. General properties of cement and admixture are reported in Tab. 1 and 2 [21, 22]. Hemp hurds were obtained from the Piedmont region of Italy and in house synthesis of inert carbonized particles was carried out in the Department of Applied Science and Technology (DISAT) of Politecnico di Torino. Details of the synthesis are given in following text.

Physical characteristics	Standard					Average values	
Density						2,800 kg/m ³	
Specific surface area	UNI EN 196-6					480 m ² /kg	
Color						Light grey	
Chemical composition	CaO	SiO ₂	Al ₂ O ₃	Fe ₃ O ₄	SO ₃	MgO	K ₂ O
% content	44	9.5	26.5	2.5	12	1.3	0.6

Table 1: Physical and chemical properties of cement [21].



Feature	Value
Appearance	Amber
Specific gravity	1.090
PH value	6.5 - 9.0
Solid content	30.50%
Recommended dosage	1.5 wt% of cement

Table 2: Properties of super plasticizer [22].

Synthesis of inert carbonized particles

The as obtained hemp hurds (Fig. 2) were dried in oven for 24 hours at $105 \pm 5^\circ\text{C}$. The dried hemp hurds were carbonized in a small air-tight quartz reactor under inert atmosphere. The inert atmosphere was obtained by the constant flow of argon gas under a pressure of 0.2 bar. The heating ramp of the furnace was fixed at $1^\circ\text{C}/\text{sec}$. The hemp hurds were carbonized at 850°C for 1 hour. After the completion of carbonization process, the carbonized hemp hurds were cooled and then removed from quartz reactor. The carbonized material was grinded by mortar and pestle and passed through ASTM sieve #120 (aperture size of $125\mu\text{m}$). The sieved powder was then ball milled by using 10 mm diameter agate beads for 120 hours. The particle size was determined by means of a laser granulometer after ball milling and the average particle size was less than $14\mu\text{m}$. Then, the size of ground material was further reduced with the help of attrition milling. Attrition milling was carried out for 1 hour by using 2 mm alumina balls and distilled water as grinding media. After the attrition milling the powder was dried in oven and stored in air tight container for further use.

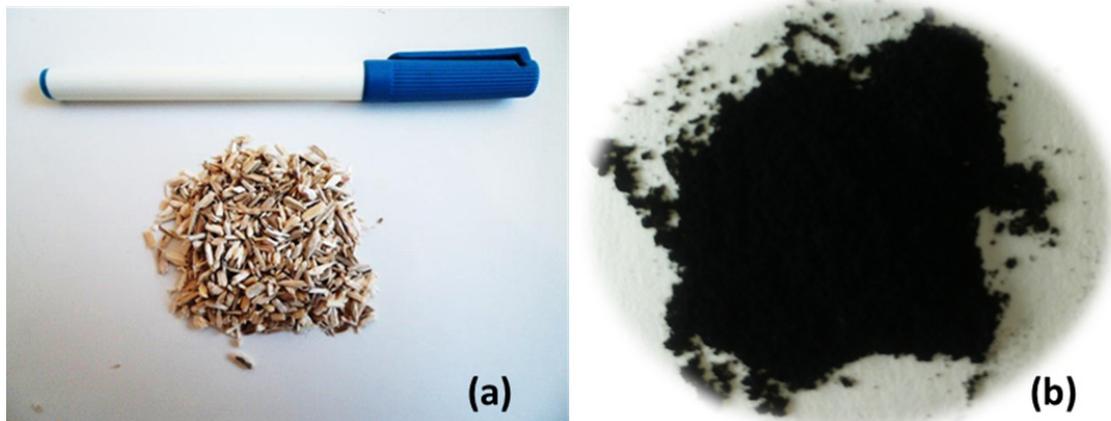


Figure 2: (a) As obtained hemp hurds (b) Carbonized and grinded hemp hurds.

Material characterization

The synthesized inert carbonized particles were observed by means of “Supra-40 Carl Zeiss” field emission scanning electron microscope (FESEM) for their microstructure and morphology. The FESEM micrographs are reported in Fig. 3. FESEM micrographs of ground-carbonized particles show their smooth texture and glossy surface. The edges of particles are sharp and highly angular indicating their brittleness. The size of particles varies from several nanometers (approx. 200 nm) to few micrometers (approx. $3\mu\text{m}$).

