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RESEARCH

Combination between organic polymer and geopolymer for production of eco-friendly metakaolin composite

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Abstract

The target of the present paper is to polymerize ethylene glycol monomer in geopolymer binder forming hybrid organic and inorganic polymer composites. Ethylene glycol monomer used in different ratios from 0.5 to 2% from the total binding weight, where as geopolymer composites made from metakaolin activated by 45% sodium silicate. The aim of the present paper is to study the enhancement in produced organic–inorganic composites by measuring compressive strength, flexural strength and tensile strength, while tracing and identification of the formed aluminosilicate composites using FTIR (Fourier transformer infra red), XRD (X-ray diffraction), DTG (differential thermogravimetry), TGA (thermogravimetric analysis) and SEM (scanning electron microscopy). Results showed an enhancement in mechanical characteristics with about more than 100% gain in compressive strength as compared with control geopolymer mix; however, the gain in flexural and tensile strength increases by about 50% on using 1.5% ethylene glycol after 90 days of curing; also, there is better modification in microstructural properties by using ethylene glycol up to 1.5%. However, the total weight loss by burning the sample up to 1000 °C using DTG is lower than 7.5% for all mixes which is much lower than the pure organic polymer which acquires total loss up to 80% up on firing to 1000 °C.

Keywords Metakaolin · Geopolymer · Ethylene glycol · Sodium silicate

Introduction

Geopolymers are emerging as a new class of high-performance materials because of their excellent properties, since the latter half of the twentieth century with growing interest by researchers, engineers and technologists in generating new materials with array properties exhibited by these materials over other conventional materials including the low cost of raw materials and their environmentally friendly manufacturing process. Geopolymers are fire and high-temperature resistant up to 1300 °C [1]; they are stable and can perform without any loss of properties at high temperatures; have high resistance to UV radiation [2]; have high compressive strength, long-term durability and heavy metal ion fixation [3, 4]; and also they possess high acid and sulphates resistance and develop rapid strength up to 70% within 4 h of casting [5, 6].

Geopolymers are easily casted, applicable and have high affinity to be sticked to many materials as metals and concretes with glassy textures. These materials are designated as "green materials" because of the low-energy consumption and low-toxic gas emission during preparation. Geopolymers can be synthesized using alumino-silicate reach waste materials as natural raw material as kaolinite as well as their amorphous transformed structure upon firing at high temperature producing metakaolinite and industrial wastes as slag, fly ash and volcanic ash, where the second type can be considered as more eco-friendly type and can help in preserving natural raw materials as well as help in getting rid of those waste materials using geopolymer technology [4]. The produced geopolymer materials from the aforementioned types give excellent compressive strength, which can exceed 120 MPa, depending on the used starting materials, activators type and ratio.

In spite these advantages, geopolymers have not been used in their full potential as of today there are some technical as

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well as commercial obstacles that hinder the growth of geopolymer industry; one of the outstanding problem with geopolymers is their processability [7, 8]; also, geopolymers present a typical brittle mechanical behaviour with the consequent low ductility, low flexural strength and low fracture toughness [9] which can restrict their applications in structural material.

Scientists tried to resolve these disadvantages by using organic polymers in geopolymer formation [10–13]. One important factor in choosing the added organic polymer is to be stable or become reactive under extreme basic condition of the geopolymer which can be satisfied by ethylene glycol. The study by Zhang et al. [3] mentioned the requirement of organic component for mineralization process of inorganic materials. It also mentioned the function of organic component to bind the microcrystals of inorganic materials and arrange their orientation to form natural composite materials with superior mechanical properties as compared to ceramics.

Polyethylene glycol (PEG) is a polyether compound with many applications in industrial manufacturing and is one of the most well-known water-soluble polymers, while it can also be dissolved in many organic solvents including aromatic hydrocarbons. PEGs are synthesized by polymerization of ethylene oxide in the presence of water or ethylene glycol and alkaline catalysts [14].

Catauro et al. [15] investigated the effect of PEG on properties of geopolymer composites, where the control mix exhibited steady-state strength with time as a result of the chemical composition of the reacted materials, whereas control mix can reach final mechanical values faster than hybrid. On the other hand, inclusion of PEG resulted in high elasticity to the base material as well as elongated time for reaching the final strength values with the increase of flexural and compressive strengths with aging time.

Lamanna et al. [13] compared the compressive strength of polymer mortars with control that is non-modified and studied their ability in restraining microcrack propagation. Authors concluded the decreased total porosity with the addition of organic polymer, and this might contribute in improved durability. Authors explored also the optimum PEG which was 10% that can be added to geopolymer systems, in order to improve their properties.

Zhang et al. [3] studied the addition of various polymers in the ratio of 1% on uncalcined kaolinite geopolymeric matrix; results elaborated an increasing strength up to 29% as well as 65% gain in bending. Authors elaborated also the high resistance of the polymer modified geopolymer to crack propagation with high bridging efficiency. Ferone et al. [9] attained also pronounced increase in compressive strengths and toughness in hybrid epoxy–geopolymer composite as control with the control mix.

In the present work, we are going to prepare hybrid metakaolin geopolymer enhanced with organic ethylene glycol monomer in different ratio and study their effect on the produced composite by FTIR, DTG, XRD, SEM, as well as differential thermal analysis. The aging effect and variation in the ratio of ethylene glycol (EG) monomer on the microstructural characteristics as well as mechanical performance also studied.

