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Synthesis, spectroscopic and mechanical properties of K and (K, Na)-geopolymers based on Algerian clays

K. Bouguermouh[1*], N. Bouzidi[1], L. Mahtout[1], S. Rossignol[2]

[1] *University of Bejaia, Materials Technology Laboratory of Process Engineering (LTMGP). Targua Ouzemmour Road, Bejaia 06000, Algeria.*

[2] *Science des Procédés Céramiques et de Traitements de Surface (SPCTS), Ecole Nationale Supérieure de Céramique Industrielle, 12 rue Atlantis, 87068 Limoges Cedex, France.*

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bouguermouh.kari@yahoo.fr
(K. Bouguermouh);
Phone: +213669941164

Abstract

Algerian kaolinic clay from Tamazert and two alkalines solutions (potassium silicate and mixed potassium sodium silicate solutions) whose Si/K and Si/(K+Na) molar ratio of 0.58 and 0.80 respectively are used for the preparation of geopolymers. The raw material calcined at 750°C characterized by XRD and DTA/TG. The results carried out by infrared spectroscopy during the K-geopolymer formation process shows the observation of the displacement of the band located at 980 cm^{-1} which proves the reorganization of network and consequently the polymerization. It was demonstrated that mechanical properties by compressive strength of (Na,K)-geopolymer are higher than that recorded for K- geopolymer which are respectively 40 MPa and 16 MPa what allows their use in the field of construction.

1. Introduction

The term of geopolymer introduced in the 70s by the Professor Davidovits, defines a class of materials obtained by the reaction between aluminosilicate powder and an alkaline solution [1]. Basically, these materials were developed as alternatives to organic polymers. The first applications are therefore found in the field of shipbuilding [2], resins [3], protection of wooden structures [4], adhesives resistant to high temperatures [5, 6], refractory [7, 8]. Geopolymers are currently of considerable interest because of their good thermal [9], chemical [10] and mechanical properties [11] and their potential for use as a green cementitious binder. The geopolymer are based on the amorphous nature of these materials and the coordination numbers of silicon and aluminum. Their three dimensional structure is composed by SiO_4 and $MAlO_4$ tetrahedra, where M is a monovalent cation, typically Na^+ or K^+. This network is comparable to that of some zeolites but differs in its amorphous character. The polymeric character of these materials increases with the Si/Al ratio, as the aluminum atoms cross link chains of SiO_4 tetrahedra. In general, their chemical formulation is in the form $\{M^{+n}(SiO_2)z, AlO_2\}n$,wH_2O, where z is the Si/Al molar ratio, M^+ is the monovalent cation and n is the polymerization degree [1]. Altering the Si/Al ratio in geopolymers thus allows the synthesis of materials with different structures. The geopolymerization mechanism is particularly difficult to study. However, most authors agree that the mechanism involves dissolution, followed by gel polycondensation [12].

It is well known that the primary properties of geopolymer materials depend on (i) the alkali cation (Na^+ or K^+) and (ii) the Si/Al molar ratio [13]. However, regardless of the Si/Al ratio or the alkali cation used, one of the main parameters in the polycondensation reaction is related to the primary raw material, (i.e.: the aluminosilicate source). The use and the applications of geopolymers must be compatible with a large number of clay precursors containing secondary minerals, which come from clay deposits. According to the literature, studies on the influence of the raw materials appear to be focused on the nature of the primary raw materials, the presence of impurities and the role of the calcination temperature. Some papers report on the use of 2:1 clay minerals [14, 15] and metakaolin as the main precursor in the formation of geopolymeric products [14, 16, 17]. According to the literature, this practice is due to the high reactivity and purity of metakaolins compared to other materials [14]. However, source materials can also be byproducts of industrial processes, such as silica fume, slag and fly ash. Nevertheless, several studies have shown that ideal temperature for the calcination of kaolin to metakaolin is around 750°C [18, 19].

