THE EFFECT OF CURING TEMPERATURE ON THE PROPERTIES AND STRUCTURE OF GEOPOLYMER COMPOSITE BASED ON POTASSIUM SILICATE AND METAKAOLIN

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A carbon fibre/geopolymer composite whose matrix was based on potassium silicate and metakaolin was subjected to different curing temperature modes. The effect of the treatments was evaluated by testing the stiffness and water uptake resistance of the composite. The structure of the composites was analysed by scanning electron microscopy, X-ray diffraction and nuclear magnetic resonance. It was determined that the highest stiffness was achieved by the primary curing at 80°C. Contrary to this, curing at temperatures higher than 100°C increased the resistance to water uptake, resulting in smaller decrease in the storage modulus. Structural changes of the geopolymer were linked to the course of the curing temperature mode. Two types of the curing were suggested for the use of the carbon fibre/geopolymer composite in heat stress applications and in a humid environment, respectively.

INTRODUCTION

Geopolymer resin is a heterogeneous system consisting of solid particles with a mean size of about three micrometres, which polymerises by means of a water-generating condensation mechanism and that is cured in a strongly alkaline environment. The process of geopolymer curing, according to current knowledge, is based on the formation of a polymeric spatial structure formed by silicon and aluminium atoms coordinated by oxygen atoms acting as bridges. The ratio between the silicon and aluminium atoms is usually at least one, i.e., $Si/Al > 1$. The composition of the geopolymer resin is, according to convention, expressed using the following empirical formula: $M_x(-(SiO_2)_y AlO_2) \cdot nH_2O$, where M is an alkali ion and x, y and n give the molar representation of the respective atoms [1]. The equivalent expression using molar ratios is $M_2O: Al_2O_3 = x$, $SiO_2: Al_2O_3 = 2y/x$ and $H_2O: Al_2O_3 = n$. The empirical formula suggests that it is a structure composed of spatially structured chains of tetrahedra of aluminium and silicon atoms. These tetrahedra are connected through their vertices, not through their edges. Chains of tetrahedra form an irregular spatial network, with alkali ions and water molecules in the gaps. The strength of the bond of the water molecules to the spatial network is not constant. The formula further indicates that it is a non-stoichiometric compound. The structure loses water by drying; microstructures are formed in the structure and the material becomes harder and more brittle. The ratio between the atoms of

alkali and aluminium in the structure is significant. This ratio should be $0.8 < K_2O/Al_2O_3 < 1.2$ [1]. Small ratios can reduce the conversion during a geopolymerisation reaction, while large ratios lead to the generation of free alkali and white efflorescence of alkali carbonates. The structure of the geopolymer network was designed by Davidovits and Barbosa [1,2]. The greatest breakthrough in the study of the structure occurred through the analysis of the aluminosilicate spectra by nuclear magnetic resonance (NMR). For the first time, this method was mentioned in the work of Lippmaa et al. [3], which dealt with a chemical shift of crystalline silicates and aluminosilicates.

They assume that aluminosilicates are formed by covalent bonds between silicon atoms and aluminium, with oxygen atoms being the bridge. The silicon atom is then surrounded by other silicon or aluminium atoms in the second sphere. They found that the number of aluminium atoms in the second sphere of the coordination is proportional to the chemical shift in the spectrum ^{29}Si NMR. Similarly, in the case of ^{27}Al, the study of the solutions of polyaluminates and aluminosilicates established that the chemical shift of ^{27}Al is dependent on the coordination of the aluminium atoms by the oxygen atoms. This was reported for the first time in [4, 5]. Another important finding of the study of the structure of aluminosilicates is the Loewenstein rule, which forbids the connection of an aluminium atom in the second sphere of the coordination to another aluminium atom [6].