Material and methods

Materials

Material used in this investigation was kaolinite collected from El-Dehesa, South Sinai, Egypt, which was upon thermally treated at 800 °C for 2 h with a heating rate of 5 °C/min, and produces metakaolinite (Mk) that possesses higher reactivity than crystalline kaolinite materials for geopolymer formation. This temperature was chosen on the basis of an earlier research works as the optimum temperature [16–19]. Liquid sodium silicate (LSS, $Na_2SiO_3{\cdot}9H_2O$) from Fisher company consists of 32% SiO_2 and 17% Na_2O with silica modulus SiO_2/Na_2O equal 1.88, and its density is 1.46 g/cm^3 used as alkali activator. Ethylene glycol monomer was sourced from Biochem Company, India with the purity of 99%.

The chemical compositions of fired and unfired kaolinite materials are given in Table 1, whereas their mineralogical characterization represented in Fig. 1. From their chemical composition table, kaolinite mostly composed of aluminium oxide and silicone oxide of about 83%; however, the mineralogical pattern confirms the complete transformation of kaolinite into amorphous constituents.

Geopolymer preparation and curing

Geopolymers were prepared from mixed organic and inorganic materials, where organic was ethylene glycol monomer which added in the ratio from 0.5 to 2.0%, while inorganic binder was metakaolinite activated by 45% sodium silicate. Metakaolin was sieved to obtain a fine powder with an average grain size of 90 μm. The water–binder material ratio (w/b) as well as mix design are recorded in Table 2. All mixes were casted in cubic shaped mould of 2.5 cm length, left to cure undisturbed under ambient temperature for 24 h and then subjected to curing temperature of 40 °C with a 100% relative humidity (R.H.). At testing time, specimens were removed from their curing condition, dried well at 80 °C for 24 h and then subjected to compressive strength measurements, whereas the resulted crushed specimens were immersed in stopping solution of methyl alcohol/acetone [20, 21] in order to prevent further hydration and then preserved in a well tight container until time of examination. Tensile

Table 1 Chemical composition of starting materials (mass, %)

Oxide content (%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	TiO_2	MnO	P_2O_5	Cl–	L.O.I	Total
Kaolin	56.33	27.61	1.32	0.18	0.06	0.06	0.04	0.08	3.73	–	0.13	0.05	10.17	99.97
MK (fired kaolin at 800 °C for 2 h)	57.50	35.10	1.59	0.64	0.17	0.25	0.15	0.12	2.85	0.00	0.13	0.06	1.14	99.70

strength measured according ASTM C496/C496M-17 [22] and flexural strength measured according to ASTM C78-18 [23] of the studied composites were measured on cylinders of 150 mm diameter and 300 mm height and beams of size 500 × 100 × 100 mm ^{3}, respectively, which they are measured at 7, 28 and 90 days, whereas compressive strength performed on cubic samples according to ASTM C109 M [24] at 7, 21, 28, 60 and 90 days.

Methods of investigation

Chemical investigation for starting materials performed using XRF-Axios (PW4400) WD-XRF Sequential Spectrometer, while mineralogical characterization was done by Philips PW 3050/60 diffractometer using a Cu Kα source. Mechanical testing was carried out using 5 tons German Brüf digital compression testing machine with a loading rate of 100 kg/min. FTIR used for elucidation of the amorphous constituents of geopolymer composites using Jasco-6100 with the aid of KBr binder in the range from 400 to 4000 cm^{-1} [25, 26]. The microstructure of the hardened specimens was studied using scanning electron microscopy—SEM Inspect S (FEI Company, the Netherlands) equipped with an energy-dispersive X-ray analyzer (EDX). Thermogravimetry conducted using DT-50 Thermal Analyzer (Shimadzu Co-Kyoto, Japan), where the samples were crushed, transferred immediately to an alumina crucible, held under isothermal conditions for 60 min at 40 °C to equilibrate in a nitrogen environment (N2 flowing at 200 ml/min) and then heated to 1000 °C at 10 °C/min in the same gas environment.

Results and discussion

FTIR and XRD investigations

FTIR spectra of 28 days hardened geopolymer specimens having various ratios of EG content are shown in Fig. 2, where there is a gradual increase in hydration bands with increasing ethylene glycol content as reflected on the stretching vibrations of O–H band at about 3455–3700 cm^{-1} as well as bending vibration of H–O–H bond at about 1630 cm^{-1}, as should be connected to the hygroscopic nature of ethylene glycol. Bands at about 2330–2355 cm^{-1} assigned to KBr binder were used in sample preparation for FTIR. There is a gradual increase in the main asymmetric band of T–O–Si at about 1030 cm^{-1} with the minor shifting to lower wave number, where T = Si or Al with increasing ethylene glycol content up to 1.5% as resulted from activation by ethylene glycol to geopolymer reaction forming amorphous N-A-S-H type gels, where EG bind the microcrystals of inorganic materials and arrange their orientation to form natural composite materials with superior properties [3]. The shift of asymmetric band is as a consequence of the aluminosilicate framework reorganization which occurs due to the geopolymerization reactions as proved also by the appearance of some weak bands in the region of bending modes of the Si–O–Si and Si–O–Al bonds (800–430 cm^{-1}) [27, 28]. There is a noticeable decrease in asymmetric band for non-solubilized silica at about 1150 cm^{-1} up to 1.5% EG, confirming the activation done by ethylene glycol. On increasing ethylene glycol to 2%, a sharp decrease in the main asymmetric band with the shifting of the peak to higher wave number gives an indication about the increase of zeolite content on the expense of amorphous

