PROPERTIES OF METAKAOLIN-BASED GEOPOLYMER MORTAR INCORPORATED WITH MULTI-WALLED CARBON NANOTUBES

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The use of alternative materials, predominantly with high levels of supplementary cementitious materials and geopolymer composites for the development of the construction industry is proposed. Metakaolin-based geopolymer mortar along with corn cob ash (CCA) and multi-walled carbon nanotubes (MWCNTs) were characterized and tested. In this paper, the properties of geopolymer mortar was studied by varying the concentrations of multi-walled carbon nanotubes (0%; 0.25%; 0.5%; 0.75% and 1%) along with the replacement levels of metakaolin with corn cob ash (0...10% about 2.5% increment). From the scanning electron microscope analysis, it was depicted that the MWCNTs were distributed uniformly within the geopolymer matrix at 0.50%, while at 1% these were poorly distributed and agglomerated within the matrix. Experimental investigation revealed that there was a significant increase in compressive strength of metakaolin-based geopolymer mortar when CCA and MWCNTs were combined at 5% of CCA and 0.5% of MWCNTs, but beyond this combination, there was a reduction in strength.

Keywords: *carbon nanotubes, compressive strength, metakaolin, scanning electron microscope.*

Для розвитку будівельної галузі запропоновано альтернативні матеріали. Досліджено геополімерний будівельний розчин на основі матакаоліну разом із золою качанів кукурудзи (CCA) і багатошаровими вуглецевими нанотрубками (NMCNT). Вивчено його властивості за зміною кількості багатошарових вуглецевих нанотрубок (0%; 0,25; 0,5; 0,75 та 1%), а також ступінь заміни метакаоліну кукурудзяною золою (0...10% та 2,5% приросту). За результатами сканувального електронного мікроаналізу встановлено, що NMCNT рівномірно розподілені в геополімерній матриці за вмісту концентрації 50%, тоді як за вмісту 1% – слабо розподілені та агломеровані всередині матриці. Зафіксовано значне збільшення міцності на стиск геополімерного розчину на основі метакаоліну за поєднання 5% CCA та 5% MWCNTs.

Ключові слова: *вуглецеві нанотрубки, міцність на стиск, метакаолін, сканувальний електронний мікроскоп.*

Introduction. During the manufacturing of cement, large amount of carbon dioxide is released necessitating the replacement of cement with other materials such as rice husk ash, corn cob ash (CCA), fly ash, bottom ash, ground granulated blast furnace slag etc. The full or partial incorporation of supplementary cementitious materials in the production of green concrete, not only minimizes the environmental impact but also improves the mechanical [1–3], workability [4], durability [5–6] and economic properties of concrete [7]. Most of the corncobs produced are disposed as waste leading to environmental pollution and hence, the recycling of CCA for geopolymer production is of paramount importance. Geopolymer is a new concept which helps in reducing the emission of carbon dioxide up to 80% [8–10]. Different researchers focussed on determining the properties of formulations of fly ash [11–12], blast furnace slag [11–12] and metakaolin (MK) based [13] geopolymers which proved the capability of geopolymer

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cement development for the construction industry [14]. Generally, the compressive strength of geopolymer depends on various factors such as molar ratio, curing mode and source materials [15]. The feasibility of using MK as a source material in geopolymer mortar or concrete has been investigated by various researchers. According to Bernal Susan et al. [16], addition of ground granulated blast furnace slag in metakaolin-based geopolymer concrete has enhanced its performance at high temperature. The geopolymer mortar made of blended source material has a higher strength than the geopolymer mortars made of single source material [17]. An attempt has been made to develop high strength by using corn cob ash and metakaolin in geopolymer mortar.

For the strengthening purposes of the composites, the use of carbon nanotubes is advocated. Carbon nanotubes, categorized as single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs), are one of the promising nanomaterials which have greater strengths than the other fibres thereby improving the overall mechanical properties of the composites. The effect of different concentrations of MWCNTs (0%; 0.1%; 0.5% and 1% by weight) on the properties of fly ash-based geopolymer was investigated and it was found that geopolymer matrix containing 0.1 and 0.5% of MWCNTs was uniformly distributed, while 1% of MWCNTs was poorly distributed and rigorously agglomerated [18]. The addition of less than 1% of MWCNTs greatly enhances the mechanical properties of the composites [19]. In this study the effect of MWCNTs on blended geopolymer mortar has been investigated by evaluating the compressive strength and microstructure properties of 8M molar concentration of NaOH.

