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GEOPOLYMERNÍ KOMPOZITNÍ SYSTÉMY VYZTUŽENÉ VLÁKNY MIKROMETROVÝCH, SUBMIKROMETROVÝCH A NANOMETROVÝCH ROZMĚRŮ - PŘÍPRAVA A MECHANICKÉ VLASTNOSTI

GEOPOLYMER COMPOSITE SYSTEMS REINFORCED BY MICROFIBERS, SUBMICROFIBERS AND NANOFIBERS: STUDY OF PROCESSING AND MECHANICAL PROPERTIES

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DECLARATION

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ABSTRAKT

Tématem práce je studium přípravy geopolymerních kompozitních systémů vyztužených vlákny mikrometrových, submikrometrových a nanometrových rozměrů a hodnocení jejich vybraných mechanických vlastností. Vyztužujícími vlákny byla recyklovaná uhlíková vlákna a komerční nanovlákna na bázi oxidu křemičitého. Geopolymerní matrice byla připravována z komerčního produktu s označením Bauxis L 160.

Vzorky byly připravovány ze základní geopolymerní matrice, do které byla přidávána vlákna odlišných rozměrů a složení a v rozdílném množství. Systémy byly připravovány standardním způsobem – odléváním směsí do forem. Z forem byly po základní době vytvrzování vyjmuty a poté dotvrzovány při rozdílných teplotách a to v rozmezí od laboratorní teploty až po teploty 900^0C. Základní doba vytvrzování činila 24 hodin, doba dotvrzování při zvýšených teplotách byla proměnlivá. Na základě znalostí o procesu vytvrzování geopolymerních materiálů byly všechny vzorky testovány až po 28 dnech.

Pro hodnocení vlivu krátkovlákenného plniva na geopolymerní matrici byla na základě zkušeností z předchozích prací zvolena zkouška tlakem, která byla doplněna zkouškou houževnatosti. Homogenita rozložení vláken a jejich adheze k matrici byla posuzována na základě snímků z rastrovacího elektronového mikroskopu. K základnímu hodnocení chemického složení byla použita EDX analýza.

Z výsledků provedených experimentů je zřejmé, že přídavek vyztužujících vláken všech uvedených rozměrů vede ke zvýšení mechanických vlastností a to jak meze pevnosti, tak modulu pružnosti. V případě recyklovaných uhlíkových vláken mikrometrových rozměrů bylo nejvyšších hodnot dosaženo při plnění 8%, kdy dochází ke zvýšení meze pevnosti na 42,4 MPa oproti 22,3 MPa u neplněné geopolymerní matrice. V případě recyklovaných uhlíkových vláken submikrometrových rozměrů byla zaznamenána nejvyšší hodnota meze pevnosti 39,8 MPa při plnění 0,7 %. Nanovlákna oxidu křemičitého mají největší vliv, neboť mez pevnosti dosahuje až 49,7 MPa při plnění 0,7%. Kombinace výztuží obou typů v poměru 0,5% submikrometrových vláken a 0,5% nanovláken oxidu křemičitého vedla k dosažení hodnoty meze pevnosti 41,8 MPa. Použitím nanovláken bylo sice dosaženo nejvyšších hodnot zkoumaných mechanických parametrů, ale tato vlákna jsou oproti uhlíkovým vláknům drahá a není zcela ověřen jejich vliv na živý organismus. Při dalším plnění dochází k rychlému poklesu mechanických vlastností, které jsou vysvětlovány nadměrným množstvím vláken v matrici a zvýšením nehomogenity systému.

Ke zvýšení zkoumaných mechanických vlastností vlivem výše uvedených plniv dochází i navzdory špatné adhezi mezi uhlíkovými vlákny a geopolymerní matricí. Optimálním teplotním intervalem pro vytvrzování navržených systémů byl nalezen rozsah 60^0C až 100^0C. Doba vytvrzování při těchto teplotách je obvykle 24 hodin, následně dochází k dotvrzování při laboratorní teplotě. Při vyšších teplotách sice dochází k dokonalejšímu rozpouštění částic geopolymeru, které poté vytvářejí homogennější matrici, ale voda nacházející se v systému se mění ve vodní páru, následkem tohoto procesu se tvoří porézní struktura a dochází ke snížení mechanických vlastností.

Optimálním plnivem geopolymerní matrice jsou na základě provedených experimentů recyklovaná uhlíková vlákna submikrometrových rozměrů. Při použití tohoto plniva v tomto rozměru dochází ke zvýšení meze pevnosti v tlaku na 39,8 MPa ačkoli je použito množství vláken menší než 1%, respektive 0,7%.

Klíčová slova: geopolymerní kompozitní systémy, recyklovaná uhlíková vlákna, nanovlákna oxidu křemičitého, vytvrzování geopolymeru, mechanické vlastnosti.

ABSTRACT
The theme of the thesis is the preparation of geopolymer composite systems reinforced by micron, submicron and nanometer scale fibre and the evaluation of their selected mechanical properties. As reinforcing fibres have been selected recycled carbon fibres and commercial silicone dioxide nanofibres. Geopolymer matrix was prepared from the commercial product with brand the Baucis L 160.
Samples were prepared from the basic geopolymeric matrix which was filled by fibres of different dimensions and composition and in different amounts. Systems were prepared in a standard manner - casting of mixtures into molds. Samples were took out from the molds after the primary curing time and then post-cured at different temperatures in range from room temperature to 900^{0}C temperature. Basic curing time of systems was 24 hours, the time of hardening at different higher temperatures was variable. Based on the knowledge about the process of hardening of geopolymer materials, all samples were tested after 28 days.
Based on the knowledge from the previous thesis the compressive strength was used to evaluation of influence of short fibre filler to geopolymer matrix. The compressive strength was completed by the evaluation of composite system toughness. The homogeneity of fibres distribution and their adhesion to the geopolymer matrix was evaluated on the basis of the scanning electron microscope micrographs. The EDX analysis was used to the evaluation of the basic chemical composition.
The results of the experiments show evident increase of the mechanical parameters - the compressive strength and modulus due to adding of reinforcing fillers. In the case of recycled carbon fibre in micrometer dimension, the highest values were obtained in the performance of 8%, which leads to increase in strength MPa to 42.4 MPa versus 22.3 for unfilled geopolymer matrix. In the case of recycled carbon fibre in submicron dimensions were recorded the highest value of yield strength of 39.8 MPa in the performance of 0.7%. Silica nanofibers have the greatest impact, as ultimate tensile strength of up to 49.7 MPa in the performance of 0.7%. Combinations of both types of reinforcement in a proportion of 0.5% submicron carbon fibres and 0.5% of silica nanofibres led to achieve values of yield strength of 41.8 MPa. Nanofibers shows the highest values of mechanical parameters, but these fibres are expensive compared to carbon fibres and it is not verified their effects on living organisms. Due to next filling of geopolymer matrix a rapid decrease in mechanical properties was recorded. This behaviour can be explained by excessive amounts of fibres in the matrix and increasing inhomogeneity of the system.
The increase of the examined mechanical properties is achieved by the aforementioned fillers influence in spite of the poor adhesion between carbon fibres and geopolymeric matrix. The optimal temperature curing interval of proposed systems was found in the range 60^{0}C to 100^{0}C. Curing times at these temperatures is generally 24 hours, followed by post-curing occurs at room temperature. At higher temperatures more efficient dissolution of geopolymer particles runs and forms a more homogeneous matrix, but the water found in the system turns into water vapour. As a result of this process highly porous structure creates and reduces the mechanical properties of system.
Based on the experiments the optimal filler for geopolymeric matrix are recycled carbon fibres of submicron dimensions. Using the filler in this dimension increases the compression strength at 39.8 MPa, although the fibres amount is less than 1% exactly 0.7%.

Keywords: geopolymer composite systems, recycled carbon fibres, silicone dioxide nanofibers, geopolymer curing, mechanical properties.

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1 INTRODUCTION

1.1 Generation

After wood, concrete is the most often used material in industry. Concrete is made from the ordinary Portland cement (OPC) as the primary binder. The environmental issues associated with the production of OPC are well known, during the production of Portland cement is consumed large amount of energy and at the same time is contributed a large volume of CO_2 into the atmosphere.

The taxes related to CO_2 and energy consumtion are focusing essentially on fuel consumption, not on actual CO_2 emission measured at the chimneys. Ordinary Portland cement used in the aggregates industries, results from the calcination of limestone (calcium carbonate) and silica according to the reaction:

$5CaCO_3 + 2SiO_2 \Rightarrow (3CaO, SiO_2)(2CaO, SiO_2) + 5CO_2$ (1-1)

The production of 1 tonne of cement directly creates a 0.55 tonne of chemical CO_2 and requires about 0.4 tonne of CO_2 to combustion of carbon-fuel. To simplify: 1 T of cement = 1 T of CO_2 [1].

Geopolymers have been developed mostly by French researcher Joseph Davidovits but the advancement of these materials to current base of knowledge has been done by all over the world [2]. Davidovits [3], [4] 1978 named that kind of material as Geopolymers, and stated that these binders can be produced by a polymeric synthesis of the alkali activated material from geological origin or by-product materials such as the fly ash and the rice husk ash.

On the opposite, geopolymer cements do not make a use of calcium carbonate and therefore generate much less of CO_2 during the production, i.e. a reduction in the range of 40% to 80-90% [1], [5]. With similar investment, lower energy cost, and identical carbon dioxide emission, the chemistry enables the producing of 5 to 10 times more of geopolymer cement than Portland cement technology. Siutable not only for environmental uses, but also for construction and civil engineering. Its use would reduce a carbon-dioxide emission caused by the cement and concrete industries by 80 to 90% [1].

Some of the literature sources mention the term “geopolymer” as a matrix consisting of an aluminosilicate source (such as metakaoline, furnace slag, fly ash, mineral clay,

mine tailing...) which is activated by the alkaline potassium/sodium silicate solution at ambient temperature or slightly elevated temperature [4]. It has two kinds of networks- polysialate and siloxane bonds are built of chain Al-O-Si in polysialate and siloxane with Si-O-Si bonds. The chemistry of polysialate forms the basis tool of microstructural properties of geopolymer. The chemical compositions of geopolymer are similar to zeolite. The difference between geopolymer and zeolite can be seen using the Xray study which shows an amorphous structure of geopolymer and highly crystalline structure of zeolites [4], [6].
The common properties of geopolymer have been listed as [4], [6]–[11]:

- ✓ Average density of 2.1g/cm^3
- ✓ Largely amorphous structure
- ✓ Contains aggregates of slag
- ✓ Micro-cracks are prevalent
- ✓ Withstand at high temperature (up to 1200^{0}C)
- ✓ Acid resistance with approximately 7% break down in 5% H_2SO_4
- ✓ Excellent mechanical properties
- ✓ Simple preparation technique

In general, geopolymers with a Si/Al ratio of 1 to 2 will present a rigid three-dimensional network and may be used for bricks, ceramics, cements, concretes but also for fire protection and the immobilisation of nuclear and toxic waste [4]. These are products and applications normally known in connection with cement and ash.

1.2 Aims of the research

As mentioned earlier, the most of the published research about geopolymers and composite materials based on long reinforcing fibres (carbon fibres, glass fibres, basalt fibres) studied the behaviour of pastes with the various types of source materials. The present study deals with the manufacture of short fibers-based geopolymer concrete, the parameters influencing the mixture proportioning, and the short-term engineering properties in the hardened states.
The aims of research are:
A. Preparation of geopolymer matrix and its characterization
- Mechanical properties of pure geopolymer matrix
- Structure of pure geopolymer matrix

B. Preparation of geopolymer composites with different types of fibres and their characterization (carbon micro fibres, submicro carbon fiber and silicon dioxide fibres)
- Mechanical properties of fibres reinforced geopolymer matrix
- Structure of fibres reinforced geopolymer matrix

Experiments of the study were directing systematically. The main properties of the reinforced geocomposite system, include:

1. Microstructure and mechanical properties of selected geopolymer matrix.
2. Effect of curing time on mechanical properties of selected geoploymers reinforced by fibres.
3. Effect of curing temperature on mechanical properties of selected fibers reinforced geopolymer.
4. Optimal percentage of fibers for the geocomposite system.

5. Observation of mechanical properties of geopolymer composite systems at high temperature.
6. Mechanism of reinforcing geopolymer by selected fibers.

1.3 Thesis Arrangement

The rest of the thesis is arranged as follow: Chapter 2 describes the theory about geopolymers, reinforced geopolymer by short fibers and also provides a brief literature review of geopolymer technology.
Chapter 3 describes the experimental work which was carried out to develop the mixture proportions, the mixing process, and the curing regime of geopolymer concrete. The tests performed to study the behaviour and characteristics of pure geopolymer are described.
Chapter 4 reports about the effect of curing time and curing temperature on mechanical properties of nanofiber SiO_2 based geopolymer, mechanical properties of reinforced geopolymer by carbon microfibers at high temperature. It indicates the effect of elevated temperature on mechanical properties of reinforced geopolymer by carbon sub-microfibers from room temperature to high temperature. In this chapter, mechanism of fibers reinforced geopolymer was also investigated.
Chapter 5 presents the conclusions and recommendations for further research.

2 LITERATURE REVIEW

This chapter provides an introduction to theory about geopolymers and properties of selected synthesis fibres used as a reinforcement in geopolymer composite systems. The available published literature about geopolymer technology is also briefly reviewed.

2.1 Geopolymers

2.1.1 Geopolymer terminology

The term "geopolymer" has been firstly used in 1979 by a French professor Joseph Davidovits [4]. Some literature refers the term "geopolymer" as a matrix consisting of an aluminosilicate source (usually in the form of fly ash, metakaolin and blast furnace slag) which is activated by an alkaline sodium/potassium silicate solution at ambient conditions or slightly elevated temperatures [12]. Geopolymers are a member of the family of inorganic polymers with a chain structures formed on a backbone of Al and Si ions. The chemical composition of this geopolymer material is similar to the natural zeolitic materials, but they have an amorphous microstructure instead of crystalline [4], [8], [13], [14]. The structure of prezeolite gel contains of Si and Al tetrahedral randomly distributed along the polymeric chains that are cross-linked so as to create cavities of sufficient size to adapt to the charge of balancing hydrated sodium ions. Davidovits [6] defined that the amorpohous to the semi-crystalline three dimensional silico-aluminate structures as the geopolymers based on silico-aluminate. Davidovits [6] further categorised the geopolymers structure based on the ratio of Si/Al following:

Polysialate: M_n – (– Si–O–Al–O–)n with Si:Al=1:1
Polysialate-siloxo: M_n – (–Si–O–Al–O–Si–O–)n with Si:Al=2:1
Polysialate-disiloxo: M_n – (–Si–O–Al–O–Si–O–Si–O–)n with Si:Al=3:1

(M is monovalent cation such as Na^+ or K^+, n is the degree of polycondensation).

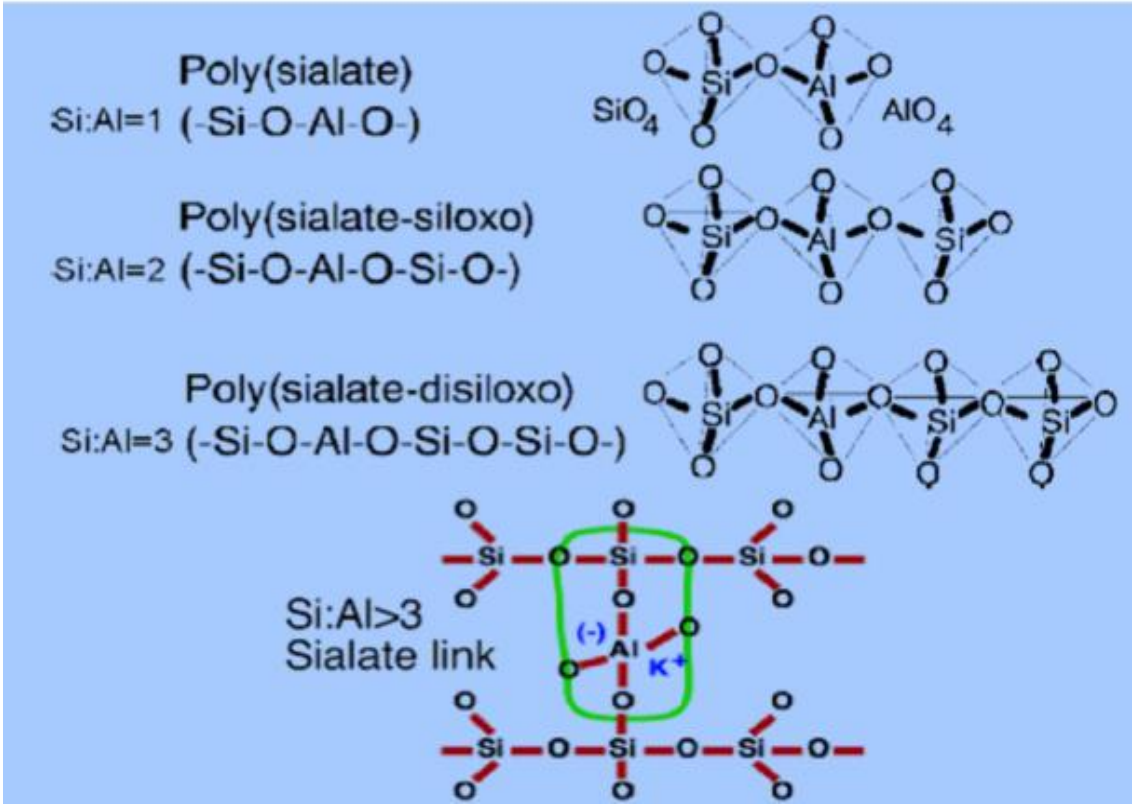

Figure 2.1 The model of the geopolymer structure [3], [4], [15]

And polysialate-multisiloxo with Si:Al > 3:1, the polymeric structure results from the cross linking of poly(silicate) chains, sheets or networks with a sialate link (–Si–O–Al–O–).

The common properties of geopolymers have been recorded as [13], [16]:

- ✓ Average density of 2.1 g/cm^3
- ✓ Amorphous structure
- ✓ Contains aggregates of slag on addition
- ✓ Micro-cracks are prevalent
- ✓ Average compressive strength of 35 MPa (even though much higher strengths have been proven under specific conditions).
- ✓ Acid resistance with approximately 7% breakdown in 5% H_2SO_4.

2.1.2 Process of geopolymerization

Any material that contains mostly silicon (Si) and aluminium (Al) in amorphous form can be used for the manufacture of geopolymer. Several minerals and industrial by-product materials have been investigated in the past. Metakaolin or calcined kaolin [3], [17], ASTM Class F fly ash [18], [19], natural Al-Si mineral [14], combination of calcined minerals and non calcined materials [13], combination of fly ash and metakaolin [13], [19], and combination of granulated blast furnace slag and metakaolin were investigated as source of materials for making geopolymers. Metakaolin is preferred by product developers of geopolymers due to its high rate of dissolution in the reactant solution, easier control of the Si/Al ratio and the white colour [20]. However, for making concrete in a mass production state, metakaolin is very expensive. United States Geological Survey estimates that the U.S. was the largest producer of the raw kaolin clay from which metakaolin is produced. In 2009, U.S. produced 5.2 milion tons of metakalolin; other major producers include the

Czech Republic (3.4 Mt), Germany (3.2 Mt), and Brazil (2.1 Mt), which was widely expected to pass the U.S. as the world's largest kaolin exporter by 2013 [21], [22].
Davidovits [3] calcined kaolin clay for 6 hours at 750^0C. He termed this metakaolin as KANDOXI (KAolinite, Nacrite, Dickite Oxide), and used it to make geopolymers. For the purpose of making geopolymer concrete, he suggested that the molar ratio of Si-to-Al of the material should be about 2.0.
Due to the nature of the source material, it was stated that the calcined source materials, such as fly ash, slag, calcined kaolin, demonstrated a higher final compressive strength compared to those made using non-calcined materials, for instance kaolin clay, mine tailings, and naturally occurring minerals[17]. However, Xu and van Deventer [13], [23] found out that using a combination of calcined (e.g. fly ash) and non-calcined material (e.g. kaolinite or kaolin clay and albite) resulted in significant improvement in compressive strength and reduction of reaction time.
Natural Al-Si minerals have shown the potential to be the source materials for geopolymerisation, although quantitative prediction on the suitability of the specific mineral as the source material is still not available, due to the complexity of the involved reaction mechanisms [14]. Among the by-product materials, only the fly ash and slag have been proved to be the potential source materials for making geopolymers. Fly ash is considered to be advantageous due to its high reactivity that comes from its finer particle size than slag. Moreover, less calcined fly ash is more desirable than slag for geopolymer feedstock material. The ash from the rice husk is highly porous and lightweight with a very high external surface area and contains silica in high a content (usually 90 - 95 wt.%).
The most common alkaline activator used in geopolymerisation is a combination of sodium hydroxide (NaOH) or potassium hydroxide (KOH) and sodium silicate or potassium silicate. The usage of a single alkaline activator has been reported. [18] Palomo concluded that the type of activator plays an important role in the polymerisation process. Reactions occur at a high rate when the alkaline activator contains soluble silicate, either sodium or potassium silicate, compared to the use of only alkaline hydroxides. Xu and van Deventer [14] confirmed that the addition of sodium silicate solution to the sodium hydroxide solution as the alkaline activator enhanced the reaction between the source material and the solution. Furthermore, after a study of the geopolymerisation of sixteen natural Al-Si minerals, they found out that generally the NaOH solution caused a higher extent of dissolution of minerals than the KOH solution.
The schematic formation of geopolymer material can be shown as described by equations (2-1) and (2-2) [4], [11], [24]. These formations indicates that all materials containing mostly silicon (Si) and aluminium (Al) can be processed to make the geopolymer material.

$n(Si_2O_5,Al_2O_2)+2nSiO_2+4nH_2O+NaOH$ or $KOH \Rightarrow Na^+,K^+ + n(OH)_3\text{-Si-O-Al-O-Si-}(OH)_3$
(Si-Al materials)

$|$

$(OH)_2$

(Geopolymer precursor) (2-1)

$n(OH)_3\text{-Si-O-Al-O-Si-}(OH)_3$ + NaOH or KOH ==> $(Na+,K+)\text{-(-Si-O-Al-O-Si-O-)}\ 4nH_2O$ (with | bonds above and below Si, Al, Si; O O O below)

($(OH)_2$

(Geopolymer backbone) (2-2)

To date, the exact mechanism of setting and hardening of the geopolymer material is not clear, as well as its reaction kinetics. However, the most of proposed mechanism consists of the following [4], [8], [10]:

- ✓ Dissolution of Si and Al atoms from the source material through the action of hydroxide ions.
- ✓ Transportation, orientation or condensation of precursor ions into monomers.
- ✓ The thermal polymerization is used due to similarity of this process to process in organic chemistry.

1. Dissolution (described by the complexing action of hydroxide types)
Solid: $Al{-}Si+MOH=M^+OSi(OH)^- + M^+Al(OH)^-$ (2-3)
Here M denotes the alkali cation Na+ or K+. The complexing reaction shown in equation 2-1 illustrates the intricate reaction mechanism in the geopolymer system. Although this mechanism is not yet fully understood. Some researchers [25] have proposed that the amount of soluble silicates in the system promotes the dissolution process of the aluminosilicate species. Keyte [26] recommended that the soluble silicates increase the initial concentration of dissolved silicon, therefore resulting in faster deprotonation and consequently in better dissolution. Others [14] suggested that the OH- species hydrolyse the oxide bonds at the surface of the aluminosilicate source, therefore promoting the aqueous products shown in equation 2-1. The first factor should allow that the dissolution process will be different in case of fly ash and metakaolin systems, where metakaolin is a calcinated clay and do not have a glass structure like the fly ash [26]. The dissolution will differ due to the particle size and shape, as well as the stability of the Al-Si source. It is where the initial Al and Si are generated at the start of the reaction.
2. Transportation, orientation or condensation of precursor ions into the monomers
$OSi(OH)_3^- + M^+OSi(OH)_3^- + M^+ = M^+OSi(OH)_2{-}OSi(OH)_3 + MOH$ (2-4)
Xu & van Deventer [13] suggested that it was mainly a physical electrostatic reaction, where the M+ cation reacted in a cation-anion pair condensation with the divalent-orthosilic acid and trivalent-orthosilic acid ions to balance the resulting Coulombic electrostatic repellence. For the other ceramic and zeolite materials this reaction is believed to proceed via a nucleation reaction, where the nuclei are formed and linked to commence the gel phase [3]. The presence of nucleation in the geopolymer synthesis process is yet to be proven as an accepted model, although Provis [27] discussed the theoretical approach in the likelihood of this model.

3. Setting or polycondensation/polymerisation of monomers into the polymeric structures (sometimes described hardening of the geopolymer matrix). This segment of the geopolymer reaction describes the gel formation and the final hardening process. It is believed that dissolution of the raw materials continues simultaneously with the condensation reaction from the formed species in the gel [28]. This is followed by the evaporation of water from the matrix and the final hardening of the geopolymer [29].

The binding properties of the matrix are believed to be those of a 3-dimensional amorphous silica network, with the general formula [30]:

$M_n - [\,[-Si-O_2]_z-Al-O]_n + wH_2O$

Where:

M refers to the alkali element

z is 1, 2, 3 or >>3

n is the degree of polycondensation

w refers to the water in the matrix

The monomers can be also shown graphically in figure below.

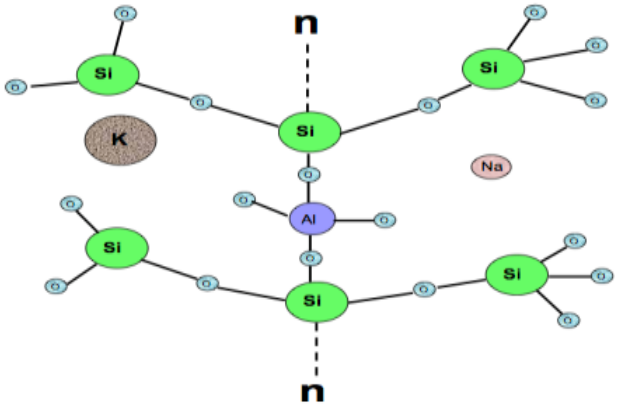

Figure 2.2 Geopolymer monomers [31]

Figure 2.3 displays a highly simplified reaction mechanism of geopolymerization [5], [25]. The reaction mechanism shown in the figure which outlines the key processes occurring in the transformation of a solid aluminosilicate source into a synthetic alkali aluminosilicate. It should be noted that the essential requirement for the processing of initial raw materials is the fine grinding and heat treatment may vary the reactivity of aluminumsilicate in the system.

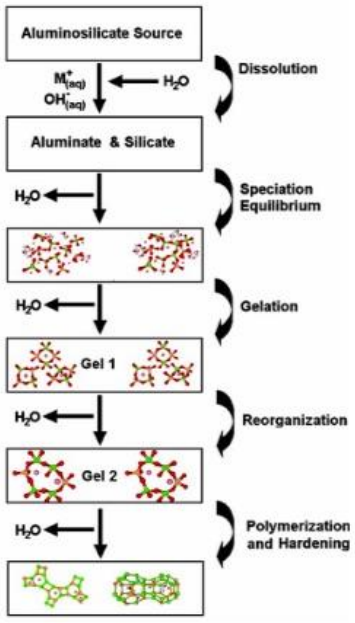

Figure 2.3 Process of geopolymerization [4], [7], [32], [33]

The dissolution of the aluminosilicate solid source by alkaline hydrolysis produces the aluminate and silicate. The volume of data available in the field of aluminosilicate dissolution and weathering represents a whole field of scientific endeavor. It is important to note that the dissolution of solid particles at the surface (resulting in the liberation of aluminate and silicate, most likely in monomeric form) into the solution has always been assumed to be the mechanism responsible for conversion of the solid particles during the geopolymerization.

A thermodynamic statistical model of alumino-silicates [27] was developed, which provides a quantitative, fundamentally based model. The latter describes the observed Gaussian trends and allows for analysis of the effects, especially when considering a change in composition and parameters of synthesis on the chemical ordering of the geopolymer. As a part of the investigation by Provis [27] it was established that an estimation of 10% unreacted material is commonly found in the general geopolymer structure.

Higher temperature implies higher rate of reaction according to the Arrhenius model, but lower degree of supersaturation [27]. However, this is related to slow nucleation and crystal growth, therefore production of semicrystalline or polycrystalline products during the synthesis at higher temperatures [25].

The presence of more nuclei will produce the crystalline product with a smaller average crystal size. Conversely, less of nuclei will produce larger crystals and induce slower solidification. The larger crystals will not be able to pack as densely with the binder phase as theirs smaller counterparts, thus producing a more porous geopolymer [27]. To avoid these porous structures and for optimum final strengths, Van Jaarsveld [25] recommended a curing temperature from 40°C to 60°C. This recommendation is largely based on the consideration of the significance of crystal water within the matrix, which reduces the cracking of the structure.

The fly ash resulting from the coal burning in a coal-fired boiler contains minerals such as kaolinite, pyrite and calcite [26]. These minerals are not burned when they pass through the flame, but they are melting due to the adequate flame temperature. Some differences between the amorphous silica sources, which may be caused due

to differences in furnace temperature and coal composition were noted [34]. Ultimately, these initial differences may alter the final geopolymer product.
Provis [27] represented a process of polymerization which is shown in Figure 2.4.

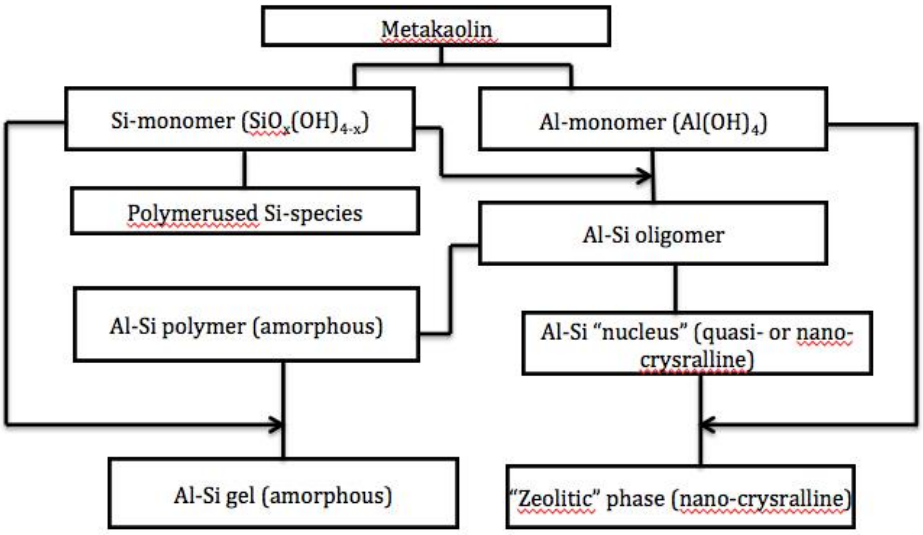

Figure 2.4 Schematic of polymerization by Provis [27]

The Faimon´s [35] model is ideal for the occurrence of the dissolution of a primary mineral into the Al- and Si-monomers, the association of these monomers via either or both addition and autocatalytic polymerization. Finally the formation of an unidentified 'secondary mineral' phase will be present. Its relevance for the geopolymerization is therefore uncomplicated, requiring only the incorporation effect of Si-oligomerization in the concentrated Al-Si gel component of the geopolymeric binder. This must also include a second pathway by which the zeolitic material/phases are observed in the formation of geopolymers.

2.1.3 Geopolymer mechanical parameters characterization

High compressive strength of geopolymers is one of the major tailored property which may lead to their wide use. It is also the widest used property in current research, primarily due to the low cost and simplicity of the compressive strength testing. Unfortunately the results gained from the different research groups or authors can not be directly compared in any accuracy sense, due to the variety of product sizes and geometry, strength testing apparatus and procedures followed by each person [36]. Research proved a valuable testing of a mixture of kaolinite, albite and fly ash [13], the addition of zirconia to the basic matrix [2], the effect of ionic contaminants in the matrix and many other investigations [13]. It is partly due to the fact that the work presented further in this study does not primarily rely on the compressive strength results, even though is this measurement included as an auxiliary comparison method within the investigation. The addition of fibers, flyash and silica sand aggregate has been proposed by the previous researchers to increase the physical strength, which may possibly have a direct relation to the expected geopolymer durability. Yip & van Deventer investigated the effect of calcium addition to the basic geopolymer matrix [30]. They established that the coexistence

of gel and phases during the early stage geopolymer activation was a major contributor to the mechanical and physical properties of the samples. A reactive source of calcium, must also be present.

An optimum ratio of metakaolin and ground granulated blast furnace slag exists [30] regardless to the ratio of SiO_2:Na_2O. A maximum strength was found out for matrixes with 20% (wt) of ground granulated blast furnace slag after ± 7 days. The addition of 40% (wt) or more of ground granulated blast furnace slag is the cause of destruction of the matrix strength. The improved strength is the result of originate extra Ca-species of ground granulated blast furnace slag brought to the geopolymeric matrix at a high pH (≈ 14). Keyte [26] found that the same limit holds for fly ash based geopolymers.

Adding too much of Ca^{2+} to a geopolymer gel leads to the formation of calcium silica hydrates (cementious based material), which can contribute to a more brittle, weaker matrix. Amorphous calcium silica hydrates may be the major component (if they are correctly controlled), which contributes to the overall strength [37] and its formation can significantly affect the properties such as acid resistance [36].

Other researchers suggested that addition of granular sand increase the compressive strength [13], enhanced density and minimised shrinkage during drying [36].

Generally it was found that a higher pH contributes to a geopolymer with higher compressive strength [38], [39]. K-geopolymers (as opposed to Na- geopolymers) in most cases exist at a higher pH, associated with higher dissolution rates and lower amounts of present unreacted material. The experiments in this thesis have used of both cations in the quest to limit the cost associated with the potassium activation.

Although this method is not used in this work, has been proved that the addition of fibre to the matrix significantly improve the flexural strength and fracture toughness of the geopolymer in comparison to a geopolymer paste [40].

The presence of some nano-crystalline zeolites [41] have been identified in geopolymer matrixes by electron microscopy, especially matrixes constructed with a high reaction time. Crystallisation with the high silica contents also seems to be less prevalent. Crystallinity has not yet been excluded as a means of strength development in the geopolymeric systems. Also, the extent of crystalline phase in the process of dissolution in the geopolymer mix [42] was not promoted nor inhibited by the presence of salt contaminants, restricted by the instrumentation detection limits. Generally, high degrees of crystallinity [2] are found at pH values greater than 12, while zeolite formation [38] is favoured at lower activating ratio of solution (Na_2O/SiO_2) and higher temperatures.

In fly ash systems was observed another interesting aspect, Keyte [26] found that the removal of iron from the fly ash source does not improve the compressive strength of the matrix.

Feng [43] proposed to use the ultrasound which can improve the compressive strength of geopolymer. The major disadvantage of this technique is the creation of 'hot-spots' within the structure resulting in a flawed sections. Less cracks have been found with the use of ultrasound which can form a substantially more evenly distributed gel-phase. These are important factors when considering the eventual strength of the matrix.