Raman analysis of ground powder was carried out by using “Renishaw Ramanscope” operating at 514.5 nm wavelength. The results of analysis are represented in Fig. 4. In Raman spectra, two distinct peaks occurring at 1352 cm^{-1} & 1578 cm^{-1} are related to D-band & G-band, respectively. G-band refers to the graphitic structure of the carbon material and it is used as a measure of material’s quality. D-band is the defect band indicating the presence of defects in the crystal structure of material. The intensity peak ratio of D & G-bands (I_D/I_G) of carbonized hemp powder is 0.66 indicating degree of structural defects concentration in the ground carbonized hemp hurds.

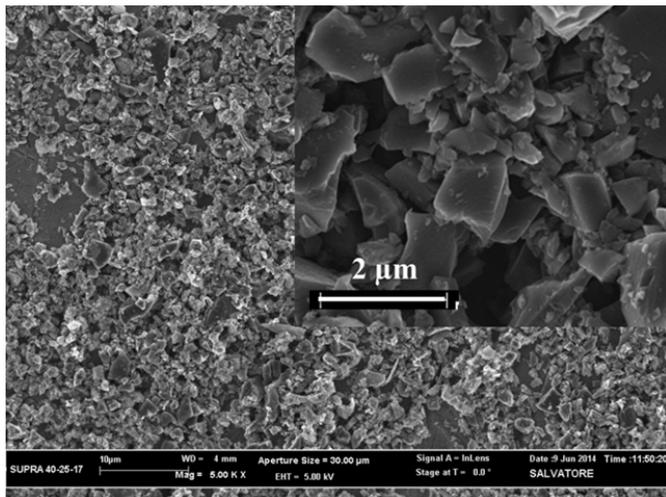


Figure 3: FESEM micrographs of carbonized and ground hemp hurds.

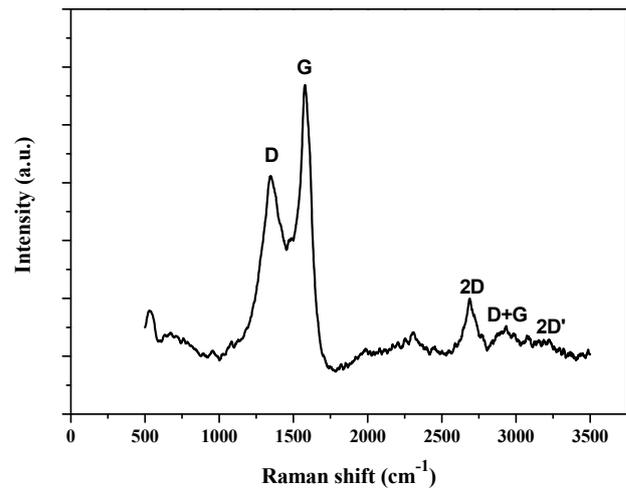


Figure 4: Raman analysis of carbonized hemp powder.

Preparation of composite samples

Five cement composites were prepared: four with various contents of inert carbonized particles and one without any inclusion to be used as reference. Composition details of cement mixes are reported in Tab. 3.

Notation	Inert carbonized particles	
	Weight (%)	Weight (mg)
CEM	0	0
CEM +0.08% HH	0.08	171
CEM +0.20% HH	0.20	428
CEM +1.00% HH	1.00	2140
CEM +3.00% HH	3.00	6420

*For each mix 214 g cement, 75 g water and 3.21 g HRWRA were used.

Table 3: Composition of cement composites.