Material. In this investigation metakaolin was used as a source material. It was partially replaced by corn cob ash prepared by burning of corn cobs procured from Maize Section, Punjab Agricultural University (Ludhiana). The MWCNTs obtained from Platonic Nanotech Private Limited, Jharkhand were used.

Table 1. Properties of different materials

Sr. No.	Metakaolin		Corn Cob Ash		Multi-walled carbon nanotubes	
	Chemical Composition	Values, %	Chemical Composition	Values, %	Specification	Values
1	SiO_2	52 ± 1	Carbon	0.43	Physical form	Fluffy, Very light powder
2	Al_2O_3	42 ± 1	Oxygen	55.02	Colour	Black
3	TiO_2	≥ 0.5	Sodium	0.01	Diameter	5 ~ 15 nm
4	Fe_2O_3	< 1.3	Magnesium	4.37	Length	10 ~ 15 μm
5	CaO	< 0.5	Aluminium	0.51	Purity	97%
6	MgO	< 0.5	Potassium	20.20	Metal content	2%
7	Na_2O, K_2O	0.5...2.5	Silicon	16.13	Bulk density	0.06 ~ 0.09 g/cm^3
8	Loss on ignition	0.8...1.2	Phosphorus	2.24	Specific surface area	220 m^2/g

Sodium silicate solution consisting of SiO_2 – 25...28% and Na_2O – 7.5...10% while sodium hydroxide (NaOH) in pellets form was used as an alkaline activating solution for the geopolymerization process. Fine aggregates conforming to zone II with a fineness modulus of 2.87 and specific gravity of 2.63 were used. The properties of metakaolin, corn cob ash and MWCNTs are listed in Table 1.

Dispersion and preparation of multi-walled carbon nanotubes. For the dispersion of MWCNTs in the metakaolin-based geopolymer mortar, a solution of polycarboxylate-based superplasticizer (5% by weight of binder) and water was prepared with an appropriate amount of MWCNTs in it. The solution was ultrasonicated in water bath for about 1 h. Twenty-five mixes of geopolymer mortar were prepared by employing different proportions of MWCNTs (0%; 0.25%; 0.5%; 0.75% and 1%) along with the replacement levels of metakaolin with corn cob ash (0...10% at the rate of 2.5% interval).

Preparation of the samples. The alkaline activator solution of 8 M was prepared one day prior to casting and then mixed with sodium silicate one hour before the casting of cube specimens with a mass ratio of 1:2.5. Firstly, metakaolin was alkali activated by employing alkaline activating solution and mixing was continued for about 2...3 min. Fine aggregates were added to the mix. The ultrasonicated solution in addition to extra water was added to the alkali activated mix and then the mixing was continued and homogeneity of the mix was ensured.

Table 2. Mix proportion of metakaolin-based geopolymer mortar

Mix	AA/B	W/S	MK	CCA	MWCNTs	AAS		SP	FA	W
						SH	SS			
			g			g				
M1	0.6	0.6	1800	0	0	308.6	771.4	0	5400	597.89
M2	0.6	0.6	1755	45	0	308.6	771.4	0	5400	597.89
M3	0.6	0.6	1710	90	0	308.6	771.4	0	5400	597.89
M4	0.6	0.6	1665	135	0	308.6	771.4	0	5400	597.89
M5	0.6	0.6	1620	180	0	308.6	771.4	0	5400	597.89
M6	0.6	0.6	1800	0	4.5	308.6	771.4	90	5400	597.89
M7	0.6	0.6	1755	45	4.5	308.6	771.4	90	5400	597.89
M8	0.6	0.6	1710	90	4.5	308.6	771.4	90	5400	597.89
M9	0.6	0.6	1665	135	4.5	308.6	771.4	90	5400	597.89
M10	0.6	0.6	1620	180	4.5	308.6	771.4	90	5400	597.89
M11	0.6	0.6	1800	0	9	308.6	771.4	90	5400	597.89
M12	0.6	0.6	1755	45	9	308.6	771.4	90	5400	597.89
M13	0.6	0.6	1710	90	9	308.6	771.4	90	5400	597.89
M14	0.6	0.6	1665	135	9	308.6	771.4	90	5400	597.89
M15	0.6	0.6	1620	180	9	308.6	771.4	90	5400	597.89
M16	0.6	0.6	1800	0	13.5	308.6	771.4	90	5400	597.89
M17	0.6	0.6	1755	45	13.5	308.6	771.4	90	5400	597.89
M18	0.6	0.6	1710	90	13.5	308.6	771.4	90	5400	597.89
M19	0.6	0.6	1665	135	13.5	308.6	771.4	90	5400	597.89
M20	0.6	0.6	1620	180	13.5	308.6	771.4	90	5400	597.89
M21	0.6	0.6	1800	0	18	308.6	771.4	90	5400	597.89
M22	0.6	0.6	1755	45	18	308.6	771.4	90	5400	597.89
M23	0.6	0.6	1710	90	18	308.6	771.4	90	5400	597.89
M24	0.6	0.6	1665	135	18	308.6	771.4	90	5400	597.89
M25	0.6	0.6	1620	180	18	308.6	771.4	90	5400	597.89