A geopolymer resin can be used to prepare composites reinforced with various kinds of fibres. One of the commonly used manufacturing technologies of conventional organic composites can be applied to the geopolymer composite preparation. It is the manual lamination intensified by placing the prepared reinforcement/matrix structure in a plastic bag under a vacuum, the so called vacuum bagging. In this work, we aimed at optimising the curing process of the geopolymer composite prepared by lamination of a carbon fabric using vacuum bagging.

The preparation of carbon fibre/geopolymer composite using vacuum bagging together with curing at 80 - 85°C was reported in [7]. The authors also discuss the necessity of drying the composite to remove the contained water and the size of geopolymer resin particles, which makes it difficult to penetrate into the bundles of carbon fibres. A geopolymer composite with 3.5 - 7.5 wt. % of short carbon fibres was prepared in a mould, cured during vacuum bagging at 80°C and then dried at 120°C [8]. A maximum flexural strength of 0.097 GPa was reached for the fibre content of 4.5 %. Foden et al. used a slightly modified process as they dried each fabric layer saturated with the geopolymer resin for 30 s at 80°C before lamination [9]. Curing was undertaken at 80°C during vacuum bagging. The composite was pressed for three hours and, finally, dried at 80°C for 24 hours. The rather complicated curing process is described in [10]. It is comprised of the preparation of the prepreg, its layering, which is interrupted by 10-minute intervals of drying at 65°C. The resulting composite was cured in a vacuum at 65°C, taken out of the vacuum and then gradually dried at 95, 135 and 205°C. Thang et al. [11] mixed geopolymer resin with Al_2O_3 nano-fibres and the resulting resin was used to impregnate the carbon fabric. In this case, the vacuum bagging started at the laboratory temperature and then it was raised to 80°C. The final drying of the composite was performed at 80°C at a normal pressure. The combination of the geopolymer resin and a chopped basalt fibre, in the concentration up to 10 wt. %, was tested in [12]. The mixture was cured in a silicon mould at 50°C for 24 hours. The exposition of the composite at 500°C had a negative effect on the bending strength which was reduced by 75 %.

The stated works dealing with the preparation of fibre reinforced geopolymer composites present certain general features, such as:

● use of low viscosity resin,
● absence of particle fillers,
● the requirement of the smallest possible particles,
● use of nano-fibres in order to reduce the cracks in the matrix,
● preventing water evaporation during the first phase of curing and drying in the following curing phase.

In this paper, a geopolymer synthesised from the following raw materials was studied:

● a potassium silicate solution with a high content of dry matter and a high modulus, i.e., a molar ratio of SiO_2/K_2O,
● an amorphous silica, which is produced as waste from zirconium production,
● a finely ground burnt clay shale as the source of the aluminium component.

It was shown that the selection of a suitable curing temperature mode has a significant effect on the properties of the resulting geopolymer composite. This was demonstrated by testing the composite strength and the resistance against the effects of boiling water.

EXPERIMENTAL

Materials

The geopolymer resin was prepared by alkaline activation of the burnt clay shale Mefisto L05 (České lupkové závody, a.s., Czech Republic) and an amorphous silica (Thermal silica, Saint-Gobain, France). The alkali activator of the reaction was an aqueous solution of potassium silicate DV 1.7 (Vodní sklo, a.s., Czech Republic). The ratio of the raw materials was set according to our previous development of the geopolymer with the best strength properties; the exact chemical composition is classified information within the project.

A Dispermat CA60-M1 (VMA-GETZMANN GmbH, Germany) with a gear wheel of 40 mm in diameter was used for mixing the raw materials. The mixing vessel was placed in a container cooled by running water. First, the amorphous silicon dioxide was mixed for 20 minutes at 9600 rpm in a solution of potassium silicate cooled to 3°C, the mixture was cooled at -20°C for 20 minutes and then metakaolin was mixed in it for 5.5 minutes at 9600 rpm and finally, the mixture was placed in a freezer for 10 min and then degassed by stirring in a vacuum.