According to Rangan and Hardijito [44], compressive strength of geopolymer concrete is very high compared to the ordinary Portland cement concrete.

Geopolymer concrete also showed very high initial strength. The compressive strength of geopolymer concrete is about 1.5 times higher than the compressive strength of the ordinary Portland cement concrete, with the same mix. The geopolymer concrete showed a good workability as in case of the ordinary Portland Cement Concrete.

2.1.4 Geopolymer applications

Geopolymers can be used in the commercial applications as a construction material, but they also have the valuable alternative qualities - resistance against the fire and acids, thermal resistance and ability to encapsulate the medium. Their superiority over the plastics, ceramics and other organic composites also strengthens the apparent need for geopolymer technology. These superior qualities are:

- ✓ Easy production and handling, whereas high temperatures are not required.
- ✓ Higher heat tolerance than in case of organic composites (resisting temperatures up to 1200^0C)
- ✓ Resistant to all organic solvents, but it can be affected by strong HCl and H_2SO_4.
- ✓ Fast setting (especially in pre-cast applications).

The production of geopolymer emits on average 5 times less of CO_2 compared to the OPC [5]. This may be a large contributing factor to incorporate geopolymers into Cement and Concrete applications. As we know the CO_2 emissions from OPC kilns play a significant role in the global greenhouse gas concentrations [36].
In wider applications, particularly in the field of medicine, it has even been proposed that geopolymer-calcium-phosphate composites may be the answer to the synthetic bone replacement [27].
Davidovits [4], [6] proposed some possible applications for the geopolymer material depending on the molar ratio of Si to Al, as given in Table 2.1.

Table 2.1 Applications of geopolymer material

Si/Al	Application
1	Bricks, ceramics, fire protection
2	Low CO_2 cements, concrete, radioactive & toxic waste encapsulation
3	Heat resistance composites, foundry equipments, fibre glass composites
>3	Sealants for industry
20<Si/Al<35	Fire resistance and heat resistance fibre composites

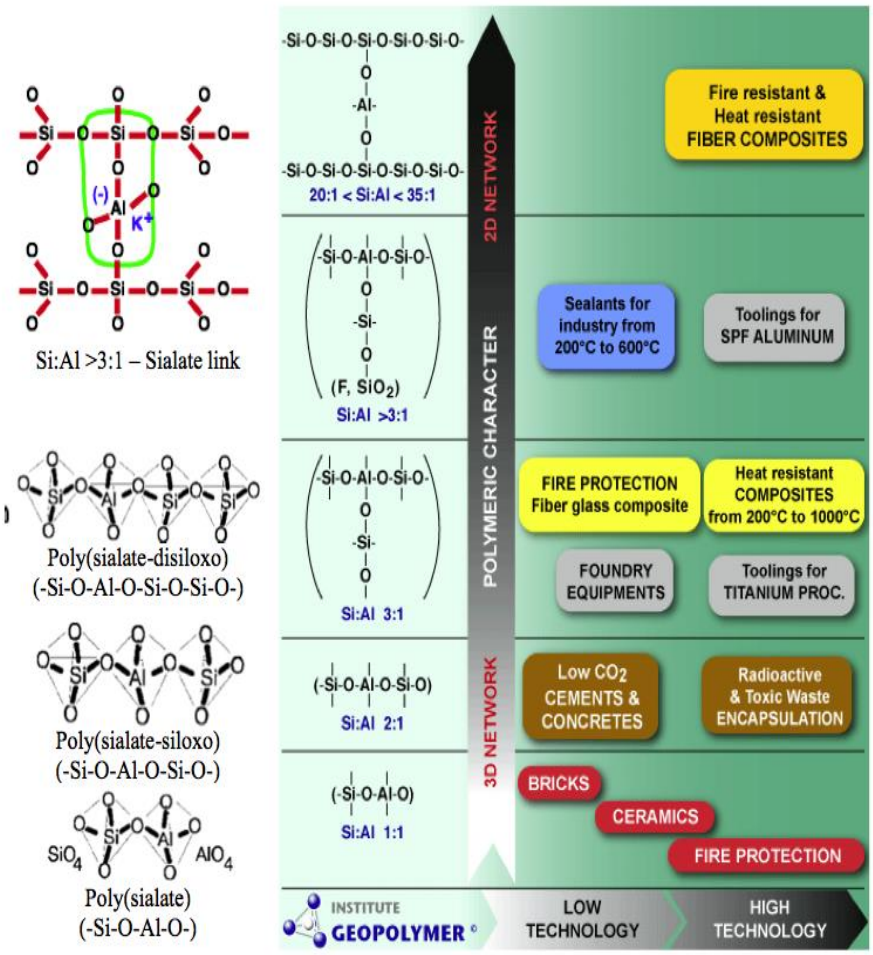

Figure 2.5 Geopolymers and possible applications [4], [6], [45], [46]

2.2 Reinforcing fibres

2.2.1 Carbon fibres

Carbon fibers have been studied scientifically since the late 1950s and fabricated in 1963. They are important material in structural composites for racing car, aerospace industry and sporting goods industry. Some carbon fibers have a stiffness that are ten times higher then in case of glass fibers and densities that have half of values compared to the glass fibers [47]. Although many carbon fibers have a high strength, they are generally not as strong as glass fibers or aramid (Kevlar) fibers. The thermal properties of carbon fibers are outstanding. They protect from the oxidation above 1000^0C they are stable up to 2000^0C. Above that temperature they will thermally decompose.

Carbon fibers are chemically inert and they are not susceptible to corrosion or oxidation at temperatures below 1000°C. Unlike glass fibers, carbon fibers have a very high fatigue strength that is transmitted to their composites [47]. The specific strength and modulus of carbon fibres-reinforced plastics show the highest value for all engineering materials, due to high performance of the carbon fibres constituents [47]. More recently, carbon fibres reinforced cement have been applied in the construction industry and civil engineering applications. Carbon fibres are prepared from the organic precursors. This preparation is generally done in three steps - stabilization of an organic fibre (at 300^0C) to form precursor, carbonization of fibre precursor (at 1100^0C), and subsequent graphitization (above 2500^0C). In narrow sense, commonly called "carbon fibres" undergoing only by the first two steps of development, while the fibres undergoing by all three steps are called "graphite fibres". "Carbon fibres" are generally used for their high strength, while the "graphite fibres" are used for their high modulus [47]. The most extensively used method is the conversion of polyacrylonile (PAN) to carbon and then to graphite. PAN is formed by the polymerization of the acrylonitrile monomer.

Basic properties of carbon fibres can be grouped into [47], [48]:

- ✓ Ultra-high-modulus, type UHM (modulus >450GPa)
- ✓ High-modulus, type HM (modulus between 350-450GPa)
- ✓ Intermediate-modulus, type IM (modulus between 200-350GPa)
- ✓ Low modulus and high-tensile, type HT (modulus < 100GPa, tensile strength > 3.0GPa)
- ✓ Super high-tensile, type SHT (tensile strength > 4.5GPa).

There are a few drawbacks of carbon fibers especially in comparison with glass fibers. The primary drawback is their cost. The lowest cost of carbon fibers is twice as expensive as S-glass, but some grades can be 100 times more expensive than E-glass. [47]. This high cost has excluded the carbon fibers from many market applications, such as the automotive market. They have found the greatest use in areas where the cost is not the primary consideration: military aircraft, spacecraft and sporting goods. Carbon fibers are quite anisotropic. Their strength and stiffness can be 10 to 100 times higher in the fiber direction than in the transverse direction.

2.2.2 Ceramics nanofibres

Nanofiber technology is developed for future army lightweight protective clothes. Application of nanofibers for ballistic, chemical and biological protection are investigated, but the thermal properties and theirs potential protection against the

cold are unknown [49]. Nanofibers are an exciting new category of materials used for several applications such as medical applications, filtration, barriers, wipes, personal care products, composites, garments, insulations and energy storages. Special properties of nanofibers make them suitable for a wide range of applications e.g. medical products, consumer products, industrial and high-tech applications for aerospace, capacitors, transistors, drug delivery systems, battery separators, fuel cells, and information technology [50].

At recent year, the polymeric nanofibers has been produced by an electrospinning process. Electrospinning is a process that spins fibers of diameters ranging from 10nm to several hundred nanometers. This method has been known since 1934 when the first patent about the electrospinning was filed. Properties of fibres depend on uniformity, polymer viscosity, intensity of electric field and DCD (distance between nozzle and collector). The advancements in microscopy such as scanning electron microscopy has enabled us to better understand the structure and the morphology of nanofibers. At the present the production rate (process of measured grams per hour) is low. Other technique to produce the nanofibers is spinning of bi-component fibers such as "Islands-In-The-Sea" fibers with amount of filaments from 240 to 1120 (1-3 denier) surrounded by dissolvable polymer. Dissolved polymer leaves the matrix of nanofibers, which can be further separated by stretching or mechanical agitation. The most often used fibers by this method are nylon, polystyrene, polyacrylonitrile, polycarbonate, PEO, PET and water-soluble polymers. The polymer ratio is generally „80% islands and 20% sea“. After the dissolving of the "sea" polymer component the resulting nanofibers have a diameter of approximately 300 nm. Compared to theelectrospinning, nanofibers produced by this technique will have a very narrow diameter range, but they are coarser [50]. Nanofibers have special properties mainly due to the extremely big surface to weight ratio compared to conventional nonwovens. They also have a low density, large surface area and high pore volume. The pore size makes the nanofiber nonwoven fabrics appropriate for a wide range of filtration application [50].

We know that the nanofiber is smaller compared to a human hair which is 50-150 μm thick. The elastic modulus of polymeric nanofibers smaller than 350 nm is found to be 1.0±0.2 GPa [50], [51].

Nanofibers can be used in medicine as e.g. artificial organ components, tissue engineering, materials for implants, drug delivery, wound dressing, and medical textile materials [50]. Nanocomposites have an excellent strength and hardness which could help with the problem of mechanical wear and reduce of the need for the periodic replacement. Many metallic nanocomposites could have this problem. Nanoceramics, such as the nanocrystalline zirconium oxides, are also particularly interesting because they can be made extremely hard, wear-resistant and more porous [50].

2.3 Geopolymer composite systems

2.3.1 Geopolymer systems reinforced by long fibers

A variety of processing techniques can be employed to produce the geopolymer composites. The fabrication method depends on the type of reinforcement. In addition to particles and tablets a various types of fibrous materials can be used. The most common reinforcement made of fibres used in geopolymer composites is

based on carbon, basalt or glass fibres, but also the other inorganic fibres such as silicon carbide, alumina, mullite or boron can be utilized.

In case of the geopolymer systems reinforced by long fibres, two different methods can generally be applied: (i) impregnation of fibre tows or fabrics to the form a pre-preg followed by a winding or lay-up process to build up the composite, or (ii) winding, weaving or lay-up of dry fibre tows or fabrics into a preform and subsequent infiltration of the preform with the liquid geopolymer binder [45], [52]. However, the pre-impregnation methods as in (i) are more commonly used; the woven fabrics are usually used because of their greater ease of handling during the lay-up process and give better reproducibility compared with unidirectional fibre composites. Nevertheless, the composites made of unidirectional fibres can be manufactured in a similar way. Firstly, layers of fibres are impregnated with the geopolymer binder using the squeegees and rollers to ensure the complete wetting of the fibres. The fibre layers are then stacked so they can to build up the laminate, this step is followed by the curing process. However, the lamination and curing processes for geopolymer composites are not trivial, because the properties of the final product can be influenced by many factors.

Hung T.D [53] studied the effect of curing temperature on the flexural strength properties of the geopolymer composites based on carbon reinforced by silica. He found that the proper temperature of the curing process for achieving a good mechanical properties of this geopolymer composite based on carbon reinforced by silica varies in relative large range from 70°C to 100°C and at 75°C the composite achieves the maximum of flexural strength which is about 570 MPa, the bending modulus is about 64 GPa and the relative deformation is 0.98%. He [40] also demonstrated that the geocomposites based on the thermal silica geopolymer matrix which is reinforced by fibres can be fabricated and cured at the optimal temperature interval with a range of 60 to 90°C. In three stages of process: for 1 hour at room temperature and 1 hour at optimal elevated temperature with the vacuum bagging technique; drying for 5 hours or more in a forced air heated box at the same temperature as in the previous stage. The mechanical properties of geopolymer reinforced by carbon fibres are always higher than those of geopolymer based on E-glass fibres and basalt fibres in case of the same curing time and curing temperature.

Lyon [54] showed that composites made of 3k (mark of fibre) carbon fabric with a plain weave and geopolymer had a tensile strength of 327 MPa and a flexural strength of 245 MPa. Both of these values are comparable to the strengths of the similar composites made of an organic matrix. Samples of geopolymer composite retained 63% of their flexural load carrying ability even after 1 h of exposure at 800^0C. The geopolymer samples had strength of 14 MPa in shear. This strength decreases to a value of 4.6 MPa for samples heated to1000^0C for 1 h.

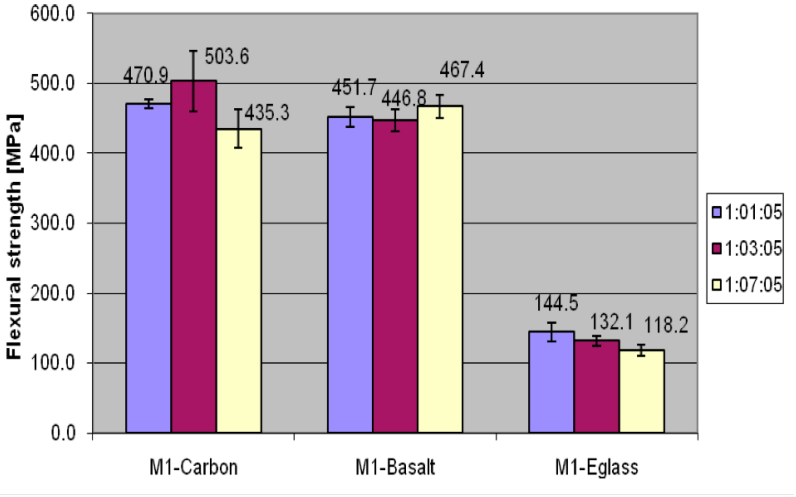

Figure 2.6 Flexural strength of geocomposite [40]

Giancaspro and Balaguru [55] indicate that plates from the hybrid composite manufactured using 3k unidirectional carbon tape exhibit the increases in flexural capacity for approximately 700% compare to those manufactured using alone E-glass fibers. For the laminate composites made just from carbon, the highest flexural strength was exhibited in case of the 3k unidirectional carbon composite at the value 466 MPa, followed by the 3k woven carbon and glass composite with a value of 429 MPa.

Shan and Liao [56] studied the epoxy matrix composite reinforced by the unidirectional glass fiber and glass–carbon fiber. The hybrid samples made of carbon–glass showed a better retention in fatigue life in water than samples made only from glass fibers, to up to 107 cycles. Therefore, by hybridization with appropriate amount of the carbon fibers, resistance to environmental fatigue the degradation of plastics reinforced by glass-fibers can be enhanced.

Papakonstantinoua [57] investigated the geocomposites made from carbon, glass and combinations of carbon and glass fibers. All the composites with monofilament fibers like the SCS-6 from Textron and Saphikon, with diameters of 140 and 125 μm, exhibit the low tensional and flexural strength. Composites made with T300 carbon and polysialate provide the mechanical properties that are comparable with the other carbon–carbon (high temperature) and ceramic matrix composites. With curing temperatures below 150°C and an easy fabrication method, composites made with polysialate are much less expensive to produce and hence have more potential for wider uses.

Blissett [58] studied the aluminosilicate glass-ceramic matrix composite made of silicon carbide fibre calcium. The Young's modulus measurement on material indicated a 150 GPa compared to the unidirectional which showed the 120 GPa. Thermally shocked samples showed a reduction in modulus for temperature differentials greater than 500°C, similar to the trend was exhibited by the unidirectetional material. The flexure strenghth of the as-received cross-ply material was from 500MPa to a value of 980 MPa for the unidirectional composite.

Anderson [59] studied four different types of the pultruded composites immersed in a highly alkaline solution. The composites were all composed of glass fibers and either polyester or vinyl ester resin. After 2 days, the specimens showed the signs of

the moisture absorption. The polyester specimens became too soft to measure after exposure in the solution for 56–112 days. During the first several weeks of exposure the fibers started to be visible and the outside surfaces became rougher in case of the polyester specimens. The strength loss was paralleled with a weight loss. The vinyl ester specimens did not deteriorate like the polyester specimens.
Foerster [60] indicated that other reinforcing types of fibres are superior to carbon, essentially due to the better fibre infiltration and wetting. In particular, aluminosilicate-based fibres can improve the strength significantly in comparison with the carbon fibres. The carbon fibres are chemically stable, aluminosilicate fibres containing B_2O_3 which shows the major degradation of fibres.

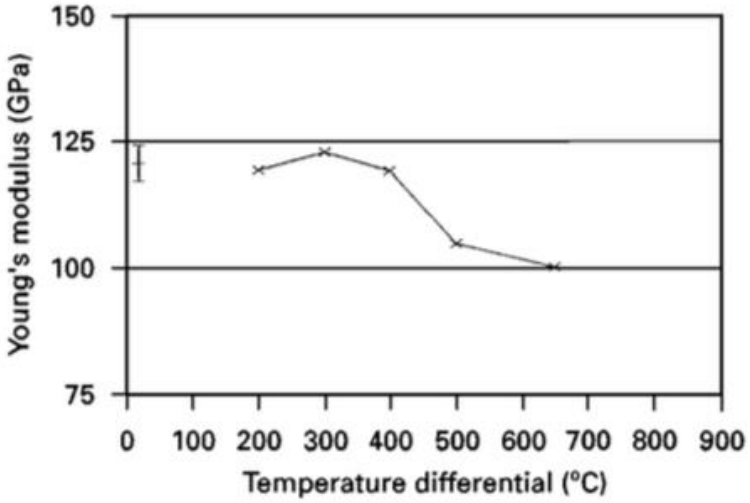

Figure 2.7 Young's modulus of a unidirectional Nicalon/CAS after six cycles of thermal ageing for 1 h and quenching [58]

2.3.2 Geopolymer systems reinforced by short fibers

Concrete is a brittle material with a low tensile strength, flexural strength and the strain capacity. The fibres are ductile or quasi-ductile material with improved tensile strength, flexural strength, strain capacity, toughness and energy absorption. The binder in fibre-reinforced cement composites (FRCCs) is mainly the Portland cement. Environmental awareness in the construction industry is promoting of alternative binders to reduce the amount of released CO2. The binders in FRCCs can be replaced with the inorganic binders, called geopolymeric cement, to create a fibre-reinforced geopolymer composites (FRGCs), which are greener. The mechanical properties of FRGCs reinforced with short fibres were discussed. The geopolymer composites reinforced with the ductile fibres shows a strain hardening and multiple cracking in flexure as is presented [53], [59], [61], [62].
The woven fabrics, mats or unidirectional fibers such as carbon, E-glass, Kevlar or basalt fibers have been so far the most widely used to cast the continuous fiber-reinforced composites in civil engineering applications. More recently, structural composite materials obtained from the inorganic matrixes have been designed to deal with the major drawbacks deriving from the use of the organic polymer resins. As a matter of fact, a significantly low resistance to UV radiation and high-temperatures is largely limiting organic matrixes to use in a wide field of applications [63].

The conventional mortars made from a sodium silicate activated by a blend of fly ash/metakaolin have been investigated by Yunsheng [64], [65]. Polyvinyl alcohol (PVA) fibers (14 μm in diameter, 6 mm in length) were added at amount of 0%, 1%, or 2% to the composites which were produced using a single-screw extruder. The samples were allowed to cure at room temperature and they were tested after 28 days. During the flexural tests it came to the substantial increases in mid-point deflection (i.e. from less than 1 mm to 16 mm) and distributed microcracking were observed. In this system the fly ash was shown to play a complex role [64]. On the one hand, it came to the greatly improved rheological characteristics of the mixture and lowering of the pressures needed for extrusion (compared with the PVA fibers - increased the pressure, making processing more difficult). On the other hand, increasing the quantity of fly ash caused the decreases in flexural strength, possibly because of the fly ash is less reactive than the metakaolin and 'dilutes' the strength-bearing phases. This was also observed during the analysis of the failure mechanism, which varied from the fiber fracture (low fly ash) to fiber pullout (high fly ash), as the weakening of the matrix due to reduced geopolymer formation which can alter the fiber/matrix bonding. Zhang [66] later investigated the impact of the properties of these formulas after freezing/thawing cycles and exposure to the acid [65]. It was found that the fiber reinforcement improved the impact of the resistance and the energy absorbance after 20 freeze–thaw cycles and also the increasing of the content of fly ash improved the behavior of the composite. The authors speculate if that was due to a number of reasons: (a) fly ash is so dense that water cannot penetrate the pores, and (b) fly ash is less reactive than metakaolin, it continued to reacting and forming of the geopolymer products over the weeks required to perform the freeze/thaw tests. The long-term properties of geopolymers containing the fly ash might, therefore, be much improved over those were initially reported. A similar phenomenon (where increasing of the fly ash content improved the impact resistance) was observed after the composites were exposed to the sulfuric acid, possibly because the acid encourages the production of the amorphous geopolymer products by altering the aluminum bonding environment.

Natali [67] have used four types of fibers: HT-carbon fibers (average fiber diameter: 10 μm), commercial E-Glass fibers (average fiber diameter: 10 μm, PVA fibers (average fiber diameter: 18 μm) and PVC fibers (average fiber diameter: 400 μm) with 7±1 mm in length. New fiber-reinforced composite materials based on sustainable geopolymer matrixes have been investigated. All the selected fibers were found to have a good adhesion properties and they are being able to control micro-cracks propagation along the matrix and creating a favorable bridging effect. A better behaviour of polymer fibers has been observed compared to that which was showed by glass fibers. Moreover, obtained results showed that a fraction equal to 1% wt. of reinforcing fibers embedded in the geopolymer matrix is able to determine a flexural strength increment, ranging from 30% up to 70% depending on the fiber type, compared to the unreinforced material. Geopolymers blended with PVC and carbon fibers exhibited the best energy absorption capacity: for those types of fibers the post-crack behavior was significantly improved. This results in an enhanced ductility of the material after the reaching of the first crack load. Maximum values were found for carbon fiber reinforced sample.

Giancaspro [63] investigated the geopolymers based on carbon and glass woven fabric. Based upon the observations and test results obtained during the preparation

and testing of the biocomposite materials, a number of conclusions may be drawn regarding the feasibility and strength of this materials. First, the material is viable in terms of production without using heat, pressure or any specialized casting equipment. This yields a relatively environmentally benign composite material that consumes little energy during the manufacture and produces the virtually no waste productsDuring the manual casting process is easy to pour the wet mixture. The shape and dimensions of the molds may be customized to fit any specified needs. The compressive strength, workability, and density are highly dependent upon the proportions of sawdust and resin in the mix. However, this is resulted in substantially lower compressive strengths and the modul of elasticity. From a processing standpoint, the sawdust content could be increased up to 29% (with 71% inorganic matrix binder) without compromising workability. The resulting biocomposite material had a density (View the MathML source) 1254kg/m3, and a compressive strength and modulus of 6.8 MPa and 0.64 GPa, respectively. When biocomposite cores were reinforced with high strength fibers and tested in flexure, the following conclusions were reached:

- ✓Both glass and carbon are useful to obtaining the increased strength and stiffness values manufactured by sandwich beams. The type of reinforcement applied to the core particleboard beam strongly influences the moment capacity of the beam. In general, carbon will provide better reinforcement than either AR-glass or E-glass.
- ✓The adding of the additional reinforcement to the sandwich beam will increase the both its strength and its stiffness.
- ✓Carbon fibers significantly increased the strength by 151% (using high-modulus carbon) and stiffness by 118% (using carbon fabric) without significantly increasing the sandwich beam mass. This is a very useful trait in fields such as aerospace technology.

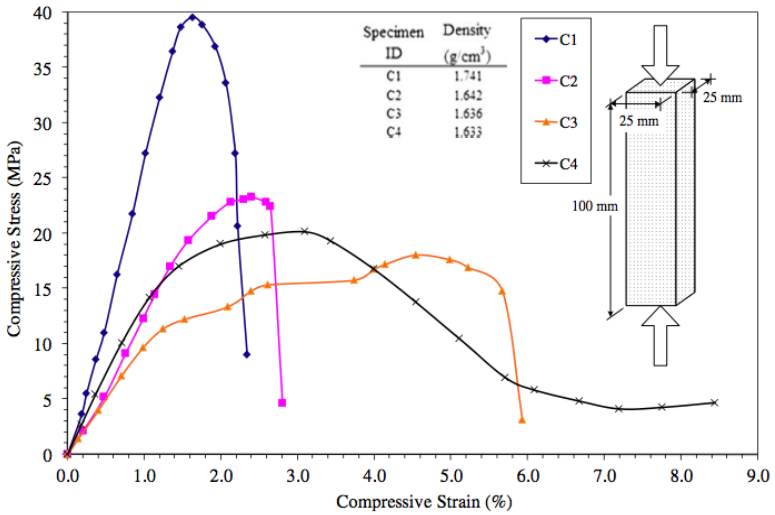

Figure 2.8 Compressive strength versus strain [63]

The Impact properties were also the focus of research by Li and Xu [68] on sodium silicate activated by slag/fly ash blends with less than 0.3% (vol.%) of basalt fibers. Tests using a Split Hopkinson Pressure Bar system revealed no change in dynamic compressive strength, but improvements in deformation characteristics and a marked increase in energy absorption were observed. Geopolymer based on 0.3%

(vol.%) basalts fiber was estimated to be the optimal fiber loading in case of energy absorption. Strain hardening was not observed. The composite properties (energy absorbed, etc.) were determined to be strain rate dependent to the impact loading.
The increased tensile properties of fiber-reinforced geopolymers can have other beneficial side effects. When working with the sodium silicate activated by fly ash/metakaolin geopolymers Zhang, Yao, Zhu, Hua, and Chen [69] found that the incorporation of polypropylene (PP) fibers (10 μm diameter, 3 mm length) increased not just the flexural strength and absorbed energy, but increased compressive strength and alleviated issues due to the drying shrinkage. Workability, however, is worse. This group os scientists later investigated the geopolymers based on sodium silicate activated by metakaolin/slag incorporating of PP fibers and an MgO as the expansive agent for marine coating applications [70]. The addition of slag increased the workability of the matrix, as slag requires less liquid than metakaolin for particle wetting, which helped to lower the porosity and water permeability. However, amounts of slag above 10% resulted in the cracking due to the drying shrinkage. It was expected that the cracking could counteracted through the use of the expansive agent and the PP fibers. The system also shown to have good anti-corrosion properties and excellent adhesion to OPC-based mortars. However, the details of the mechanical behavior such as the failure mode was brittle or ductile, were not provided.
Sun and Wu [71] investigated the NaOH activated fly ash with PVA fibers processed by a hydrothermal hot pressing technique. A variety of pressing variables, fly ash types and volume fractions of the fiber reinforcement (all below 1.5%) were explored. The largest quantity of fiber led to very poor workability, but all volumes were successful in endowing the matrix with a high tensile strength and a ductile failure mechanism. Increasing the pressing temperature led to increased the strength, but only up to 200°C, when the fibers melted the composite returned to displaying brittle behavior. The same was true when the hot-pressing was carried out for longer time than 1 h.
Thaumaturgo [72] investigated the geopolymeric cement concretes reinforced with basalt fibers with a volume of 0%, 0,5% and 1%. The addition of 1.0% of basalt fibers resulted in 26.4% reduction of the compressive strength and 12% reduction of the splitting tensile strength in case of the concrete. With the fiber percentage increased, the probability of crumpling these fibers together and leaving voids in the matrix was greater. Concrete with Vf equal to 0.5% presented negligible changes in the compressive and splitting tensile strength relative to concrete without fibers.
Alomayri [73] describes the physical, mechanical and fracture behaviour of fly-ash based geopolymer reinforced with cotton fibres (0.3–1.0 wt%). Increasing the content of cotton fibres (up to 0.5 wt%) increases the flexural strength, flexural modulus and the fracture toughness of the composites. However, further increase in cotton fibre content aove 0.5 wt% caused a reduction in the mechanical properties due to the poor workability which led to the formation of voids and fibre agglomerations. The density of geopolymer composites decreases with an increase in fibre content. The [74] thermal, mechanical and fracture behaviour of fly-ash based geopolymer composites reinforced with cotton fabric (0–8.3 wt.%) were also presented. The compressive strength of composites is higher in the case of horizontally oriented fabric compared to that laid in vertical direction. This can be due to the ability of horizontally laid cotton fabric to directly absorb and distribute

the load uniformly throughout the cross-section. In addition, this significant enhancement of compressive strength in the horizontal direction is due to the fact that the interface between the fabric and the matrix is not exposed to any shear loading which in turn reduces the possibility of fabric detachment or delamination from the matrix at high loads. Compressive strength of the composites containing cotton fabrics increases with increase in fabric layers (i.e. the fibre contents) oriented in both directions. The increase in compressive strength with fibre loading may be due to the ability of the cotton fibres to absorb the stress transferred from the matrix.

Giancaspro [75] used a waste sawdust as filler and an inorganic potassium aluminosilicate as a binder. Relative to 15 other wood plastic composites that utilize the organic polymers, the inorganic biocomposite generated the lowest heat release rate during 5 min of the fire exposure. The addition of fiber reinforcement facings decreases the amount of smoke released by the biocomposite sandwich plates. Biocomposite with reinforcement based on carbon produced 5 times less smoke than facings with both glass and carbon fibers.

Lin [76] demonstrates that the geopolymer matrix composites were reinforced with a kind of sheet-like short carbon fibers preform prepared with the help of the ultrasonic scattering treatment, which exhibit the excellent mechanical properties. In this experiment the carbon fibers are used with a diameter of 6–8 μm and an average length of 2, 7 and 12 mm, respectively. The composite reinforced by the carbon fibers of 7 mm in length shows a maximum flexural strength as well as the highest work of fracture, which are nearly 5 times higher than in case of the geopolymer matrix.

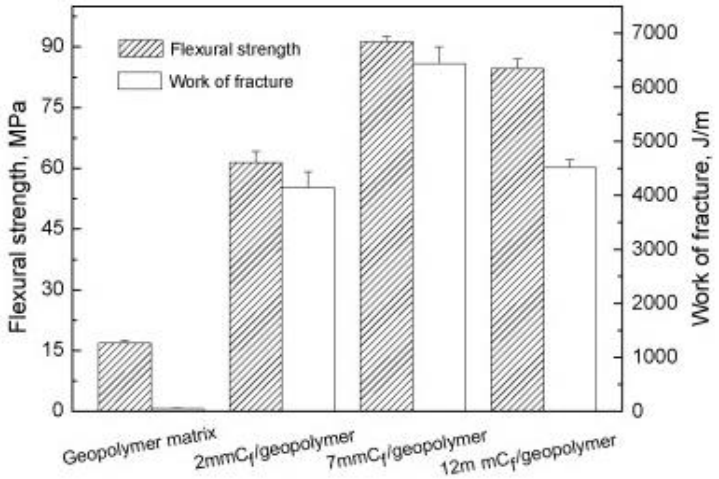

Figure 2.9 Variation of flexural strength and work of fracture of geopolymer matrix and Cf/geopolymer composites with starting fiber [76]

Lin [77] investigated the crack growth in situ. Observation during the three-point flexural test shows that lots of micro cracks form on the whole surface of the beam sample. With the increase of the bending load of the beam sample keeps a nearly elastic deformation behavior at initial stages and exhibits an obvious displacement.

P.He [78] shows that after the heat treatment of the composite at 1100°C, many short oval cracks in the radial direction of carbon fibers were formed. These oval cracks were resulted from the large volume shrinkage caused by viscous sintering of the geopolymer matrix at high temperature. Mechanical properties of the unidirectional carbon fiber reinforced geopolymer composite can be greatly improved by the heat treatment in a wide range of temperatures from 1100 to 1300°C. Especially for C-1100, flexural strength and Young's modulus got values, 234.2 MPa and 63.8 GPa, respectively. The increase in mechanical properties could be contributed to the matrix densification and the lucite formation as well as the proper Cf/matrix strength of the interface bonding. When the composite are heat treated at 14000C, the strengthening effect of the carbon fibers is dramatically decompensated. It is resulted from the serious fiber degradation and the much stronger fiber/matrix interface bonding. So, the composite shows substantially decreased mechanical properties and fractures in a very brittle manner.

Zhang [79] studies on carbon fiber with the length, diameter and density of chopped fibers are 6 mm, 7 μm and 1.76-1.80 g/cm^3 respectively. And four different mass contents of 0, 0.5%, 1% and 2% of chopped carbon fibers to metakaolin-flyash precursor were considered. Bending strength of geopolymers at ambient temperature gets significantly enhanced with an increase in carbon fibers content, but the compressive strength at ambient temperature is not affected to a great extent. After exposure to 500^{o}C, bending and compressive strength decreases greatly for all specimens, though the specimens with higher carbon fibers content exhibit relative higher strength retention.

The addition of chopped carbon fibers to the geopolymers provides an effective crack control mechanism under the high temperature exposure and this in turn enhances bending strength at temperatures of 20-500°C. The addition of chopped carbon fibers in geopolymers does not significantly influence the compressive strength of geopolymers at temperatures of 20-700°C. The fly ash-based geopolymers cured at ambient temperature provide lower strength at ambient temperature compared to metakaolin-based geopolymers. However, geopolymers with higher content of fly ash and lower content of metakaolin exhibit greater strength retention after exposure to high temperature, due to the lower mass loss and sintering reactions of un-reacted fly ash at high temperatures. Geopolymer consisting of 50% fly ash and 50% metakaolin and 2% of carbon fibers (wt.%) provides an optimum bending and the compressive strength properties at ambient temperature after the exposure to high temperature and it is therefore suited for the fire resistance applications.

2.3.3 Geopolymer systems reinforced by nanofibers

Saafi [80] studied the effect of multiwalled carbon nanotubes on the mechanical and electrical properties of the geopolymeric composites based on fly ash. The load–deflection response was linear for all beams. The addition of multiwalled carbon nanotubes in amount up to 0.5-wt% significantly increased the flexural strength, stiffness and toughness of the beams. The number of multiwalled carbon nanotubes bridging the micro-crack in samples with 0.5-wt% was higher than in samples with 0.1-wt%. Due to the agglomeration, only a few multiwalled carbon nanotubes were near the crack.