Note: AA/B = Alkaline activator to binder ratio; W/S = Water to solid ratio; MK = Metakaolin; CCA= = Corn cob ash; MWCNTs = Multi-walled carbon nanotubes; AAS = Alkaline activator solution; SH = = Sodium hydroxide; SS = Sodium silicate; SP = Superplasticizer; FA = Fine aggregates; W = Water.

No surfactant (polycarboxylate-based superplasticizer) was used for the preparation of plain metakaolin-based geopolymer mortar. Freshly prepared geopolymer mortar was poured into cubes of standard size of 70.6×70.6×70.6 mm for the determination of compressive strength. Consequently all the cube specimens were placed on a vibrator for about 2 min to remove the excess air voids. After an hour of casting, the cube specimens were placed in an oven for 24 h at 40°C for thermal curing. The cubes were removed and demoulded after 24 h and then placed at room temperature until testing. Three iterations of geopolymer mortar for different ages were made for different concentrations of MWCNTs and various replacement levels of corn cob ash. The mix proportion of metakaolin-based geopolymer mortar is given in Table 2.

Characterization methods. The compressive strength of geopolymer mortar was measured at an age of 3; 7 and 28 days of curing. Scanning Electron Microscope (SEM) test was performed on fractured samples (that is, M1, M13 and M23) to determine the quality of MWCNTs dispersion and the crack-bridging mechanism. Energy dispersive X-ray spectroscopy (EDS) technique was used to determine the elemental composition of different geopolymer mortar mixes (M3, M8, M13, M18 and M23).

Results and discussion. ***Compressive strength.*** The effect of CCA replacement and incorporation of MWCNTs at different ages of curing (3; 7 and 28 days) on the compressive strength (CS) of metakaolin-based geopolymer mortar is shown in Fig. 1.

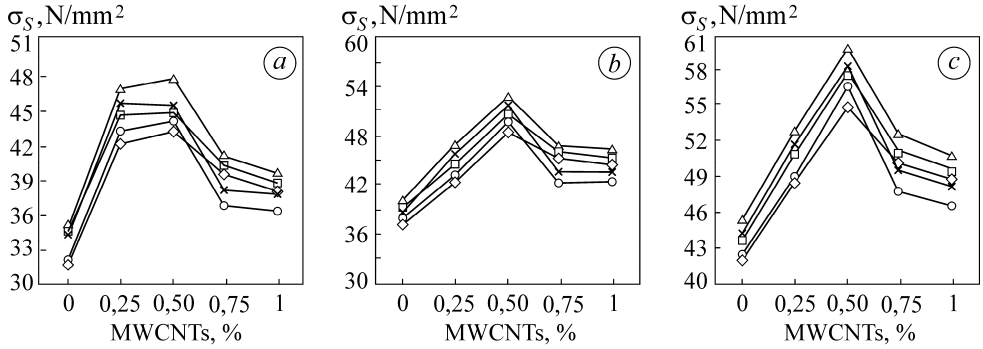

Fig. 1. Compressive strength of geopolymer mortar at 3 (*a*), 7 (*b*) and 28 (*c*) days:
◇ – 0%; □ – 2.5; △ – 5; × – 7.5; ∗ – 10%.