Preparation of the composite specimens

The geopolymer resin was applied manually with a spatula to ten layers of carbon fabric in the form of a plain weave with a surface density of 93 g·cm^{-2}, 1K (Havel Composite CZ s.r.o.), at a dosage of 282 g per square metre of the fabric. The pieces were layered and pressed by rolling and the last layer was covered with P3 perforated separation foil and a non-woven distribution fabric. The plate was then enclosed in a PP foil and a vacuum was generated inside. The vacuum was maintained for 72 hours at 23°C. The cured plate was cut into test pieces with dimensions of 10 × 80 × 1.7 mm.

The dimensions were selected to suit the dynamic mechanical analyser (DMA) and the low thickness of the sample also showed greater sensitivity to the corrosion processes when the samples were exposed to boiling distilled water.

The test specimens were primarily cured at 80°C for 18 hours, then weighed, and their storage modulus was measured. Then they were divided into eight groups, A1 to A8, each of which was subjected to a higher thermal exposure. Group A1 – 100°C/2 hours, A2 – 100°C/2 hours + 110°C/2 hours and so on, according to Tables 1 and 2. After the thermal exposure, the storage modulus and the changes in the weight of the pieces were measured and the pieces were exposed to boiling distilled water. After the water uptake resistance and dry weight had been measured, the storage modulus was measured again.

Characterisation of the geopolymer resin and composite

To study the microstructure of the pure geopolymer resin, a cylinder 40 mm in diameter and 3 mm thick was prepared, cured at 80°C, broken and a shard was analysed. To study the carbon fibre/geopolymer composite, a small piece was cut off and analysed. The analysis of the microstructures of the geopolymer composites was performed by scanning electron microscopy (SEM) using a Vega3SBU scanning electron microscope (Tescan, Czech Republic) at an accelerating voltage of 30 kV in the mode of back-scattered electrons (BSE) and at a low pressure (20 to 30 Pa) and a working distance of 6 to 15 mm.

X-ray diffraction was used to analyse the metakaolin structure of the Mefisto L05 and Thermal Silica as the source material and the pure resin powder sample that had been cured at 80°C for 18 hours; the measurement was performed at room temperature. The measurement was made using a PANalytical PW 3040 X-ray diffractometer with CuKα radiation (K-Alpha1 = 1.54060 Å, K-Alpha2 = 1.54443 Å, U = 40 kV, I = 30 mA, K-A2/K-A1 ratio = 0.50) with an X'Celerator detector. The output was processed with the software High Score Plus.

The elemental composition of the raw materials was determined by X-ray fluorescence using the PANalytical AXIOS 3 kW with a Rh SST-mAX anode and a dispersing crystal LiF220, GE, PE002, PX1. The output was determined by a fundamental parametric method based on six measured scans. The PANalytical ICSD FIZ Karlsruhe 2012 mineral database was used to interpret the spectra.

The nuclear magnetic resonance measurement was performed using a Bruker Avance II HD500 WB/US-NME (Karlsruhe, Germany) on a rotating sample at a frequency of 5 - 10 kHz and with the axis of rotation at an angle to the vector of the magnetic induction (MAS – magnetic angle spinning). The sample was placed in a 4-mm ZrO_2 rotor and exposed to a standard single pulse. During the data transfer, SPINAL 64 dipolar decoupling was applied to eliminate the spin-spin interaction. The flip pulse length was 4.8 μs. The nutation frequency of the B1 excitation field (^{29}Si and ^{27}Al) was 62.5 kHz and the repetition interval was 4 s. The atoms of ^{29}Si and ^{27}Al were calibrated by M_8Q_8 and $AlNO_3$ as external standards (-109.8 and 0.0 ppm, respectively). The samples were converted to powder form by grinding them in a porcelain mortar.

Table 1. Storage modulus and weight loss depending on curing in the range of 100 to 170°C, the dwell time was 2 hours; 100 % weight corresponds to the condition after primary curing.