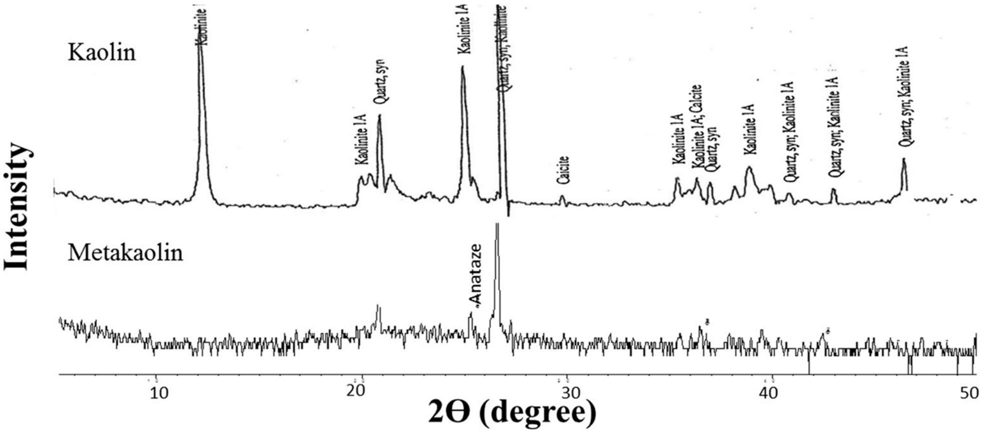


Fig. 1 X-ray diffraction pattern of the starting raw materials

Table 2 Composition of the geopolymer mixes (mass, %)

Mix no.	Meta-kaolin (MK) (%)	Sodium silicate (%)	Ethylene glycol (%)	Water/binder (%)	T.M20/ Al2O3	SiO2/ Al2O3	T.M2O/ SiO3	T. water/ T.M2O
E0	100	45	0.0	0.390	0.369	2.05	0.11	17.07
El	100	45	0.5	0.396	0.369	2.05	0.11	17.33
E2	100	45	1.0	0.400	0369	2.05	0.11	17.50
E3	100	45	1.5	0.410	0369	2.05	0.11	17.94
E4	100	45	2.0	0.411	0.369	2.05	0.11	17.99

geopolymer structure. Also, there is an increased intensity in the non-solubilized silica at about 1150 cm^{-1}, as a result of an increased viscosity by the added glycol monomer, and absorbs water necessary for geopolymer formation and so it hinders the formation of 3-D branched geopolymer chains [29].

Increasing the geopolymerization rate to 90 days (Fig. 3), one can notice a shoulder band at about 845 cm^{-1} aligned for Si–O stretching and OH bending (Si–OH); these bands reflect efficiency of alkaline dissolution of in metakaolin precursors upon forming free terminal active hydroxide chains that upon time incorporated in geopolymer formation as observed from its decreased intensity with time as well as increased intensity of the main asymmetric band at about 1030 cm^{-1}.

Also, as geopolymerization increases, the intensity of hydration bands decreased with the increase of asymmetric band for amorphous geopolymer structure as compared with 28 days. This may be connected to the increased polymerization of ethylene glycol with curing time, while the broad hydration band for mix incorporating 2% ethylene glycol is observed and confirms the increased swelling effect by monomer to the necessary water for reaction even at later ages and so retard the geopolymerization reaction as reflected on the lower intensity of asymmetric band [29].

XRD pattern of 90 days hardened alkali-activated MK-geopolymer composites reinforced with various ratios of ethylene glycol are shown in Fig. 4. The pattern illustrates that there is a broadness in the region of 20 to 35° 2*θ* characterizing glassy phase of geopolymer constituent [30]; this region increased with ethylene glycol up to 1.5% reflecting the increased activation for geopolymerization reaction by the added glycol; however, faujasite phase of zeolite appeared in the control mix as well as in the mix incorporates high EG (2%) which indicates the retardation effect upon using high EG as confirmed by FTIR, leading to the formation of short crystalline chains rather than three-dimensional amorphous geopolymer chains which are responsible for growth of geopolymer framework.

Thermal investigation

Differential thermogravimetric curve of Mk-geopolymer incorporating various ratios of ethylene glycol (Fig. 5) showed a characteristic two endotherms at temperature lower than 60 °C as well as endothermic band lower than 105 °C. The first associated with the loss of freely evaporable water was present in large pores of the aluminosilicate type product