Gengying Li [81] studied the Portland cement, fly ash with nano SiO2. The addition of nano-SiO2 to the high-volume and the high-strength concrete leads to an increase of both short-term strength and long-term strength. The high volume of the fly ash in high-strength concrete has an increase in 3 days strength of 81% with respect to high-volume of fly ash in the high-strength concrete, and the 2 years strength was 115.9 MPa which is higher than the strenght of a high-volume fly ash high-strength concrete reached about 108 MPa and the Portland cement concrete reached about 103.7 MPa. The cement mortars with four contents of nano-SiO_2 particles (3%, 6%, 10%, and 12% of the weight of cement) were tested. The increase of strength of the mortars was found with increased content of the nano-SiO_2 from 3% to 12%. The microstructure of the mixture containing nano-SiO_2 revealed a dense compact formation of hydration products and a reduced number of $Ca(OH)_2$ crystals [82].
Senff [83] studied the Porland cement after adding nanosilica with a content of 0%, 3.5% and 7% (wt.%). The values of compressive strength have increased compared to mortars without mineral additions. However, if the higher amount of cement is substituted or the mixtures become difficult to mould (nanosilica = 7%) the performance is decreased. The factorial design showed that the unrestrained shrinkage and the weight loss of the mortar did not follow a linear regression model and the mortars with nanosilica after 7 days the shrinkage increased to 80%, while at 28 days it increased to 54%.
Givi [84] investigated the effects of SiO_2 nanoparticles to mechanical properties and physical properties of binary blended concrete. Nanoparticles with average particle size of 15 nm were used. The mixtures were prepared with the cement replacement of 0.5%, 1.0%, 1.5% and 2.0% by weight. The comparison of the results from the 7, 28 and 90 days of samples shows that the compressive strength increases with partial cement replacement by SiO_2 nanoparticles up to 1.0%. And the use of 2.0% of SiO2 nanoparticles decreases the compressive strength to a value which is near to the control concrete.
Nazari [85] studied effects of TiO2 nanoparticles on concrete containing “ground granulated blast furnace slag” as binder. The results show that the compressive strength increases by adding up to 3.0 wt.% TiO2 nanoparticles as replacements and then it decreases with adding of 4.0 wt.% of TiO2 nanoparticles. That produces specimens with much higher compressive strength with respect to ground granulated blast furnace specimens with content of 1.0 and 2.0 wt.% of TiO2 nanoparticles. He also [86] studied the effect of the lime on the strength and percentage of water absorption of Al2O3 nanoparticles blended concrete. The compressive strength of the specimens cured for 7, 28 and 90 days increases with added nanoparticles Al2O3 up to 1.0% as replacement and then it decreases, although the results of 2.0% as replacement are still higher than in case of the ordinary cement concrete.
Meng [87] investigated effect of nanoparticles TiO_2 on mechanical properties of the cement mortar. The compressive strength of specimen cured for 1 day increased to 60% and the compressive strength of the sample which was cured for 28 days also increased to 15% comparing to the first sample. So superplasticizer and slag powder was helpful to modify the strength of the cement mortar with nanoparticles of TiO_2 even if the improvement on fluidity was not obvious.

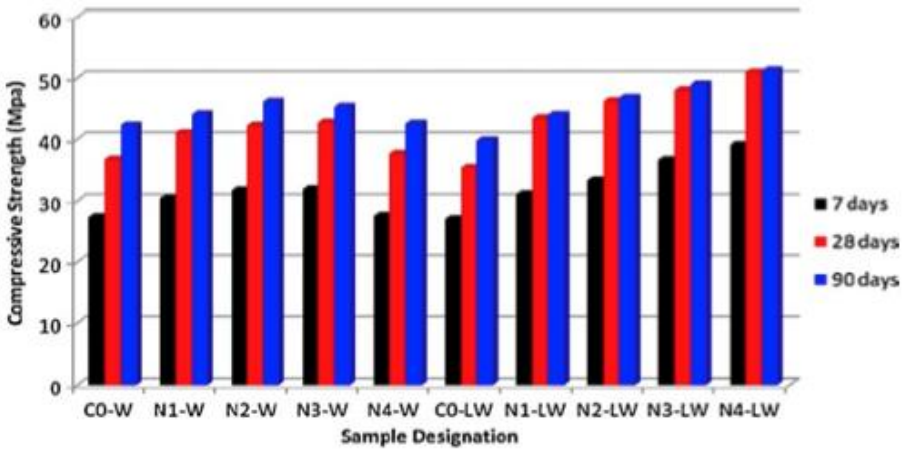

Figure 2.10 Compressive strength of nano-Al_2O_3 particles blended concrete specimens [86]

Stefanidou [88] studied the nanoparticles of SiO_2 with the size of 14 nm with 0%, 0.5%, 1%, 2% and 5% of weight. The maximum compressive strength for the amples without superplasticizer was recorded for samples with 0.5% amount of nanoparticles SiO_2 and it reached 50 MPa after curing for 28 days. Also, compressive strength increased with time. The specimens with high content of nano-SiO_2 presented lower strength in relation to the other samples. There was a 25% average increase in compressive strength if 0.5% of nano-SiO_2 was added compared to the reference samples. This increase was 20% in the case of 1% and 2% (wt.%) of nano-SiO_2 content.

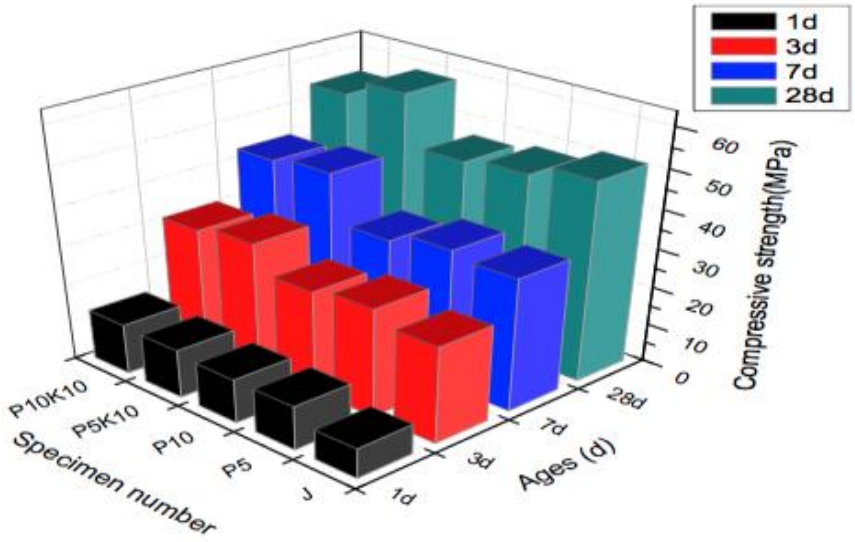

Figure 2.11 Compressive strength of cement mortar [87]

Said [89] studied the effect of nanosilica on the ordinary cement concrete and on the binary binders (ordinary cement + Class F fly ash). Results from 7 and 28 days showed that the increase in the dosage of nanosilica from 0% to 6% (wt.%) decrease the compressive strength values from 32.38 MPa to 18.54 MPa. The low

rate of strength development for concrete incorporating the Class F fly ash can be controlled by the addition of nanosilica. For long-term strength the mixtures containing a nanosilica can gain the relatively high strength after the curing for 28 days.

Aly [90] studied the nanosilica composites based on the waste glass cement. Waste glass improves the compressive strength up to 40% at 28 days of hydration compared to the control specimen. The mixture of 40 wt.% of the waste glass and 3 wt.% of nanosilica achieved a 26% increase in compressive strength with respect to the control specimen. This increase indicates that the hybrid combination of nanosilica and the waste glass greatly improves the mechanical performance of the cement matrix. Also the incorporation of nanosilica improved the impact strength of waste specimens compared to the control specimens.

Hou [91] investigated the addition of nano SiO_2 to a cement–fly ash pastes. The compressive strength of samples with content of fly ash mortars 0%, 40% and 60% increased to 9%, 50% and 64% at 7 days in case of samples with 5% (wt.%) of nanosilica added to the cement mortars. While the enhancement degrees are 10% and 20% for the 0.75% and 1.5% content of added nanosilica to the cement mortars.

Behfarnia [92] demonstrates that the compressive strength is developed in concretes containing nanoparticles in every case higher than that of control specimens. The compressive strength of concrete was considerably improved by using nano silicon dioxide particles as a part of cementitious materials. The 28-days compressive strength of concrete was enhanced as much as 16.67% in comparison to the ordinary concrete by replacing of 3 wt.% of the cement by nanosilica particles. The compressive strength increased from 16.67% to 30.13% in case that the content of nanosilica increased from 3 wt.% to 5 wt.% and then it decreased to 23.58% when the nanosilica content increased to 7 wt.%. The increase of the compressive strength of the concrete containing nanosilica in comparison to the control concrete can be attributed to the pozzolanic reaction of nanosilica.

Tanakorn [93] studied the effect of addition of nano-SiO_2 and nano-$Al2O_3$ on the properties of high calcium fly ash geopolymer pastes. Nano-particles were added to the fly ash at the dosages of 0%, 1%, 2%, and 3% of weight. At 90 days, the compressive strengths of pastes containing of 2% of the nano-SiO_2 and nano-$Al2O_3$ increased to 51.8 and 56.4 MPa, respectively compared with 39.4 MPa of the control paste. At 90 days, the flexural strengths of pastes containing of 2% nano-SiO_2 and nano-$Al2O_3$ were 5.98 and 5.92 MPa compared with 4.31 MPa of the control paste. The addition of 3% of the nanoparticles, however, started to adversely affect the strength of geopolymer. The compressive strengths at 90 days of samples with a 3% of nano-SiO_2 and nano-$Al2O_3$ reduced to 48.1 and 46.1 MPa, whereas the corresponding flexural strengths dropped to 5.23 and 5.26 MPa, respectively.

Oltulu [94] studied the cement mortars produced by the addition of silica fume and nano-SiO_2, nano-$Al2O_3$ and nano-Fe_2O_3 powders in singular, binary or ternary combinations in 3 different proportions (0.5%, 1.25% and 2.5% of weight) of the binder content. The use of nano-SiO_2 powder at proportions of 0.5% and 1.25% has increased the compressive strength in parallel to decreasing capillary absorption coefficient of the mortars, while a proportion of 2.5% has displayed the opposite effect.

Shih [95] studied the nanosilica particles with a spherical diameter of about 20 nm, that was incorporated into the Portland cement paste. The compressive strength

after 7, 14, 28 and 56 days increases with the increase of the amount of nanosilica until it reaches an optimal amount of 0.6% and then drops to some lower values in case of addition of 0.8%. With 0.6% nanosilica the mixture achieves the highest compressive strengths with the highest value of 65.62 MPa at time of 56 days.

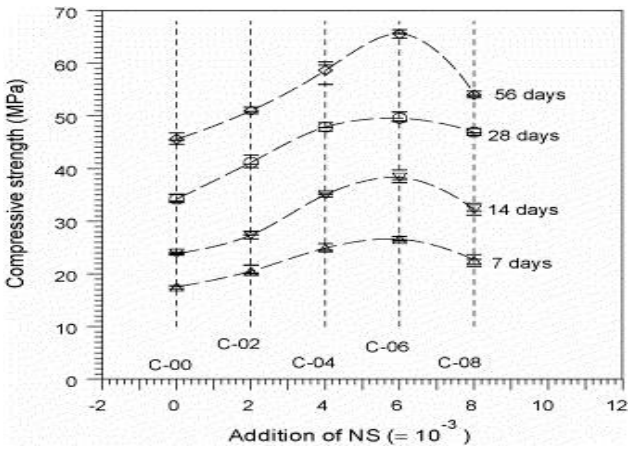

Figure 2.12 Effects of nanosilica particles on the compressive strength [95]

3 EXPERIMENTAL PROGRAM

This chapter presents the details about the development of the process of making the geopolymer concrete based on short fibers. From 2004 to present, a very little knowledge and know-how of making of geopolymer concrete based on short fibers is available in the published literature.
The technology to manufacture and test the ordinary Portland cement (OPC) is currently in use. The aim of this study was to make the promotion of this 'new' material in the concrete industry.
In order to simplify the development process, the compressive strength was selected as the decisive parameter. This is not unusual because compressive strength has an intrinsic importance for the structural design of the concrete structures [96].
Although geopolymer concrete can be made using the various sources of materials, in the present study is used only the geopolymeric mixture of baucis and the activator. In order to minimize the effect of the properties of the aggregates on the properties of geopolymer based on short fibers it was used the commonly used baucis L160 and activator L160.

3.1 Materials

3.1.1 Geopolymer L160

Geopolymer resin contained only from the ground aluminosilicate fly dust as the powder binder (baucis) and activator. The most common alkaline activator used in geopolymerisation is a combination of sodium hydroxide (NaOH) or potassium hydroxide (KOH) and sodium silicate or potassium silicate. In this study, the activator contains of Na2SO3 solution with NaOH solution which produce the alkaline silicate solution with modulus of 1.50. The ratio of H2O/Na2O used for experiments was 12. Some pure geopolymer samples with a ratio of 4:5 of weigth of the activator/baucis were tested for mechanical properties, SEM and EDX was done as well. The tested material in this study is L160 geopolymer.

Pinto [97] found that the fresh geopolymer mortar became very stiff and dry under the mixing and it also exhibited a high viscosity and cohesive properties. He suggested that the forced mixer type should be used for mixing the geopolymer materials, instead of the gravity type mixer. An increase of the mixing time caused increased the temperature of the fresh geopolymers and hence reduced the workability. To improve the workability, he suggested the use of admixtures to reduce the viscosity and cohesion.
Xu and van Deventer [13] has confirmed that the addition of sodium silicate solution into the sodium hydroxide solution as the alkaline activator enhanced the reaction between the source material and the solution.

Table 3.1 Chemical composition of geopolymer L160

Element	Na_2O	MgO	Al_2O_3	SiO_2	SiO_3	K_2O	CaO	TiO_2	FeO	Σ
Wt %	9.24	2.12	24.03	50.94	0.44	0.61	10.08	0.97	0.85	99.28

Table 3.1 shown the ratio of Si/Al and Na/Al molar ratio of 2.0 and 0.8 respectively, that is polysialate-siloxo.

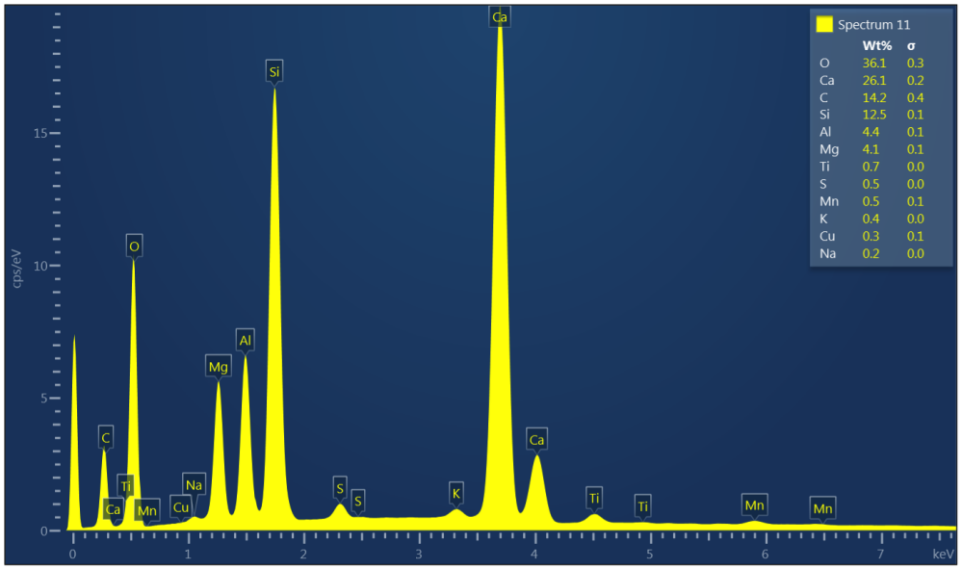

Figure 3.1 EDX of powder baucis L160 geopolymer

Figure 3.1 shows the percentage of elements in components of baucis L160.

Figure 3.2 Photo and SEM picture of powder baucis L160 geopolymer

3.1.2 Carbon fibers (CF)

Concrete is brittle and has low tensile and flexural strength and strain capacity. Fibres are ductile or quasi-ductile with the improved tensile and flexural strength, strain capacity, toughness and energy absorption. Carbon fibers are wellknown organic fibers. Carbon fibers have been the most widely used material to make composites reinforced fibers in the civil engineering applications. In this study, micro-carbonfibers (CMF) and submicro-carbonfibers (CSMF) were used.

Carbon fiber material has a wide range of applications and they can be formed at various densities in limitless shapes and sizes. Carbon fibers are often shaped into the tubing, fabric, and cloth and they can be custom-formed into any number of composite parts and pieces. In this study, carbonfibers were received from the Aerospace Eesearch and Test Institute of Prague, Czech republic as material from the recycling process reuse of carbon fibres from the aerospace industry. The CSMF was milled by a machine for about 30 minute in labrotary in The Institute for Nanomaterials, Advanced Technology and Innovation is a research centre of the Technical University of Liberec.

Table 3.2 Characteristic of used carbon fibers

Kind of fiber	Length (µm)	Diameter	Density (g/cm^3)
CMF	177	8 µm	1.75
CSMF	8.2	1.1 µm	1.75

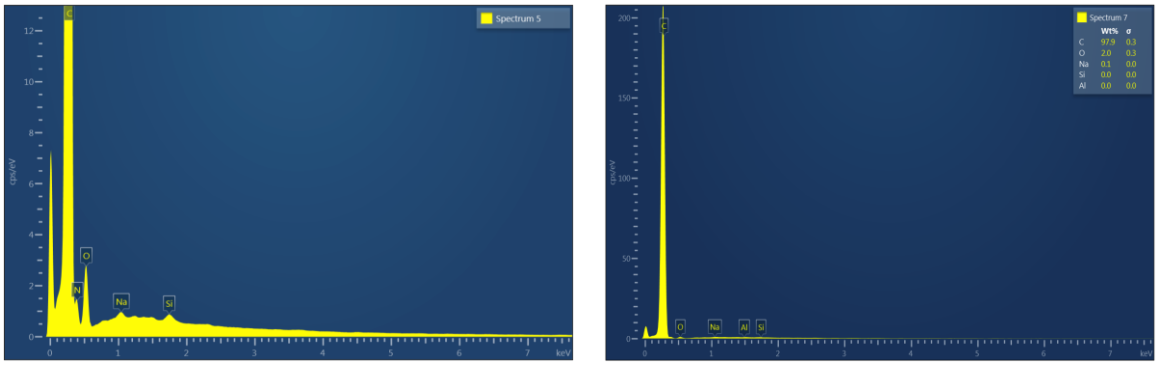

Figure 3.3 EDX spectrum of micro carbon fibers (left) and submicro fibres (right)

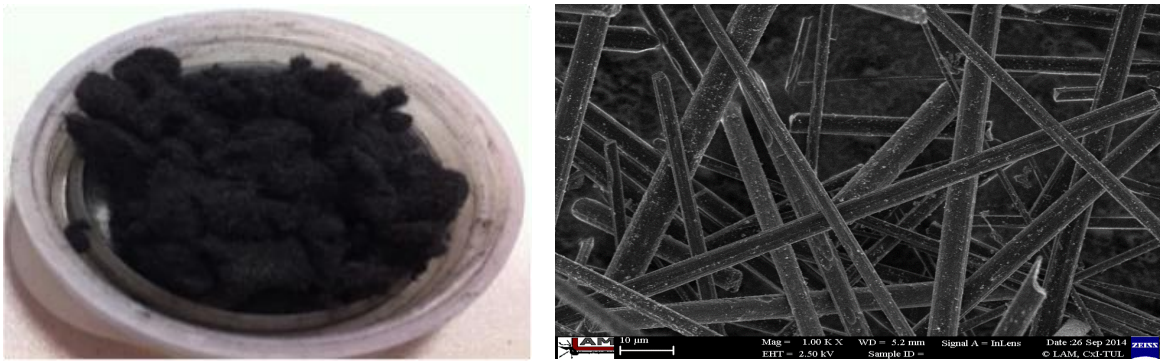

Figure 3.4 Photo and SEM of micro carbon fibers

Figure 3.5 Photo and SEM of submicro carbon fibers (milled fibers)

3.1.3 Silicon dioxide nanofibres

Silicon dioxide nanofibers are inorganic fibers. Silicon dioxide nanofibrous powder is a novel kind of the ceramic material produced by the industrial production technology operated by the company KERTAK (PARDAM nanotechnology), s.r.o. in the Czech Republic [85]. Nanofibrous products are fully comprised of ceramic basis of silicon oxide with a minor amount of porous particles of the same material. The properties and characteristics of this inorganic nanofiber material is a high specific surface area which is highly accessible for fluid media, the high collision of air draft

vs. nanofibrous surface “many times higher than regular powders”, predestine the SiO_2 nanofibrous materials as the applications in many products.

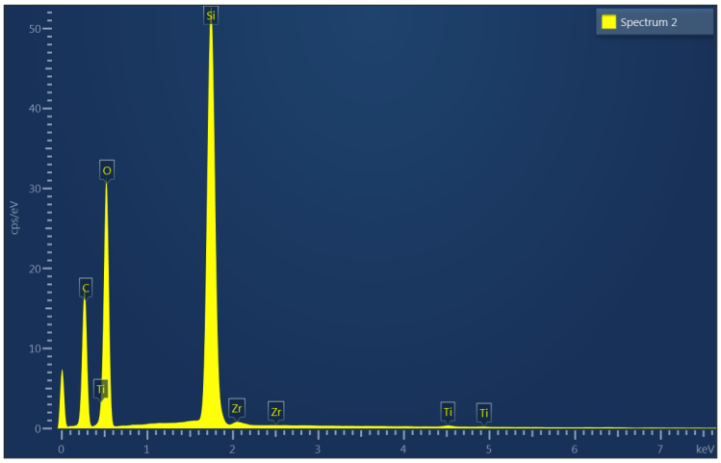

Figure 3.6 EDX of nano silicon dioxide fiber

Nanofibres have parameters: length 80.68-139.5 µm,
diameter 540 nm density 0.02 g/cm3

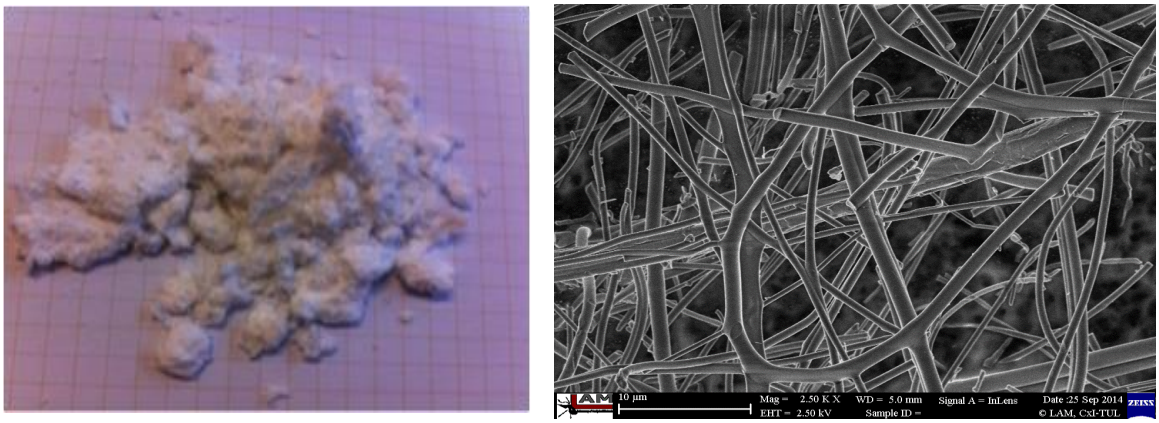

Figure 3.7 Photo and SEM of nano silicon dioxide fibers

In figure 3.7 is shown not a pure SiO2, it appear Zr, Ti in spectrum because they use the same tool for a production of the many kind of nanofibres.

3.2 Methods

3.2.1 Preparation of samples

In the beginning the big amount of trial mixtures of geopolymer concrete were manufactured.The samples were tested in the form cylinders with the size of 80 x 10 x 4 mm, 30 x 20 mm or 30 x 12 mm. Initially, the mixing was done by the mixer. However, this method was determined as impractical for large volumes .
The main objectives of the preliminary laboratory work were:

- To familiarize with the making of the geopolymer concrete based on short fibers;

- To understand the effect of the sequence of adding the alkaline activator to the solids constituents in the mixture;
- To observe the behaviour of the fresh geopolymer concrete;
- To develop the process of mixing and the curing
- and
- To understand the basic mixture proportioning of short fibers-based geopolymer concrete.

The preliminary laboratory work revealed the following:

3.2.1.1 Mixing

It was found that the fresh Cf-based geopolymer concrete was dark in colour (due to the dark colour of the Cf), and it has a lighter colour with nanosilica (not white) (due to the white colour of the white naosilica), and was cohesive.

Davidovits [3], [4] suggested that it is preferable to mix the sodium silicate solution with the sodium hydroxide solution before the adding it to the solid constituents. He also suggested that the sodium silicate liquid obtained from the common market should be in the form of a dimer or a trimer, instead of a monomer, and mixing it together with the sodium hydroxide solution assists the polymerisation process.

Based on the preparatory work, it was decided that it will used the following standard mixing process.

- Mix the baucis and activator with 4:5 in ratio (wt.%) for 3 minutes by hand;
- Mix the mixture for 5 minutes by mixer;
- Add fibres into the mixture and continue in mixing for 5 minutes to make the mixture homogeneous (Appendix A);
- Add the activator (if needed) and continue in mixing;
- Pour the mixture into the mould and
- Vibrate with the specimens for 3-5 minutes.

Figure 3.8 Baucis and activator geopolymer L160

Figure 3.9 Mixing process and moulding of samples

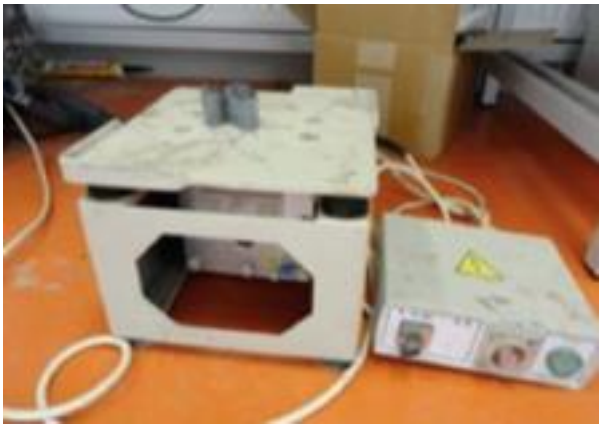

Figure 3.10 Vibration process for 3-5 minutes

3.2.1.2 Curing

Geopolymer concrete specimens should be wrapped during curing at elevated temperatures in a dry environment (in the oven) to prevent an excessive evaporation. Unlike the small geopolymer paste specimens, which can be easily wrapped by placing a lid on the mould, a suitable method was needed for large size of geopolymer concrete specimens. Extensive trials revealed wrapping of concrete specimens by using a vacuum bagging film which is effective for temperatures up to 100°C for several hours (or several days) of curing. To tighten the film of the concrete moulds was utilized. Later it was used in all further experimental work due to its simplicity and economic ease.

When specimens were cured at high temperature (from 200°C up to 1200°C), were specimens demoulding after one or two days at room temperature and then were put in the furnace (see figure 3.7). Specimens were subjected to temperatures of up to 900°C at an incremental rate of 5^0C/min from room temperature. The temperature was set at 900°C for 1 hour (3h,5h...) then the specimens were allowed to cool naturally to room temperature inside the furnace. Meanwhile, the unexposed samples were left undisturbed at ambient temperature.

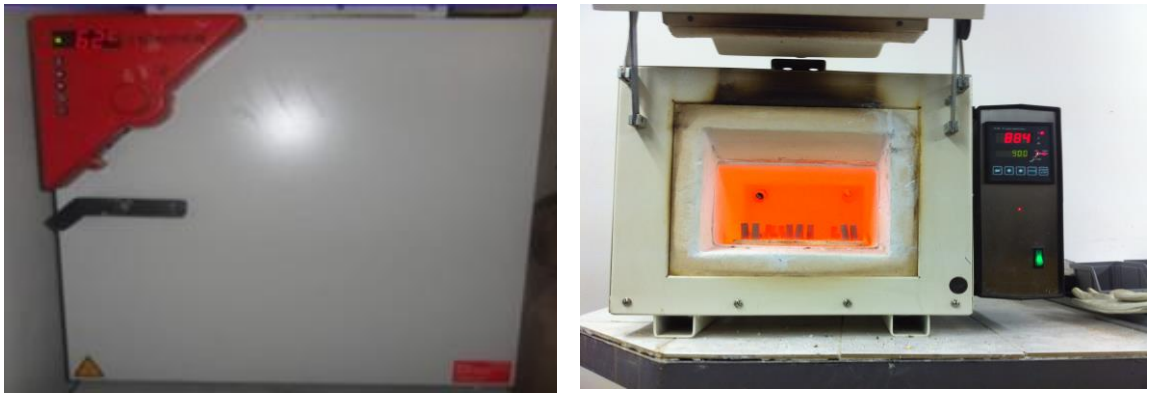

Figure 3.11 Ovens for the curing process in the Department of Material Science (TUL)

3.2.2 Samples structure and chemical analysis

The basic characterization of the geopolymer systems structure was conducted using a Carl Zeiss Ultra Plus scanning electron microscope. Before the microscopic analysis a film of gold with the thickness of 3 nanometres was vacuum-deposited on the specimens. The same instrument was used for the EDX analysis of the chemical composition.

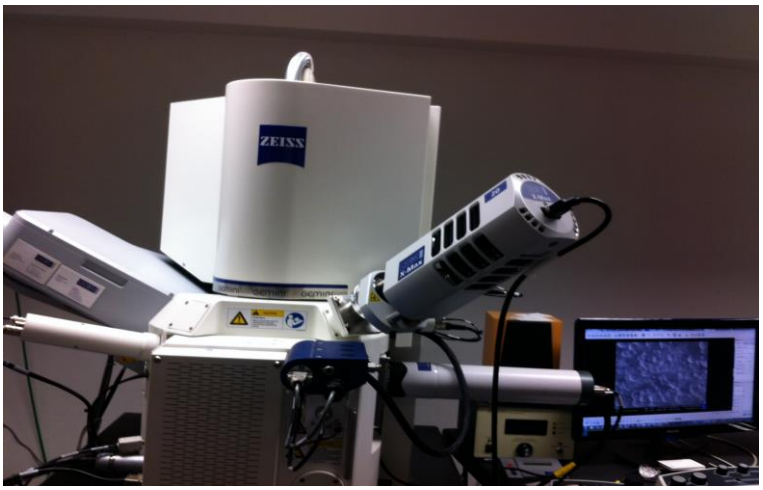

Figure 3.12 ZEISS microscope in the Department of Material Science (TUL)

3.2.3 Mechanical analysis of samples

3.2.3.1 Compressive strength tests

The compressive strength of all geopolymer mortars and concretes after 28 days was measured by testing machine Instron LaborTech 2.050, TUL (see figure 3.8). The samples were cured and tested in accordance with the Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens ASTM C39/C39M-01 [86].

Five samples of each formulation were tested and the average data were reported. The loading was controlled by displacement with a constant rate of 2 mm/min for all the tests. The compressive strength of mortar (R_m) was calculated using equation:

$R_m = F_{max}/S_0$ (3-1)

Where: R_m is compressive strength, [MPa];
F_m is the maximum load, [N];
S_0 is the original cross-sectional area of a specimen in a compression test, mm^2

3.2.3.1.1 Modulus of elasticity in compresion

According to Hardjito [100], modulus of elasticity in compression was calculated using equation:

$E_m = 2707 \times \sqrt{Rm} * 5300$ (3-2)

Where
E_m is modulus of elasticity in [MPa];
R_m is compressive strength [MPa].
The prediction of the modulus of elasticity by that equation is close to the test results and this equation is used to calculate the modulus of elasticity of geopolymer concrete, presented in this study.

3.2.3.2 Impact test

The thin small stick specimens (at 28 days) with the dimensions of 80 mm × 10 mm × 4 mm were prepared and tested for the impact test by the instrument impact tester Zwick according to European Standard EN ISO 179-1 [101]. When a test starts, the punch is raised to a specific height and then pushed down by high-pressure gas. The peak resistant load, fracture energy, and load gradient of the specimen can be measured and recorded.

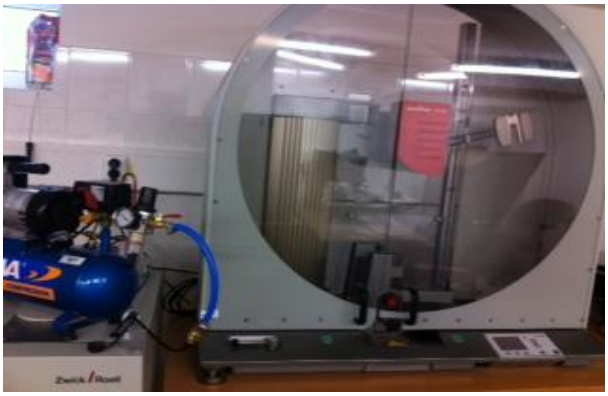

Figure 3.13 Zwick for impact test (KMT-TUL)

To caculate the Charpy impact strength of specimens without notched, a_{cU}, expessed in kilojoules per square metre, the following equation was used:

$a_{cU} = [E_c/(h.b)] \times 10^3$ [3-3]

Where
E_c is the corrected energy in J, absorbed by breaking the test specimens;
h is the thickness in [mm];

b is the width in [mm].

3.2.3.3 Hardness

In this study, the MH 180 Portable Leeb Hardness Tester was used to measure the hardness of geopolymers. This equipment can test any angle, even upside down. The hardness scales are convertable among hardness units: HRB (Rockwell Hardness B Scale), HRC (Rockwell Hardness C Scale), HV (Vicker), HB (Brinell), HS (Shore), HL (Leeb). The basic principle of this equipment is the use of an impact of the body with a certain weight against the tested surface under the certain test force, then measure the impacting velocity and the rebounding velocity of the impact body respectively when the spherically test tip is located 1 mm above the testing surface.

Figure 3.14 MH 180 Portable Leeb Hardness Tester

3.2.3.4 Fracture toughness test

Rectangular bars (after 28 days) were used in the fracture toughness measurements and tested according to ASTM D 5045 – 99 Standard Test Methods for Plane-Strain Fracture Toughness and Strain Energy Release Rate of Plastic Materials [102]. A crack with a length and thickness (depth) (a/W) ratio of 0/4 was introduced into the specimen using the 0.4 mm diamond blade to evaluate the fracture toughness. The fracture toughness KIC was calculated using the following equation:

$K_{IC} = [P_m/BW^{1/2}] \times f(a/W)$

where

where

Pm is the maximum load at crack extension [N];

B is the specimen width [mm];

W is the specimen thickness [mm];

And a is the crack length [mm];

f(a/W) is the polynomial geometrical correction factor:

f(a/W)=

$$f(x) = 6x^{1/2}\frac{[1.99 - x(1-x)(2.15 - 3.93x + 2.7x^2)]}{(1+2x)(1-x)^{3/2}}$$

Figure 3.15 Testing machine Instron (KMT-TUL)

4 RESULTS AND DISCUSSIONS

4.1 Pure geopolymer systems

Geopolymerization is an important process that determines the microstructure of geopolymer materials and their mechanical properties. There are many factors that affect the geopolymerization process such as source materials including solid raw materials, chemical and mineral additives, alkali activators, and plasticizers. Other factors are processing conditions such as pressure curing temperature and curing time [6], [103], [104].