Set of samples	A1	A2	A3	A4	A5	A6	A7	A8
Temperature exposure	80°C/18 h							
	100°C	110°C	120°C	130°C	140°C	150°C	160°C	170°C
Modulus after curing at 80°C [GPa]	29.18	32.05	31.6	30.34	31.42	29.98	29.95	31.84
Modulus after target curing [GPa]	28.45	30.82	30.23	28.24	27.96	26.84	25.76	25.85
Wt. after target curing [%]	98.78	98.49	98.02	97.55	96.84	96.87	96.07	95.90

Table 2. Corrosion test in boiling distilled water and the effect on the modulus size depending on curing at 100 to 170°C, while maintaining each temperature for 2 hours.

Set of samples	A1	A2	A3	A4	A5	A6	A7	A8
Temperature exposure	80°C/18 h							
	100°C	110°C	120°C	130°C	140°C	150°C	160°C	170°C
Modulus before test [GPa]	28.45	30.82	30.23	28.24	27.96	26.84	25.76	25.85
Modulus after drying [GPa]	0.81	1.45	1.74	3.04	5.5	7.24	12.32	15.19
Wt. before test [%]	98.93	98.67	98.17	97.7	97.09	97.09	96.25	96.07
Wet wt. [%]	140.2	135.5	128.1	114.5	108.3	103.1	99.19	98.5
Dry wt. [%]	75.65	77.95	79.87	83.7	84.16	85.6	88.65	89.79

Testing of the geopolymer
composite

The non-destructive measurement of the storage modulus was performed using a DMA Q800 (TA Instruments, USA) at a frequency of 1 Hz and a strain amplitude of 20 µm. The storage modulus is the real part of the complex modulus of elasticity and is related to the sample's stiffness.

The test of immersing the specimens in boiling distilled water for 150 min allowed the evaluation of the behaviour of the composites prepared by carbon fabric lamination, which tend to form a high internal surface between the fibres and the polymer that contributes to the reduced resistance to aggressive water. The amount of absorbed water was determined immediately after the sample had been pulled out of the water (wet weight) and after drying at 105°C (dry weight) and the weight loss resulting from the dissolution of the polymer was measured. This test documents the degree of the cross-linking of the polymer, where the non-cross-linked polymer swells by absorbing water and disintegrates.

RESULTS AND DISCUSSION

Influence of curing on the strength and corrosion properties

The storage modulus of the CF/geopolymer composite after primary curing is 30.80 GPa on average as can be seen in Table 1. After the consequent curing steps in the range of 100 to 170°C, the storage modulus gradually decreases; the greatest loss, 6 GPa, was determined at 170°C, which was more than eight times the loss at 100°C. The storage modulus is assumed to document both the degree of curing of the polymer and the quality of the adhesion between the matrix and the fibre reinforcement. Thus, the loss of stiffness shows that the connection between the fibre and the geopolymer was

subject to structural changes and that the geopolymer itself was subject to changes, which is also indicated by the differences in weight.