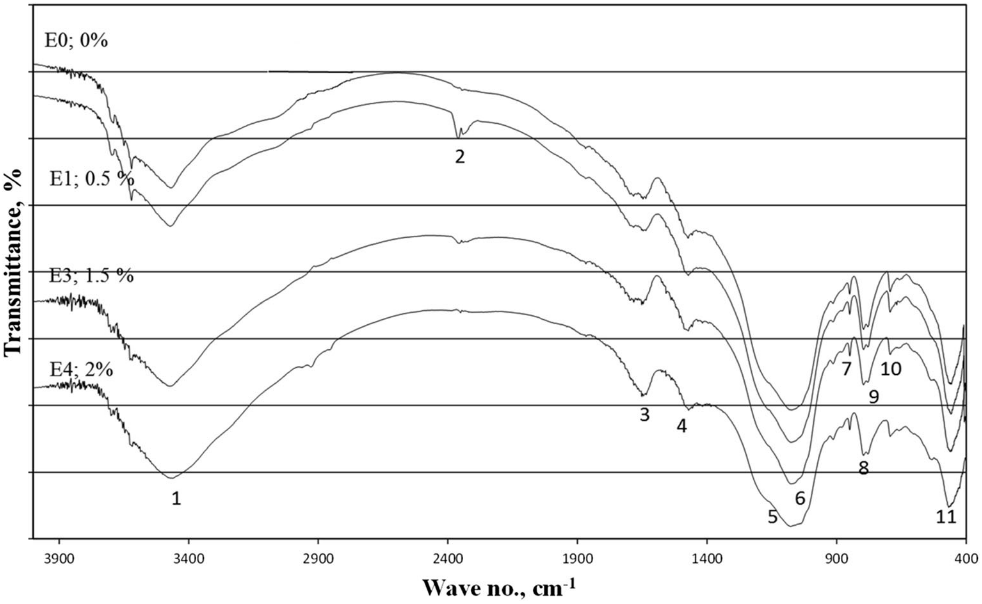


Fig. 2 FTIR spectra of 28 days alkali-activated MK geopolymer specimens enhanced with various ratios of ethylene glycol. (1: Stretching vibration of O–H bond; 2: stretching vibration of KBr; 3: bending vibration of (HOH); 4: stretching vibration of CO_2; 5: asymmetric stretching vibration (Si–O–Si); 6: asymmetric stretching vibration (T–O–Si); 7: symmetric stretching vibration (Si–O–Si); 8, 9: symmetric stretching vibration (A1–O–Si); 10: symmetric stretching vibration (Si–O–Si); 11: bending vibration (Si–O–Si and O–Si–O))

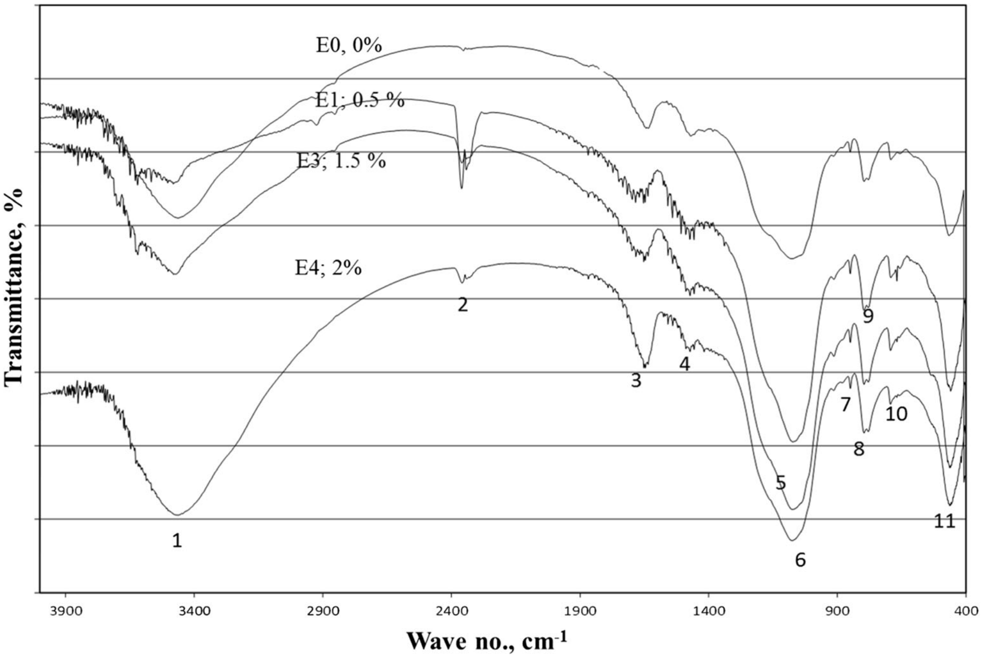


Fig. 3 FTIR spectra of 90 days alkali-activated MK geopolymer specimens enhanced with various ratios of ethylene glycol. (1: Stretching vibration of O–H bond, 2: stretching vibration of KBr; 3: bending vibration of (HOH), 4: stretching vibration of CO_2, 5: asymmetric stretching vibration (Si–O–Si), 6: asymmetric stretching vibration (T–O–Si), 7: symmetric stretching vibration (Si–O–Si); 8, 9: symmetric stretching vibration (A1–O–Si); 10: symmetric stretching vibration (Si–O–Si); 11: bending vibration (Si–O–Si and O–Si–O))

(geopolymer gel) for Mk-geopolymer [31]; this endotherm increases with ethylene glycol up to 1.5% and then decreased sharply with further monomer increase. The increased band intensity associated with activation done by ethylene glycol as it polymerizes under alkaline medium [14], forming well-arranged geopolymer composite, while further increase in ethylene glycol hinders the geopolymer formation by increased viscosity as mentioned before. The behaviour of the first endothermic peak is inversely proportional to the second endotherm that assigned to water present in zeolite [32], where the increased intensity of the first endotherm with ethylene glycol was accompanied by lowering the intensity of the second endotherm with shifting to lower temperature; however, further increase in EG beyond 2% results in an increased broadness as well as shifting to high temperature.