Firstly, geopolymer was prepared by a mixing of raw material and akaline activator (baucis alkaline and baucis activator L160). The compound was mixed for 3 minutes by hand and then was mixed for 5 minutes by mixer at room temperature until the solution was homogenized. After mixing, the fresh mortar was poured in the cylindrical plastic moulds with the dimensions of 12x 30 mm cylinder (diameter x high).

The pure geopolymer G0 (without fibers) was cured at room temperature, at 60°C for 24 hours, at 100°C for 24h, at 200°C for 8h, at 300°C for 8h, at 600°C for 3h and at 800°C for 3h.

From tables 4.1, 4.2 and figures 4.1, 4.2, the results indicate that compressive strength of pure geopolymer achieves the highest value after curing at 60^0C during 24 hours with a value of 25.36 MPa which is increased for 10.07 % compared to curing at room temperature. After curing in range from 200^0C to 800^0C, compressive strength and the modulus of elasticity of geopolymer concrete decreases while increasing temperature and time. Especially this decrease is very quickly in range temperature from 600^0C to 800^0C. From 300^0C, there small cracks on surface of samples, it is to see clearly at 600^0C and 800^0C. Geopolymer can withstand the high temperature (at 800^0C on this experiment).

From figure 4.3, after analyzing of different areas by SEM scans, we concluded that bonding between elements of geopolymer was very good. Some trapped voids could be observed at several places, especially at high temperature. At 800^0C for 3 hours, matrix of geocomposite contains a lot of pores, it look like honeycomb.

Table 4.1 Properties of pure geopolymer system at diffirent temperature and diffirent times

	Hardness [HV]	Density [g/cm^3]	Compressive strength [MPa]	Modulus of elasticity compression [GPa]
at room temperature	268 ± 3.4	1.716	23.04 ±1.17	18.29 ±0.33
At 60^{0}C-24h	270 ± 4.8	1.71	25.36 ±2.23	18.93 ±0.59
At 100^{0}C-24h	280 ± 3.8	1.695	22.39 ±0.79	18.11±0.22
At 200^{0}C-8h	265 ± 4.1	1.691	20.23±2.69	17.48 ±0.78
At 300^{0}C-8h	250 ± 3.2	1.682	20.04 ±1.57	17.42 ±0.46
At 600^{0}C-3h	172 ± 2.3	1.674	10.07 ±3.04	13.89 ±1.21
At 800^{0}C-3h	161 ± 2.7	1.656	4.37 ±2.75	10.96 ±1.56

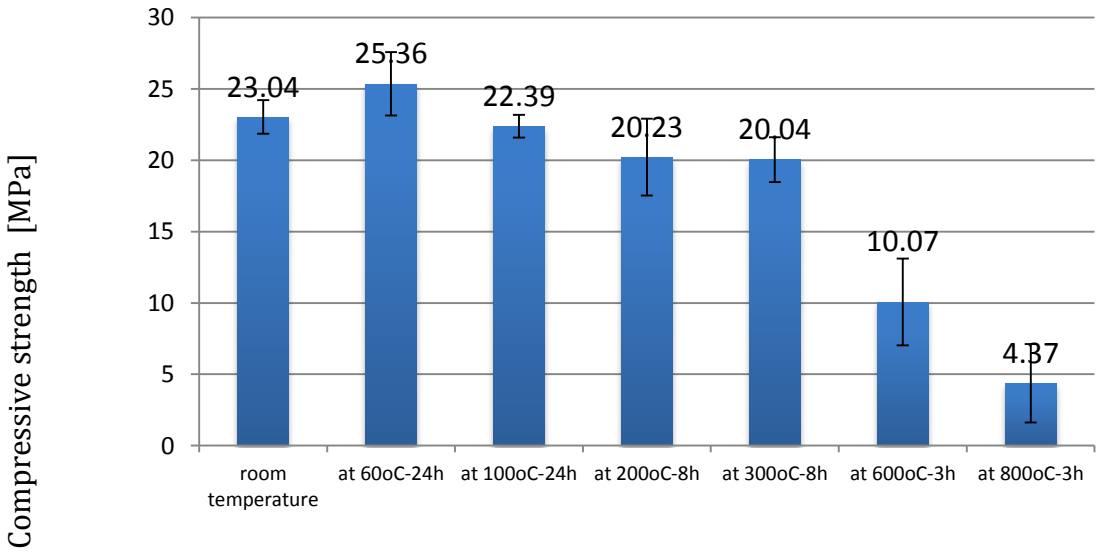

Figure 4.1 Compressive strength of pure geopolymer samples that were hardned curing at diffirent temperature and diffirent times

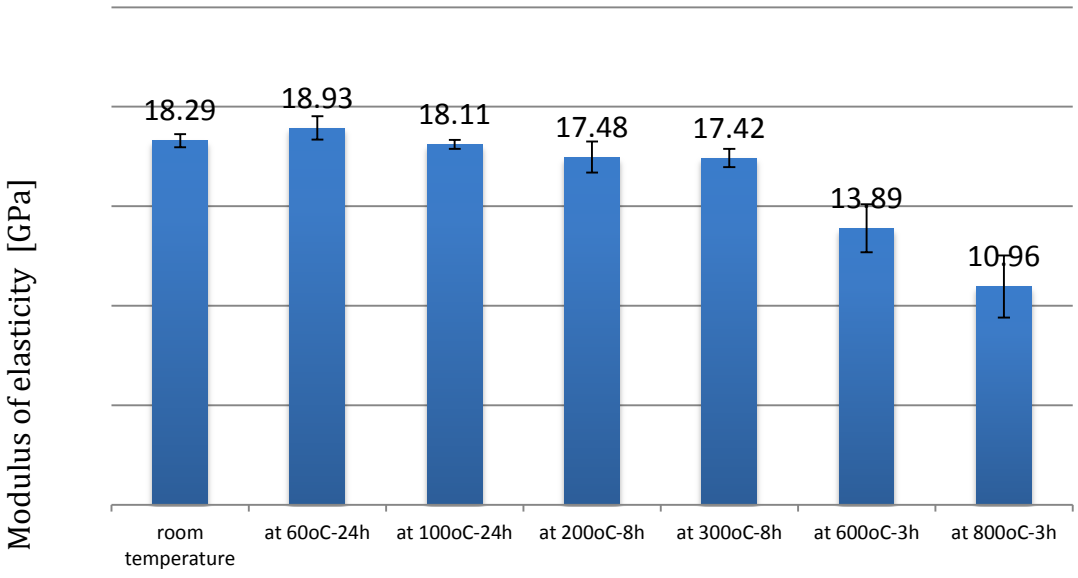

Figure 4.2 Modulus of elasticity in compression of pure geopolymer samples that were hardned curing at diffirent temperature and diffirent times

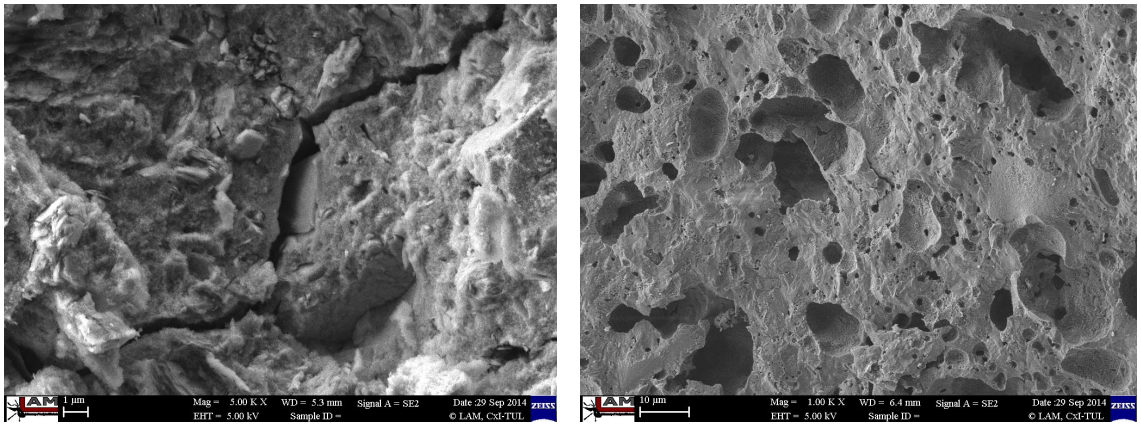

Figure 4.3 SEM pictures of pure geopolymer samples that were hardned and cured at 60^0C-24h (left) and at 800^0C-3h (right)

4.2 Geopolymer composite systems reinforced by carbon micro fibers

Cost of Nanosilica fibres are very expensive (about 8€/g, producer KERTAK company, Czech Republic) whereas carbon microfibers are 133 times less expensive compare to the cost of nanosilica (0.036-0.06 €/g). That is why the carbon microfibers is recommended to use widely.

Over the past years, various kinds of geopolymer based composites, including particulate, continuous fibers and short fibers reinforced geopolymer composites have been extensively investigated. The continuous fiber reinforced geopolymer composites have generated a great deal of attention due to their adaptability to the conventional polymer composites manufacturing techniques. Meanwhile, the high strength and modulus of the fibers can prevent the catastrophic brittle failure in composites.

In this part the properties of carbon microfibers reinforced geopolymer at high temperature were investigated.

4.2.1 Sample preparation

Firstly, geopolymer was prepared by a mixing of raw material and akaline activator (baucis alkaline and baucis activator L160). The compound was mixed for 3 minutes by hand and then was mixed for 5 minutes by mixer at room temperature until the solution was homogenized. Then the carbon microfibers with 1% (GMC1), 3% (GMC3), 5% (GMC5), 7% (GMC7), 8 % (GMC8) and 10 % (GMC10) of weight was added to the geopolymer resin mixture. The slurry was mixed for 5 minutes. After the mixing the fresh mortar was poured in the cylindrical plastic moulds with dimensions of 20x 30 mm cylinder (diameter x high). The samples were vibrated for 3 minutes and then they were wrapped.

After 1-2 days, the samples were demoulded and put into the oven (to cure at 60^0C for 24 hours, at 200^0C for 8 and 16 hours and at 300^0C for 8 and 16 hours) or furnace (up to 1200^0C) with treatment at 600^0C and at 800^0C for 1hour, 3 hours and 5 hours. Specimens were subjected to desired temperatures up to 800°C at an incremental rate of 50C/min from room temperature. The temperature was sustained at desired temperature for some hours then the specimens were allowed

to cool naturally to room temperature on the air. Meanwhile, the unexposed samples were left undisturbed at ambient temperature. Samples could be tested after 28 days.
It is difficult to mix compounds, which contains higher percentage of fibers (from 7% in weight, and with 10% fibers added, extra activator is needed).

4.2.2 Properties of carbon micro fibres based geopolymer

Properties of carbon micro fibres reinforced geopolymer are shown in tables 4.3, 4.4 and in Appendixes C1-C3.
Densities were measured in range of 1.176- 1.708 g/cm^3. Density was reduced while increasing temperature of the treatment and curing time. At 800^{0}C for 5 hours in furnace the density of sample with a content of 10% carbon fibres achives the lowest value 1.176 g/cm^3.
Hardness of samples was measured easily after curing at lower temperature. But it was very difficult to determine it after curing at high temperature (at 600^{0}C and 800^{0}C). Actually just a few papers investigated the hardness of geopolymer at high temperature.
In part 4.1, the values of measured compressive strength and modulus of elasticity of pure geopolymers were 23.04 MPa and 18.29 GPa (at room temperature), 25.36 MPa and 18.93 GPa (cured at 60^{0}C for 24 hours).
From table 4.3, 4.4 and figure 4.4, 4.5, the mechanical properties of carbon micro fibres reinforced geopolymers are always higher than values of pure geopolymers (without fibres in matrix). After curing of samples at 60^{0}C for 24 hours, compressive strength and modulus of elasticity of geopolymer composite content 8 % fibres shows the highest value of 42.37 MPa, and 22.92 GPa, respectively. The compressive strength of GMC8 is 1.67 times higher than value of pure geopolymer, and near to the value of GNS5- mixture containing 0.5 % of nanosilica fibres (44.83MPa).
It is easy to see that under the same curing condition, mixture content 8 % (GMC8) of carbon micro fibres achives the highest value of mechanical properties.
Figures 4.5- 4.9 show the strength loss of the geopolymers after being exposed to elevated temperatures. It can be observed that the geopolymer paste possesses the highest strength loss at 600°C and 800°C. Further, the geopolymer composite loses its strength after exposure to elevated temperatures of 800°C. Comparing of the thermal behavior of the carbon fibres based geopolymer with equivalent OPC paste system exposed to elevated temperatures up to 800°C, Kong and Sanjayan [105] reported that the geopolymer have superior fire resistance over the OPC paste which lost its strength at temperature of 400°C.
In addition, in this study the geopolymer paste showed a 73.4% loss of strength at 800°C, unlike the thermal performance of the geopolymer paste in the current study which lost its strength at temperature range of 600–800°C.

Table 4.2 Properties of carbon microfibers based geopolymer at 800^0C with diffirent composition and diffirent time of curing

Mixture		Hardness [HV]	Density [g/cm^3]	Compressive strength [MPa]	Modulus of elasticity compression [GPa]
GMC1	At 800^0C-1h	202 ± 4.19	1.578	10.43 ± 1.32	14.04 ± 0.56
	At 800^0C-3h	192 ± 2.7	1.575	8.34 ± 2.31	13.12 ± 0.87
	At 800^0C-5h	--*	1.542	7.84 ± 0.62	12.88 ± 0.28
GMC3	At 800^0C-1h	195 ± 3.2	1.533	8.73 ± 1.07	13.30 ± 0.47
	At 800^0C-3h	--	1.531	7.34 ± 1.57	12.63 ± 0.62
	At 800^0C-5h	--	1.625	9.08 ± 2.4	13.46 ± 1.15
GMC5	At 800^0C-1h	--	1.525	12.92 ± 2.51	15.11 ± 0.89
	At 800^0C-3h	--	1.492	11.90 ± 0.37	14.64 ± 0.17
	At 800^0C-5h	--	1.490	8.80 ± 1.34	13.33 ± 0.63
GMC7	At 800^0C-1h	179 ± 3.2	1.401	9.87 ± 0.72	13.80 ± 0.2
	At 800^0C-3h	--	1.387	9.36 ± 1.47	13.58 ± 0.47
	At 800^0C-5h	--	1.369	9.96 ± 1.57	13.84 ± 0.56
GMC8	At 800^0C-1h	--	1.376	12.92 ± 2.01	15.03 ± 0.73
	At 800^0C-3h	--	1.367	12.81 ± 2.73	14.99 ± 0.81
	At 800^0C-5h	--	1.360	10.92 ± 2.19	14.25 ± 0.75
GMC10	At 800^0C-1h	--	1.219	8.24 ± 0.92	13.07 ± 0.42
	At 800^0C-3h	--	1.191	8.01 ± 1.19	12.96 ± 0.53
	At 800^0C-5h	--	1.176	5.59 ± 1.73	11.70 ± 0.81

* it was not possible to read value.

Table 4.3 Properties of carbon microfibres based geopolymer at room temperature and curing at 60^0C for 24 hours

Mixture		Hardness [HV]	Density [g/cm^3]	Compressive strength [MPa]	Modulus of elasticity in compression [GPa]
GMC1	At room temperature	262 ± 3.6	1.708	24.46 ± 1.2	18.69 ± 0.23
	At 60^0C-24h	268 ± 4.8	1.681	26.48 ± 0.89	19.23 ± 0.32
GMC3	At room temperature	270 ± 2.9	1.658	25.43 ± 0.72	18.95 ± 0.28
	At 60^0C-24h	272 ± 5.1	1.651	27.95 ± 1.15	19.61 ± 0.17
GMC5	At room temperature	274 ± 4.1	1.647	26.48 ± 0.42	19.23 ± 0.72
	At 60^0C-24h	277 ± 3.3	1.638	31.16 ± 1.43	20.41 ± 0.69
GMC7	At room temperature	280 ± 5.6	1.612	27.54 ± 1.23	19.51 ± 0.64
	At 60^0C-24h	283 ± 6.2	1.593	33.57 ± 0.73	20.98 ± 0.38
GMC8	At room temperature	284 ± 1.9	1.567	36.77 ± 1.17	21.71 ± 0.31
	At 60^0C- 24h	286 ± 2.1	1.536	42.37 ± 0.82	22.92 ± 0.59
GMC10	At room temperature	287 ± 2.8	1.517	25.93 ± 2.1	19.08 ± 0.52
	At 60^0C-24h	290 ± 1.7	1.497	29.54 ± 1.3	20.01 ± 0.67

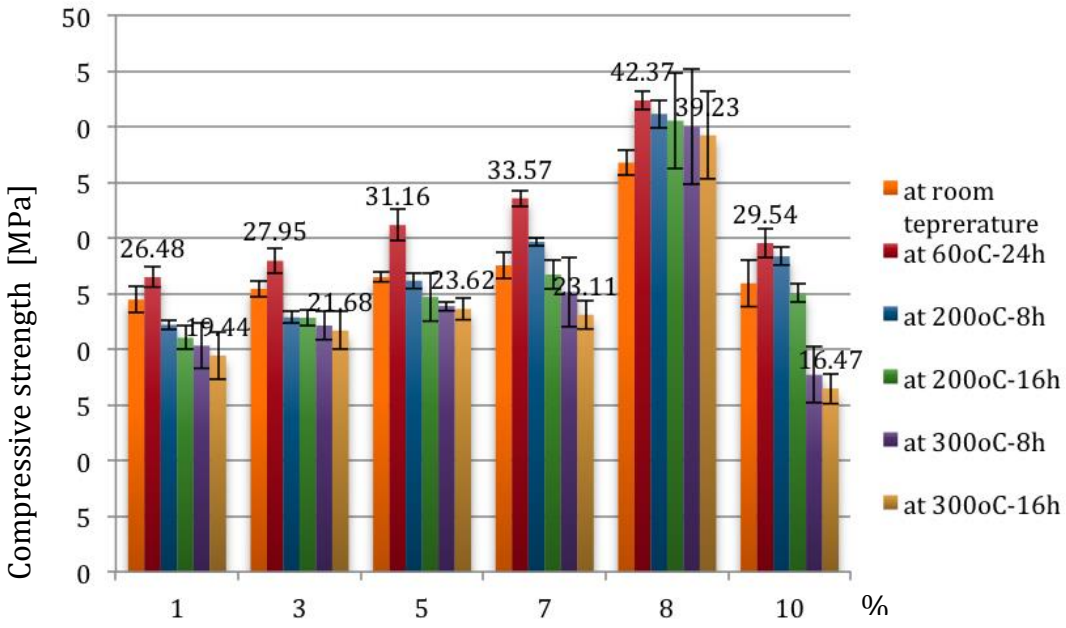

Figure 4.4 Compressive strength of carbon micro fibres based geopolymer cured at diffirent temperature and filled with diffirent amount of CMF

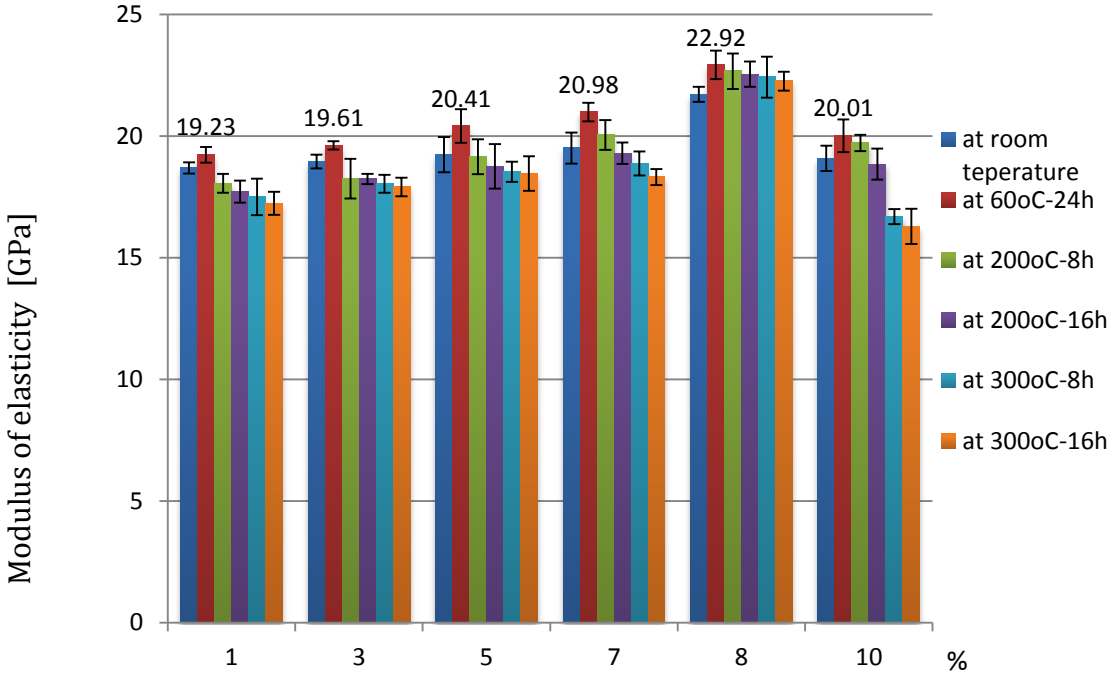

Figure 4.5 Modulus of elasticity in compression of carbon micro fibres based geopolymer cured at diffirent temperature and filled with diffirent amount of CMF

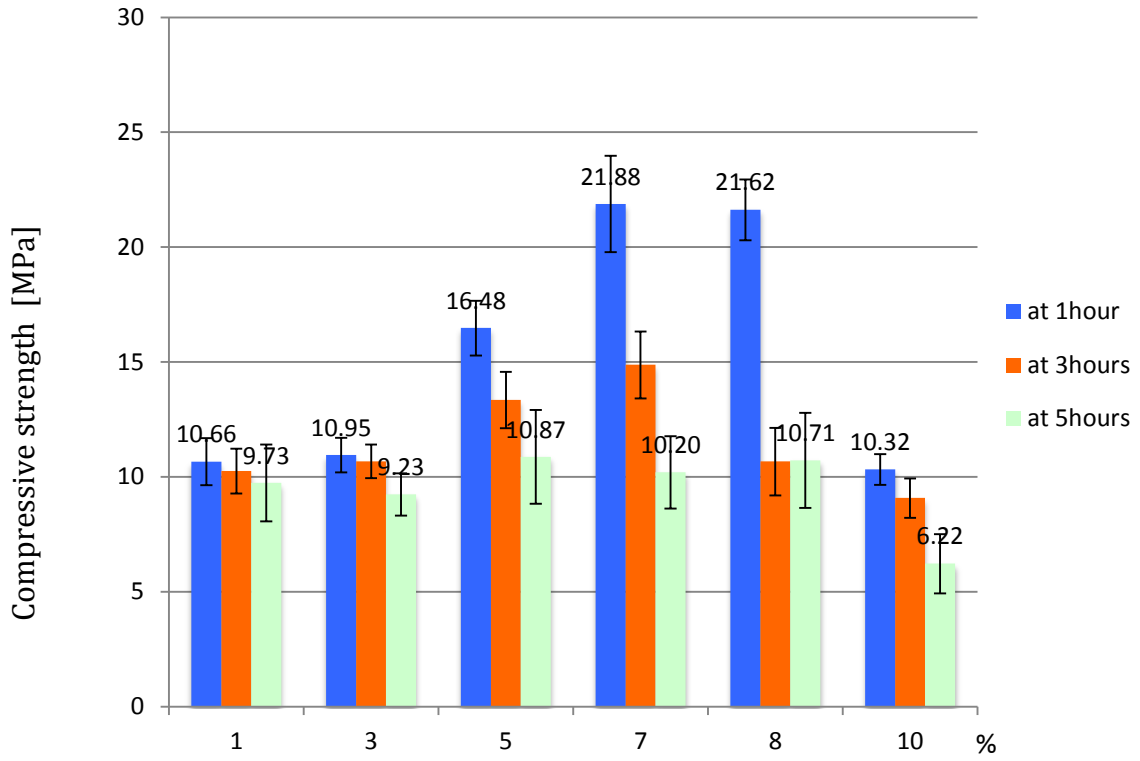

Figure 4.6 Compressive strength of carbon micro fibres based geopolymer at 600^{0}C filled with diffirent amount of CMF

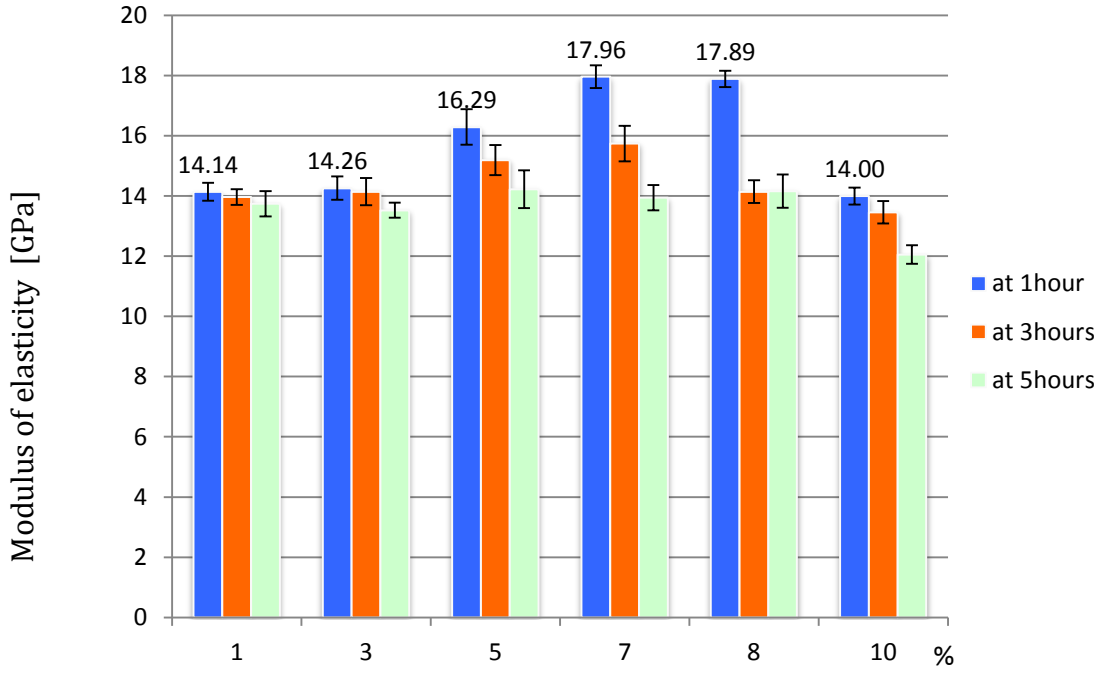

Figure 4.7 Modulus of elasticity in compression of carbon micro fibres based geopolymer at 600^{0}C filled with diffirent amount of CMF

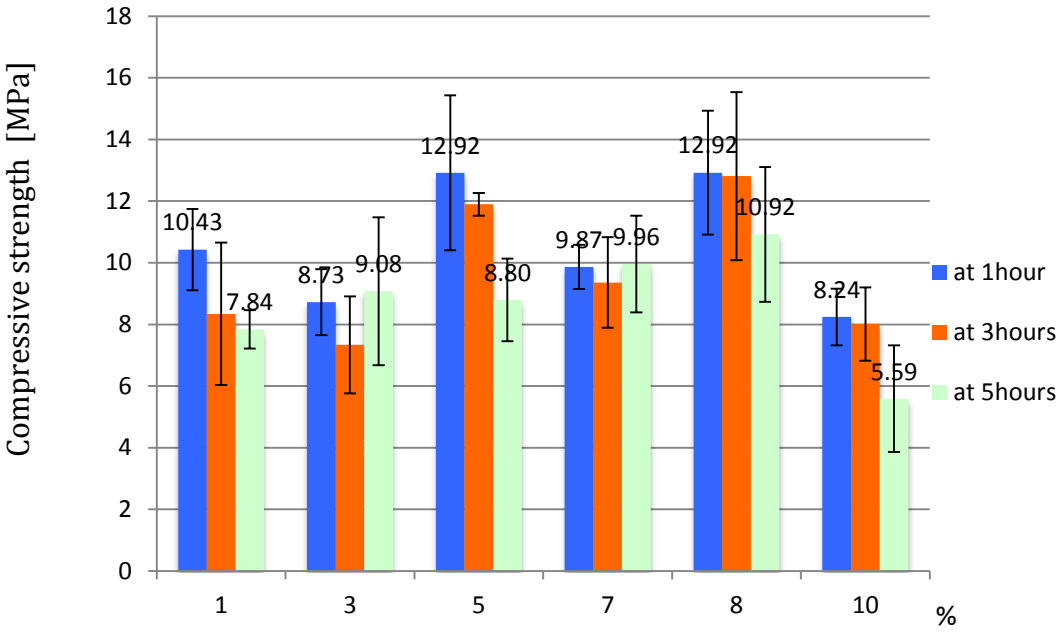

Figure 4.8 Compressive strength of carbon micro fibres based geopolymer at 800^{0}C filled with diffirent amount of CMF

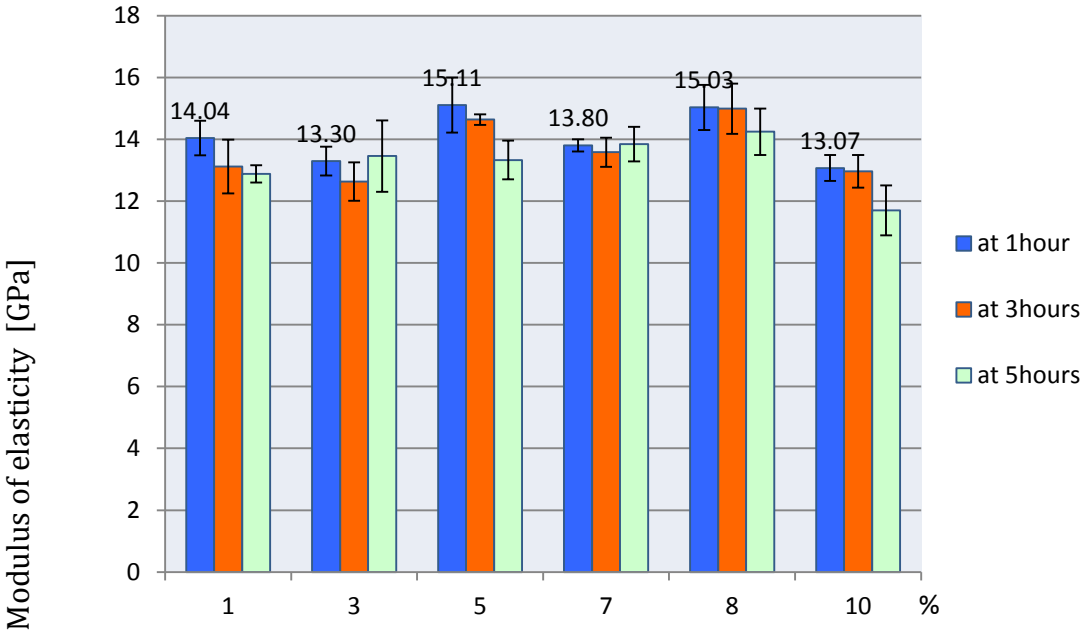

Figure 4.9 Modulus of elasticity in compression of carbon micro fibres based geopolymer at 800^{0}C filled with diffirent amount of CMF

Bakharev [106], Abdulkareem [107] and Kong [105], [108] investigated an influence of high temperature on mechanical properties of geopolymer (from 200^{0}C to 1200^{0}C). They demontrated that the thermal incompatibility between the geopolymer matrix and its aggregate components is the most likely cause of

strength loss in geopolymer concrete specimens at elevated temperatures. Bakharev shows that after curing 800^{0}C for 4hours, compressive strength of geopolymer is around 5 MPa (in this study, at 800^{0}C for 5 hours, compressive strength of geopolymer composite achieves 5.59 MPa in value).
In this study a 78.44 % of strength loss of GMC 10 at 800^{0}C for 5 hours (compared to the strength of GMC 10 at room temperature) which is shown in figure 4.7 and 4.8. The compressive strength and modulus of elasticity was decreased while elevated temperature (from 200^{0}C to 800^{0}C) and longer treatment time.
When the geopolymer composite are heat treated at 800^{0}C, the strengthening effect of the carbon fiber is dramatically decompensated. It is resulted from the serious fiber degradation and the much strong interface bonding strength of fiber/matrix. So, the composite shows substantially decreased mechanical properties and fractures.
At 800°C, geopolymer composite can withstand with a low value of 5.59 MPa in compressive strength and 11.7 GPa of modulus of elasticity in compression (GMC10-5hours).
There are some cracks and fractures in the matrix after treatment at high temperature (above 300°C).

4.2.3 Microstructure of matrix of carbon micro fibers based geopolymer concrete

The Scanning Electron Microscopy was used to the study of the microstructure of geocomposites cured at ambient conditions as well. Which can be seen from figures 4.10, 4.11 and appendixes C4-C5.
One of the possible issues was bonding and adhesion between the reinforcing fibers and the geopolymer matrix. We were not sure if the fiber would be saturated enough and if the bonding between the fibers and geopolymer glue would be sufficient. After the analyzing of samples by SEM, we recieved an information about bad adhesion between reinforcing elements and the geopolymer matrix. Some trapped voids was observed at several places, especially at high temperature. At 600^{0}C for 3 hours, matrix of geocomposite contains a lot of pores, it look like honeycomb. These pores are likely caused by two reasons: (1) the residual of air bubbles that were introduced into the geopolymer precursor through the mixing or trapped inside the geopolymer when the precursor was poured into the mold; and (2) the space that was previously occupied by water created a cavity after water evaporating.