The opposite effect of the temperature was observed in the corrosion test, as stated in Table 2. The wet weight values show that with an increase in the temperature at which the geopolymer samples were cured, the water absorption of the samples decreased. The best result was achieved when curing was performed at the maximum temperature of 170°C; the weight gain in this sample was
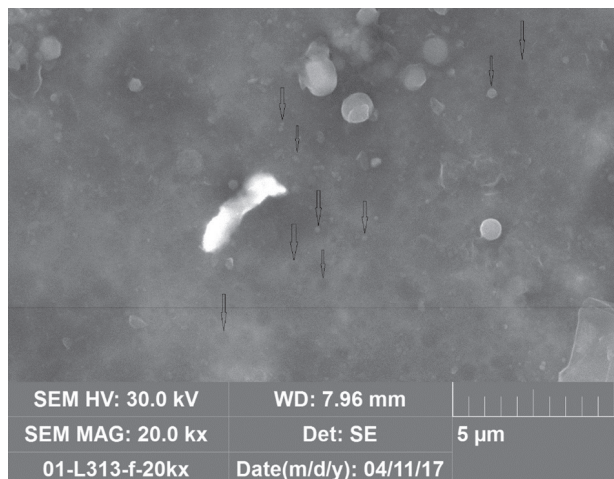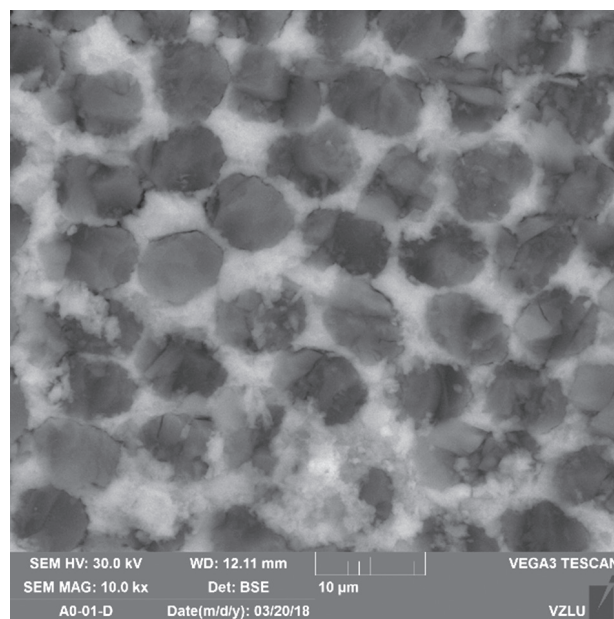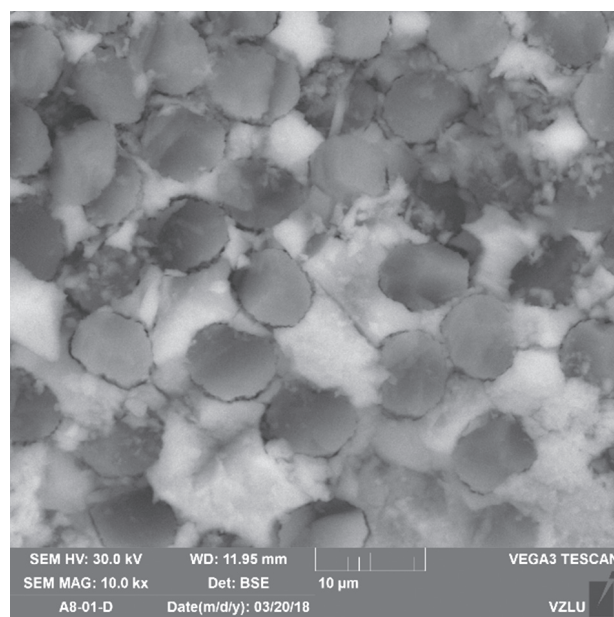

a)

b)

Figure 2. SEM images of the structure of the section of the composite A0 (a) and A8 (b) cured at 80 and 170°C, respectively, acc. to Table 2; the fibres are oriented perpendicularly to the section.

Figure 1. SEM image of the fracture surface of the pure geopolymer; the spherical structures are marked by arrows.

only 2.4 %. On the other hand, at a curing temperature of 100°C, the weight of the composite grew by more than 40 %, which indicates that a composite of resin cured at this temperature would be very sensitive to moisture. The effect of increasing the curing temperature is also confirmed by the comparison of weight and mechanical changes after drying the wet samples at 105°C. The least affected sample was the one cured at 170°C, where the weight decreased by 6 % and the modulus by 41 %, while in the sample cured at 100°C, the weight decreased by 23 % and the modulus by as much as 97 %.