The aim of this work is the comparison between two geopolymers: K-geopolymer and (Na, K)–geopolymer based on calcined clay at 750°C from Tamazert (north eastern Algerian) actived with alkaline potassium silicate solution and mixed sodium and potassium silicate solution respectively and curing at 70°C. The products are characterized by XRD and FTIR. The water absorption and mechanical properties of the two materials are then compared.

2. Experimental

2.1. Raw materials and sample preparation

The raw materials used for the various syntheses are: calcined clay named MKT from Tamazert north eastern Algerian. The clay named KT was initially crushed and sieved through a sieve of 80 microns particle size, and then calcined at 750°C for 4 hours. Two commercial potassium and sodium silicate solutions were used, which were denoted as SiK and SiNa supplied by chemical labs (USA) whose water content of 76 wt % and 64 wt % respectively with Si/K and Si/Na molars ratios of 1.7 and pH values of 11.4 and 11.30, respectively. To compare the two alkaline solutions, the Si/K and Si/(K+Na) molars ratios were maintained at Si/K=0.58 and Si/(K+Na)=0.80 by dissolving potassium hydroxide pellets (VWR, 85.7 % pure) into the two starting silicate solutions. Then, calcined clay was added. The obtained mixtures were placed in a closed sealable polystyrene mold in an oven at 70°C for 24 h. The process of the obtained samples is presented on Figure 1. The compositions of the prepared mixtures are reported in Table 1. The samples were named GPK and GPKNa based on SiK+KOH and SiNa+KOH respectively.

Table 1: The composition and water absorption of the mixtures prepared according to the molar ratio of the species.

Samples	Si/K	Si/Na	Si/Al	Water absorption (wt%)
GPK	1.24	-	1.9	26
GPKNa	2.43	3.03	2.4	19

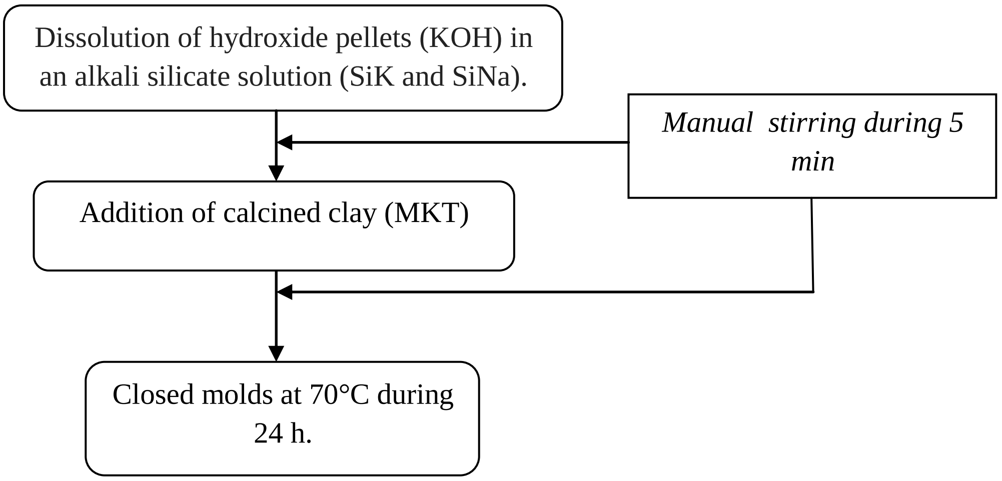


Figure1: Processing stages of geopolymer elaboration.

2.2. Sample characterization

2.2.1. X fluorescence analysis

The chemical composition of kaolin KT was determined by using the X fluoressence (PanAnalytical PerlX 3).

2.2.2. XRD analysis

The various diffractograms of the powders presented were obtained on an apparatus Brucker D 8 of Debye-Sherrer type using radiation Cu Kα (λKα = 1.5406 Å) and a back graphite monochromator. The range of analysis lies between 5 and 60° with a step of 0.02° and a time of acquisition of 8 s. the crystalline phases present in material are identified by comparison with standards pdf (Powder Diffraction Files) of the ICDD (International Center for Diffraction Dated).