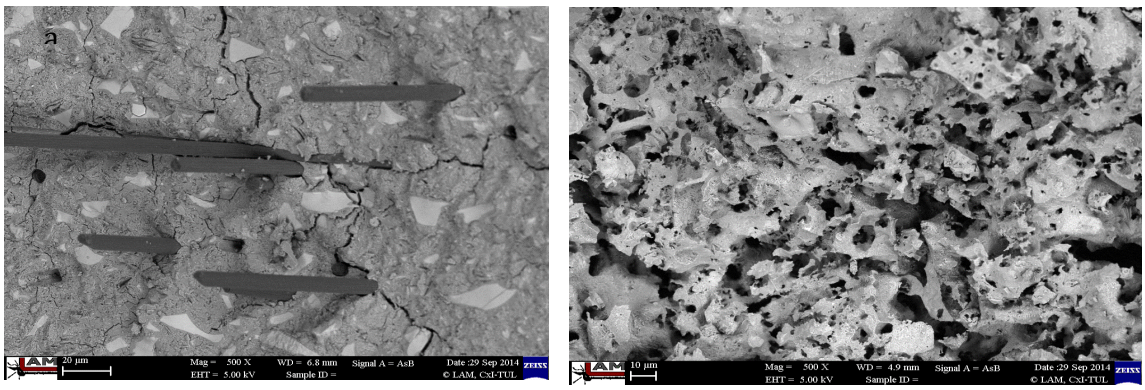

Figure 4.10 SEM of 10 % carbon micro fibres based geopolymer at 60^{0}C-24h (left) and at 600^{0}C-3h (right)

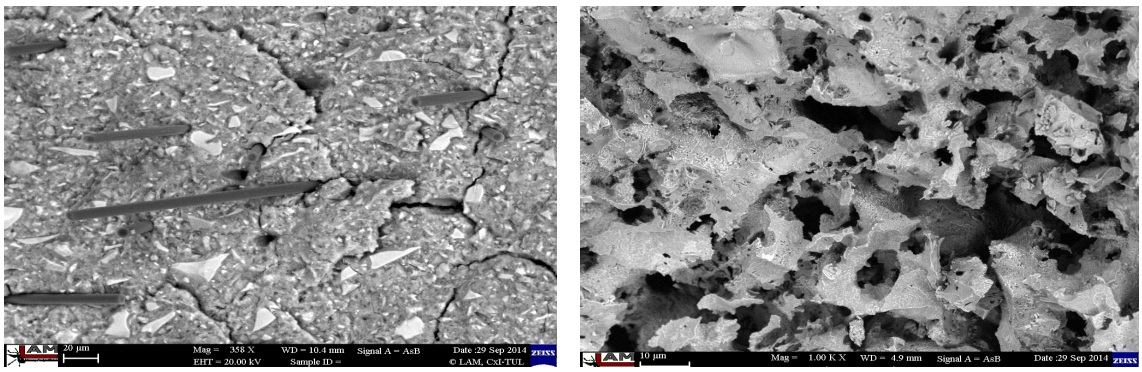

Figure 4.11 SEM of 7 % carbon micro fibres based geopolymer at 60^0C-24h (left) and at 800^0C-5h (right)

4.2.4 Conclusions

The emphasis of this chapter was to indicate the properties of carbon micro fibres reinforced geopolymer treated at high temperature (from at 200^0C and 300^0C for 8, 16 hours and at 600^0C, 800^0C for 1, 3, 5 hours). The main results of this chapter can be summarised following:

- ✓ Densities were measured in range 1.176- 1.708 g/cm^3. Density were reduced while increasing treatment temperature and curing time. At 800^0C for 5 hours in furnace the density of 10% carbon fibres content achives the lowest value 1.176 g/cm^3.
- ✓ Mechanical properties of carbon micro fibres reinforcing geopolymer are always higher than value of pure geopolymer (without fibres in matrix).
- ✓ After curing at 60^0C for 24 hours the compressive strength and modulus of elasticity of geopolymer composite with content 8 % of fibres samples reached the highest values of 42.37 MPa, and 22.92 GPa, respectively. The compressive strength of GMC8 was 1.67 times higher than value of pure geopolymer, and near to the value of GNS5- mixture contains 0.5 % of nanosilica fibres (44.83MPa).
- ✓ Under the same curing conditions the mixture with contents 8 % (GMC8) of carbon micro fibres achieved the highest mechanical properties.
- ✓ A 78.44 % loss of compressive strength of GMC10 at 800^0C for 5 hours (compared to strength of GMC10 at room temperature) was shown.
- ✓ The compressive strength and the modulus of elasticity decreased while elevated temperature (from 200^0C to 800^0C) and longer treatment time increased.
- ✓ At 800^0C, geopolymer composite can withstand with low values 5.59 MPa of compressive strength and 11.7 GPa of modulus of elasticity in compression (GMC10-5hours).
- ✓ At 600^0C and 800^0C, the composite systems shows substantially decreased mechanical properties and fractures with very brittle manner.
- ✓ After the analyzing using SEM of different areas of the reinforcing surfaces, we concluded that bonding between the carbon fibers and geopolymer was bad.
- ✓ Some trapped voids was observed at several places, especially at high temperature.

4.3 Geopolymer composite systems reinforced by carbon sub-micro fibers

In part 4.2 the carbon micro fibres reinforced geopolymer were investigated. Cost of Nanosilica fibres are very expensive (about 8€/g, producer KERTAK company, Czech Republic) whereas carbon microfibers are 133 times less expensive compare to the cost of nanosilica (0.036-0.06 €/g). These fibres were milled from the carbon micro fibres by milling machine Retsch CryoMill in CxI laboratory.

4.3.1 Sample preparation

Carbon sub-micro fibres were milled by the machine for 30 min in total.
The geopolymer was prepared by a mixing of raw material and akaline activator (baucis alkaline and baucis activator L160). The compound was mixed for 3 minutes by hand and then was mixed for 5 minutes by mixer at room temperature until the solution was homogenized. Then the carbon microfibers with 1% (GMC1), 3% (GMC3), 5% (GMC5), 7% (GMC7), 8 % (GMC8) and 10 % (GMC10) of weight was added to the geopolymer resin mixture. The slurry was mixed for 5 minutes. After the mixing the fresh mortar was poured in the cylindrical plastic moulds with dimensions of 20x 30 mm cylinder (diameter x high). The samples were vibrated for 3 minutes and then they were wrapped.
After 1-2 days, the samples were demoulded and put into the oven (to cure at 60^0C for 24 hours, at 200^0C for 8 and 16 hours and at 300^0C for 8 and 16 hours) or furnace (up to 1200^0C) with treatment at 600^0C and at 800^0C for 1hour, 3 hours and 5 hours. Specimens were subjected to desired temperatures up to 800°C at an incremental rate of 50C/min from room temperature. The temperature was sustained at desired temperature for some hours then the specimens were allowed to cool naturally to room temperature on the air. Meanwhile, the unexposed samples were left undisturbed at ambient temperature. Samples could be tested after 28 days.

4.3.2 Properties of carbon sub-micro fibres based geopolymer

Properties of carbon sub-micro fibres reinforced geopolymer are shown in tables 4.5, 4.6 and in Appendixes D1-D4.
Densities were measured in range 1.412- 1.697 g/cm^3. Densities of samples were reduced while increasing treatment temperature and curing time. At 900^0C for 5 hours in furnace, density of sample with content of 1% carbon sub-micro fibres achieved the lowest value of density 1.412 g/cm^3.
Hardness was measured after the curing at lower temperature. But it was very difficult to determine the hardness after curing at high temperature (above 600^0C).
In part 4.1, the compressive strength and the modulus of elasticity of pure geopolymer showed values of 23.04 MPa and 18.29 GPa (at room temperature), 25.36 MPa and 18.93 GPa (curing at 60^0C for 24 hours).
After curing at 60°C for 24 hours, compressive strength, and modulus of elasticity of geopolymer composite with content of 8 % carbon micro fibres had the highest value of 42.37 MPa, and 22.92 GPa, respectively. After curing at 60°C for 24 hours the compressive strength and the modulus of elasticity of geopolymer composite with content of 0.7 % nano fibres SiO2 had values of 47.69 MPa and 23.99GPa (see part 4.4). In table 4.5, it is shown that at 60°C for 24 hours the compressive strength and the modulus of elasticity of geopolymer composite with content of 0.7 % carbon sub-micro fibres had values of 39.81 MPa and 22.38 GPa. It means that

mechanical properties of fibres based geopolymer are always higher than values of pure geopolymer (without fibres).

From part 4.4 indicates that after 600C for 24 hours the compressive strength and modulus of elasticity of geopolymer composite with content of 0.7 % carbon sub-micro fibres are higher than other geopolymer composite with 0.3 % nano fibres SiO_2. Due to the commercial price, carbon micro fibres and carbon sub-micro fibres are recommended to use widely.

Under the same curing conditions the geopolymer composite with 0.7 % of sub-micro fibres achieved the highest mechanical properties. The samples had value of 39.81 MPa of the compressive strength and 22.38 GPa of the modulus of elasticity in compression to curing at 60^0C for 24 hours. Compressive strength of GSC7 was 1.69 times higher than value of pure geopolymer

The compressive strength and modulus of elasticity were decreased with increasing temperature of curing and tretment time (from 200^0C to 900^0C).

As risen temperature from 40° to 600°C the average strength loss was for about 17.2 % in case of all of specimens (appendix D1, D2).

As risen temperature from 60° to 800^0C, the average strength loss was for about 22.3 % in case of all of specimens (appendix D2, D3).

As risen temperature from 80° to 900^0C, the average strength loss was for about 25.93 % in case of all of specimens (shown in table 4.6 and appendix D3). It reduced very quickly.

Table 4.4 Properties of carbon sub-micro fibres based geopolymer at room temperature and at 60^0C for 24 hours

Mixture		Hardness [HV]	Density [g/cm^3]	Compressive strength [MPa]	Modulus of elasticity in compression [GPa]
GSC1	At room temperature	263 ± 3.6	1.697	24.51 ± 0.93	18.70 ± 0.47
	At 60^0C-24h	270 ± 4.8	1.685	24.91 ± 1.34	18.81 ± 0.34
GSC3	At room temperature	272 ± 2.7	1.668	31.85 ± 1.06	20.58 ± 0.55
	At 60^0C-24h	274 ± 4.3	1.657	37.08 ± 1.67	21.78 ± 0.63
GSC5	At room temperature	275 ± 3.8	1.654	32.92 ± 0.55	20.83 ± 0.39
	At 60^0C-24h	280 ± 2.3	1.648	38.96 ± 0.76	22.20 ± 0.54
GSC7	At room temperature	279 ± 3.1	1.623	39.41 ± 2.15	22.29 ± 0.63
	At 60^0C-24h	285 ± 4.5	1.612	39.81 ± 1.92	22.38 ± 0.61
GSC10	At room temperature	288 ± 3.4	1.598	34.76 ± 1.35	21.26 ± 0.71
	At 60^0C-24h	295 ± 2.2	1.575	36.92 ± 0.77	21.75 ± 0.52

Table 4.5 Properties of carbon sub-micro fibres based geopolymer at 900^0C

Mixture		Hardness [HV]	Density [g/cm^3]	Compressive strength [MPa]	Modulus of elasticity in compression [GPa]
GSC1	At 900^0C-3h	--	1.597	9.25 ± 0.89	13.53 ± 0.75
	At 900^0C-5h	--	1.585	7.74 ± 0.83	12.83 ± 0.81
GSC3	At 900^0C-3h	--	1.572	9.42 ± 0.34	13.61 ± 1.06
	At 900^0C-5h	--	1.561	7.94 ± 0.75	12.93 ± 0.89
GSC5	At 900^0C-3h	--	1.532	9.52 ± 0.73	13.65 ± 1.12
	At 900^0C-5h	--	1.527	8.02 ± 0.87	12.97 ± 0.56
GSC7	At 900^0C-3h	--	1.512	9.78 ± 1.04	13.77 ± 1.21
	At 900^0C-5h	--	1.491	8.31 ± 0.94	13.10 ± 0.92
GSC10	At 900^0C-3h	--	1.467	8.93 ± 1.23	13.39 ± 1.21
	At 900^0C-5h	--	1.412	6.71 ± 1.06	12.31 ± 0.45

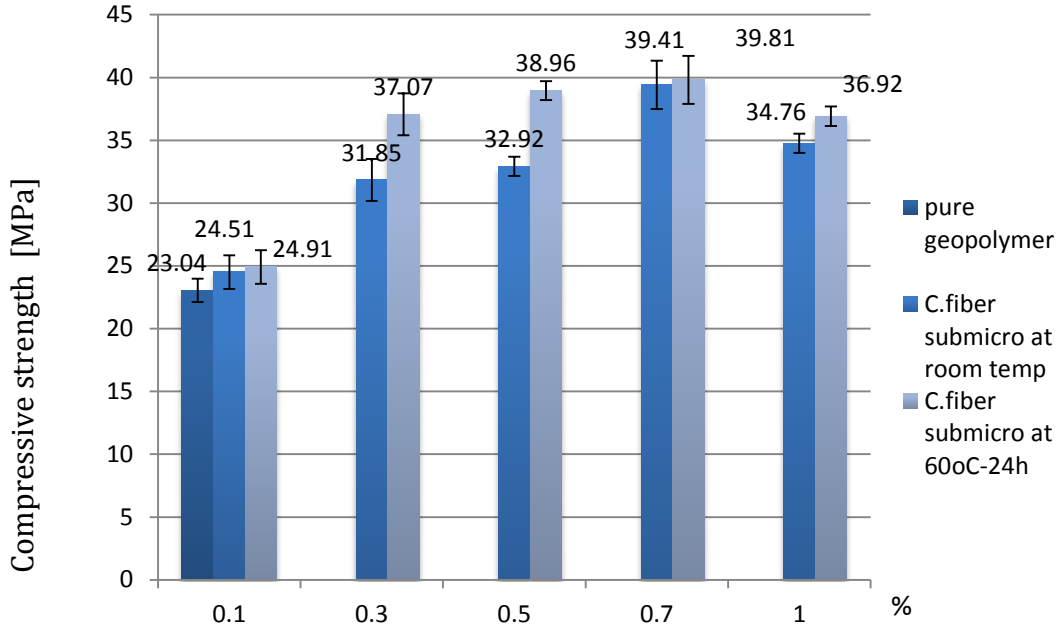

Figure 4.12 Compressive strength of carbon sub-micro fibres based geopolymer at room temperature and at 60^0C-24h filled with diffirent amount of CSMF

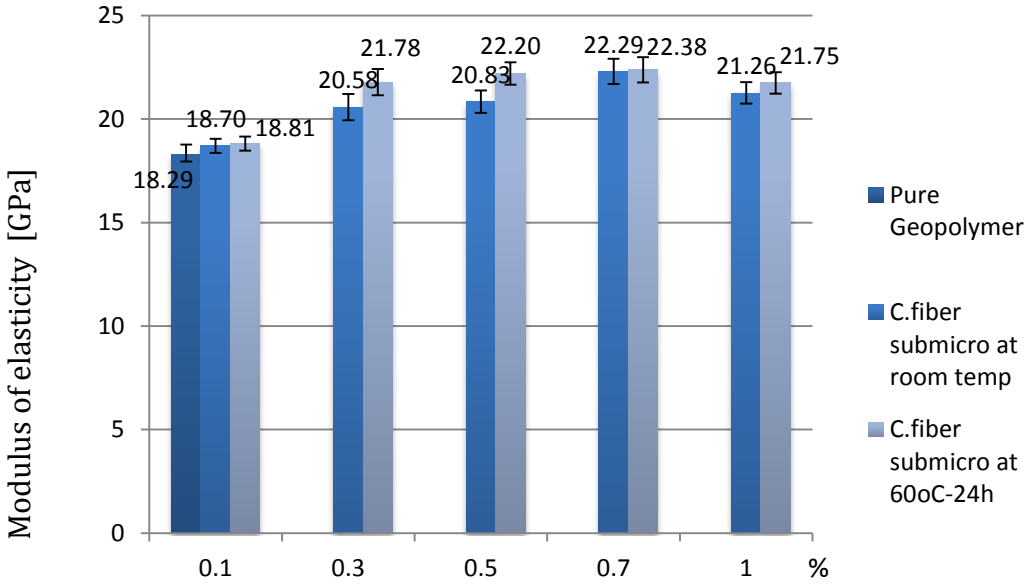

Figure 4.13 Modulus of elasticity in compression of carbon sub-micro fibres based geopolymer at room temperature and at 60^0C-24h filled with diffirent amount of CSMF

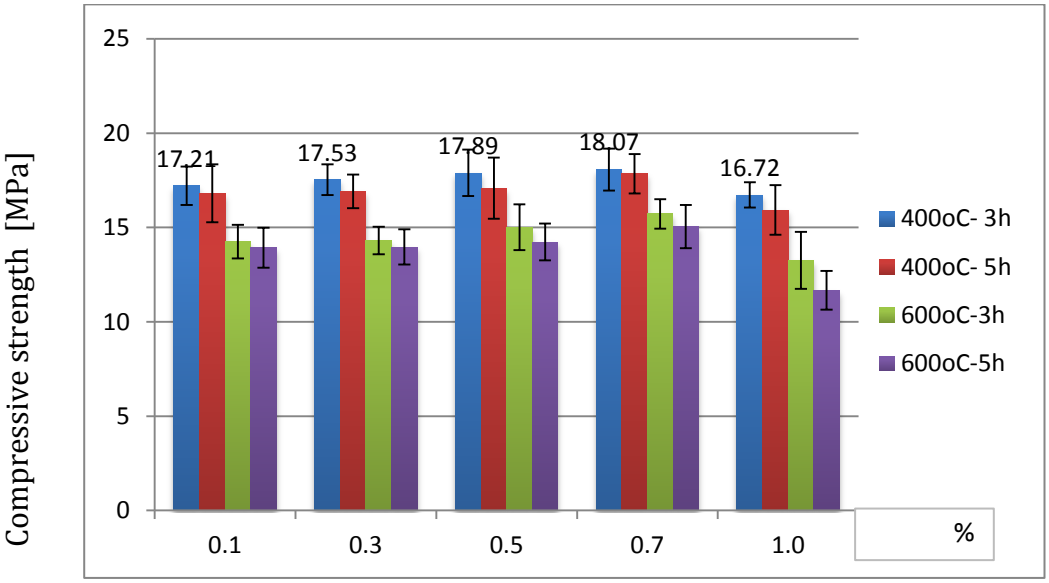

Figure 4.14 Compressive strength of carbon sub-micro fibres based geopolymer at 400^0C and at 600^0C filled with diffirent amount of CSMF

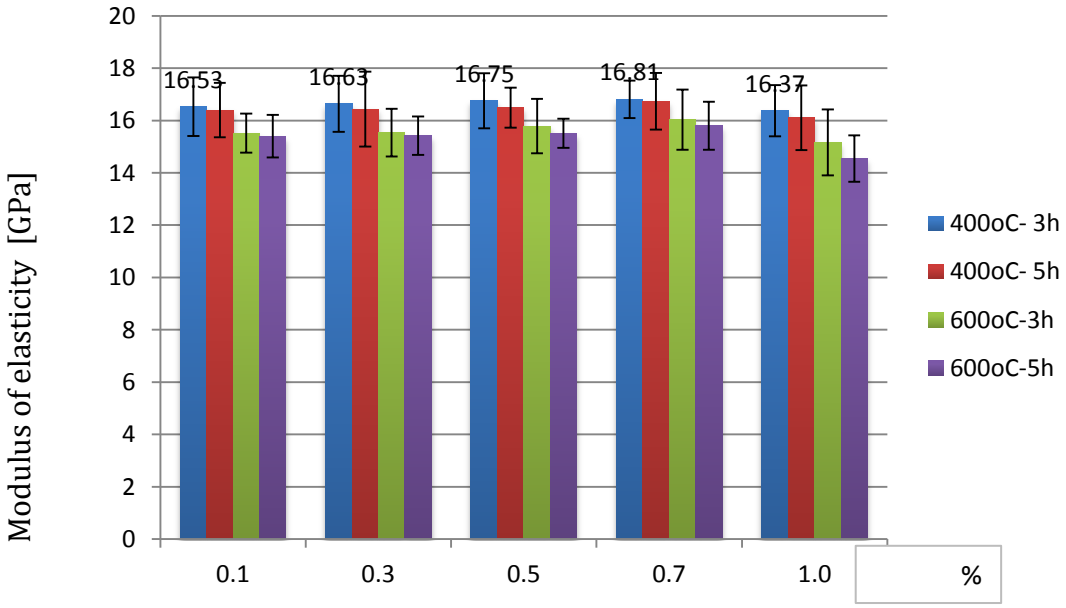

Figure 4.15 Modulus of elasticity in compression of carbon sub-micro fibres based geopolymer at 400^0C and at 600^0C filled with diffirent amount of CSMF

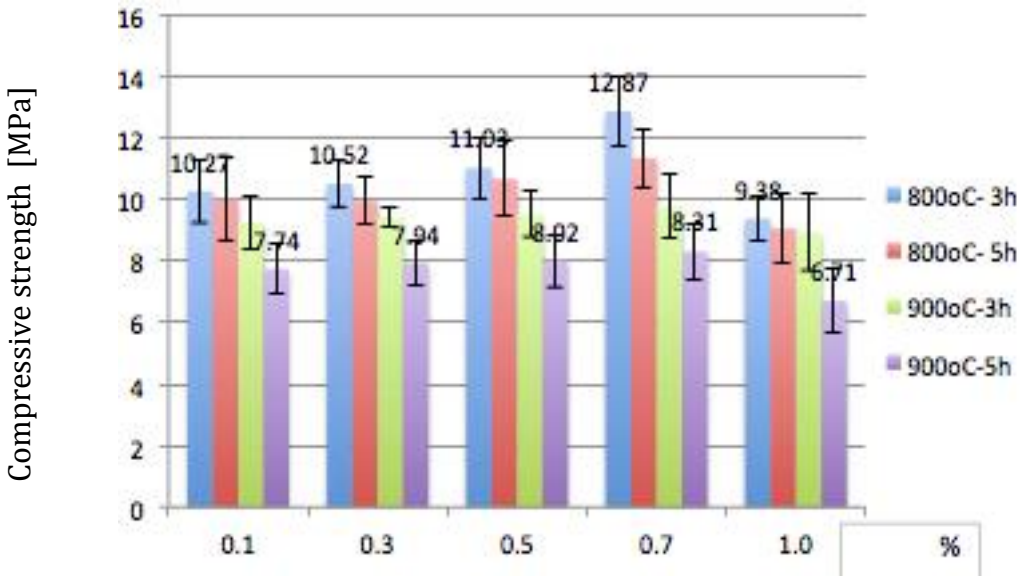

Figure 4.16 Compressive strength of carbon sub-micro fibres based geopolymer at 800^{0}C and at 900^{0}C filled with diffirent amount of CSMF

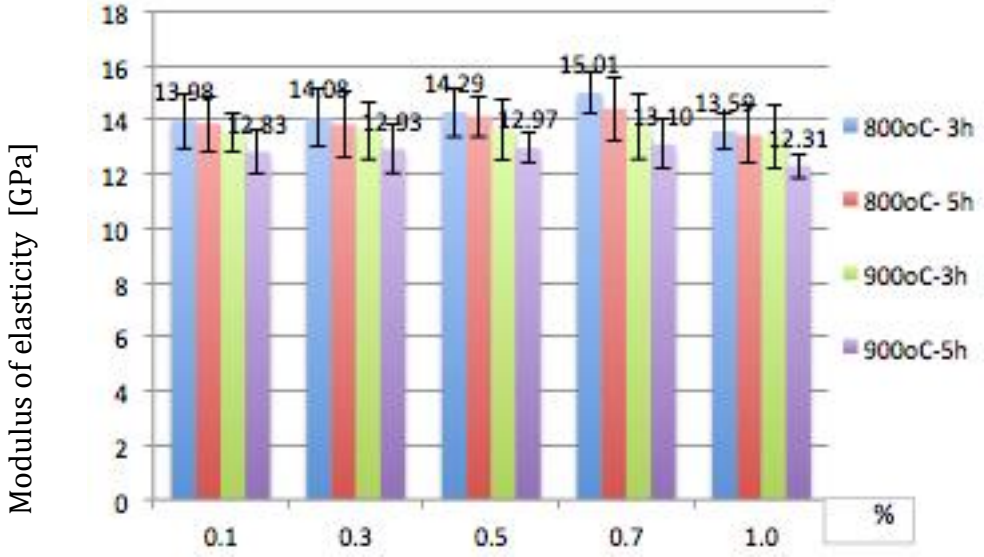

Figure 4.17 Modulus of elasticity in compression of carbon sub-micro fibres based geopolymer at 800^{0}C and at 900^{0}C filled with diffirent amount of CSMF

In this study the geopolymer can withstand up to 900^{0}C with a value 6.71 MPa of compressive strength and 12.31 GPa of modulus of elasticity in compression to GSC10. After the fire exposures the geopolymer concrete specimens were found to suffer less damage in terms of cracking than the OPC concrete specimens. The OPC concrete cylinders suffered severe spalling for 800^{0}C and 1000^{0}C exposures, while there was no spalling in the geopolymer concrete specimens. The geopolymer concrete specimens generally retained higher strength after temperature exposition than the OPC concrete specimens [109].

When the geopolymer composite are thermal treated at 900^{0}C the strengthening effect of carbon fiber is dramatically decompensated. It is resulted from the serious fiber degradation. So, the composite shows substantially decreased mechanical properties and fractures and also showed a very brittle manner.

Sarker [109], Zhang [110], Bakharev [106] and Kong [108] also investigated the effect of elevated temperature on geopolymer. They show that heat transport is faster in geopolymer concrete than in OPC concrete when the samples were exposed to fire. Significant spalling occurred in the OPC concrete specimens for fires at tempeatures of 800 and 1000^0C. The spalling did not occur in the geopolymer concrete specimens which were exposed to the same fire temperatures. Extensive surface cracking appeared in the OPC concrete cylinders after the fire exposure at 400, 650, 800 and 1000^0C. From appendix D4 is evident that the mixture of nanosilica and carbon sub-micro fibers based geopolymer had highest value of 41.79 MPa of the compressive strength and 22.8 GPa of modulus of elasticity (after curing at 60^0C for 24hours) with 0.5 % nanosilica and carbon sub-micro fibres.

4.3.3 Microstructure of matrix of carbon sub-micro fibers based geopolymer concrete

The geopolymer microstructure remained stable after exposure to high temperature (about 100^0C). It can be found that a small amount of microcracks on the surface of the specimens in below figures, when the specimens were cured at room temperature for 28 days. Some of small caverns can be seen on the surface of the SEM micrographs for all of specimens after exposure to elevated temperatures from 400 to 900^0C in. However, as the specimen is heated at 900^0C, a lot of big caverns can be seen on the surface of micrographs, which is probable owing to the partial collapse of geopolymer matrix caused by the weight loss, matrix decomposition and phase transformations.

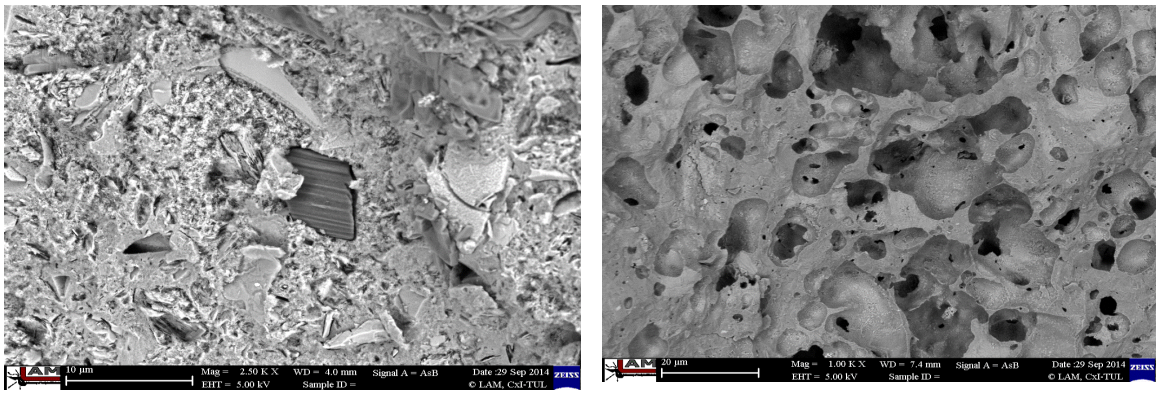

Figure 4.18 SEM of 0.5 % carbon sub-micro fibres based geopolymer at 60^0C-24h (left) and at 900^0C-3h (right)

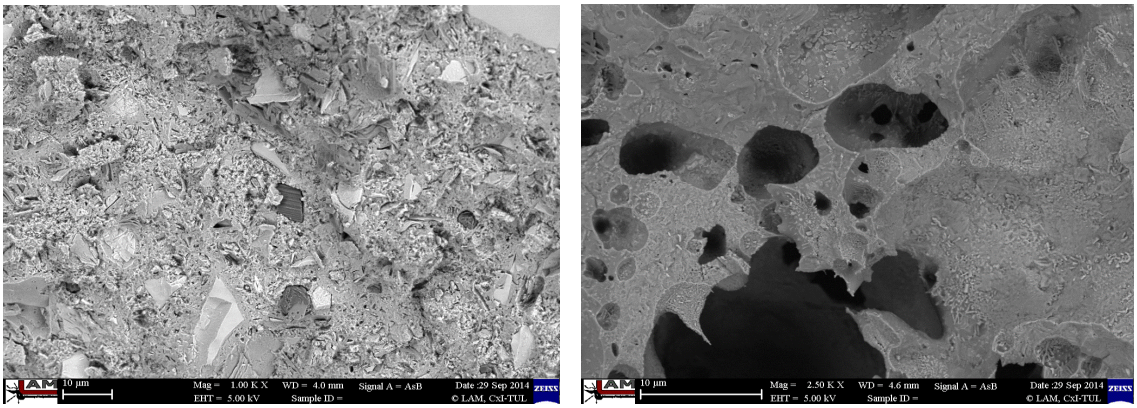

Figure 4.19 SEM of 0.7 % carbon sub-micro fibres based geopolymer at 60^0C-24h (left) and at 600^0C-3h (right)

4.3.4 Concluding remarks

Densities were measured in range 1.412- 1.697 g/cm^3. Densities were reduced while increasing treatment temperature and curing time. At 900^{0}C for 5 hours in furnace, the density of samples with 1% of carbon sub-micro fibres achieved the lowest value of 1.412 g/cm^3.

Hardness was measured after the curing at lower temperature. But it was very difficult to determine it after curing at high temperature (above 600^{0}C).

After curing at 60^{0}C for 24 hours the compressive strength and the modulus of elasticity of geopolymer composite with content of 8 % carbon micro fibres had the highest value of 42.37 MPa, and 22.92 GPa, respectively. After curing at 60^{0}C for 24 hours the compressive strength and modulus of elasticity of geopolymer composite with content of 0.7 % SiO_2 nano fibres had value of 47.69 MPa and 23.99GPa, respectively. In table 4.4, it is shown that at 60^{0}C for 24 hours the compressive strength and the modulus of elasticity of geopolymer composite with content of 0.7 % carbon sub-micro fibres had value of 39.81 MPa and 22.38 GPa. It means that geopolymer composite systems has values of mechanical parameters always higher than the pure geopolymer.

After 60^{0}C for 24 hours the compressive strength and the modulus of elasticity of geopolymer composite with content of 0.7 % carbon sub-micro fibres was than geopolymer composite with 0.3 % nanofibres SiO_2. Due to the commercial price, the carbon micro fibres and carbon sub-micro fibres are recommended to use widely.

Under the same curing conditions the geopolymer composite with 0.7 % of sub-micro fibres achieved the highest mechanical properties. The compressive strength was about 39.81 MPa and 22.38 GPa of modulus of elasticity in compression after curing at 60^{0}C for 24 hours. The compressive strength of GSC7 was 1.69 times higher than values of pure geopolymer.

The strength and modulus were decreased while elevated temperature (from 200^{0}C to 900^{0}C) and longer treatment time.

As risen temperature from 400 to 600^{0}C, the average strength loss was 17.2 % for all of specimens.

As risen temperature from 600 to 800^{0}C, the average strength loss was 23.2 % for all of specimens.

As risen temperature from 800 to 900^{0}C, the average strength loss was 25.93 % for all of specimens. It is reduced very quickly.

Some of small amount of microcracks could be seen on the surface of the specimens.

Some of small caverns on the surface pictured by SEM micrographs are presented in case of all of specimens after the exposure to elevated temperatures from 400 to 900^{0}C.

However, as the specimen was heated to 900^{0}C a lot of big caverns emerged on the surface of micrographs, which was probable owing to the partial collapse of geopolymer matrix caused by the weight loss, matrix decomposition and phase transformations.

4.4 Geopolymer composite systems reinforced by silicon dioxide nanofibres

4.4.1 Sample preparation

The geopolymer was prepared by a mixing of raw material and akaline activator (baucis alkaline and baucis activator L160). The compound was mixed for 3 minutes by hand and then was mixed for 5 minutes by mixer at room temperature until the solution was homogenized. Then the nanofibers SiO_2 with 0.1% (GNS1), 0.3% (GNS3), 0.5% (GNS5), 0.7% (GNS7) and 1 % (GNS10) of weight was added to the geopolymer resin mixture. The slurry was mixed for 5 minutes. After the mixing the fresh mortar was poured in the cylindrical plastic moulds with dimensions of 20x 30 mm cylinder (diameter x high). The samples were vibrated for 3 minutes and then they were wrapped.

The specimens were placed into the oven (up to 300^0C) at 60^0C, 70^0C, 80^0C, 95^0C, 105^0C, (extra 150^0C and 200^0C) for 24 hours. Finally, the samples were removed from the moulds and left in the laboratory ambient conditions until the testing day.

4.4.2 Effect of curing temperature on mechanical properties of nanofibers SiO_2 reinforced geopolymer concrete

The nano fibers based geopolymer specimens were cured for 24 hours at 60^0C, 70^0C, 80^0C, 95^0C, 105^0C, (extra curing at 150^0C and 200^0C). When adding nano fibers into mixture of geopolymeric slurry, it was needed to add the fibers slowly. Increasing volume of nano fibers SiO_2, change the colour of mixture to the lighter colour. The colour of mixture was milk-white in case of sample with 1 % fibers inside.

In tables 4.1, 4.2 and figures 4.1, 4.2 is shown that the pure geopolymer achievd the highest mechanical properties at curing temperature of 60°C for 24 hours with value of 25.36 MPa of compressive strength and 18.93 GPa of the modulus elasticity in compression. The compressive strength of geopolymer after the curing at higher temperature is higher for 10.07 % compared to the sample cured at room temperature. Mechanical properties of this geopolymer systems decreased with increasing temperature but it could withstand at 800°C with value 4.37 MPa of compressive strength (and 10.96 GPa of modulus of elasticity).

But from temperature about 2000C were present some small cracks on surface of specimens and they were larger with higher curing temperatures and time of curing.

Some literature demonstrated [4], [54], [111] the fire resistance of geopolymers.

Various physical and mechanical properties of nanofibers SiO2 based geopolymer obtained at different conditions are listed in tables 4.7 and appendixes B1-B3. Hardness of geopolymer was measured in range 262 HV to 303 HV. Alomayri [112] investigated the geopolymer hardness and values of hardness which was measured in this study are similar to his result. Densities of the geopolymer were in the range of 1.492–1.673 g/cm3, and decrased with increasing temperature and nanofibers concentration, maybe because of evaporation of water.

Figures 4.20 to 4.23 shown that mechanical properties of geopolymer composite (adding nanofibers) obtained higher values than in case of pure geopolymer and increased with increasing percentage of nanofibers from 0.1% to 0.7%. the geopolymer composite with 0.7% of nanofibers had the highest compressive strength with a value of 49.73 MPa (2.2 times higher compared to the pure geopolymer), and 24.39 GPa of modulus of elasticity (at 105°C for 24 hours). Mechanical properties of geopolymer composite with nano fibres SiO_2 were also

increased while increasing temperature as in figures 4.20 and 4.21 from 600C to 80°C. The mechanical properties with curing temperature of 95°C is lower than in case of 80°C for 24 hours. Although at 105°C the compressive strength was higher than in case of 95°C. So for the range of temperatures for curing 60°C, 70°C and 80°C. At 60°C for 24 hours the compressive strength is higher for about 5.4 % than at room temperature. The curing temperature higher than 60°C did not provide so big increases of mechanical properties (2.1%).