On investigating their thermogravimetric pattern (Fig. 6), one can see that their total weight loss varied with ethylene glycol giving ~7.25, ~7.37, ~7.53 and ~6.85% for 0, 0.5, 1.5 and 2% ethylene glycol, respectively. The total weight loss reflected the increased the amorphous aluminosilicate content with EG up to 1.5%, while decreasing its content with further increase EG as resulted from retardation effect of high dose of ethylene glycol. On comparing weight loss of the resulted composite, it can be noticed that it is much lower than the pure organic polymer composite which has weight loss between 50 and

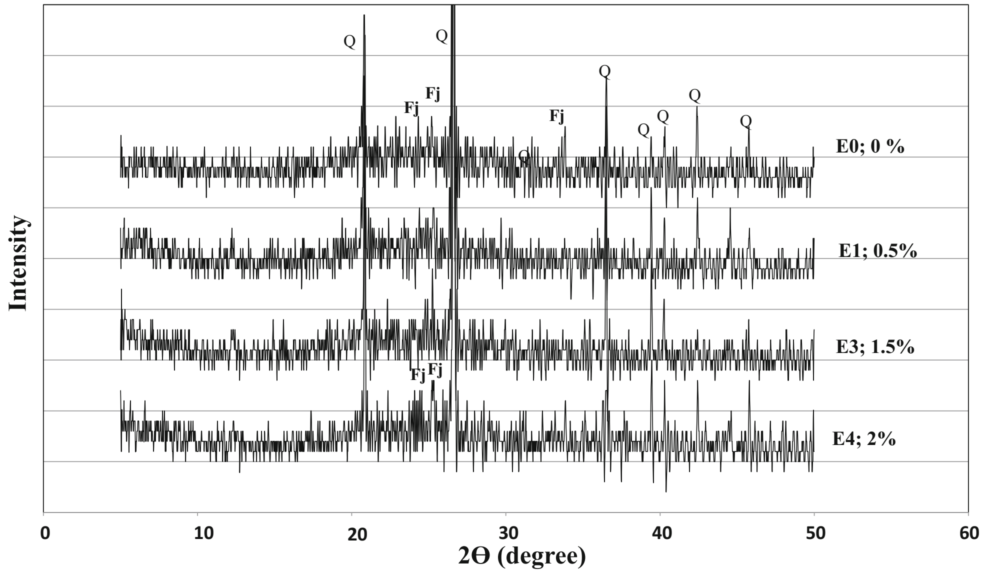
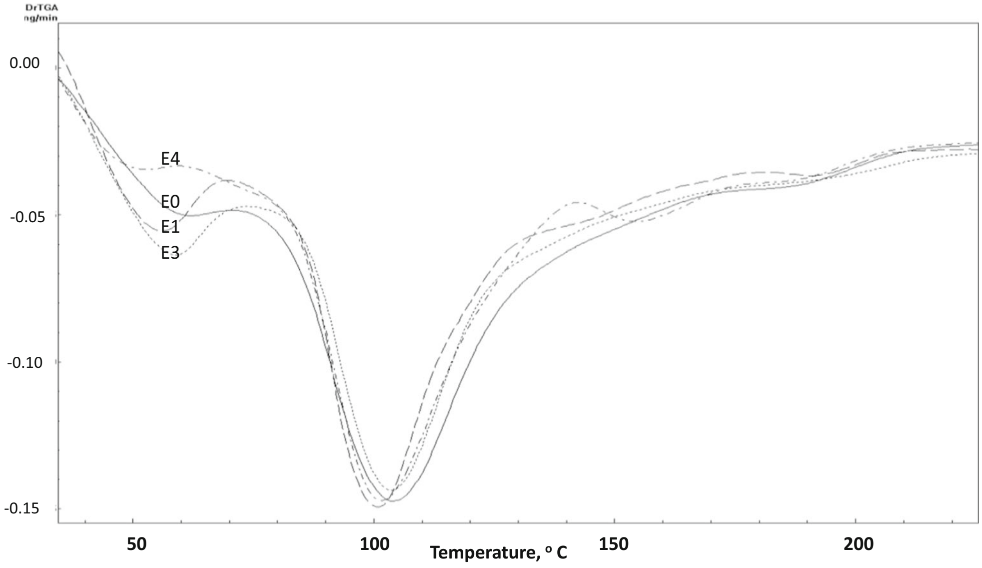


Fig. 4 XRD pattern of 90-day alkali-activated MK geopolymer specimens enhanced with various ratios of ethylene glycol (Q quartz, Fj faujasite)

Fig. 5 Differential thermogravimetric pattern of 90-day alkali-activated MK geopolymer specimens enhanced with various ratios of ethylene glycol