2.2.3. FTIR analysis

Differential thermal analyses (DTA) and thermogravimetric analyses (TG) were performed with the sample held in a Pt crucible between 25°C and 1200°C using a SDTQ600V20.9. The sample was heated at a rate of 5° C min^{-1} in a dry air low.

FTIR spectra were acquired using a Thermo Fisher Scientific 380 infrared spectrometer (Nicolet) via the attenuated total reflection (ATR) method. The IR spectra were acquired between 500 and 4000 cm^{-1} with a resolution of 4 cm^{-1}. A macro was used to monitor the geopolymer formation, which enabled the acquisition of spectra (64 scans) every 10 min for 13 h. The acquisition began with the deposition of a drop of sample onto a diamond substrate. Ultimately, 72 overlaid raw spectra were obtained and corrected to remove contributions from atmospheric CO_2 between 2400 and 2280 cm^{-1}. The spectra were also corrected using a baseline, which was used to normalize the spectra, and then the spectra were compared. Monitoring the material during formation enabled the geopolymerization process to be observed, which was shown by the variation of the main peak position observed at approximately 980 cm^{-1}.

2.2.4. Compressive strength

Mechanical compressive tests were performed on a Lloyd EZ 20 load testing machine. Eight cylindrical specimens for each formulation whose diameter was set at 15 mm and length equal to twice the diameter were tested with a maximum compression of 20 kN. The measurement of displacement was given by the crosshead displacement. The specimen was placed between two compressive modules, and the inferior modulus was equipped with a ball for better load alignment during testing. The compressive tests were performed until the sample rupture data constant displacement velocity of 0.1 mm/min.

2.2.5. Water absorption measurement

Water absorption test was carried out on GPK and GPKNa geopolymers; this test consist on weighing samples of cylindrical shape previously heated at 105°C in an oven and record the initial mass (m_i), then emerged in distilled water and carried to boiling for 2 hours then weighting samples after wiping with absorbent paper, the mass was noted at the end (m_f) calculating the % absorption is done using the (Eq. (1)) [20]:

$$\%Abs=((mi-mf)/mf)\times 100 \qquad (1)$$

3. Results and discussions

3.1. Raw material investigation

The chemical composition results are listed in (Table 2) which shows that the KT clay is composed mainly of 50 wt % SiO_2, 33 wt % Al_2O_3. L.O.I (loss on ignition) is equal to 11.38 less than that of perfect kaolinite which is 14 wt %. Mineralogical analysis shows that the mass ratio SiO_2/Al_2O_3 is 1.52 whereas of about 1.1 for pure kaolin. This discrepancy suggests the presence of free silica (quartz) [21].

Table 2: Chemical and mineralogical composition of kaolin KT.

Oxides (%)	KT
SiO_2	49.56
Al_2O_3	32.66
Fe_2O_3	2.18
TiO_2	0.39
CaO	0,12
MgO	0.46
K_2O	2.94
Na_2O	0.18
P_2O_5	0.16
LOI	11.38

SiO_2/Al_2O_3	1.52

LOI : loss on ignition

The thermogram of KT clay (Figure 2) shows two endothermic phenomena: the first is at approximately 50°C which is accompanied by a weight loss of 3 wt % and is related to the elimination of physisorbed water, and the second of low intensity at approximately 200°C due to the presence of organic matter. An endothermic phenomenon around 480°C which is accompanied by a weight loss of 8.7 wt % and arises from the structural dehydroxylation of kaolinite. In addition, an exothermic peak at 970°C which is attributed for the transformation of metakaolin (i.e: structural reorganization of metakaolin) to mullite [22-24]. The kaolinite content is estimated to be 50 % based on the mass loss at approximately 490°C.