Procedure followed for the preparation of the cement composite samples is given below:

- The inert carbonized particles were added in to the solution of water and superplasticizer,
- The mixture was then sonicated for 15 minutes,
- After sonication the mixture was transferred into the mixing bowl and mixer was started,
- Mixer speed was kept at 440 rpm and the cement was added gradually in the mixing bowl within 60 seconds,
- After the addition of cement the mixing was carried out for another 60 seconds at constant speed (i.e. 440 rpm),
- Then, the speed was increased to 630 rpm and mixing was done for 2 more minutes, hence making the total mixing time of 4 minutes,
- After completion of the mixing, the paste was transferred into the acrylic molds of $20 \times 20 \times 75 \text{ mm}^3$,
- The molds were then kept in air tight boxed having humidity level of 90%,
- After the completion of 24 hours of sample preparation, the samples were removed from molds and kept in water for immersed water curing of 28 days,
- At the completion of curing period the samples were removed and 2 mm thick and 6 mm deep U shaped notches were made,

Testing methods

The cured and notched cement composite samples were tested for their strengths in flexure and compression. For flexural strength the cement samples were analyzed in three point bending according to the ASTM C348 [23] by using a single column Zwick-Line Z010 testing machine. The crack mouth opening displacement (CMOD) controlled mode was



selected for all the specimens and displacement rate was fixed at 0.003 mm/min. The portions of broken prisms were tested in compression according to ASTM C349 [24]. For compression, the displacement rate was kept at 0.50 mm/min and 0.80 mm/min for loading and unloading the specimens. Typical test setup for flexural and compression test is shown in Fig. 5(a) and 5(b).

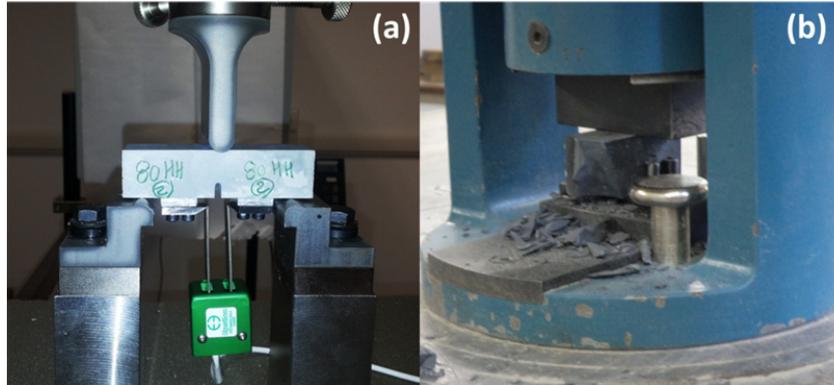


Figure 5: Test setup for: (a) Flexural strength test & (b) Compressive strength test

Small broken pieces of specimens from compression tests were analyzed by FESEM for their microstructure. FESEM images are shown in Fig. 6.

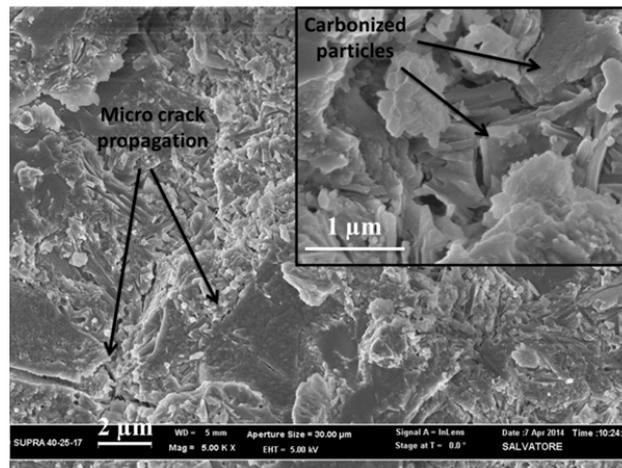


Figure 6: FESEM images of cement composite containing inert carbonized particles

RESULTS AND DISCUSSIONS

The notched specimen were tested in three point bending. Minimum three specimens were tested for each composition and their average modulus of rupture (MOR) was evaluated according Eq. (1):

$$\sigma_{max} = \frac{3 F_{max}^2 l}{2 w b^2} \quad (3)$$

where

F is the maximum force in the load deflection curve,

l is the span length,

w is the specimen width,

b is the specimen height.

Typical load-CMOD curves and fracture surfaces as experimentally recorded for cement composite specimens with and without micro carbonized inerts are shown in Fig. 7 and 8. The comparison of average modulus of rupture of cement composite mixes is given in Fig. 9.