It is observed that the CS of geopolymer mortar for different concentrations of MWCNTs (0%; 0.25%; 0.5%; 0.75% and 1%) increased up to the replacement level of 5% CCA with metakaolin and decreased thereafter. The lower compressive strength at both early and later stages is attributed due to lower amount of reactive silica or alumina in the composites. The CS of geopolymer mortar increased up to 0.5% of MWCNTs and then it started showing decreasing trend as the incorporation of MWCNTs in the matrix tend to reduce the growth of microcracks up to a certain level. Also, the addition of MWCNTs decreased the porosity of composites by filling the pores resulting into compacted form. The CS of geopolymer mortar at 1% of MWCNTs was higher than the mixes without MWCNTs but it was lower than the mixes which contained 0.5% of MWCNTs. This can be due to the agglomeration of MWCNTs in the geopolymer matrix. Dispersion concerns and agglomeration sometimes cause the reduction in strength in case of inclusion of more quantity of MWCNTs as compared to that of small fraction of MWCNTs as depicted by Gillani et al [20]. The overall trend shows that the addition of small amounts of MWCNTs gives better results.

Morphology of metakaolin-based geopolymer composites. The SEM micrographs of the sample M1 (Fig. 2*a*) suggest that the plain metakaolin-based geopolymer mortar contains many un-reacted metakaolin particles. There were pores and microcracks present in the sample M1 which resulted into the decreasing trend of compressive strength of plain metakaolin-based geopolymer mortar. Fig. 2*b* depicts that the mix M13 has a uniform distribution of individual MWCNTs thereby bridging the microcracks present in the mix. At 1% MWCNTs there is agglomeration of MWCNTs as these are not properly dispersed in the matrix (Fig. 2*c*). The EDS analysis shows (see Table 3) that the amount of carbon detected in the mixes increase with the increase in content of MWCNTs which greatly affects the compressive strength of geopolymer. Table 3 reveals that the strength of geopolymer decreases with the increase in the Si/Al ratio.

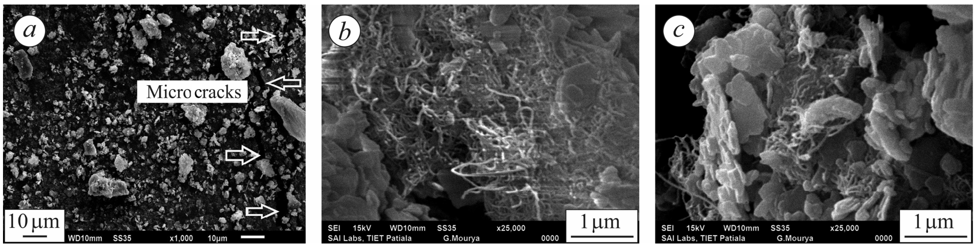

Fig. 2. Plain geopolymer mortar (*a*), geopolymer with 0.5% (*b*) and with 1% (*c*) MWCNTs.

Table 3. Element percentage of the mixes having CCA 5%

Element, weight, %	C	O	Na	Al	Si	K	Ca	Ti	Fe
Mix M3	18.50	51.34	1.98	10.91	15.91	0.29	0.22	0.58	0.27
Mix M8	21.09	46.44	2.19	11.89	16.77	0.34	0.29	0.69	0.30
Mix M13	22.27	41.64	2.32	14.74	17.11	0.39	0.31	0.88	0.34
Mix M18	29.12	39.18	2.49	10.90	16.36	0.54	0.16	0.79	0.46
Mix M23	36.65	37.84	2.63	7.06	13.80	0.71	0.08	0.62	0.61

CONCLUSIONS

The study examined the MK-CCA-based geopolymer and its effects on the compressive strength and microstructure properties using 8 M of NaOH. The following conclusions are drawn. For all curing periods, the compressive strength of MK-CCA blended geopolymer mortar increases up to 5% of replacement of metakaolin with CCA and then it decreases. This decrease in strength is attributed to the lower amount of reactive silica or alumina in the composites. The strength of MK-CCA blended geopolymer reinforced with MWCNTs increases up to the incorporation of 0.5% of MWCNTs in the matrix, thereafter it decreases. The reduction in strength is due to the agglomeration of MWCNTs in the composites. SEM analysis confirms that the MWCNTs help in bridging the microcracks to produce the maximal amount of compressive strength instead of plain metakaolin-based geopolymer mortar. EDS analysis testifies that the strength of geopolymer decreases with the increase in the ratio of Si/Al. The authors recommend using 5% CCA as a partial replacement for metakaolin in geopolymer mortar along with 0.5% MWCNTs as there is a significant increase in compressive strength with this combination.

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Received 29.12.2020