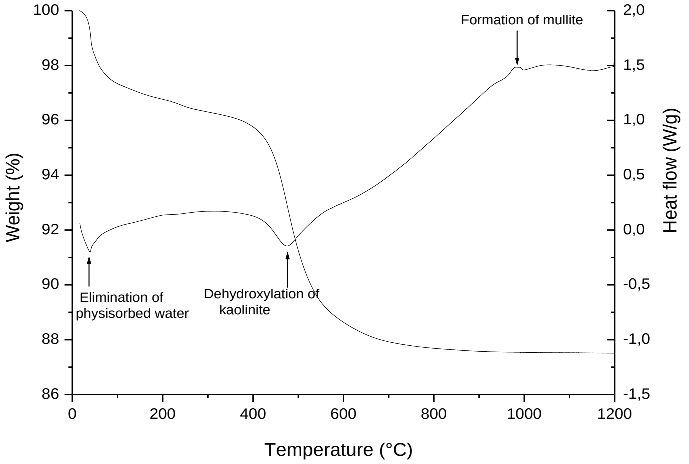


Figure 2: Thermal curves **(**DTA-TGA) of KT clay.

The X-ray diffractogram of KT clay presented in Figure 3 shows that the product is a complexe mixture of several mineralogical phases; we note that the kaolinite is the majority mineralogical phase. Further, there is existence of impurities: quartz, muscovite and much less of albite. After calcinations at 750°C for 4h peaks corresponding to kaolinite disappear. In addition, the peaks related to quartz and muscovite remains unchanged after heat treatment. During the heat treatment (Figure 3) peaks corresponding to kaolinite, disappear due to the formation of metakaolin (the dehydrated kaolinite) or amorphization of metakaolinite represented by the dome at 22-32 °2θ, the heat treatment therefore causes the transition from a crystalline (kaolinite) in a disordered phase (metakaolinite) by a collapse of the crystal lattice phase, as confirmed in the thermogravimetric analysis shown in Figure 2. From these data, clay KT appears to have greater abundance of kaolinite which transform to metakaolinite after calcination and other secondary minerals as quartz and muscovite are also found in XRD spectra results which is in agreement with those deducted from DTA/TG analysis.

3.2. Characterization of binders based on geopolymer formulations

3.2.1. Preparation of geopolymers

During the preparation of geopolymers, we note that the potassium alkaline solution is less viscous compared to that mixed potassium and sodium silicate alkaline solution consequently the paste of GPK is less viscous than of GPKNa. Figure 4 shows Photos of developed materials; the cylindrical specimens (GPK and GPKNa) treated at 70°C for 24 h, were left 7 days at laboratory temperature. Then, they were released from their casting paste. Finally, the samples were shaped. We note that samples have the same color as the starting calcined clay raw material. At the end of processing and drying, the samples do not undergo warping but only a change in color which depends on the temperature and the content of coloring impurities such as Fe_2O_3 and TiO_2 [25]; the valence state of Fe^{2+} and Fe^{3+} accentuates the color turning beige (room temperature) to red brick after heat treatment at 750°C and show efflorescence because of chemical reaction between the excess potassium hydroxide dissolved in the material and the carbon dioxide contained in the air [26].

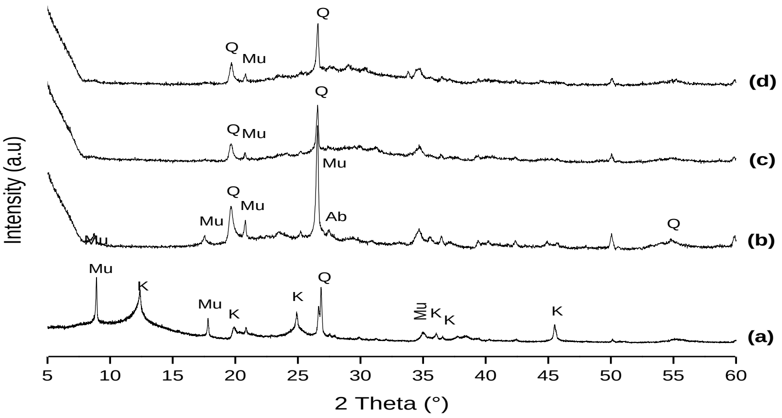


Figure 3: Patterns of (a): clay KT, (b): Calcined clay MKT, (c): GPK and (d): GPKNa geopolymers (K: Kaolinite (00-001-0527), Q : Quartz (00-001-0649), Mu : Muuscovite (00-002-0467 and Al : Albite (00-009-0466)).