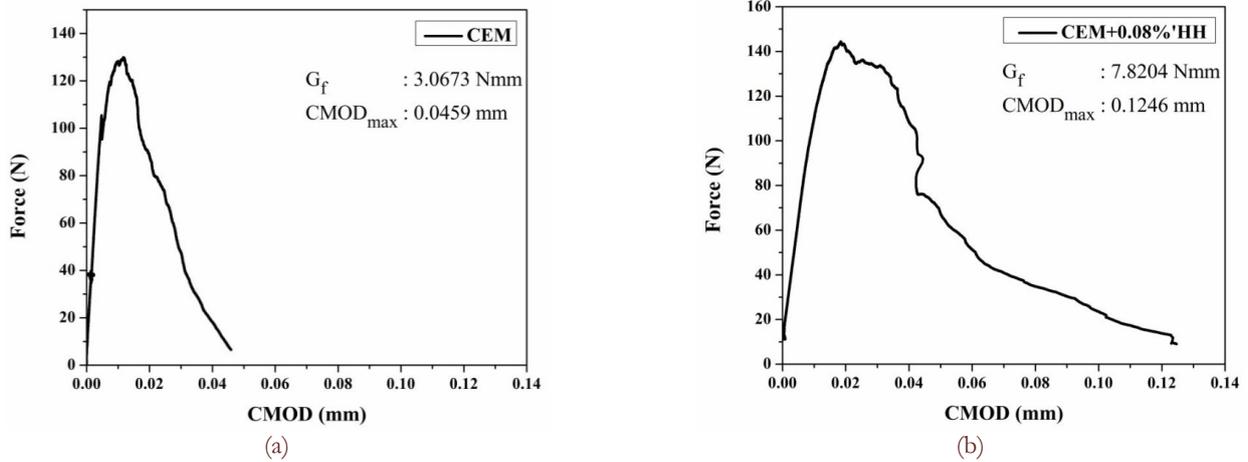


Figure 7: Typical load vs. CMOD curves for (a) Cement (b) Cement with 0.08 wt% carbonized hemp hurds



Figure 8: Fracture surface of cement composite samples (a) Cement (b) Cement with 0.08wt% carbonized hemp hurds

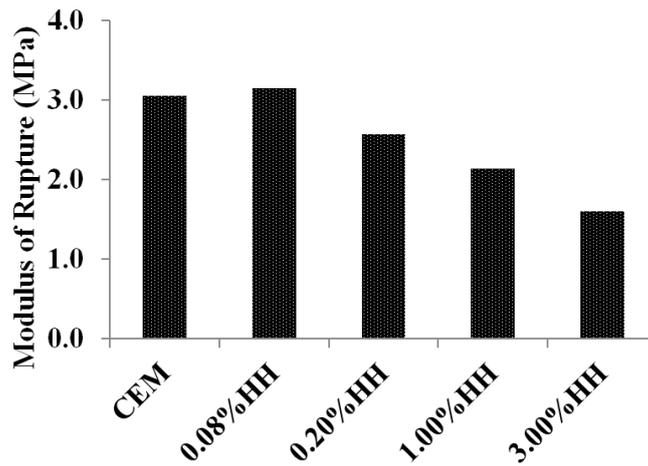


Figure 9: Comparison of flexural strength of cement composites containing various wt% of carbonized hemp hurds

The analysis of flexural strength results demonstrated some sort of mixed trend of increase and decrease in proportion to increase in the content of carbonized particles inclusions. A slight increase of 7% in MOR was achieved on addition of 0.08 wt% HH but there was noticeable decrease on further addition up to 3%. The fracture surfaces are highly affected by the inert particles inclusion. It seems that carbonized particles act as a heterogenic obstacle in the way of crack tip and



either forced it to deflect or to transform it into multiple cracks (Fig. 6). As a result, several times increase was observed in the area of fracture surface as compared to the cross section of reference cement specimen.