The optimal temperature for curing is 60°C. Nasvi [113], Xiem [114], Hung [40], Heah [115], Villareal [116] also investigated the effect of temperature on mechanical properties of geopolymer. And their optimal temperature for curing is at 60°C or at 70°C. The results from this investigating of an optimal curing temperature is not different compared too their results.

Table 4.6 Properties of nanofibers SiO_2 based geopolymer concrete at room temperature and curing at 60^0C for 24 hours

Mixture		Hardness [HV]	Density [g/cm^3]	Compressive strength [MPa]	Modulus of elasticity in compression [GPa]
GNS1	At room temperature	268 ± 4.2	1.71	24.6 ± 1.26	18.73 ± 0.32
	At 60^0C-24h	270 ± 4.8	1.691	25.36 ± 2.23	18.93 ± 0.59
GNS3	At room temperature	275 ± 3.2	1.688	37.12 ± 0.91	21.79 ± 0.63
	At 60^0C-24h	282 ± 5	1.655	39.12 ± 3.2	22.23 ± 0.81
GNS5	At room temperature	280 ± 4.1	1.674	42.39 ± 0.76	22.92 ± 0.47
	At 60^0C-24h	279 ± 3.7	1.628	44.83 ± 2.73	23.42 ± 0.44
GNS7	At room temperature	284 ± 6	1.572	45.26 ± 1.65	23.51 ± 0.31
	At 60^0C-24h	290 ± 6.2	1.583	47.69 ± 1.08	23.99 ± 0.59
GNS10	At room temperature	287 ± 2.8	1.576	35.96 ±0.59	21.53 ± 0.52
	At 60^0C-24h	295 ± 2.8	1.527	36.2 1.55	21.59 ± 0.67

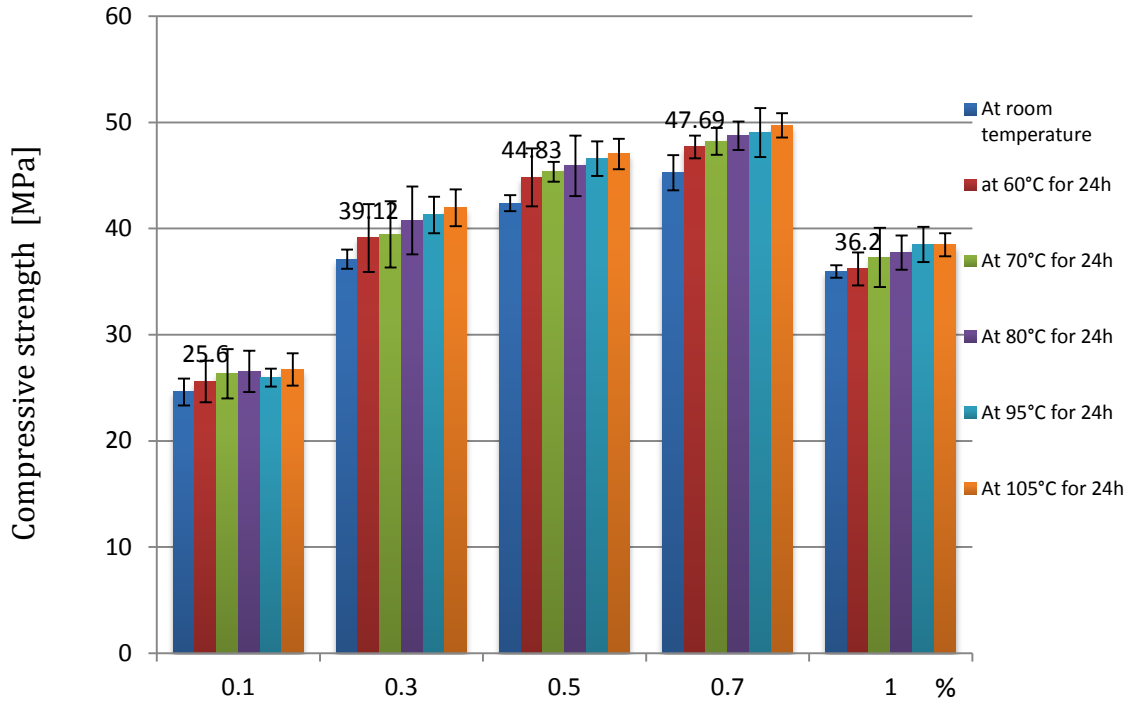

Figure 4.20 Compressive strength of nanofibers SiO_2 based geopolymer cured at diffirent temperatures and filled with diffirent amount of nanofibers SiO_2

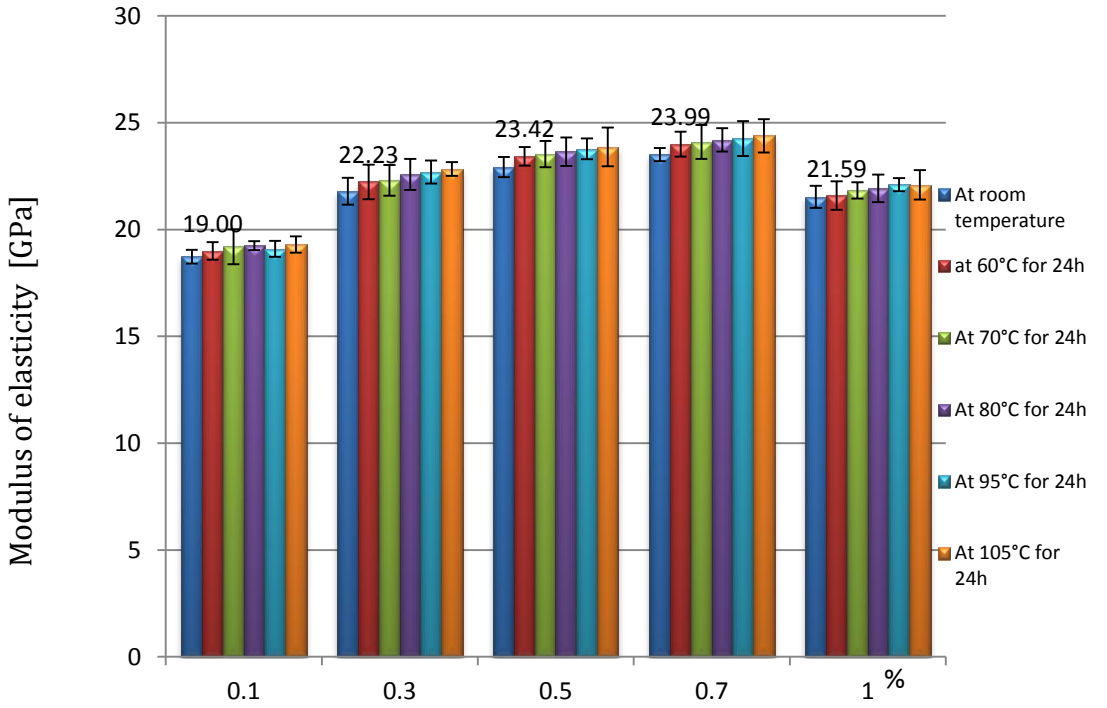

Figure 4.21 Modulus of elasticity in compression of nanofibres SiO_2 based geopolymer cured at diffirent temperatures and filled with diffirent amount of nanofibers SiO_2

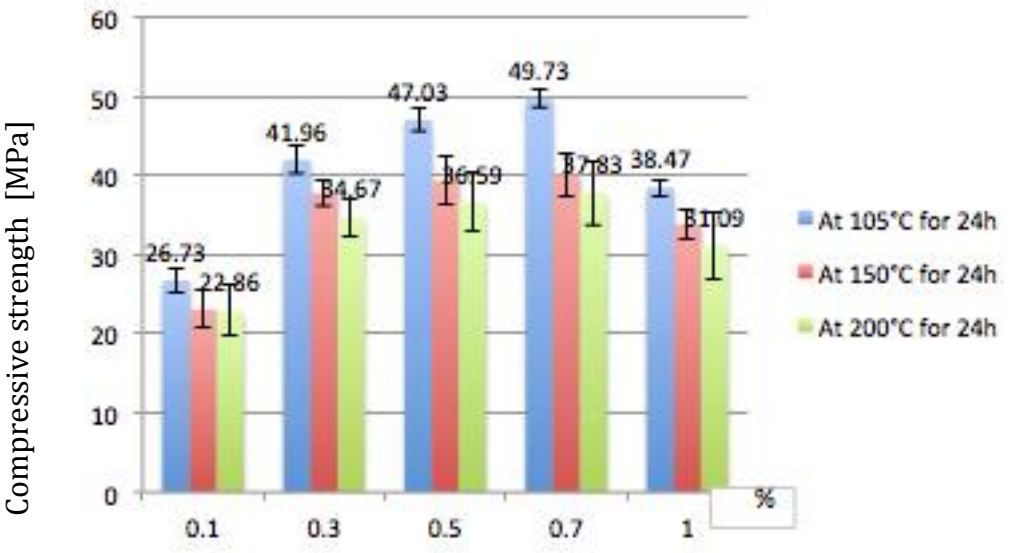

Figure 4.22 Compressive strength of nanofibres SiO_2 based geopolymer after 105^0C filled with diffirent amount of nanofibers SiO_2

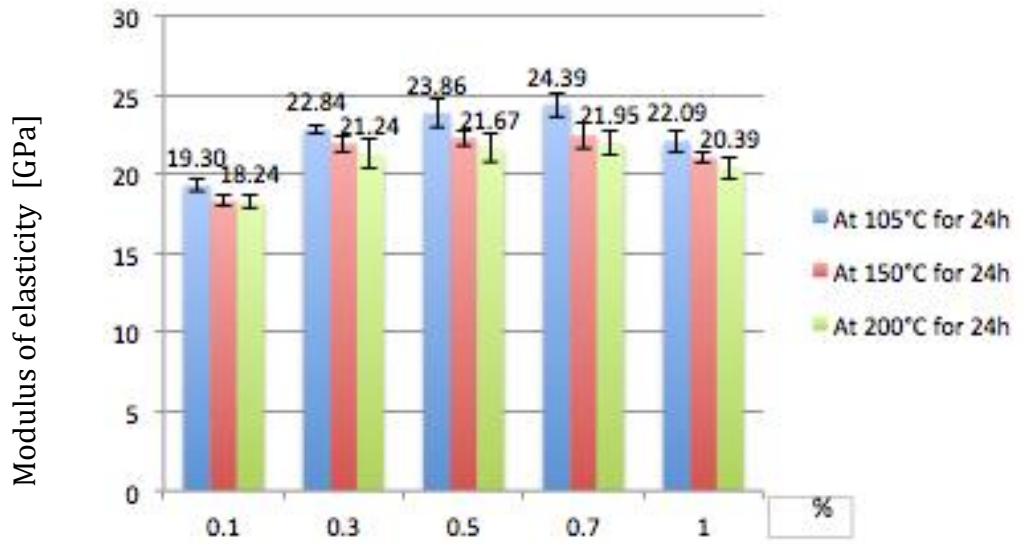

Figure 4.23 Modulus of elasticity in compression of nanofibres SiO_2 based geopolymer after 105^0C filled with diffirent amount of nanofibers SiO_2

At different temperatures the mechanical properties of geopolymer were investigated with curing time 24 hours at 105°C, 150°C, 200°C. Why should be reported with this? Because it is necessary to know "from what temperature mechanical properties are decreasing". Table 4.7, figure 4.22, 4.23 shown that from 105°C properties (physical and mechanical properties) of nanofibres SiO_2 based geopolymer are reduced. It means never to cure geopolymer at higher temperature than 100°C for improving properties.

4.4.3 Effect of curing time on mechanical properties of nanofibres based geopolymer concrete

In the part 4.4.1the curing temperature was investigated. The optimal temperature for curing was find out as 60°C. This part reports continuously abou the curing time. The specimens were cured at 60°C for diffirent time such as: for 8 hours, 24 hours, 48 hours and for 72 hours.

Why to cured the samples? Almost all geopolymer specimens are set and formed into the hard structure within 24 h after preparation except of the specimens that were cured under the lower temperature conditions. At room temperature (20°C) the dissolution of baucis particles into the activator is slow so the geopolymer gels grew slowly and geopolymer samples were still gelatinous and moist. The amounts of used precursors (primarily Al) dissolved from amorphous phases in metakaolin were in sufficient to polymerize with the amorphous Si precursors in the activators to form a plenty of aluminosilicate gels.

Properties of geopolymer composite are listed below in tables 4.8- 4.10 and figures. 4.24 and 4.25.

Tables 4.8- 4.10 shown that with addition of 0.7 % of nanofibers the mechanical properties of geopolymer obtained the highest values.

Densities of nanosilica fibers based geopolymer were in the range of 1.507–1.685 g/cm^3.

Figure 4.24 and figure 4.25 show the results with curing 60^0C, longer curing time improve polymerisation process resulting higher compressive strength and modulus of elasticity in compression. Up to 24 hours of curing time, it is rapid in rate of increasing strength. It indicates that longer curing time did not produce weaker material as claimed Harijto [44], Van Jaarsveld [117], Memon [118].

Table 4.7 Properties of nanofibers SiO_2 based geopolymer with curing at 60^0C for 8 hours and 16 hours

Mixture		Hardness [HV]	Density [g/cm^3]	Compressive strength [MPa]	Modulus of elasticity in compression [GPa]
GNS1	At 60^0C-8h	272 ± 4.3	1.685	24.71 ± 0.86	18.76 ± 0.59
	At 60^0C-16h	275 ± 2.7	1.678	24.87 ± 2.31	18.80 ± 0.82
GNS3	At 60^0C-8h	279 ± 3.2	1.648	37.43 ± 0.67	22.86 ± 0.73
	At 60^0C-16h	281 ± 3	1.635	37.79 ± 3.12	21.94 ± 0.95
GNS5	At 60^0C-8h	282 ± 4.1	1.654	42.59 ± 0.82	22.97 ± 0.46
	At 60^0C-16h	287 ± 5.2	1.663	43.2 ± 0.93	23.09 ± 0.66
GNS7	At 60^0C-8h	284 ± 4.5	1.639	45.73 ± 0.87	23.61 ± 0.59
	At 60^0C-16h	286 ± 3.2	1.619	46.87 ± 1.27	23.83 ± 0.81
GNS10	At 60^0C-8h	287 ± 2.8	1.623	36.05 ± 0.62	21.55 ± 0.67
	At 60^0C-16h	290 ± 2.2	1.61	36.14 ± 2.78	21.57 ± 0.38

Table 4.8 Properties of nanofibers SiO_2 based geopolymer concrete with curing at 60^0C for 24 hours

Mixture	Hardness [HV]	Density [g/cm^3]	Compressive strength [MPa]	Modulus of elasticity in compression [GPa]
G0	270 ± 4.8	1.71	25.36 ± 2.23	18.93 ± 0.59
GNS1	277 ± 4	1.673	25.6 ± 1.95	19.00 ± 0.41
GNS3	282 ± 5	1.655	39.12 ± 3.2	22.23 ± 0.81
GNS5	279 ± 3.7	1.628	44.83 ± 2.73	23.42 ± 0.44
GNS7	290 ± 6.2	1.583	47.69 ± 1.08	23.99 ± 0.59
GNS10	295 ± 2.8	1.527	36.2 ± 1.55	21.59 ± 0.67

Table 4.9 Characteristics of nanofibers SiO_2 based geopolymer concrete at 60^0C for 48 hours and 72 hours

Mixture		Hardness [HV]	Density [g/cm^3]	Compressive strength [MPa]	Modulus of elasticity in compression [GPa]
GNS1	At 60^0C-48h	278 ± 4.3	1.665	25.96 ± 0.83	19.09 ± 0.37
	At 60^0C-72h	282 ± 2.7	1.658	26.03 ± 1.72	19.11 ± 0.34
GNS3	At 60^0C-48h	285 ± 3.2	1.648	40.07 ± 1.72	22.44 ± 0.64
	At 60^0C-72h	287 ± 3	1.625	40.78 ± 1.68	22.59 ± 0.74
GNS5	At 60^0C-48h	283 ± 4.1	1.574	44.97 ± 0.77	23.45 ± 0.51
	At 60^0C-72h	289 ± 5.2	1.563	45.29 ± 1.43	23.64 ± 0.67
GNS7	At 60^0C-48h	294 ± 6	1.572	47.83 ± 2.3	24.02 ± 0.79
	At 60^0C-72h	296 ± 3.2	1.54	48.32 ± 0.93	24.12± 0.52
GNS10	At 60^0C-48h	297 ± 2.8	1.516	37.16 ± 1.65	21.80 ± 0.31
	At 60^0C-72h	301 ± 2.2	1.507	37.86 ± 1.09	21.96 ± 0.69

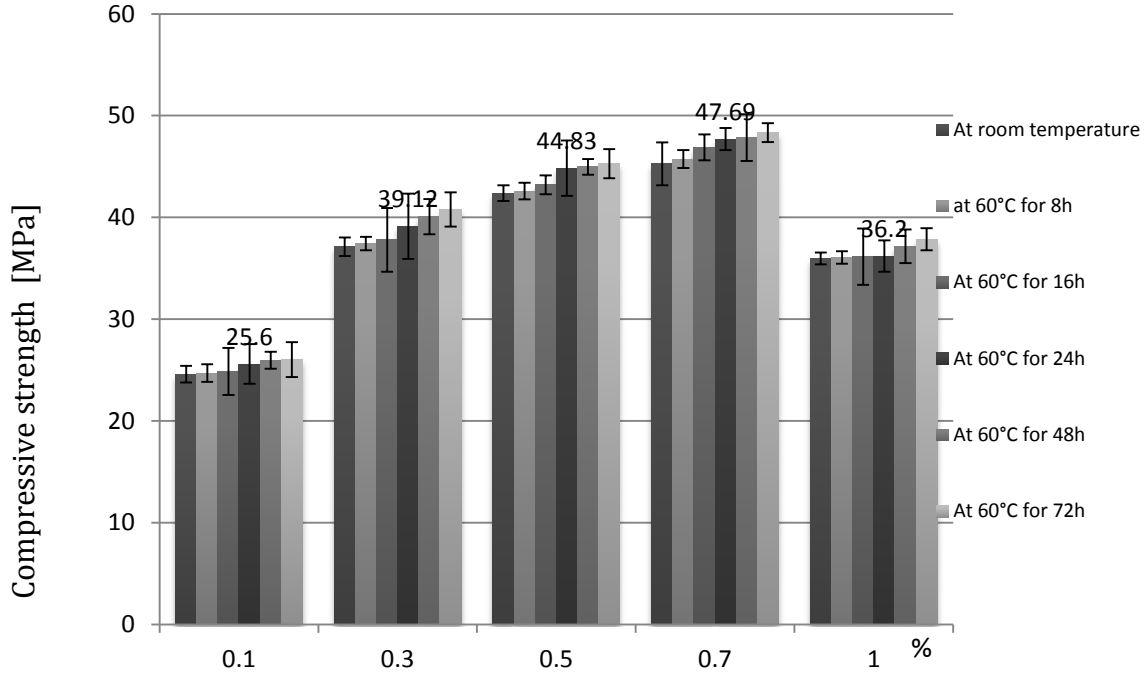

Figure 4.24 Compressive strength of nanofibres SiO_2 based geopolymer at 60^0C filled with diffirent amount of nanofibers SiO_2

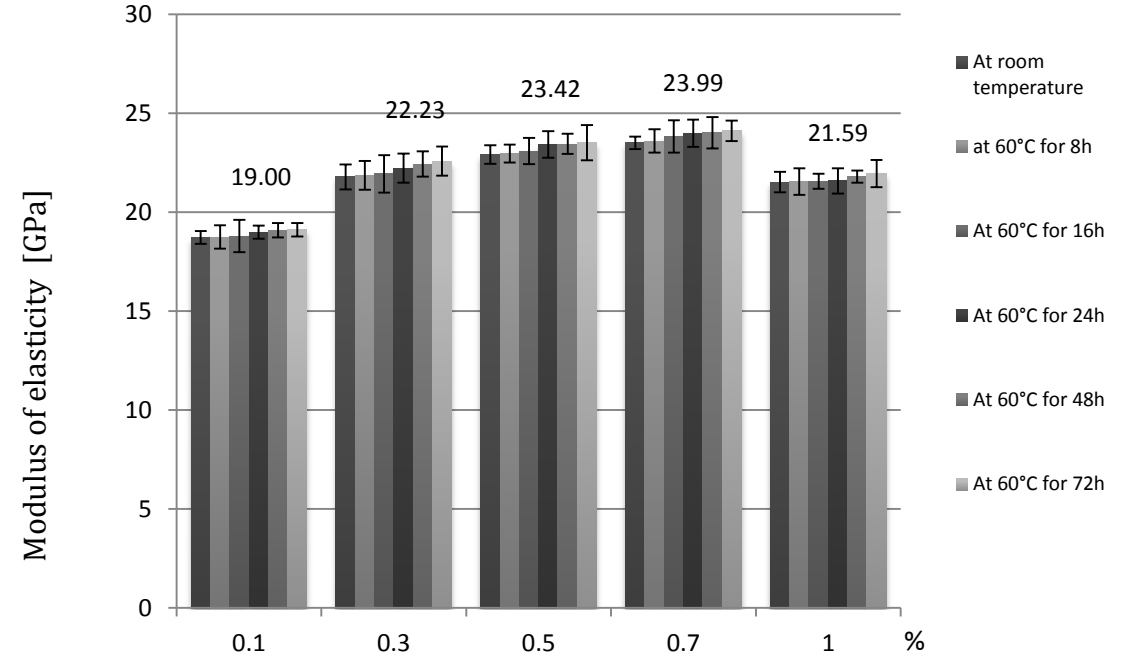

Figure 4.25 Modulus of elasticity of nanofibres SiO_2 based geopolymer with curing at 60^0C for different time and filled with diffirent amount of nanofibers SiO_2

4.4.4 Microstructure of matrix of nanofibres SiO_2 based geopolymer concrete

Using the Scanning Electron Microscopy helped to study the microstructure of geocomposites cured at 600C as well. From figures 4.26 - 4.28 can be seen that the interaction between fibers and geopolymer matrix seems good but unfortunatelly the micro-cracks on the perpendicular sections and surfaces of the composites still existed as a natural defect of ceramic matrix composites.Scanning

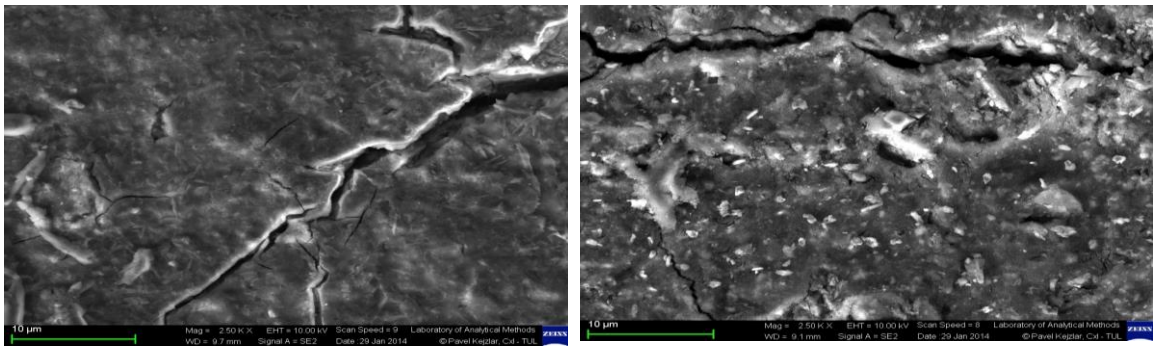

Figure 4.26 SEM of 0.1 % (left) and 0.3 % (right) nanofibers based geopolymer at 60^0C-24h

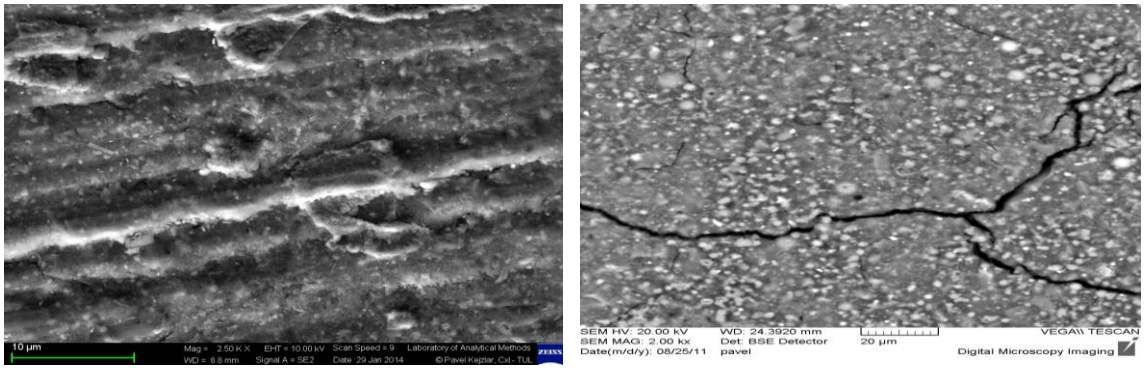

Figure 4.27 SEM of 0.5 % (left) and 0.7 % (right) nanofibers based geopolymer at 60^0C-24h

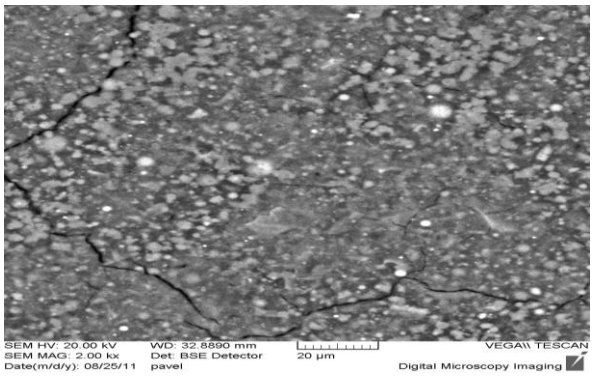

Figure 4.28 SEM of 1 % nanofibers SiO_2 based geopolymer

4.4.5 Conclusions

In this part the nanofibers SiO2 reinforced geopolymer was investigated with curing at different temperatures (from 60°C to 200°C). The curing at 60°C was done for 8 hours, 16 hours, 24 hours, 48 hours and 72 hours. The main results of this chapter can be summarised as following:

- Hardness of geopolymer was measured in range of 262 HV to 303 HV.
- Densities of the geopolymer were in the range of 1.492–1.673 g/cm^3 and decrased with increasing temperature and nanofibers concentration, because of the evaporation of water.
- The mechanical properties (compressive strength, modulus of elasticity) of the geopolymer increased with elevated temperature (range 60°C to 95°C).
- From the temperature of 105°C (150°C, 200°C) the properties (physical and mechanical properties) of nanofibres based geopolymer has reduced. This result means that it is not suitable to cure the geopolymer at higher temperatures than 100°C for improving the properties.
- Mechanical properties of geopolymer composite (with added nanofibers) were always higher than properties of pure geopolymer and increased with increasing percentage of nanofibers from 0.1% to 0.7%. The geopolymer composite with 0.7% of nanofibers SiO2 had the highest compressive strength with value of 49.73 MPa (2 times higher than pure geopolymer cured under the same conditions), and 24.39 GPa of modulus of elasticity (at 105°C for 24 hours).
- The 24 hours of curing which was quick and still resulted in increasing of strength. It indicates that longer curing time did not produced a weaker material.
- The optimal curing conditions are at 60°C for 24 hours. The compressive strength and modulus of elasticity of geopolymer obtained values of 47.69 MPa and 23.99GPa, respectively.
- The adhension between the fibers and geopolymer matrix iwas good due to the chemical similarity of reinforcing fibres and the geopolymer matrix.

4.5 Geopolymer composite systems reinforced by carbon sub-micro fibres and silicon dioxide nanofibres

The addition (combination) of silicon dioxide nanofibres and carbon sub-micro fibres based geopolymer were studied. The reinforcing mixtures were prepared as: 0.1% nanofibres and 0.1 % carbon sub-micro fibres (M11) then 0.3% nanofibres + 0.3% submicro fibres (M33), 0.5% nanofibres + 0.5 % sub-micro fibres (M55), 0.7% nanofibres + 0.7% sub-micro fibres (M77), 1% nanofibres + 1% sub-micro fibres (M110). Specimens were cured at room temperature and at 60^{0}C for 24 hours in the oven.

From figure 4.29, 4.30 it can be seen that the mixture of nanosilica and carbon sub-micro fibers based geopolymer had highest value of 41.79 MPa of the compressive strength and 22.8 GPa of modulus of elasticity (after curing at 60°C for 24hours) in case of using 0.5 % nanofiber SiO2 and 0.5 % carbon sub-micro fibres.

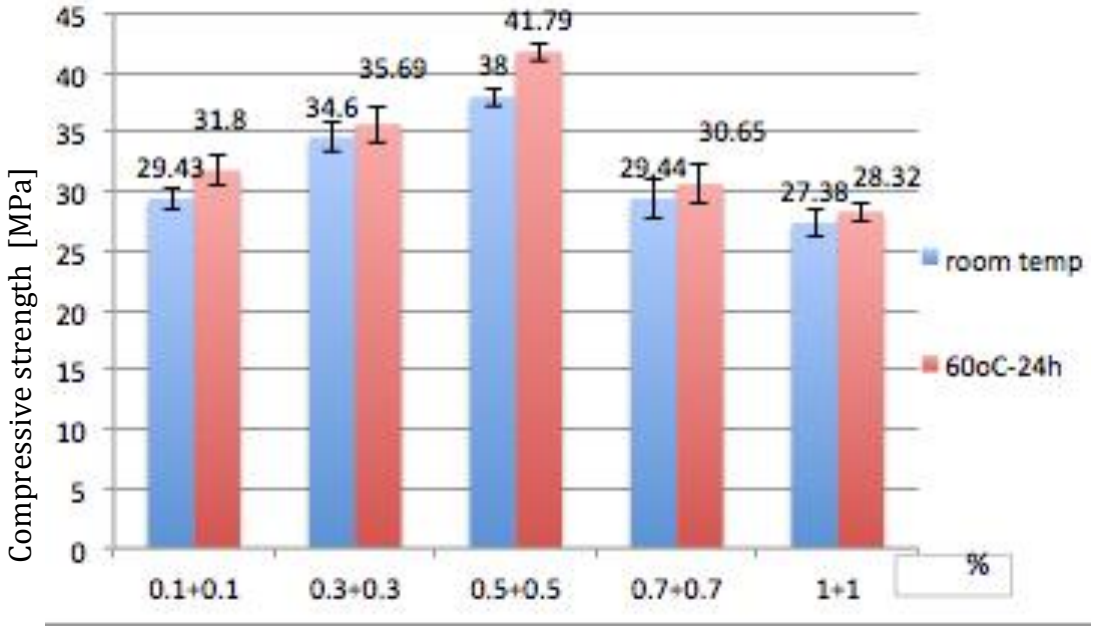

Figure 4.29 Compressive strength of reinforced geopolymer based on the mixture of nanofibers SiO_2 and carbon sub-micro fibres at room temperature and at 60^0C-24h

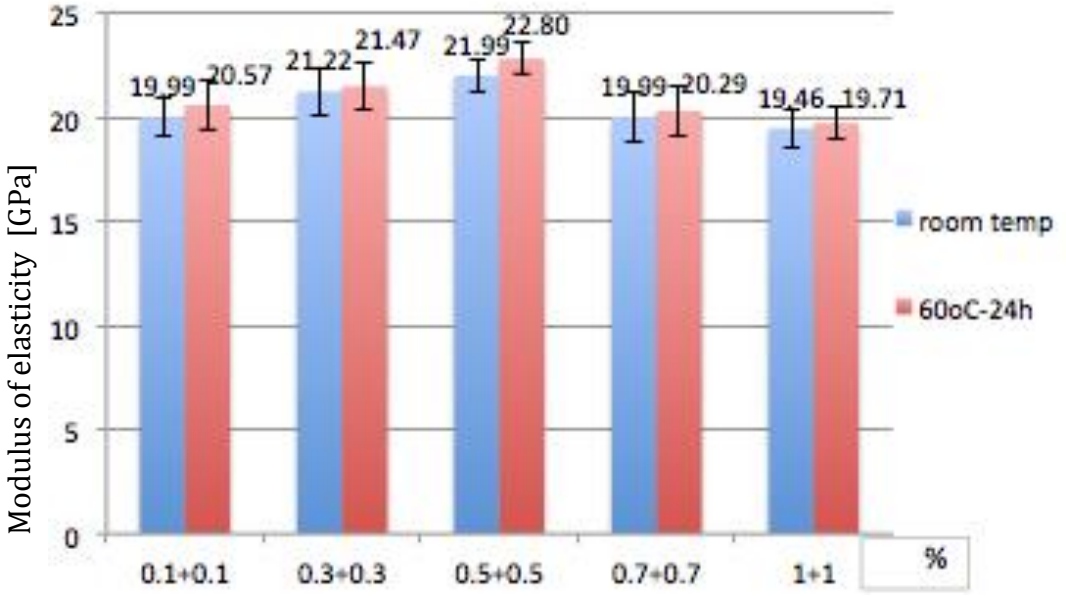

Figure 4.30 Modulus of elasticity in compression of reinforced geopolymer based on the mixture of nanofibers SiO_2 and carbon sub-micro fibres at room temperature and at 60^0C-24h

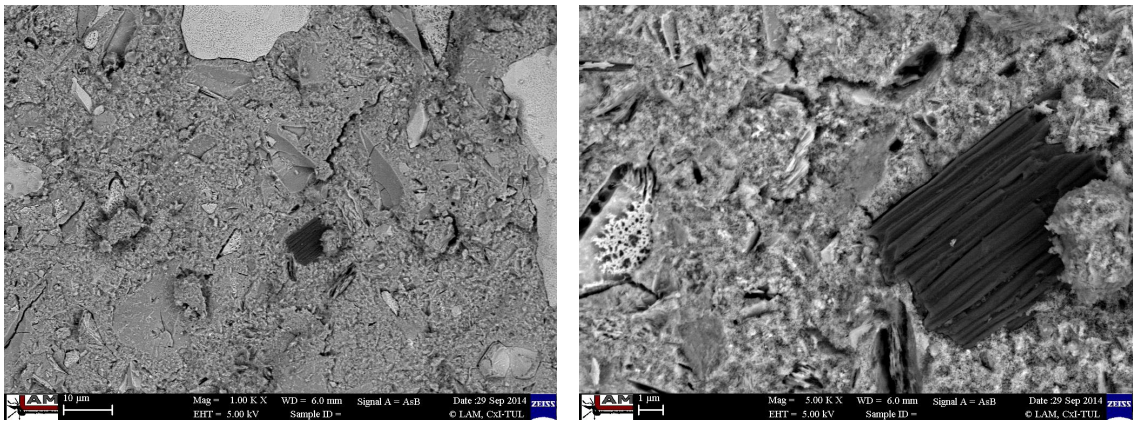

Figure 4.31 SEM pictures of 0.5% SiO_2 nanofibres and 0.5% carbon sub-micro fibres reinforced geopolymer

From figure 4.31 it can be seen different structure of geopolymer composite systems comapre to the pure geopolymer. The carbon sub-micro fibres (the black spot) can be also seen. The adhension between the carbon sub micro fibers and geopolymer matrix is poor.