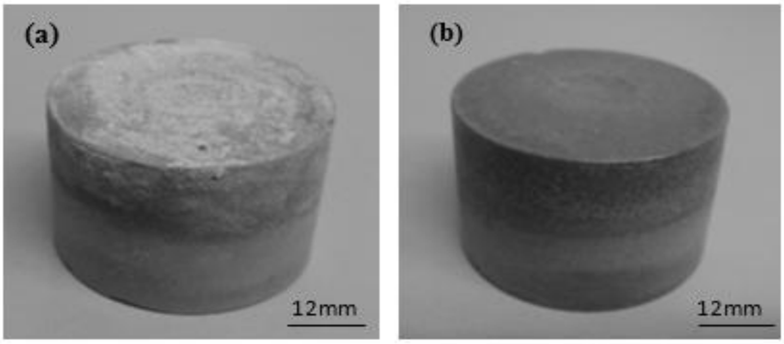


Figure 4: Photos of (a): GPK and (b): GPKNa geopolymers.

3.2.2. FTIR analysis

Figure 5(a) shows that the main band of geopolymer based on potassium (K- geopolymer) located at approximately 980 cm^{-1} is attributed to Si-O-Si. This last moves from 981.82 cm^{-1} to 963.16 cm^{-1} during formation as it is shown in Figure 5(b). There is also the presence of other bands which is visible in the infrared spectrum; The bands between 3400-3200 cm^{-1} and between 1654 and 1639 cm^{-1} are attributed to stretching vibrations (H-O) and deformation (H-O-H) in the water molecules absorbed or present in cavities in the geopolymers structure [16, 17, 22- 24]. The bond located at 1397 cm^{-1} is designed as characteristic of HCO_3^-, and 1374 cm^{-1} and 1459 cm^{-1} are identified as characteristic peaks of CO_3^{2-} [25].

Considering the rich content of K in the geopolymer and the high efflorescence of GPK (Figure 4), the carbonate species must be in the form of K_2CO_3 and $KHCO_3$. The atmospheric CO_2 can be absorbed in water on the surface or in the pores of fresh samples, in alkaline environment; this CO_2 can react quickly with the OH^- ion to produce HCO_3^- species, as in Eq. (2). Longer exposure to air allows for continued reaction of HCO_3^- species with OH^-, forming CO_3^{2-} species, as indicated in Eq. (3). The appearance of $KHCO_3$ and K_2CO_3 species (Figure 5(a)) proves this point, as does the existence of excessive KOH after the geopolymerization process. Part of this excessive KOH reacts quickly with atmospheric CO_2 to form carbonate upon exposure to air [26].

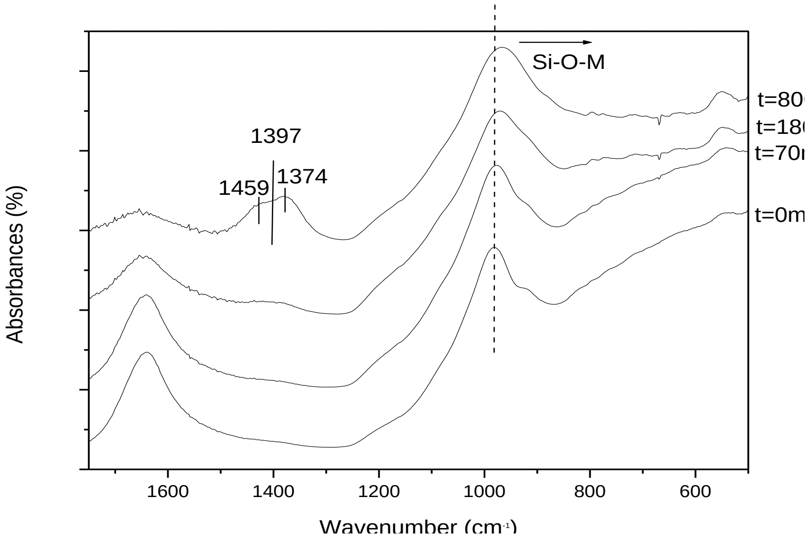
$$CO_2 + OH^- \longrightarrow HCO_3^- \qquad (2)$$