The load deflection curves were further analyzed and fracture toughness parameters were evaluated as per standard set forth in ASTM C1018 [25]. Based on eq 2(a & b) toughness indices I_5 and I_{10} were evaluated for all the compositions with and without micro-carbonized particles. Related results of I_5 and I_{10} are given in Fig 10 & 11 respectively:

$$I_5 = \frac{\text{Area under the Force \& CMOD curve up to 3 times the 1}^{st} \text{ crack CMOD}}{\text{Area under the Force \& CMOD curve up to 1}^{st} \text{ crack CMOD}} \quad (2a)$$

$$I_{10} = \frac{\text{Area under the Force \& CMOD curve up to 5.5 times the 1}^{st} \text{ crack CMOD}}{\text{Area under the Force \& CMOD curve up to 1}^{st} \text{ crack CMOD}} \quad (2b)$$

Evaluated toughness indices (I_5 & I_{10}) of the cement composites clearly demonstrate that the addition of HH (in micro-carbonized form) significantly increase the fracture toughness. The rate of increase in flexural toughness is non-linearly related to the added content of micro-carbonized HH. It is believed that presence of high number of irregular shaped carbonized particles control the cracks by increasing their lengths. This phenomenon considerably increases the energy required for crack propagation and resultantly enhances the overall fracture toughness of cement composites.

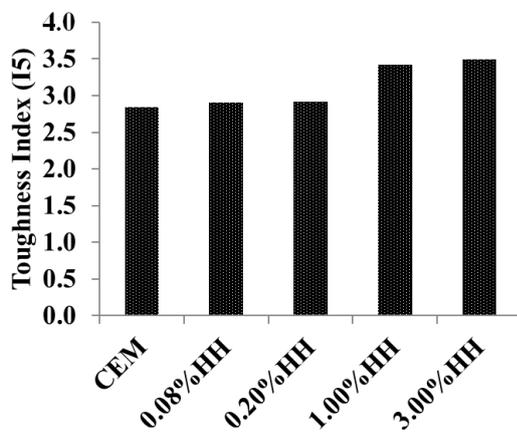


Figure 10: Comparison of toughness index I_5 of cement composites containing various wt% of carbonized hemp hurds.

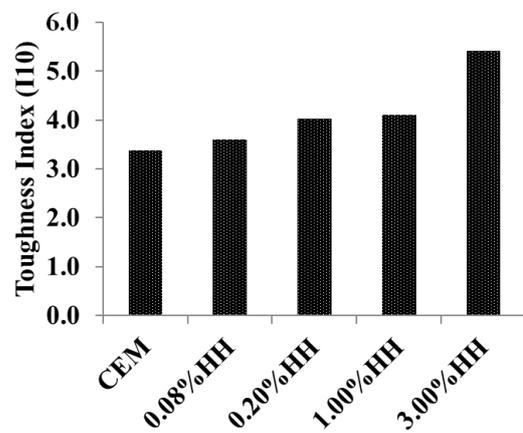


Figure 11: Comparison of toughness index I_{10} of cement composites containing various wt% of carbonized hemp hurds.

Compression tests were carried out by using the broken pieces of the prisms from flexural test. The results of compressive strength tests are reported in Fig. 12. The results showed increasing trend up to 1 wt% carbonized particles inclusion and then decrease in strength. The maximum compressive strength enhancement was about 58% at 1 wt% inclusion. This strength enhancement may be attributed to the filling action of inert particles inclusion in the cement matrix and resulting in higher packing density.

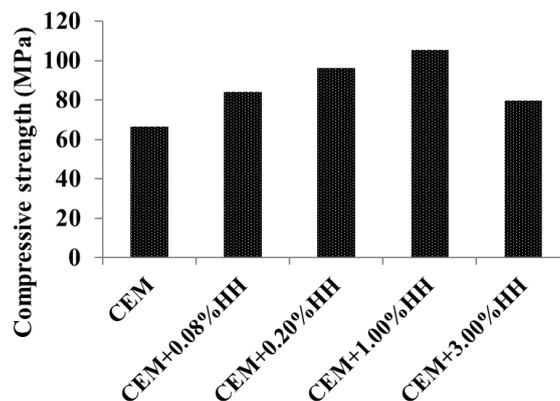


Figure 12: Comparison of compressive strength of cement composites containing various wt% of carbonized hemp hurds



CONCLUSIONS

In this work micro-carbonized particles were prepared from hemp hurd by controlled pyrolysis. These particles were found quite effective in enhancing compressive strength and fracture toughness of cement matrix composites. It is believed that irregular shaped micro particles contouring by the crack and crack pinning are the mechanisms, which can explain the increase of toughness in the composite samples.

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