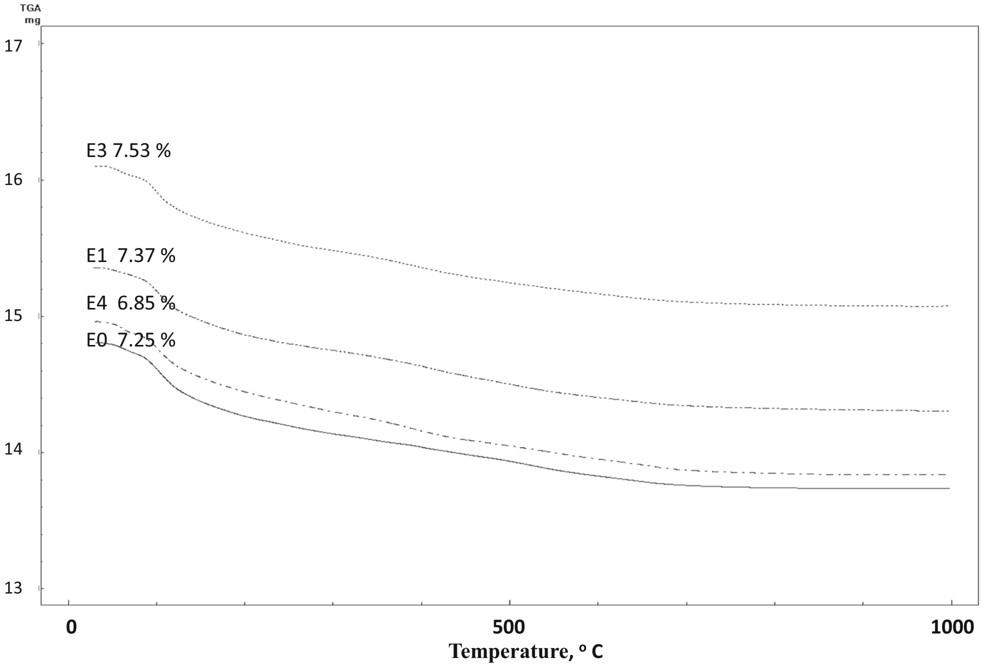


80%. This recommends the lower flammability of the resulted combined composite in addition to the very low release of toxic fume as in accordance with Bakharev [33].

Microstructural investigation

Microstructure of 90 days Mk-geopolymer composites enhanced with various ratios of ethylene glycol monomer is shown in Fig. 7. The micrograph of the control geopolymer (Fig. 7a) indicates the presence of unreacted laminar from metakaolin that spreads mostly all over the matrix; this laminar disappeared upon adding 0.5% EG (Fig. 7b) where the added monomer enhanced the polymerization of Mk forming dense microstructure, but still there are some unreacted laminars in addition to formation of pores within the matrix. These pores completely diminished with the formation more dense and compact structure upon adding 1.5% EG (Fig. 7c) as the used ratio results in extra enhancement for geopolymerization reaction by forming additional organic polymer that densified the matrix. Further increase in the EG to 2% results in the formation of wide pores spreading within the matrix, while the increased viscosity leads to low compaction between the reacting binder and formation of agglomerates within the matrix leading to the weakening of formed composite as represented in Fig. 7d.

Fig. 6 TGA of 90-day alkali-activated MK geopolymer specimens enhanced with various ratios of ethylene glycol