$$HCO_3^- + OH^- \longrightarrow CO_3^{2-} + H_2O \qquad (3)$$

The observed shift in figure 5(b) indicates the substitution of Si-O-Si bonds by Si-O-Al bonds within the material. In the case of geopolymer based on potassium (K- geopolymer), the main band moves from 981.82 cm^{-1} to 963.16 cm^{-1} during formation and the observed shift value is 19 cm^{-1} This value is characteristic of the formation of an aluminosilicate network [27] through an increase in the substitution of Si-O-Si bonds with Si-O-Al bonds.

The results of the ATR-mode measurement of the polycondensation rate prove the reactivity of calcined clay from Tamazert in an alkaline potassium silicate solution (Si/K=0.58) which allows its use in the field of the geopolymers.

(a)



(b)

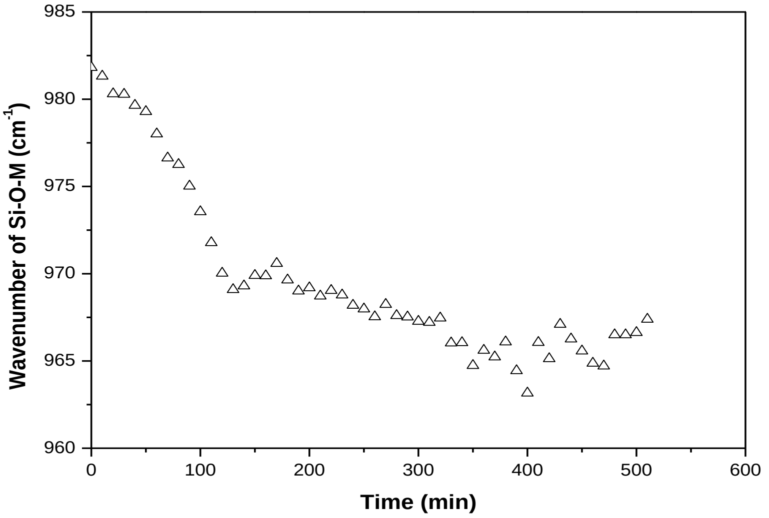


Figure 5: (a): FTIR spectra recorded during the formation during 800 min and (b): Displacement of the main band of GPK geopolymer.

3.2.3. XRD analysis

According to Figure 3, the diffractograms of geopolymers show that GPK and GPKNa have a semi- crystalline structure due to appearance of a dome at (22°2θ-32°2θ) and persistence of peaks corresponding to quartz and muscovite but their intensities were slightly lower, and after geopolymerization process, peak at (33.86 ° 2θ) appear.

The XRD patterns of raw materials and resulting geopolymers indicate that the crystallized components in the raw materials are more difficult to dissolve and hence those unreactive crystals remain as fillers in the resulting geopolymer composites. In the XRD patterns of GPK, and GPKNa geopolymer samples, there is a broad hump in the range of 22–32°2θ, which is the typical XRD pattern for the amorphous geopolymer. However, because of the high peak of quartz, the geopolymer hump is less apparent. Some peaks from the raw materials remained in the corresponding geopolymer patterns, but with reduced intensity, which is attributed to the unreacted crystalline contents, such as the quartz around 20°2θ and 26°2θ, and the Muscovite around 35°2θ [28]. It has been shown that quartz is unreactive widely [29], the persistence of peaks corresponding to the quartz and muscovite in X -ray diffraction patterns of the two types of geopolymer indicates that it does not participate in the geopolymerisation process, but their intensities were slightly lower due to a dilution effect [29,30]. After geopolymerization process, peak (33.86°2θ) appears, this last is more intense in the diffractogram of GPKNa than GPK this is due to the formation of alluminosilicate gel [29].