4.6 Mechanism of reinforcing

The main purpose of the fibers was to provide a control the cracking and increasing of the fracture toughness of the brittle matrix through the bridging action during of both micro and macro-cracking of the matrix. Debonding, sliding and pulling-out of the fibers are the local mechanisms that control the bridging action [119].

With a low ratio of Si:Al the geopolymer concrete-based materials had a low tensile strength and were inherently brittle by nature. The masonry blocks are using in the residential construction and have lower strength and ductility values compared to the structural concrete. The fibers reinforcement aids in the improvement of ductility, tensile, impact and flexural performance of the masonry and concrete buildings [120]. This enhances the structural resilience under impact loads. High and low-velocity impact behavior of cement-based materials have been studied by several researchers using Charpy, Izod, drop-weight, split Hopkinson bar, explosive, and ballistic tests [120]. In this part of study the samples were tested by Charpy method.

Lok and Zhao [121] reported that at strain rates exceeding 50 s−1, post-peak ductility of the steel fibre-reinforced concrete was lost owing to the loss of bond between the concrete fragments and steel fibres. Zhu [122] studied the impact behavior of alkali-resistant glass textile-reinforced cement composites. The maximum flexural stress and absorbed energy of the beam by specimen increased with the number of textile layers. Impact properties of polyethylene textile cement composites were investigated by Gencoglu [123] and compared to AR glass textile. The polyethylene textile composites showed higher load carrying capacity at large deflections and hence more ductile than AR glass textile composites.

In the beginning of macro-cracking the bridging action of fibers prevented and controled the opening and growth of cracks. This mechanism increases the

demand of energy for the crack to propagate. The linear elastic behavior of the matrix is not affected significantly by the low volumetric fiber fractions. However, post-cracking behavior can be substantially modified with increases of strength, toughness and durability of the material [72].

The purpose of this study was to evaluate the fracture toughness (the critical stress intensity factor – KIc) of geopolymeric concretes reinforced by different wt.% of carbon micro fibers.

In this study the carbon microfibers were used with content of 1%, 3%, 5%, 7%, 8% and 10 % of weight. All specimens ere cured at room temperature and at 60°C for 24 hours in the oven. The process of preparing the specimens is shown in chapter 3.

For the impact test the dimension of sample was 80 * 10 * 4 mm. For the fracture toughness the dimension of specimen was 120 * 25 * 12.5 mm (L*W*B). Before testing it was prepared the sharp notch on every samples by the machining with dimension of 4 * 12 mm (see figure 4.32). The angle of notch was not significant (in some paper, authors did not use sharp notch).

4.6.1 Impact Test

For the impact test the dimension of sample was 80 * 10 * 4 mm.

We used the Zwick for testing (see image in chapter 3).

Zwick machine parameters:

Velocity: 2.9 m/s
Pendulum mass: 1.19 kg
Length of arm: 330 mm
Pendulum: 5J

Table 4.10 Impact energy of geocomposite systems reinforced by carbon microfibres at diffirent weight %

% C_{mf}	Charpy impact strength (kJ/m^2)	
	at room temperature	at 60^{0}C-24h
0	0.8	0.823
1	1.22	1.41
3	1.53	1.62
5	3.13	3.21
7	3.42	3.52
8	4.28	4.37
10	3.55	3.61

From table 4.10 and figure 4.32 we can indicate that the increase of impact resistance of carbon microfibers reinforced geopolymer at ultimate failure varied from 1.52 to 5.4 times compared to the pure geopolymer. After curing at 60°C for 24 hours the impact resistance of geocomposite was always higher than at room temperature.

The maximum increase of 5.4 times was observed for fibrous concrete with content of 8% carbon micro fibres after curing at 60°C-24h. In general, it can be concluded that with increasing percentage of the fibres increase the impact resistance as well as the ultimate failure. Further, it can also be concluded that incorporation of carbon micro fibres in the plain concrete had significantly improved the impact resistance of concrete.

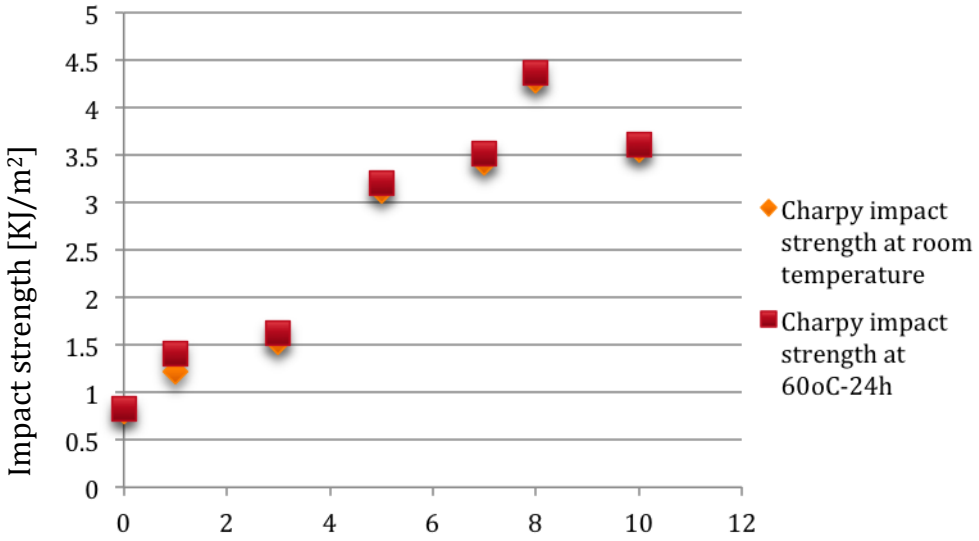

Figure 4.32 Impact strength of carbon microfibres based geopolymer

Mohammadi [124] studied the impact resistance of steel fibers in concrete. It has shown the increase in impact resistance at ultimate failure varied from the 968% to 1943%, 1076% to 2428% and 1337% to 3211% for steel fibrous concrete mixes having 1.0%, 1.5% and 2.0% of volume fraction of fibres. Wang [125] identified two damage mechanisms of fibre fracture and fibre pull-out under the impact loads. Steel fibres could bring about much greater increases in fracture energy with a transition of failure modes occurring between the steel fibre volumes of 0.5% and 0.75%.

4.6.2 Fracture toughness test

The fracture toughness was determined by the measurement of the resistance of a material to the propagation of a crack.

Three-point bending, single-edge, notched beam specimens are the current standard [102]. The critical stress intensity factor – KIC was calculated according to 3.2.3.4 (see chapter 3).

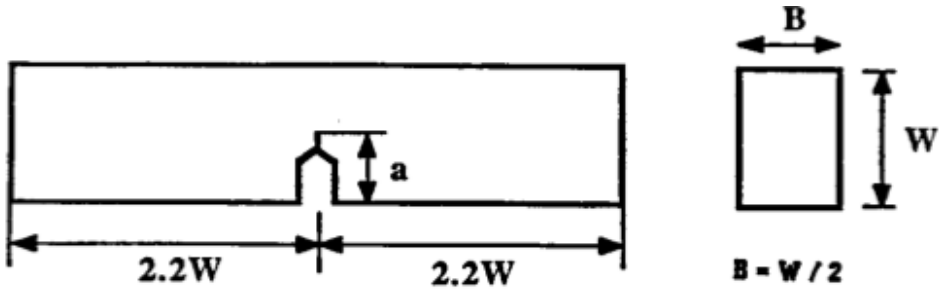

Figure 4.33 The specimen configuration in the fracture toughness test

Table 4.11 Critical stress intensity factor –KIc of carbon micro fibres reinforced geopolymer for diffirent way of hardening.

% wt of CMF	critical stress intensity factor –Kic [MPa.m^2]	
	at room temperature	at 60^{0}C-24h
0	16.48	17.32
1	21.28	23.42
3	26.89	27.5
5	33.76	35.34
7	48.16	49.3
8	69.2	71.1
10	53.1	55.3

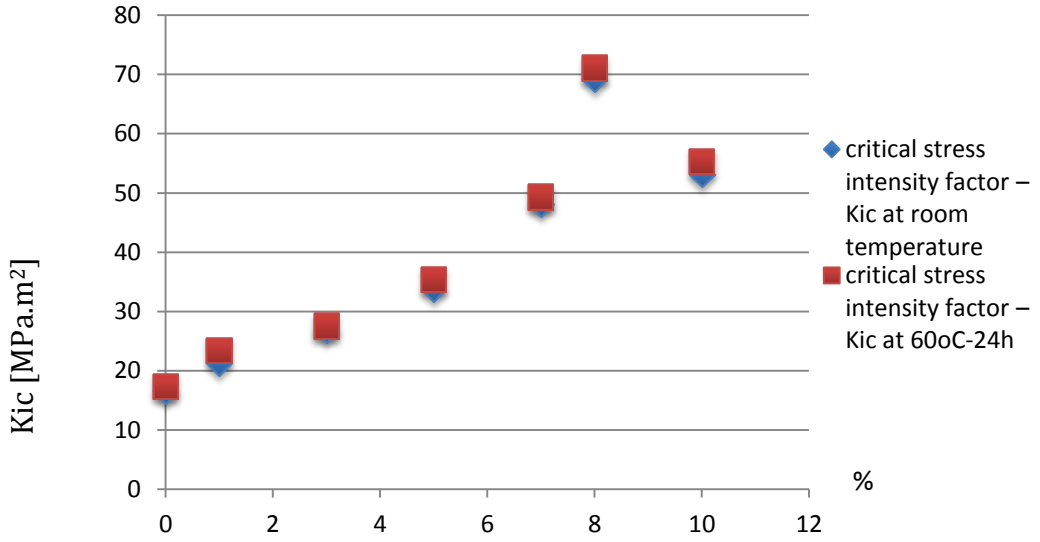

Figure 4.34 Critical stress intensity factor –KIc of carbon micro fibres reinforced Geopolymer

From above equation and figure 4.34 it can be noticed that there were a significant improvements in load capacity as well as in fracture toughness (KIc values in table 4.11). The superior load capacity and fracture toughness of fibers based concrete compare to the pure geopolymer can also be seen. The experiment showed that the KIc of carbon fibres based geopolymer was 1.3 to 4.2 times higher compared to the pure geopolymer. After curing at 60°C for 24 hours the KIc of geocomposite was always higher than at room temperature. The maximum increase of 4.2 times was observed in case of fibrous concrete with 8% of carbon micro fibres after curing at 60°C for 24h. In general, it can be concluded that the increasing percentage of fibres increase the KIc. Further, it can also be concluded that the incorporation of carbon micro fibres into the plain concrete had significantly improved the impact resistance of the concrete. F. J. Silva, J. L. and C. Thaumaturgo [126] investigated the fracture toughness of mortar composites which are utilizing the natural wollastonite micro- fiber ($Ca[SiO_3]$) and the geopolymeric cement as binder. They showed that the samples with the fiber volume up to 2% had the maximum toughness of 40 MPa.m^2 (lower than KIc in this study (71.1 MPa.m^2).

5 CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

5.1 Conclusions

The main aim of this thesis was to create the composite systems reinforced by microfibres, submicrofibres and nanofibres. Studying of their processing and the mechanical parameters. The reinforcing fibres were selected from the recycled carbon fibres and nanofibres SiO_2. Carbon fibres were selected as a waste product from the industry. The recycled carbon fibres were consequently milled in order to receive the smaller size of filler similar to particles. It was used a one size of the submicrometer range and chemicaly different material. The SiO_2 nanofibres were used as a new type of ceramic material with similar chemical composition to the geopolymer matrix.

eopolymer resin contained from the ground aluminosilicate fly dust was used as a powder binder (baucis) and activator. The most common alkaline activator used in geopolymerisation is a combination of sodium hydroxide (NaOH) or potassium hydroxide (KOH) and sodium silicate or potassium silicate. In this study the activator contained the Na_2SO_3 solution with NaOH solution to produce alkaline silicate solution with modulus of 1.50. The ratio of used H_2O/Na_2O was 12. Some of the pure geopolymer samples with a ratio of 4:5 of weigth (activator/baucis) were tested for mechanical properties, SEM and EDX. Material used in this study was the baucis L160 geopolymer.

In this study the carbon micro fibres, carbon sub-micro fibres and nanofibres of SiO_2 were used to improve the strength of geopolymer systems composite.

The geopolymer composite systems reinforced with carbon micro fibers with content of 1% (GMC1), 3% (GMC3), 5% (GMC5), 7% (GMC7), 8 % (GMC8) and 10 % (GMC10) of weight were indicated. After mixing the fresh mortar was poured into the cylindrical plastic moulds with dimensions of the cylinder 20x 30 mm (diameter x high). The samples were vibrated for 3 minutes and then they have been wrapped. After 1-2 days the samples were demoulded and put into the oven (cured at 60^0C for 24 hours, at 200^0C for 8 and 16 hours and at 300^0C for 8 and 16

hours) or furnace (up to 1200^{0}C)to treat at 600^{0}C and at 800^{0}C for 1hour, 3 hours and 5 hours.
The geopolymer composite systems reinforced with carbon sub-micro fibers with content of 0.1% (GSC1), 0.3% (GSC3), 0.5% (GSC5), 0.7% (GSC7), and 1 % (GSC10) of weight were studied. After the mixing the fresh mortar was poured into the cylindrical plastic moulds with dimensions of 12 x 30 mm (diameter x high). The samples were vibrated for 3 minutes and then they have benn wrapped. After 1-2 days the samples were demoulded and put into the oven (cured at 60°C for 24 hours), or furnace (up to 1200°C) to treat at 400°C, 600°C, 800° and 900°C for 3 and 5 hours. The specimens were subjected to desired temperatures up to 900 °C with the incremental rate of 50C/min from the room temperature.
The geopolymer composite systems reinforced with silicon dioxide nanofibers with content of 0.1% (GNS1), 0.3% (GNS3), 0.5% (GNS5), 0.7% (GNS7) and 1 % (GNS10) of weight were investigated. After mixing the fresh mortar was poured into the cylindrical plastic moulds with dimensions of 12x 30 mm (diameter x high). The samples were vibrated for 3 minutes and then they have been wrapped. Specimens were put into the oven (up to 300^{0}C) at 60^{0}C, 70^{0}C, 80^{0}C, 95^{0}C, 105^{0}C, (extra 150^{0}C and 200^{0}C) for 24 hours for finding the optimal curing temperature. The optimal temperature for curing was 60°C. To find an optimal curing time the specimens were cured at 60°C for different time such as: for 8hours, for 24 hours, for 48 hours and for 72 hours.

The following conclusions based on the experimental work reported in this study, are drawn:

A) Pure geopolymer systems:

- Densities were calculated in a range of 1.176- 1.708 g/cm^3. Densities were reduced with increasing treatment temperature and curing time.
- The hardness of geopolymer was measured in range of 175 HV to 303 HV.
- The compressive strength of the pure geopolymer achieved the highest values of mechanical parameters after curing at 60^{0}C for 24 hours with a value of 25.36 MPa which increased for 10.07 % compared to sample without curing (at room temperature).
- After curing at temperatures from 200°C to 800°C the compressive strength and the modulus of elasticity of the concrete decreased with increasing temperature and curing time.
- From the temperature of 300°C some of small cracks appeared on the surface of samples. It can be seen more clearly in case of using temperatures of 600°C and 800°C.
- Geopolymer can withstand the high temperatures (at 800°C in this experiment).

B) Geopolymer composite systems reinforced by carbon micro fibres:

- Mechanical properties of the carbon micro fibres reinforced geopolymer were always higher than value of mechanical properties of the pure geopolymer (without fibres in matrix).
- After curing at 60^{0}C for 24 hours the compressive strength and the modulus of elasticity of geopolymer composites with content of 8 % fibres had the

highest valueof 42.37 MPa, and 22.92 GPa, respectively. The compressive strength of GMC8 was 1.67 times higher than value of pure geopolymer and near to the value of GNS5- mixture contains 0.5 % nano fibres SiO_2 (44.83MPa).

- A loss of 78.44 % of the strength of GMC10 at 800^0C for 5 hours (compared to the strength of GMC10 at room temperature) was shown.
- At 800^0C the geopolymer composite colud withstand but with a low value of 5.59 MPa of the compressive strength and 11.7 GPa of modulus of elasticity in compression (GMC10-5hours).
- Geopolymer composite systems – geopolymer matrix with content of 7-8 wt % of carbon microfibres that were cured at temperature 600^0C for 1 hour recieved higher values of mechanical parameters (21.88 MPa, 17.96 GPa at 7 % CMF and 21.62 MPa , 17.89 GPa) in case of using 8 % CMF compare to the pure geopolymer cured at same conditions (10.06 MPa, 13.81 GPa). This increase of mechanical parameters was very interesting and probably it was in relation to the influence of reinforcing fibres and short time of curing at high temperatures.

C) Geopolymer composite systems reinforced by carbon sub- micro fibres:

- Under the same curing conditions the geopolymer composite with 0.7 % of sub-micro fibres achieved the highest mechanical properties. Values were 39.81 MPa of compressive strength and 22.38 GPa of modulus of elasticity in compression after curing at 60^0C for 24 hours. The compressive strength of GSC7 was 1.69 time higher than values of pure geopolymer.
- The strength and modulus decreased with elevated temperature (from 200^0C to 900^0C) and longer treatment time.
- As the temperature risen from 400 to 600^0C the average loss of strength for all samples was about 17.2 %.
- As the temperature risen from 600 to 800^0C the average loss of strength for all samples was about 22.3 %.
- As the temperature risen from 800 to 900^0C the average loss of strength for all samples was about 25.93 %. The strenght reduced very quickly.
- A small amount of small caverns were found using the SEM micrographs in case of all samples after exposure to the elevated temperatures from 400 to 900^0C.
- When the specimen is heated to 900°C a lot of big caverns on the surface can be seen on micrographs. The matrix of geocomposite also contains a lot of pores which look like a honeycomb.

D) Geopolymer composite systems reinforced by SiO_2 nano fibres:

- Curing temperatures in a range of 60^0C to 95^0C increased the values of mechanical parameters.
- From the temperature of 105^0C (150^0C, 200^0C) the physical and mechanical properties of nanofibres based geopolymer were reduced. The curing temperatures above 100^0C were not suitable for improving the mechanical properties.
- The mechanical properties of geopolymer composite (with nanofibers) were always higher than properties of pure geopolymer and they increased with

increasing percentage of the nanofibers from 0.1% to 0.7%. The geopolymer composite with content of 0.7% nanofibers had the highest compressive strength with values of 49.73 MPa (2 times higher compared to the pure geopolymer) and 24.39 GPa of modulus of elasticity (at 105^0C for 24 hours).

- Longer curing time did not produced a weaker material.
- The optimal curing conditions were at 60^0C for 24 hours. The compressive strength and the modulus of elasticity of geopolymer had values of 47.69 MPa and 23.99GPa, respectively.
- After the curing at 60^0C for 24 hours the compressive strength and modulus of elasticity of geopolymer composite with content of 0.7 % carbon sub-micro fibres were higher than the geopolymer composite with 0.3 % of nanofibres SiO_2. Due to the commercial price the carbon micro fibres and carbon sub-micro fibres are recommended to use widely.
- It was also found a small amount of microcracks on the surface of the specimens.
- The use of SiO_2 nanofibres is expensive and human do not know the influence to the enviroment and human body.

E) Geopolymer composite systems reinforced by carbon sub- micro fibres and SiO_2 nanofibres:

- The highest values of mechanical properties of 41.79 MPa of compressive strength and 22.8 GPa of modulus of elasticity (after curing at 60^0C for 24hours) with content of 0.5 % nanofiber SiO_2 and 0.5 % carbon sub-micro fibres mixtures were obtained.

F) Mechanism of reinforcing:

- Impact resistance of carbon microfibers reinforced geopolymer at ultimate failure varied from 1.52 to 5.4 times compared to pure geopolymer.
- The maximum increase of 5.4 times was observed in case of fibrous concrete with 8% carbon micro fibres after curing at 60^0C-24h.
- KIc of carbon fibres based geopolymer was 1.3 to 4.2 times higher compared to the pure geopolymer.
- The maximum KIc increase of 4.2 times (71.1 $MPa.m^2$) was observed for the fibrous concrete with content of 8% carbon micro fibres after curing at 60^0C-24h.
- Incorporation of carbon micro fibres into the plain concrete has significantly improved the impact resistance and fracture toughness of the geocomposite.

More remarks:

- The optimal curing temperature was 60^0C.
- In case of curing temperature under 100^0C the mechanical parameters of material increased with the time of curing.
- In case of curing temperature above 100^0C (600^0C, 800^0C) the time of curing decreased the mechanical parameters of material.

- Short stay – 1 hour at high temperature (600^0C)- the mechanical parameters quickly increased but after that they fall down - in case of composite systems reinforced by carbon microfibres.
- Demoulding specimens (1-2 days in mold) can change their mechanical parameters (when they were cured at high temperature and than subsequently at the lower temperature).
- The process of curing was still active after demolding, the chemical reaction run and could be hardened by increasing temperature.
- High temperature was important in dissolving of alluminium silicate particles because the homogeneousness of material could be increased. Small undissolved particles could not be found in the fracture on the surface.
- During the curing at high temperatures (100^0C- 800^0C) the water in material was changed to a steam and thus the porous geopolymer structure was created.
- This porous geopolymer structure should be studied for its thermo-insulation properties.
- The parameters of geopolymer composite materials were recieved by adding 0.7 % of the submicrofibres. This results can be explained due to the smallest amount of filler and the optimal curing at 60^0C for 24 hours.

5.2 Recommendations for Future Research

This dissertation presents the first effort to explore and validate an innovative potential of the application of short fibres based geopolymers. However, the additional work is essentially required in the future for the successful application of short fibres based geopolymers in practice.

1. Identify the possible applications of geopolymer short fibres technology due to the excellent properties.
2. Natural fibres reinforced geopolymer should be investigatedfor their physical and mechanical properties.
3. Acid resistance and shrinkage should be observed.
4. Adhension between the fiber and surface element of geopolymer is needed to be understanded.
5. Increase the adhension between the reinforcing elements and matrix.
6. Study the influence of silicon dioxide particles or fibres for pozzolanic effect in the geopolymer matrix.

6 REFERENCES

[1] Joseph Davidovits, "Carbon-Dioxide Greenhouse-Warming: What Future for Portland Cement, Emerging Technologies Symposium on Cements and Concretes in the Global Environment," 1993.
[2] J. S. J. V. D. J. W. Phair, "Effect of silicate activator pH on the leaching and material characteristics of waste-based inorganic polymers," *Miner. Eng.*, no. 3, pp. 289–304, 2001.
[3] '99 Geopolymer International Conference Proceedings. Geopolymer Institute, 1999.
[4] Joseph Davidovits, *Geopolymer Chemistry and Applications*. Geopolymer Institute, 2008.
[5] Joseph Davidovits, "Global warming impact on the cement and aggregates industries," 1994.
[6] Joseph Davidovits, Geopolymer, Green Chemistry and Sustainable Development Solutions: Proceedings of the World Congress Geopolymer 2005. Geopolymer Institute, 2005.
[7] J.G.S. Van Jaarsveld§,, J.S.J. Van Deventer§, E-mail the corresponding author,, and L. Lorenzen†, "The potential use of geopolymeric materials to immobilise toxic metals," vol. Volume 10, no. issue 7, pp. 659–669, Jul. 1997.
[8] Joseph Davidovits, "Geopolymers: Inorganic Polymeric New Materials," *Journal of Thermal Analysis*, vol. Vol 37, 1991.
[9] D. Z. Kostas Komnitsas, "Geopolymerisation: A review and prospects for the minerals industry," *Miner. Eng.*, no. 14, pp. 1261–1277, 2007.
[10] Van jaarsveld jgs, lucky gc, van deventer jsj., "The stabilisation of mine tailings by reactive geopolymerisation, In: Griffiths P, Spry A, editors. Proc. MINPREX 2000 Interna-tional Congress on Mineral and Processing and Extractive Metal-lurgy," *Aust. Inst. Min. Metall. Melb. Aust.*, Sep. 2000.
[11] "Years of Successes and Failures in Geopolymer Applications," presented at the Market trends and Potential breakthroughs, Geopolymer 2002 Conference, Melbourne, Australia (2002)., 2002.

[12] K. C. Goretta, N. Chen, F. Gutierrez-Mora, J. L. Routbort, G. C. Lukey, and J. S. J. van Deventer, "Solid-particle erosion of a geopolymer containing fly ash and blast-furnace slag," *Wear*, vol. 256, no. 7, pp. 714–719, 2004.
[13] H. Xu and J. S. J. van Deventer, "Effect of Source Materials on Geopolymerization," *Ind. Eng. Chem. Res.*, vol. 42, no. 8, pp. 1698–1706, Apr. 2003.
[14] Xu and Van Deventer JS, "Ab initio calculations on the five-membered alumino-silicate framework rings model: implications for dissolution in alkaline solutions," *Comput. Chem.*, vol. 24, no. 3–4, pp. 391–404, May 2000.
[15] Teixeira, -, and Pinto, A. Fernandez, P., and Jalali, S., "Geopolymer Manufacture and Application Main Problems when Using Concrete Technology," in *Proceeding of International Conference on Geopolymer*, Melbourne, A ustralia, 2002.
[16] K. C. Goretta, N. Chen, F. Gutierrez-Mora, J. L. Routbort, G. C. Lukey, and J. S. J. van Deventer, "Solid-particle erosion of a geopolymer containing fly ash and blast-furnace slag," *Wear*, vol. 256, no. 7–8, pp. 714–719, Apr. 2004.
[17] V. F. F. Barbosa and K. J. D. MacKenzie, "Thermal behaviour of inorganic geopolymers and composites derived from sodium polysialate," *Mater. Res. Bull.*, vol. 38, no. 2, pp. 319–331, Jan. 2003.
[18] A. Palomo, M. W. Grutzeck, and M. T. Blanco, "Alkali-activated fly ashes: A cement for the future," *Cem. Concr. Res.*, vol. 29, no. 8, pp. 1323–1329, Aug. 1999.
[19] J. C. Swanepoel and C. A. Strydom, "Utilisation of fly ash in a geopolymeric material," *Appl. Geochem.*, vol. 17, no. 8, pp. 1143–1148, Aug. 2002.
[20] A. Nazari and S. Riahi, "Al2O3 nanoparticles in concrete and different curing media," *Energy Build.*, vol. 43, no. 6, pp. 1480–1488, Jun. 2011.
[21] Freedonia Group, Inc., Navi Mumbai, India (2009), "Baharat Book Bureau-work kaolin," Mumbai, India (2009), 2009.
[22] "R.L. Virta- Clays," United States Geological Survey, Reston, VA (2010).
[23] Xu and Van Deventer JS, "Ab initio calculations on the five-membered alumino-silicate framework rings model: implications for dissolution in alkaline solutions," *Comput. Chem.*, vol. 24, no. 3–4, pp. 391–404, May 2000.
[24] J. G. S. Van Jaarsveld, J. S. J. Van Deventer, and L. Lorenzen, "The potential use of geopolymeric materials to immobilise toxic metals: Part I. Theory and applications," *Miner. Eng.*, vol. 10, no. 7, pp. 659–669, Jul. 1997.
[25] van Jaarsveld, J. G. S. ; Lukey, G. C. ; van Deventer, J. S. J. ; Graham, A., "the stabilisation of mine tailings by reactive geopolymerisation," presented at the International Congress on Mineral Processing and Extractive Metallurgy, 2000.
[26] Keyte, L. M. ; Lloyd, R. L. ; Lukey, G. C. ; van Deventer, J. S.J., "The Effect of Coal Ash Glass Chemistry on the Tailor Design of Waste-Based Geopolymeric Products," in *world of coal ash conference proceedings -cd-rom edition-; 148 world of coal ash*, 2005.
[27] P. D. John L. Provis, "Modeling Speciation in Highly Concentrated Alkaline Silicate Solutions," *Ind. Amp Eng. Chem. Res. - IND ENG CHEM RES*, vol. 44, no. 23, pp. 8899–908, 2005.

[28] W. K. W. Lee and J. S. J. van Deventer, "Use of Infrared Spectroscopy to Study Geopolymerization of Heterogeneous Amorphous Aluminosilicates," *Langmuir*, vol. 19, no. 21, pp. 8726–8734, Oct. 2003.
[29] J. S. J. van D. W. K.W. Lee, "The effect of ionic contaminants on the early-age properties of alkali-activated fly ash-based cements," *Cem. Concr. Res.*, no. 4, pp. 577–584, 2002.
[30] C. K. Yip, G. C. Lukey, and J. S. J. van Deventer, "The coexistence of geopolymeric gel and calcium silicate hydrate at the early stage of alkaline activation," *Cem. Concr. Res.*, vol. 35, no. 9, pp. 1688–1697, Sep. 2005.
[31] GOKHALE C, LORENZEN L, and PROF Jan Stephanus Jakob VAN DEVENTER, "The immobilisation of organic waste through geopolymerisation," University of Stellenbosch, 2001.
[32] M. Davidovits, N. Davidovits, and J. Davidovits, "Process for obtaining a geopolymeric alumino-silicate and products thus obtained," US5342595 A, 30-Aug-1994.
[33] Yolandi Muntingh, "durability and diffusive behaviour evaluation of geopolymeric material," University of Stellenbosch, Austrialia, 2006.
[34] Xu, H., Lukey, G.C. & Van Deventer, J.S.J.,, "The effect of Ca on activation of class C, class F-fly ash and blast furnace slag," *Cement and Concrete research.*, vol. Vol 36, Issue 7, Jul. 2006.
[35] J. Faimon, "Oscillatory silicon and aluminum aqueous concentrations during experimental aluminosilicate weathering," *Geochim. Cosmochim. Acta*, no. 15, pp. 2901–2907, 1996.
[36] Lloyd, R. R., & Van Deventer, J.S.J., "The microstructure of geopolymers synthesised from industrial wastes," Department of Chemical and Biomolecular Engineering, The University of Melbourne, Victoria 3010, Australia., 2005.
[37] C. K. Yip, G. C. Lukey, and J. S. J. van D. Dean, "Effect of Blast Furnace Slag Addition on Microstructure and Properties of Metakaolinite Geopolymeric Materials," in *Advances in Ceramic Matrix Composites IX*, N. P. Bansal, J. P. Singh, W. M. Kriven, and H. Schneider, Eds. John Wiley & Sons, Inc., 2006, pp. 187–209.
[38] J. W. Phair, J. D. Smith, and J. S. J. Van Deventer, "Characteristics of aluminosilicate hydrogels related to commercial 'Geopolymers,'" *Mater. Lett.*, vol. 57, no. 28, pp. 4356–4367, Oct. 2003.
[39] H. Xu, J. S. J. van Deventer, and G. C. Lukey, "Effect of Alkali Metals on the Preferential Geopolymerization of Stilbite/Kaolinite Mixtures," *Ind. Eng. Chem. Res.*, vol. 40, no. 17, pp. 3749–3756, Aug. 2001.
[40] Hung T.D, "thermal silica-based geopolymer composite system: study of processing and mechanical properties," Technical university of Liberec.
[41] J. L. Provis, P. Duxson, J. S. J. Van Deventer, and G. C. Lukey, "The Role of Mathematical Modelling and Gel Chemistry in Advancing Geopolymer Technology," *Chem. Eng. Res. Des.*, vol. 83, no. 7, pp. 853–860, Jul. 2005.
[42] W. K. W. Lee and J. S. J. van Deventer, "The effects of inorganic salt contamination on the strength and durability of geopolymers," *Colloids Surf. Physicochem. Eng. Asp.*, vol. 211, no. 2–3, pp. 115–126, Dec. 2002.
[43] D. Feng, H. Tan, and J. S. J. van Deventer, "Ultrasound enhanced geopolymerisation," *J. Mater. Sci.*, vol. 39, no. 2, pp. 571–580, Jan. 2004.

[44] Djwantoro Hardjito, "Studies on Fly Ash-Based Geopolymer Concrete," Curtin University of Technology, Austrialia, 2005.
[45] D. D. L. Chung, Composite Materials: Science and Applications. Springer, 2010.
[46] D. Joseph, "From ancient concrete to geopolymers," in *Arts Metiers Mag*, 1993.
[47] D. Hull and T. W. Clyne, *An Introduction to Composite Materials*. Cambridge University Press, 1996.
[48] Mechanics of Composite Materials. .
[49] D. L. Schodek, P. Ferreira, and M. F. Ashby, *Nanomaterials, Nanotechnologies and Design: An Introduction for Engineers and Architects*, 1 edition. Amsterdam; Boston: Butterworth-Heinemann, 2009.
[50] D. L. Schodek, P. Ferreira, and M. F. Ashby, Nanomaterials, Nanotechnologies and Design: An Introduction for Engineers and Architects. Butterworth-Heinemann, 2009.
[51] A. L. Andrady, *Science and Technology of Polymer Nanofibers*. John Wiley & Sons, 2008.
[52] M. C. Gupta, *Polymer Composite*. New Age International, 2005.
[53] K. D. Tran D. H, "Effect of curing temperature on flexural properties of silica-based geopolymer-carbon reinforced composite," *J. Achiev. Mater. Manuf. Eng.*, 2009.
[54] R. E. Lyon, P. N. Balaguru, A. Foden, U. Sorathia, J. Davidovits, and M. Davidovics, "Fire-resistant aluminosilicate composites," *Fire Mater.*, vol. 21, no. 2, pp. 67–73, Mar. 1997.
[55] J. W. Giancaspro, C. G. Papakonstantinou, and P. N. Balaguru, "Flexural Response of Inorganic Hybrid Composites With E-Glass and Carbon Fibers," *J. Eng. Mater. Technol.*, vol. 132, no. 2, pp. 021005–021005, Feb. 2010.
[56] Y. Shan and K. Liao, "Environmental fatigue of unidirectional glass–carbon fiber reinforced hybrid composite," *Compos. Part B Eng.*, vol. 32, no. 4, pp. 355–363, 2001.
[57] C. G. Papakonstantinou, P. Balaguru, and R. E. Lyon, "Comparative study of high temperature composites," *Compos. Part B Eng.*, vol. 32, no. 8, pp. 637–649, Dec. 2001.
[58] M. J. Blissett, P. A. Smith, and J. A. Yeomans, "Flexural mechanical properties of thermally treated unidirectional and cross-ply Nicalon-reinforced calcium aluminosilicate composites," *J. Mater. Sci.*, vol. 33, no. 16, pp. 4181–4190, Aug. 1998.
[59] L. C. B. G. R. Anderson, "Durability of Concrete Reinforced with Pultruded Fiber Reinforced Plastic Grating."
[60] S.C. Foerster, T. Graule, L.J. Gauckler, "Thermal and mechanical properties of alkali-activated alumino-silicate based high performance composites," *Adv. Sci. Technol. 7 1995*.
[61] S.-H. Shin, O. Purevdorj, O. Castano, J. A. Planell, and H.-W. Kim, "A short review: Recent advances in electrospinning for bone tissue regeneration," *J. Tissue Eng.*, vol. 3, no. 1, p. 2041731412443530, 2012.
[62] M. Y, "Durability and Diffusive Behaviour Evaluation of Geopolymeric Material.," 2006.
[63] J. Giancaspro, C. Papakonstantinou, and P. Balaguru, "Mechanical behavior of fire-resistant biocomposite," *Compos. Part B Eng.*, vol. 40, no. 3, pp. 206–211, Apr. 2009.