Influence of curing on the geopolymer structure

The cured resin resembles that of ceramics; its shard is smooth and vitreous. The curing process of the continuous phase of the pure geopolymer is documented in Figure 1. The microstructure of the pure geopolymer appears to be a homogeneous phase containing slightly visible spherical structures about 0.5 µm in diameter (i.e., within the resolution of the microscope). The comparison of two composite samples with different degrees of curing is shown in Figure 2. Sample A0 was cured at 80°C for 18 hours. Sample A8 was cured according to the procedure in Table 2. A light matrix surrounding dark fibres can be seen in both micrographs. The separation of the fibres from the matrix is more pronounced on the fracture surface of sample A8. Moreover, the fracture surfaces of the sample A0 matrix seem jagged, while those of sample A8 are more compact.

It was determined by X-ray powder diffraction that the burnt clay shale Mefisto L05 contained an amorphous phase with an admixture of quartz and a small amount of minerals – mullite, kaolinite, biotite, and anatase

(Figure 3). The thermal silica showed an amorphous phase with traces of ZrO_2 (Figure 4). The structure of the cured geopolymer is formed by an amorphous halo between 2Theta 20° and 35° and there are also traces of the minerals originating from the raw materials present as displayed in Figures 5 and 6. No additional crystalline phases which would be generated during curing were identified in the geopolymer. The highest qualitative portion of the Mefisto L05 crystalline phase is represented by quartz, other minerals are present in an insignificant amount.

X-ray fluorescence confirmed the presence of ZrO_2 in the Thermal Silica. Moreover, procedure determined not a negligible amount of amorphous Al_2O_3, which was

Table 3. X-ray fluorescence analysis of the solid components of the raw materials and the cured geopolymer (wt. %); H_2O not included.

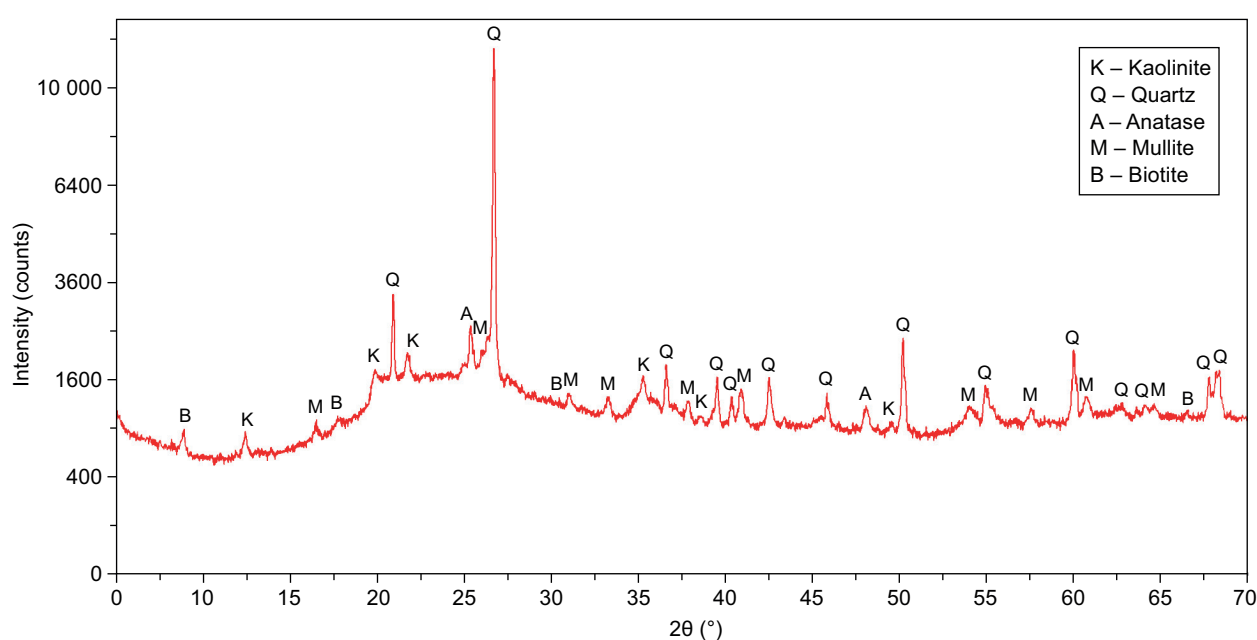| Component	Thermal Silica	Mefisto L05	Geopolymer 80°C
SiO_2	92.6	49.1	64.9
Al_2O_3	4.04	47.3	14.0
Fe_2O_3	0.21	0.90	0.46
CaO	0.04	0.20	0.10
MgO	-	0.10	-
K_2O	0.08	0.50	17.4
Na_2O	0.10	-	0.42
TiO_2	0.06	1.60	0.57
ZrO_2	1.85	-	1.35
SO_3	0.01	0.10	0.07
P_2O_5	0.40	-	0.20
As_2O_3	0.13	-	-
not ident.	0.48	0.20	0.53