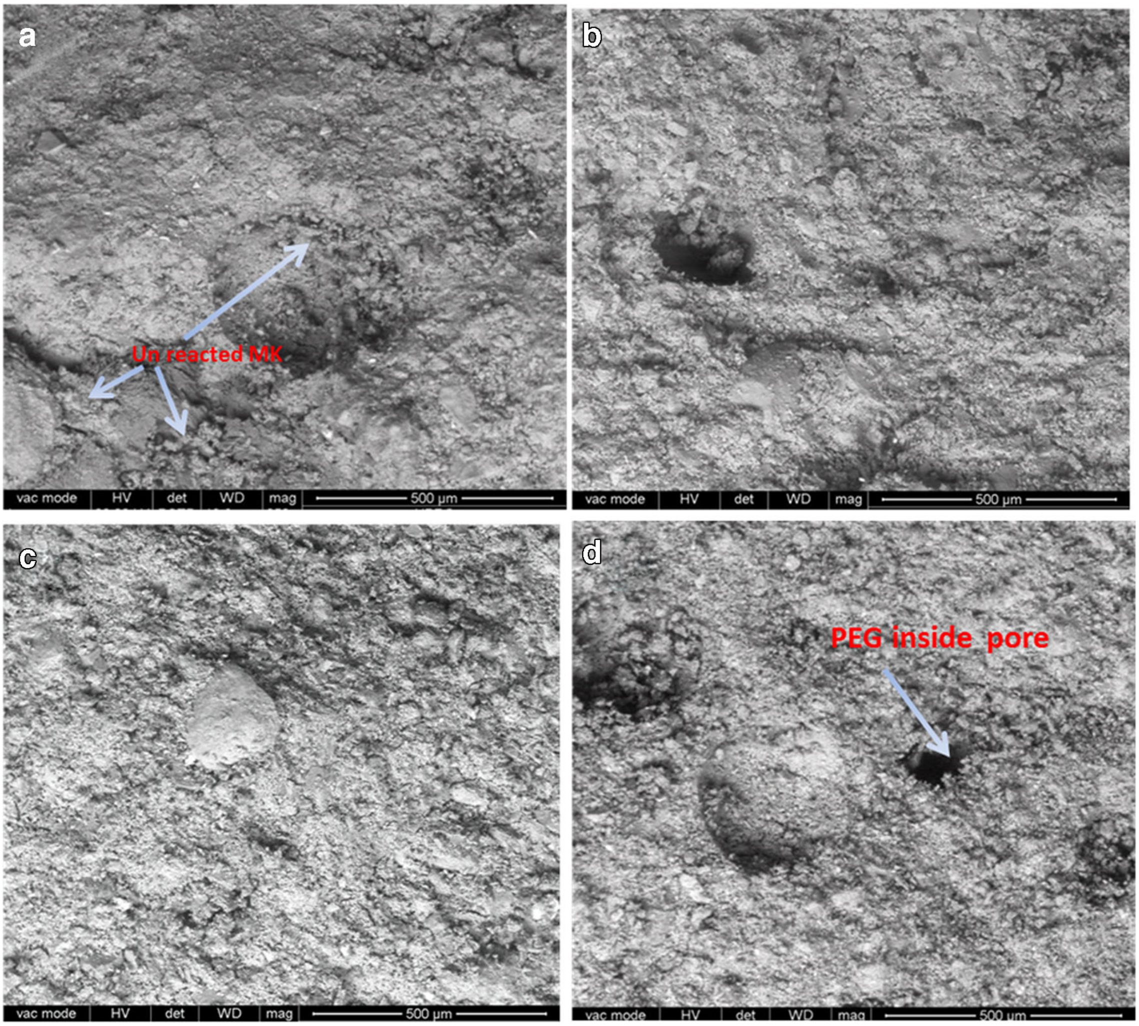


Fig. 7 SEM of 90-day alkali-activated MK geopolymer specimens enhanced with various ratios of ethylene glycol. **a** 0%. **b** 0.5%. **c** 1.5%. **d** 2%

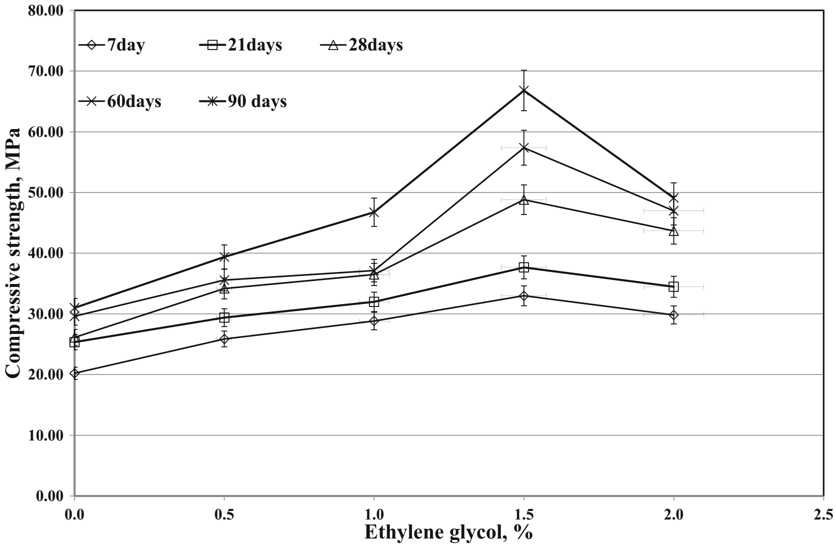
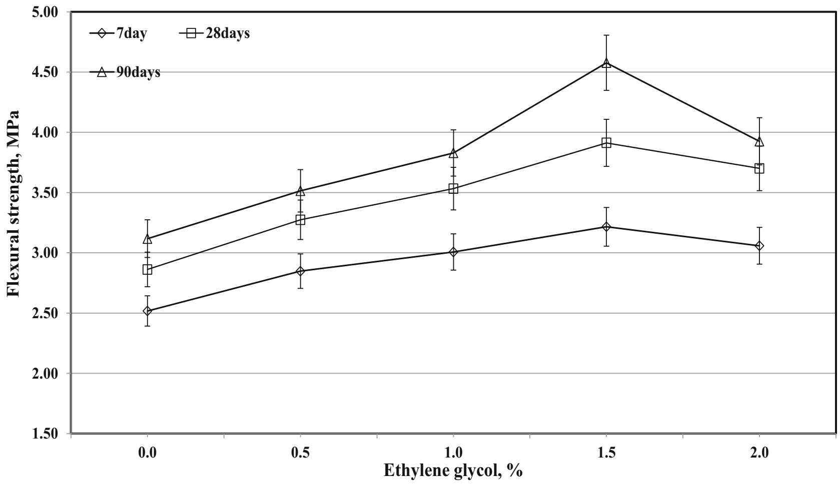


Fig. 8 Compressive strength of alkali-activated MK geopolymer specimens enhanced with various ratios of ethylene glycol

Fig. 9 Flexural strength of alkali-activated MK geopolymer specimens enhanced with various ratios of ethylene glycol