[64] Z. Yunsheng, S. Wei, Z. Li, and Z. Xiangming, "Geopolymer Extruded Composites with Incorporated Fly Ash and Polyvinyl Alcohol Short Fiber," *ACI Mater. J.*, Jan. 2009.

[65] Z. Yunsheng, S. Wei, L. Zongjin, Z. Xiangming, Eddie, and C. Chungkong, "Impact properties of geopolymer based extrudates incorporated with fly ash and PVA short fiber," *Constr. Build. Mater.*, vol. 22, no. 3, pp. 370–383, Mar. 2008.

[66] Yu Zhang, "Impact of Freeze-Thaw on Liquefaction Potential and Dynamic Properties of Mabel Creek Silt," Alaska University Transportation Center, 2009.

[67] A. Natali, S. Manzi, and M. C. Bignozzi, "Novel fiber-reinforced composite materials based on sustainable geopolymer matrix," *Procedia Eng.*, vol. 21, pp. 1124–1131, 2011.

[68] W. Li and J. Xu, "Mechanical properties of basalt fiber reinforced geopolymeric concrete under impact loading," *Mater. Sci. Eng. A*, vol. 505, no. 1–2, pp. 178–186, Apr. 2009.

[69] 张祖华 Z. Z., 晓 X. Y. 姚, 诸华军 H. Z., 华苏东 S. H., and 悦 Y. C. 陈, "Preparation and mechanical properties of polypropylene fiber reinforced calcined kaolin-fly ash based geopolymer," *J. Cent. South Univ. Technol.*, vol. 16, no. 1, pp. 49–52, Feb. 2009.

[70] Z. Yunsheng, S. Wei, and L. Zongjin, "Composition design and microstructural characterization of calcined kaolin-based geopolymer cement," *Appl. Clay Sci.*, vol. 47, no. 3–4, pp. 271–275, Feb. 2010.

[71] P. Sun and H.-C. Wu, "Transition from brittle to ductile behavior of fly ash using PVA fibers," *Cem. Concr. Compos.*, vol. 30, no. 1, pp. 29–36, Jan. 2008.

[72] D. P. Dias and C. Thaumaturgo, "Fracture toughness of geopolymeric concretes reinforced with basalt fibers," *Cem. Concr. Compos.*, vol. 27, no. 1, pp. 49–54, Jan. 2005.

[73] T. Alomayri, F. U. A. Shaikh, and I. M. Low, "Characterisation of cotton fibre-reinforced geopolymer composites," *Compos. Part B Eng.*, vol. 50, pp. 1–6, Jul. 2013.

[74] T. Alomayri, F. U. A. Shaikh, and I. M. Low, "Effect of fabric orientation on mechanical properties of cotton fabric reinforced geopolymer composites," *Mater. Des.*, vol. 57, pp. 360–365, May 2014.

[75] J. Giancaspro, C. Papakonstantinou, and P. Balaguru, "Fire resistance of inorganic sawdust biocomposite," *Compos. Sci. Technol.*, vol. 68, no. 7–8, pp. 1895–1902, Jun. 2008.

[76] T. Lin, D. Jia, P. He, M. Wang, and D. Liang, "Effects of fiber length on mechanical properties and fracture behavior of short carbon fiber reinforced geopolymer matrix composites," *Mater. Sci. Eng. A*, vol. 497, no. 1–2, pp. 181–185, Dec. 2008.

[77] T. Lin, D. Jia, P. He, and M. Wang, "In situ crack growth observation and fracture behavior of short carbon fiber reinforced geopolymer matrix composites," *Mater. Sci. Eng. A*, vol. 527, no. 9, pp. 2404–2407, Apr. 2010.

[78] P. He, D. Jia, T. Lin, M. Wang, and Y. Zhou, "Effects of high-temperature heat treatment on the mechanical properties of unidirectional carbon fiber

reinforced geopolymer composites," *Ceram. Int.*, vol. 36, no. 4, pp. 1447–1453, May 2010.

[79] H. Zhang, V. Kodur, L. Cao, and S. Qi, "Fiber Reinforced Geopolymers for Fire Resistance Applications," *Procedia Eng.*, vol. 71, pp. 153–158, 2014.

[80] M. Saafi, K. Andrew, P. L. Tang, D. McGhon, S. Taylor, M. Rahman, S. Yang, and X. Zhou, "Multifunctional properties of carbon nanotube/fly ash geopolymeric nanocomposites," *Constr. Build. Mater.*, vol. 49, pp. 46–55, Dec. 2013.

[81] G. Li, "Properties of high-volume fly ash concrete incorporating nano-SiO2," *Cem. Concr. Res.*, vol. 34, no. 6, pp. 1043–1049, Jun. 2004.

[82] B.-W. Jo, C.-H. Kim, G. Tae, and J.-B. Park, "Characteristics of cement mortar with nano-SiO2 particles," *Constr. Build. Mater.*, vol. 21, no. 6, pp. 1351–1355, Jun. 2007.

[83] L. Senff, D. Hotza, W. L. Repette, V. M. Ferreira, and J. A. Labrincha, "Mortars with nano-SiO2 and micro-SiO2 investigated by experimental design," *Constr. Build. Mater.*, vol. 24, no. 8, pp. 1432–1437, Aug. 2010.

[84] A. Naji Givi, S. Abdul Rashid, F. N. A. Aziz, and M. A. M. Salleh, "The effects of lime solution on the properties of SiO2 nanoparticles binary blended concrete," *Compos. Part B Eng.*, vol. 42, no. 3, pp. 562–569, Apr. 2011.

[85] A. Nazari and S. Riahi, "TiO2 nanoparticles effects on physical, thermal and mechanical properties of self compacting concrete with ground granulated blast furnace slag as binder," *Energy Build.*, vol. 43, no. 4, pp. 995–1002, Apr. 2011.

[86] A. Nazari and S. Riahi, "Improvement compressive strength of concrete in different curing media by Al2O3 nanoparticles," *Mater. Sci. Eng. A*, vol. 528, no. 3, pp. 1183–1191, Jan. 2011.

[87] T. Meng, Y. Yu, X. Qian, S. Zhan, and K. Qian, "Effect of nano-TiO2 on the mechanical properties of cement mortar," *Constr. Build. Mater.*, vol. 29, pp. 241–245, Apr. 2012.

[88] M. Stefanidou and I. Papayianni, "Influence of nano-SiO2 on the Portland cement pastes," *Compos. Part B Eng.*, vol. 43, no. 6, pp. 2706–2710, Sep. 2012.

[89] A. M. Said, M. S. Zeidan, M. T. Bassuoni, and Y. Tian, "Properties of concrete incorporating nano-silica," *Constr. Build. Mater.*, vol. 36, pp. 838–844, Nov. 2012.

[90] M. Aly, M. S. J. Hashmi, A. G. Olabi, M. Messeiry, E. F. Abadir, and A. I. Hussain, "Effect of colloidal nano-silica on the mechanical and physical behaviour of waste-glass cement mortar," *Mater. Des.*, vol. 33, pp. 127–135, Jan. 2012.

[91] P. Hou, K. Wang, J. Qian, S. Kawashima, D. Kong, and S. P. Shah, "Effects of colloidal nanoSiO2 on fly ash hydration," *Cem. Concr. Compos.*, vol. 34, no. 10, pp. 1095–1103, Nov. 2012.

[92] K. Behfarnia and N. Salemi, "The effects of nano-silica and nano-alumina on frost resistance of normal concrete," *Constr. Build. Mater.*, vol. 48, pp. 580–584, Nov. 2013.

[93] T. Phoo-ngernkham, P. Chindaprasirt, V. Sata, S. Hanjitsuwan, and S. Hatanaka, "The effect of adding nano-SiO2 and nano-Al2O3 on properties of high calcium fly ash geopolymer cured at ambient temperature," *Mater. Des.*, vol. 55, pp. 58–65, Mar. 2014.

[94] M. Oltulu and R. Şahin, "Pore structure analysis of hardened cement mortars containing silica fume and different nano-powders," *Constr. Build. Mater.*, vol. 53, pp. 658–664, Feb. 2014.
[95] J.-Y. Shih, T.-P. Chang, and T.-C. Hsiao, "Effect of nanosilica on characterization of Portland cement composite," *Mater. Sci. Eng. A*, vol. 424, no. 1–2, pp. 266–274, 2006.
[96] A. M. Neville, *Properties of Concrete*, 5 edition. Harlow, England ; New York: Prentice Hall, 2011.
[97] Teixeira-Pinto, Fernandes, P Jalali, "Geopolymer Manufacture and Application Main Problem when Using Concrete technology," Melbourne, 2002.
[98] "Pardam | 'We make nanofibers.'".
[99] C09 Committee, "Test Method for Compressive Strength of Cylindrical Concrete Specimens," ASTM International, 2014.
[100] Hardjito D, "The stress–strain behaviour of fly ash-based geopolymer concrete," *Dev. Mech. Struct. Mater.*
[101] "Plastics – Determination of Charpy impact properties Part 1: Non-instrumented impact test (ISO 179-1 : 2000) English version of DIN EN ISO 179-1." .
[102] D20 Committee, "Test Methods for Plane-Strain Fracture Toughness and Strain Energy Release Rate of Plastic Materials," ASTM International, 2007.
[103] S. Barbhuiya, S. Mukherjee, and H. Nikraz, "Effects of nano-Al2O3 on early-age microstructural properties of cement paste," *Constr. Build. Mater.*, vol. 52, pp. 189–193, Feb. 2014.
[104] P. He, D. Jia, T. Lin, M. Wang, and Y. Zhou, "Effects of high-temperature heat treatment on the mechanical properties of unidirectional carbon fiber reinforced geopolymer composites," *Ceram. Int.*, vol. 36, no. 4, pp. 1447–1453, May 2010.
[105] D. L. Y. Kong and J. G. Sanjayan, "Effect of elevated temperatures on geopolymer paste, mortar and concrete," *Cem. Concr. Res.*, vol. 40, no. 2, pp. 334–339, Feb. 2010.
[106] T. Bakharev, "Thermal behaviour of geopolymers prepared using class F fly ash and elevated temperature curing," *Cem. Concr. Res.*, vol. 36, no. 6, pp. 1134–1147, Jun. 2006.
[107] O. A. Abdulkareem, A. M. Mustafa Al Bakri, H. Kamarudin, I. Khairul Nizar, and A. A. Saif, "Effects of elevated temperatures on the thermal behavior and mechanical performance of fly ash geopolymer paste, mortar and lightweight concrete," *Constr. Build. Mater.*, vol. 50, pp. 377–387, Jan. 2014.
[108] D. L. Y. Kong and J. G. Sanjayan, "Damage behavior of geopolymer composites exposed to elevated temperatures," *Cem. Concr. Compos.*, vol. 30, no. 10, pp. 986–991, Nov. 2008.
[109] P. K. Sarker, S. Kelly, and Z. Yao, "Effect of fire exposure on cracking, spalling and residual strength of fly ash geopolymer concrete," *Mater. Des.*, vol. 63, pp. 584–592, Nov. 2014.
[110] Y. J. Zhang, S. Li, Y. C. Wang, and D. L. Xu, "Microstructural and strength evolutions of geopolymer composite reinforced by resin exposed to elevated temperature," *J. Non-Cryst. Solids*, vol. 358, no. 3, pp. 620–624, Feb. 2012.

[111] T. W. Cheng and J. P. Chiu, "Fire-resistant geopolymer produced by granulated blast furnace slag," *Miner. Eng.*, vol. 16, no. 3, pp. 205–210, Mar. 2003.
[112] T. Alomayri, H. Assaedi, F. U. A. Shaikh, and I. M. Low, "Effect of water absorption on the mechanical properties of cotton fabric-reinforced geopolymer composites," *J. Asian Ceram. Soc.*
[113] M. C. M. Nasvi, P. G. Ranjith, J. Sanjayan, and H. Bui, "Effect of temperature on permeability of geopolymer: A primary well sealant for carbon capture and storage wells," *Fuel*, vol. 117, Part A, pp. 354–363, Jan. 2014.
[114] Xiem N.T, "the potential applications of geopolymer materials in waste processing," Technical university of Liberec.
[115] C. Y. Heah, H. Kamarudin, A. M. M. A. Bakri, M. Binhussain, M. Luqman, I. K. Nizar, C. M. Ruzaidi, and Y. M. Liew, "Effect of Curing Profile on Kaolin-based Geopolymers," *Phys. Procedia*, vol. 22, pp. 305–311, 2011.
[116] M. S. Muñiz-Villarreal, A. Manzano-Ramírez, S. Sampieri-Bulbarela, J. R. Gasca-Tirado, J. L. Reyes-Araiza, J. C. Rubio-Ávalos, J. J. Pérez-Bueno, L. M. Apatiga, A. Zaldivar-Cadena, and V. Amigó-Borrás, "The effect of temperature on the geopolymerization process of a metakaolin-based geopolymer," *Mater. Lett.*, vol. 65, no. 6, pp. 995–998, Mar. 2011.
[117] J. G. S. van Jaarsveld, J. S. J. van Deventer, and G. C. Lukey, "The effect of composition and temperature on the properties of fly ash- and kaolinite-based geopolymers," *Chem. Eng. J.*, vol. 89, no. 1–3, pp. 63–73, Oct. 2002.
[118] Memon, Fareed Ahmed; Nuruddin, Muhd Fadhil; Demie, Samuel; Shafiq, Nasir, "Effect of Curing Conditions on Strength of Fly ash-based Self-Compacting Geopolymer Concrete," *World Acad. Sci. Eng. Technol. Issue 56 P860*.
[119] S. P. Shah, S. E. Swartz, and C. Ouyang, Fracture Mechanics of Concrete: Applications of Fracture Mechanics to Concrete, Rock and Other Quasi-Brittle Materials, 1 edition. New York: Wiley-Interscience, 1995.
[120] A. Bentur and S. Mindess, Fibre Reinforced Cementitious Composites, Second Edition. CRC Press, 2006.
[121] T. S. Lok and P. J. Zhao, "Impact Response of Steel Fiber-Reinforced Concrete Using a Split Hopkinson Pressure Bar," *J. Mater. Civ. Eng.*, vol. 16, no. 1, pp. 54–59, Feb. 2004.
[122] D. Zhu, M. Gencoglu, and B. Mobasher, "Low velocity flexural impact behavior of AR glass fabric reinforced cement composites," *Cem. Concr. Compos.*, vol. 31, no. 6, pp. 379–387, Jul. 2009.
[123] M. Gencoglu, B. Mobasher, "Static and Impact Behavior of Fabric Reinforced Cement Composites in Flexure," in *RILEM Proceedings, Pro. 53, S.A.R.L., Cachan, France*.
[124] Y. Mohammadi, R. Carkon-Azad, S. P. Singh, and S. K. Kaushik, "Impact resistance of steel fibrous concrete containing fibres of mixed aspect ratio," *Constr. Build. Mater.*, vol. 23, no. 1, pp. 183–189, Jan. 2009.
[125] N. Wang, S. Mindess, and K. Ko, "Fibre reinforced concrete beams under impact loading," *Cem. Concr. Res.*, vol. 26, no. 3, pp. 363–376, Mar. 1996.
[126] F.J. Silva, J. L., C. Thaumaturgo, "reinforcement and fracture in geopolymeric cement composites," Materials and Mechanical Engineering Department, Militar Engineering Institute - IME, Brazil.

7 APPENDICES

APPENDIX A1. PERCENTAGE OF FIBERS REINFORCED GEOPOLYMER

% (wt)	Carbon fiber (μm)	Carbon fiber(subμm)	SiO2(nm)	C (subμm) +SiO2(nm)
	3	0.1	0.1	0.1+0.1
	5	0.3	0.3	0.3+0.3
	7	0.5	0.5	0.5+0.5
	8	0.7	0.7	0.7+0.7
	10	1	1	1+1
Price	0.036÷0.06 EUR/g		8 EUR/g	
Produced	Aerospace research	Miiling from	Kertak nanotechnology	
	and test institute in Prague	Carbon fiber in μm		

APPENDIX A2. CURING PROCESS OF FIBERS REINFORCED GEOPOLYMER

Curing temperature/ curing time	Pure geopolymer	Geopolymer +carbon microfibres	Geopolymer + carbon submicrofibres	Geopolymer + silicone dioxide nanofibres	Geopolymer + carbon submicrofibres + silicone dioxide nanofibres
23°C/24 h	x	x	x	x	x
60°C/8 h				x	
60°C/16h				x	
60°C/24h	x	x	x	x	x
60°C/48h				x	
60°C/72h				x	
70°C/24h				x	
80°C/24h				x	
95°C/24h				x	
100°C/24h	x				
105°C/24h				x	
150°C/24h				x	
200°C/8h	x	x			
200°C/16h		x			
200°C/24h				x	
300°C/8h	x	x			
300°C/16h		x			
400°C/3h			x		
400°C/5h			x		
600°C/1h		x			
600°C/3h	x	x	x		
600°C/5h		x	x		
800°C/1h		x			
800°C/3h	x	x	x		
800°C/5h		x	x		
900°C/3h			x		
900°C/5h			x		

APPENDIX B1. PROPERTIES OF SILICON DIOXIDE NANOFIBRES BASED GEOPOLYMER WITH CURING AT 70^0C AND 80^0C FOR 24HOURS

Mixture		Hardness [HV]	Density [g/cm^3]	Compressive strength [MPa]	Modulus of elasticity in compression [GPa]
GNS1	At 70^0C-24h	278 ± 4.3	1.665	26.32 ± 2.31	19.19 ± 0.82
	At 80^0C-24h	282 ± 2.7	1.658	26.54 ± 1.95	19.25 ± 0.21
GNS3	At 70^0C-24h	285 ± 3.2	1.648	39.45 ± 3.12	22.30 ± 0.72
	At 80^0C-24h	287 ± 3	1.625	40.76 ± 3.2	22.58 ± 0.73
GNS5	At 70^0C-24h	283 ± 4.1	1.574	45.36 ± 0.93	23.53 ± 0.61
	At 80^0C-24h	289 ± 5.2	1.563	45.92 ± 2.85	23.64 ± 0.67
GNS7	At 70^0C-24h	294 ± 6	1.572	48.23 ± 1.27	24.10 ± 0.79
	At 80^0C-24h	296 ± 3.2	1.54	48.75 ± 1.35	24.20 ± 0.55
GNS10	At 70^0C-24h	297 ± 2.8	1.516	37.29 ± 2.78	21.83 ± 0.38
	At 80^0C-24h	301 ± 2.2	1.507	37.73 ± 1.62	21.93 ± 0.64

APPENDIX B2. CHARACTERISTICS OF NANOFIBRES SiO_2 BASED GEOPOLYMER AT 95^0C AND 105^0C FOR 24 HOURS

Mixture		Hardness [HV]	Density [g/cm^3]	Compressive strength [MPa]	Modulus of elasticity in compression [GPa]
GNS1	At 95^0C-24h	283 ± 5.3	1.645	25.96 ± 0.83	19.09 ± 0.37
	At 105^0C-24h	285 ± 3.6	1.642	26.73 ± 1.52	19.30 ± 0.38
GNS3	At 95^0C-24h	289 ± 3.2	1.639	41.27 ± 1.73	22.69 ± 0.54
	At 105^0C-24h	291 ± 2.6	1.637	41.96 ± 1.72	22.84 ± 0.94
GNS5	At 95^0C-24h	294 ± 4.1	1.592	46.59 ± 1.63	23.78 ± 0.49
	At 105^0C-24h	296 ± 2.9	1.551	47.03 ± 1.43	23.86 ± 0.91
GNS7	At 95^0C-24h	298 ± 5.2	1.564	49.05 ± 2.3	24.26 ± 0.82
	At 105^0C-24h	298 ± 2.7	1.549	49.73 ± 1.14	24.39 ± 0.78
GNS10	At 95^0C-24h	302 ± 1.7	1.506	37.29 ± 2.78	22.10 ± 0.31
	At 105^0C-24h	303 ± 3.4	1.495	38.51 ± 1.65	22.09 ± 0.69

APPENDIX B3. PROPERTIES OF SILICON DIOXIDE NANOFIBERS BASED GEOPOLYMER AT 150^0C, 200^0C FOR 24 HOURS

Mixture		Hardness [HV]	Density [g/cm^3]	Compressive strength [MPa]	Modulus of elasticity in compression [GPa]
GNS1	At 150^0C-24h	280 ± 5	1.625	23.07 ± 2.4	19.09 ± 0.37
	At 200^0C-24h	278 ± 3.6	1.619	22.86 ± 3.2	19.30 ± 0.38
GNS3	At 150^0C-24h	282 ± 2.8	1.629	37.76 ± 1.6	22.69 ± 0.54
	At 200^0C-24h	283 ± 1.8	1.616	34.67 ± 2.5	22.84 ± 0.94
GNS5	At 150^0C-24h	275 ± 3.1	1.585	39.33 ± 3.1	23.78 ± 0.49
	At 200^0C-24h	273 ± 2.5	1.548	36.59 ± 3.7	23.86 ± 0.91
GNS7	At 150^0C-24h	269 ± 4.9	1.563	40.07 ± 2.7	24.26 ± 0.82
	At 200^0C-24h	265 ± 2.7	1.529	37.83 ± 4.1	24.39 ± 0.78
GNS10	At 150^0C-24h	263 ± 4.7	1.516	33.78 ± 1.9	22.10 ± 0.31
	At 200^0C-24h	262 ± 4.3	1.492	31.09 ± 4.3	22.09 ± 0.69

APPENDIX C1. PROPERTIES OF CARBON MICRO FIBRES BASED GEOPOLYMER AT 200^0C

Mixture		Hardness [HV]	Density [g/cm^3]	Compressive strength [MPa]	Modulus of elasticity in compression [GPa]
GMC1	At 200^0C-8h	247 ± 2.9	1.676	22.19 ± 0.41	18.05 ± 0.39
	At 200^0C-16h	238 ± 4.8	1.671	22.03 ± 1.05	17.71 ± 0.45
GMC3	At 200^0C-8h	250 ± 2.9	1.668	22.87 ± 0.53	18.25 ± 0.82
	At 200^0C-16h	245 ± 3.7	1.659	22.83 ± 0.74	18.23 ± 0.21
GMC5	At 200^0C-8h	244 ± 3.2	1.623	26.16 ± 0.7	19.15 ± 0.72
	At 200^0C-16h	239 ± 4.3	1.618	24.7 ± 2.17	18.75 ± 0.92
GMC7	At 200^0C-8h	237 ± 2.6	1.590	29.65 ± 0.39	20.04 ± 0.61
	At 200^0C-16h	233 ± 6.2	1.583	26.72 ± 1.29	19.29 ± 0.44
GMC8	At 200^0C-8h	224 ± 1.9	1.554	31.15 ± 1.25	20.41 ± 0.73
	At 200^0C-16h	--	1.536	30.54 ± 4.31	20.26 ± 0.52
GMC10	At 200^0C-8h	207 ± 2.8	1.527	28.35 ± 0.78	19.71 ± 0.33
	At 200^0C-16h	190 ± 2.5	1.448	25.03 ± 0.83	18.84 ± 0.64

APPENDIX C2. PROPERTIES OF CARBON MICRO FIBRES BASED GEOPOLYMER AT 300^0C

Mixture		Hardness [HV]	Density [g/cm^3]	Compressive strength [MPa]	Modulus of elasticity in compression [GPa]
GMC1	At 300^0C-8h	207 ± 3.1	1.656	20.32 ± 2.03	17.50 ± 0.39
	At 300^0C-16h	198 ± 3.4	1.647	19.44 ± 2.15	17.24 ± 0.47
GMC3	At 300^0C-8h	190 ± 2.6	1.638	22.13 ± 1.27	18.04 ± 0.38
	At 300^0C-16h	--	1.627	21.68 ± 1.72	17.90 ± 0.41
GMC5	At 300^0C-8h	--	1.613	23.88 ± 0.42	18.53 ± 0.72
	At 300^0C-16h	--	1.591	23.62 ± 0.97	18.46 ± 0.71
GMC7	At 300^0C-8h	217 ± 2.6	1.584	25.13 ± 3.1	18.87 ± 0.49
	At 300^0C-16h	210 ± 5.1	1.573	23.11 ± 1.29	18.31 ± 0.33
GMC8	At 300^0C-8h	214 ± 1.9	1.534	30.00 ± 5.2	20.13 ± 0.84
	At 300^0C-16h	--	1.532	29.23 ± 3.91	19.94 ± 0.39
GMC10	At 300^0C-8h	187 ± 2.2	1.512	17.70 ± 2.5	16.69 ± 0.31
	At 300^0C-16h	--	1.436	16.47 ± 1.36	16.29 ± 0.72

APPENDIX C3. PROPERTIES OF CARBON MICRO FIBRES BASED GEOPOLYMER AT 600^0C

Mixture		Hardness [HV]	Density [g/cm^3]	Compressive strength [MPa]	Modulus of elasticity in compression [GPa]
GMC1	At 600^0C-1h	215 ± 3.27	1.588	10.66 ± 1.02	14.14 ± 0.30
	At 600^0C-3h	198 ± 2.5	1.585	10.25 ± 0.97	13.97 ± 0.26
	At 600^0C-5h	--	1.562	9.73 ± 1.67	13.74 ± 0.42
GMC3	At 600^0C-1h	197 ± 2.2	1.543	10.95 ± 0.75	14.26 ± 0.39
	At 600^0C-3h	--	1.539	10.67 ± 0.73	14.14 ± 0.45
	At 600^0C-5h	--	1.525	9.23 ± 0.92	13.52 ± 0.25
GMC5	At 600^0C-1h	185 ± 2.9	1.538	16.48 ± 1.19	16.29 ± 0.59
	At 600^0C-3h	--	1.534	13.34 ± 1.23	15.19 ± 0.50
	At 600^0C-5h	--	1.529	10.87 ± 2.04	14.22 ± 0.63
GMC7	At 600^0C-1h	181 ± 3.1	1.524	21.88 ± 2.1	17.96 ± 0.38
	At 600^0C-3h	--	1.517	14.87 ± 1.45	15.74 ± 0.59
	At 600^0C-5h	--	1.508	10.20 ± 1.57	13.94 ± 0.42
GMC8	At 600^0C-1h	--	1.496	21.62 ± 1.32	17.89 ± 0.27
	At 600^0C-3h	--	1.467	10.67 ± 1.47	14.14 ± 0.38
	At 600^0C-5h	--	1.460	10.71 ± 2.07	14.16 ± 0.55
GMC10	At 600^0C-1h	--	1.329	10.32 ± 0.67	14.00 ± 0.28
	At 600^0C-3h	--	1.291	9.08 ± 0.86	13.46 ± 0.0.37
	At 600^0C-5h	--	1.276	6.22 ± 1.29	12.05 ± 0.31

APPENDIX D1. PROPERTIES OF CARBON SUB-MICRO FIBRES BASED GEOPOLYMER AT 400^0C

Mixture		Hardness [HV]	Density [g/cm^3]	Compressive strength [MPa]	Modulus of elasticity in compression [GPa]
GSC1	At 400^0C-3h	190 ± 2.1	1.698	17.21 ± 1.02	16.53 ± 1.12
	At 400^0C-5h	--	1.692	16.81 ± 1.53	16.40 ± 1.04
GSC3	At 400^0C-3h	197 ± 1.8	1.689	17.53 ± 0.81	16.63 ± 1.07
	At 400^0C-5h	185 ± 2.6	1.685	16.92 ± 0.89	16.43 ± 1.43
GSC5	At 400^0C-3h	--	1.674	17.89 ± 1.23	16.75 ± 1.05
	At 400^0C-5h	--	1.668	17.09 ± 1.62	16.49 ± 0.76
GSC7	At 400^0C-3h	201 ± 1.5	1.652	18.07 ± 1.11	16.81 ± 0.72
	At 400^0C-5h	--	1.641	17.85 ± 1.04	16.74 ± 1.08
GSC10	At 400^0C-3h	--	1.598	16.72 ± 0.67	16.37 ± 0.98
	At 400^0C-5h	--	1.581	15.93 ± 1.32	16.10 ± 1.23

APPENDIX D2. PROPERTIES OF CARBON SUB-MICRO FIBRES BASED GEOPOLYMER AT 600^0C

Mixture		Hardness [HV]	Density [g/cm^3]	Compressive strength [MPa]	Modulus of elasticity in compression [GPa]
GSC1	At 600^0C-3h	--	1.691	14.25 ± 0.89	15.52 ± 1.12
	At 600^0C-5h	--	1.687	13.92 ± 1.06	15.40 ± 1.04
GSC3	At 600^0C-3h	183 ± 2.1	1.673	14.31 ± 0.73	15.54 ± 1.07
	At 600^0C-5h	--	1.665	13.97 ± 0.94	15.42 ± 1.43
GSC5	At 600^0C-3h	178 ± 2.3	1.652	15.01 ± 1.21	15.79 ± 1.05
	At 600^0C-5h	--	1.648	14.23 ± 0.98	15.51 ± 0.76
GSC7	At 600^0C-3h	180 ± 3.1	1.637	15.72 ± 0.78	16.03 ± 0.72
	At 600^0C-5h	--	1.631	15.05 ± 1.15	15.80 ± 1.08
GSC10	At 600^0C-3h	--	1.587	13.26 ± 1.51	15.16 ± 0.98
	At 600^0C-5h	--	1.572	11.67 ± 1.03	14.55 ± 1.23

APPENDIX D3. PROPERTIES OF CARBON SUB-MICRO FIBRES BASED GEOPOLYMER AT 800^0C

Mixture		Hardness [HV]	Density [g/cm^3]	Compressive strength [MPa]	Modulus of elasticity in compression [GPa]
GSC1	At 800^0C-3h	176 ± 2.4	1.672	10.27 ± 1.02	13.98 ± 1.03
	At 800^0C-5h	--	1.654	10.01 ± 1.34	13.86 ± 1.04
GSC3	At 800^0C-3h	184 ± 2.6	1.623	10.52 ± 0.76	14.08 ± 1.07
	At 800^0C-5h	--	1.596	9.95 ± 0.76	13.84 ± 1.23
GSC5	At 800^0C-3h	179 ± 2.2	1.591	11.03 ± 1.01	14.29 ± 0.91
	At 800^0C-5h	175 ± 1.7	1.583	10.67 ± 1.23	14.14 ± 0.76
GSC7	At 800^0C-3h	--	1.575	12.87 ± 1.17	15.01 ± 0.77
	At 800^0C-5h	--	1.551	11.35 ± 0.96	14.42 ± 1.18
GSC10	At 800^0C-3h	--	1.532	9.38 ± 0.72	13.59 ± 0.67
	At 800^0C-5h	--	1.514	9.06 ± 1.15	13.45 ± 1.07

APPENDIX D4. PROPERTIES OF NANOSILICA AND CARBON SUB-MICRO FIBRES BASED GEOPOLYMER AT ROOM TEMPERATURE AND AT 60^0C-24HOURS

Mixture		Hardness [HV]	Density [g/cm^3]	Compressive strength [MPa]	Modulus of elasticity in compression [GPa]
M11	At room temperature	265 ± 3.1	1.677	29.43 ± 0.93	19.99 ± 0.93
	At 60^0C-24h	272 ± 4.2	1.655	31.8 ± 1.34	20.57 ± 1.18
M33	At room temperature	275 ± 2.3	1.648	34.6 ± 1.2	21.22 ± 1.15
	At 60^0C-24h	278 ± 4.3	1.635	35.69 ± 1.55	21.47 ± 1.16
M55	At room temperature	277 ± 2.8	1.624	38 ± 0.78	21.99 ± 0.78
	At 60^0C-24h	282 ± 2.6	1.618	41.79 ± 0.76	22.80 ± 0.73
M77	At room temperature	279 ± 3.1	1.597	29.44 ± 1.73	19.99 ± 1.21
	At 60^0C-24h	287 ± 3.7	1.591	30.65 ± 1.62	20.29 ± 1.23
M110	At room temperature	285 ± 3.5	1.588	27.38 ± 1.2	19.46 ± 0.94
	At 60^0C-24h	297 ± 2.8	1.582	28.32 ± 0.8	19.71 ± 0.8

List publications of author

[1] Thi Linh Trinh, D.Kroisova, Petr Louda, and Xiem N. Thang, "Compressive strength of flyash based geopoymer adding nanofiber," presented at the Workshop Svetlanka 2011, 2011.

[2] Thi Linh Trinh, D.Kroisova, and Petr Louda, "Curing At High Temprature On mechanical Of Geopolymer Adding Carbon Fiber," presented at the The 1st International Virtual Conference on Advanced Scientific Results Slovakia, 2013.

[3] Thi Linh Trinh, D.Kroisova, and Petr Louda, "Effect of curing time and curing temperature on mechanical properties of Carbon fiber based geopolymer," in *conference proceedings*, 2013.

[4] Thi Linh Trinh, D.Kroisova, Petr Louda, and Nguyen Thang Xiem, Pavel Kejzlar, "Effect of nanofiber on mechanical properties of geopolymer," presented at the Potential Application of Plasma and Nanomaterials - PAPN 2013, 2013.

[5] Thi Linh Trinh, D.Kroisova, Petr Louda, and Pavel Kejzlar, "Effect of nanofiber (SiO2) on mechanical properties of geopolymer," presented at the Conference Postgraduate symposium on nanotechnology- chemical enginerrig, university of Birmingham, England, 2011.

[6] Linh Tr.Th, D. Kroisova, and Petr Louda, P.Kejzlar, "Effect of Nano-Fiber (Sio2) on Mechanical Properties of Geopolymer," in *3rd International seminar on applied technology,science, and arts*, Indonesia, 2011, pp. 69–72.

[7] Linh Tr.Th, D.Kroisova, and Petr Louda, "Experimental study on nano fibers based geopolymer," presented at the Interdisciplinary Scientific International Conference for PhD students and assistants, Czech Republic, 2014.

[8] Linh Tr.Th, D. Kroisova, and Petr Louda, "Experiment on short fiber reinforced geopolymer," *J. Mech. Civ. Eng. India*, vol. 11, 2014.

[9] Thi Linh Trinh, D.Kroisova, and Petr Louda, "Geopolymer environmental-friendly material," presented at the Workshop Svetlanka 2012, 2012.

[10] Thi Linh Trinh, D.Kroisova, and Petr Louda, "Nanofiber and applications," presented at the NanoThailand 2012: Nanotechnology for benefits of Mankind, 2012.

[11] Thi Linh Trinh, D.Kroisova, and Petr Louda, "Potential of geopolymer technology on green building in construction," presented at the Mezinárodní Masarykově konferenci prosince 2012, MAGNANIMITAS, 2012.