Figure 3. X-ray powder diffraction pattern of the metakaolin Mefisto L05.

Table 4. Amount of amorphous phase and identified minerals in the geopolymer and the raw materials.

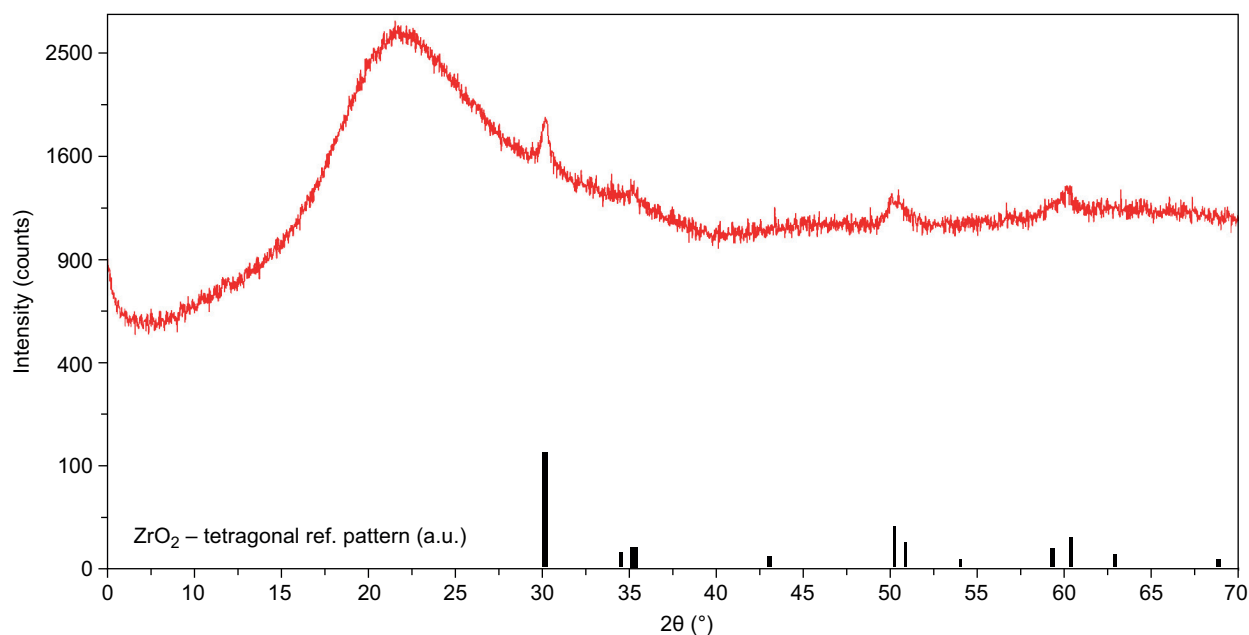| Mefisto L05	Thermal silica	Geopolymer 80°C
Approx. 85 % amorphous phase	Almost amorphous phase	Almost amorphous phase
Approx.7 % Quartz		
Remained crystalline phase with identified traces of Mullite, Anatase, Biotite and Kaolinite	Identified traces of ZrO₂ hexagonal	Identified traces of Quartz, ZrO₂ hexagonal, Mullite, Biotite, Kaolinite and Anatase