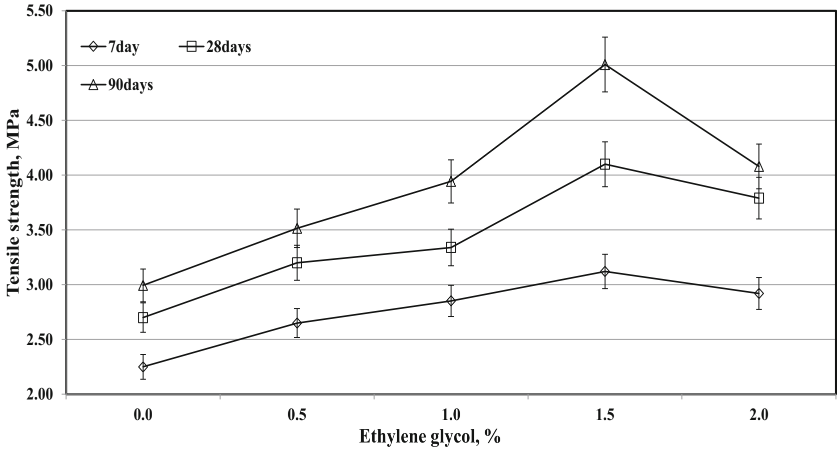
Mechanical properties

The results of mechanical properties (compressive, flexural, tensile strength) of metakaolin geopolymer composites enhanced with various ratios of ethylene glycol up to 2.0%, cured up to 90 days, are shown in Figs. 8, 9 and 10. The patterns illustrate an increase in mechanical strength values with EG up to 1.5% as well as with increasing curing time and then decreases with further EG. It can be seen from the figures also the increased flexural strength with ethylene glycol up to 1.5% giving about 4.6 MPa after 90 days and then decreases to about 3.9 MPa up on using 2% EG. On the other hand, tensile strength increased to about 5 MPa with EG increase to 1.5% as related to the increased elasticity with the aid of the hybridization between organic and inorganic polymers and then decreases to about 4.1 MPa with increasing EG to 2% which is still higher than control mix that give about 3.1 MPa after 90 days.

It is observed from Table 2, the molar oxide ratios were $SiO_2/Al_2O_3 = 2.05$, total alkalis/$Al_2O_3 = 0.369$, and total alkalis/$SiO_2 = 0.11$. From the previous data and as stated by Duxson et al. [34] for $Si/Al \geq 1.65$, the specimens showed a homogenous microstructure as elucidated from Fig. 7, where there is an increased compaction as revealed from interaction between geopolymer and organic polymer leading to an extra enhancement in matrix performance up to 1.5% as positively reflected on their mechanical properties, while increasing monomer to 2% results in an increased viscosity forming wide pores by the increased water content, as confirmed by the hygroscopic nature of the added monomer which reflected negatively on the matrix cohesion by increasing porosity and decreasing mechanical properties.

The increased strength with EG up to 1.5% emphasized by the activation for geopolymerization reaction by EG forming well compacted structure as compared with lower doses as well as control Mk-geopolymer composite. XRD, FTIR and SEM result showed that the amorphous phase, including organic and inorganic polymers were probably present during the geopolymerization of Mk powders which suggested that geopolymer–organic polymer composite had been formed. FTIR showed the bands of amorphous geopolymer at about 1030 cm^{-1} with shifting to lower wave number upon increasing EG to 1.5%, as confirmed by SEM which reflected the formation of well compacted and homogeneous composite

Fig. 10 Tensile strength of alkali-activated MK geopolymer specimens enhanced with various ratios of ethylene glycol



with high mechanical properties where EG is polymerized to form polyethylene glycol (PEG) in open pores under extremely alkaline condition and affecting positively compressive strength [29].

The results of compressive strength values that illustrate the strength gain for control mix can reach its final values faster than hybrid system [15] which possesses continuous hydration and polymerization rate that enrich the strength values with time, where the 7 days compressive strength of the control mix is about 20 MPa and reaches to about 31 MPa after 90 days. However, mix enriched with 1.5% EG encounters strength gain from about 33 MPa at 7 days to about 67 MPa at 90 days which can be considered more than 100% strength gain.

Also, the compressive strength gain reaches up to more than 100% as compared with control mix after 90 days up on adding 1.5% EG while the tensile and flexural strength increased by about 67% and 47%, respectively; however, 2% EG still possesses higher mechanical strength as compared with control mix as well as lower doses of EG. These results can offer dual organic and geopolymer composite with superior properties with high flexibility as well as high elasticity in addition to their high mechanical properties that can applied for various construction purposes. So the previous data enhance the production of well compacted and dense structure and favour high adhesion to steel substrates and so can be applied for steel coatings as well as for restoration of historic heritages [35–37].

Conclusions

The main concluded remarks are listed below:

1) Addition of ethylene glycol monomer to metakaolin geopolymer composites enhances morphological as well as mechanical characteristics up to 1.5% reaching to more than 100% compressive strength gain after 90 days.
2) Tensile and flexural strength gain up to more than 67 and 50% up on adding 1.5% EG after 90 days.
3) The FTIR, XRD and DTG proved an increased amorphous structure with EG up to 1.5%, whereas SEM confirms the compact and dense microstructure, while increasing EG to 2% results in an increased agglomeration as well as decrease the intensity of the formed geopolymer.
4) The total weight loss varied with ethylene glycol giving ~ 7.25, ~ 7.37, ~ 7.53 and ~ 6.85% for 0, 0.5, 1.5 and 2% ethylene glycol, respectively. The increased loss reflected an increased geopolymer content with glycol up to 1.5%, whereas these values were much lower than the pure organic polymer composites which possess weight loss between 50 and 80%.
5) The results can offer duel organic and geopolymer composite with superior properties that can be applied for various potential applications as steel coatings, restoration and conservation domain.

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