3.2.4. Water absorption study

The water absorption results (table 1) carried out three months after the preparation. These results show that the water absorption of the two samples is high, the GPK geopolymer water absorption is 26 wt % greater than those recorded to GPKNa geopolymer which is equal to 19 wt %. Therefore, the material based on (Na,K)-geopolymer is less porous than K-geopolymer. A previous study of Steins et al. [31] shows that the use of two alkali ions (Na + and K +) differing by their size and by their kosmotropic or chaotropic properties allowed us to demonstrate that pore size, shape and distribution depend on the alkali activator. The potassium geopolymer has a greater specific surface area than the sodium geopolymer because the pores are smaller and more numerous. In the other hand, according to the scattering results, therefore the most striking difference between sodium silicate solution and potassium silicate solution is the disparity in their respective viscosities [32], which may be due to the differing extents of hydration of Na^+ and K^+. This reflects the small concentration of free water in the sodium silicate solution as compared to that in the potassium silicate solution. However, the viscosity of the initial mixture is a very important parameter for the geopolymerisation process, and can influence the structure, porosity, pore distribution, pores diameter, etc.[33]. Prud'homme et al [13] in the case of in situ geopolymer foam formation, found that the viscosity increases during formation due to the reaction temperature, 70°C, which causes a significant loss of water. Thus, the balancing foam formation requires a particular viscosity, and the departure of water increases the viscosity and hinders the development of bubbles [13]. Thus, the pore samples structure depends primarily on the heat treatment and increasing the compressive strength is possibly a result of a continuous geopolymerization without hydration.

3.2.5. Compressive test

Figure 6 shows the compression test results which are performed on eight samples for each composition. The results show that the GPKNa specimens has an elastic behavior with a brittle failure, whereas, GPK samples have a ductile elastic behavior with a strong softening phase before specimen failure characterizing the resistance of the material to the sudden propagation of cracks. However, the geopolymer GPKNa ((Na,K)-geopolymer) whose Si/Al molar ratio equal to 2.4 gives a resistance to the compressive force of 40 MPa higher than that recorded for the GPK geopolymer whose Si/Al molar ratio is 1.9 and gives 16 MPa. Indeed, previous studies have shown that the mixed-alkali specimens exhibit strengths in excess of the Na or K systems, which may be the result of a 'mixed-alkali effect' (MAE) [34].

The mechanical properties of geopolymers may be understood by applying the existing knowledge of the effects of alkali cation on the molecular structure of an aluminosilicate framework. However, the current understanding of geopolymerization does not extend so far as to include aspects of alkali interactions, especially at high Si/Al ratio, that may account for the emergence of a positive MAE, which is observed to become more prominent over time and the deterioration of strength in pure alkali specimens. There has been limited study into the mechanical properties of mixed alkali aluminosilicate materials, namely because the MAE is primarily concerned with processes that involve the transport of ions within a material structure [34]. As such, there has been little investigation of the mechanism of mixed-alkali interactions in terms of mechanical properties.

Duxson suggested that alkali metal cations have a role of against load anions with $Al\ (OH)^{4-}$ in the pores for Si/Al < 1.40. For higher ratios of Si/Al, the $Al\ (OH)^{4-}$concentration's and aqueous alkali were decreased. Theoretically, any type of alkaline metal can be used for the synthesis of geopolymer; however, most authors have focused their work on the use of sodium and potassium ions [35,36]. Na^+ cation have a smaller size than K^+, and display strong pair formation with smaller silicate oligomers (such as monomers). But due to their large sizes, K^+ cations favor the formation of larger silicate oligomers with which $Al(OH)^{4-}$ prefers to bind [35-37].

The addition of KOH tends to increase the degree of polycondensation in alkali metal silicate solutions, while the addition of NaOH may increase the quantity of monomeric silicates. It is generally admitted that both Na^+ and K^+ change the degree of polycondensation but in different ways, and it is observed in this case that both undergo dissolution and ionization reactions at different rates [36, 37]. According to Van Jaarsveld alkali metal cations change in almost all stages of geopolymerization and in particular during gel hardening and crystal formation, since cations contribute to the structure formation of geopolymers [38]. Besides, the type and the composition of alkali metal control the development of the mechanical properties of geopolymers [37, 39-41].

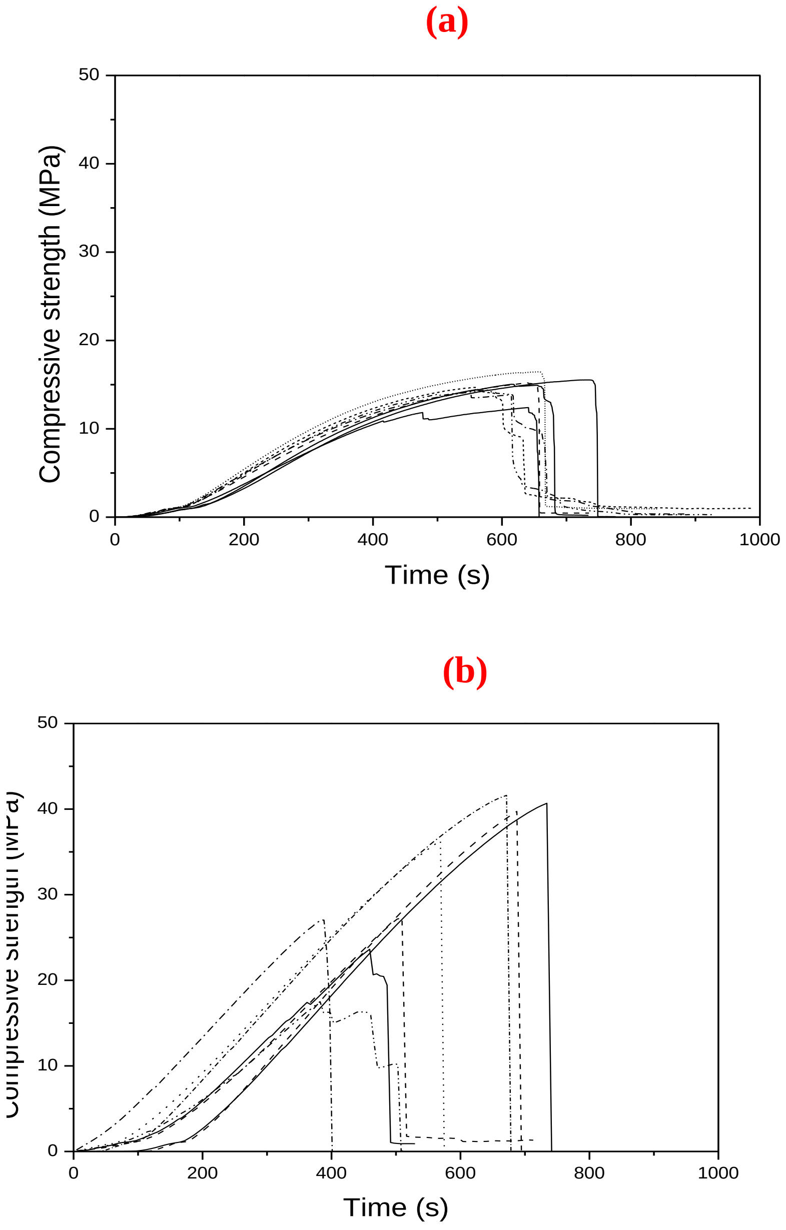


Figure 6: Compressive strength of (a): GPK and (b): GPKNa geopolymers.

5. Conclusions

Algerian clay from Tamazert is reached in kaolinitre according to XRD and DTA/TG results what allows its use in field of geopolymers. Two alkalines solutions of potassium silicate and mixed alkalis silicate solutions were used to synthesis two geopolymers which were characterized by FTIR, XRD, water absorption and compressive strength. Results show that:

i) Algerian clays from Tamazert show a good reactivity in alkaline potassium silicate solution (Si/K=0.58) according to ATR-mode measurement.

ii) Geopolymers have a semi- crystalline structure due to the persistence of non-reactive phases such as quartz and muscovite.
iii) The type of alkali silicate solution, namely potassium and sodium silicate solution used in the formulation of geopolymers plays an important role in the porous structure and consequently the resistance to the compression force of the final material.

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