Figure 4. X-ray powder diffraction pattern of the Thermal Silica with a reference pattern of ZrO$_2$ tetragonal.
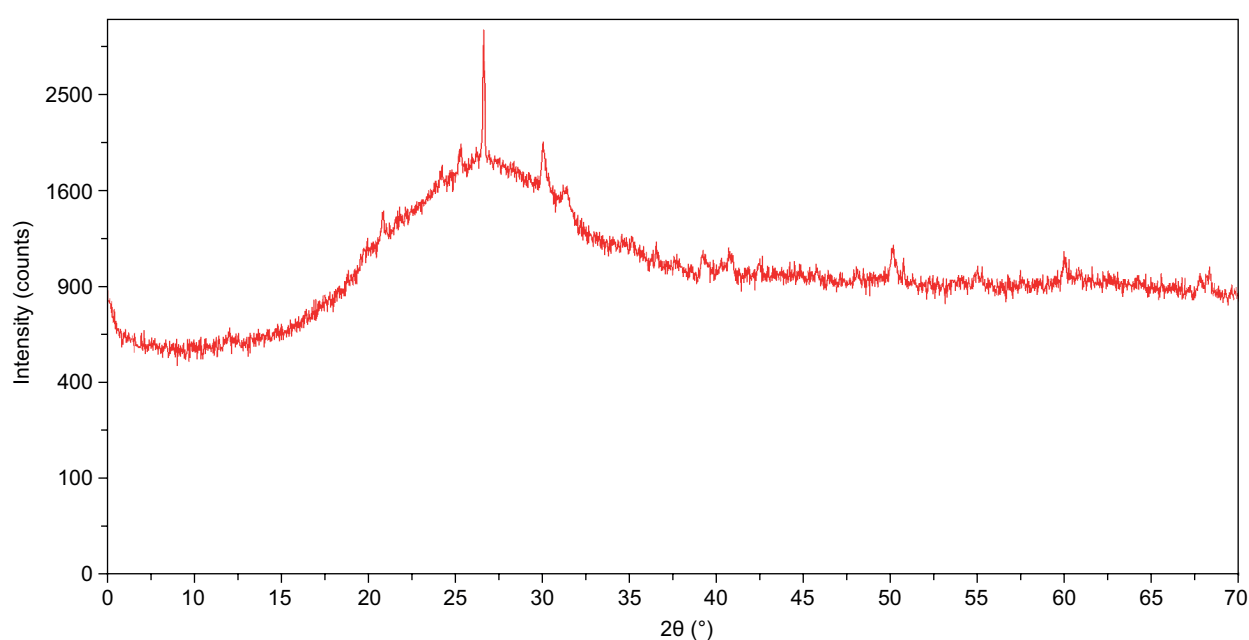

Figure 5. X-ray powder diffraction pattern of the geopolymer cured at 80°C.

not detected by X-ray diffraction. The content of TiO_2, which shows a signal as anatase in the X-ray diffraction spectrum, was analysed as well as a significant amount of Fe_2O_3, which causes a grey colouring of the raw material.

X-ray diffraction was supplemented by the NMR method, which was used to assess the effect of the curing temperature mode according to Table 5 on the change in the structure of the geopolymer resin. In the case of the metakaolin raw material, which was analysed as a reference sample, there is a broad peak for ^{29}Si and ^{27}Al in the spectra, see Figure 7. The peak of 5 ppm ^{29}Al in the metakaolin represents the form of $Al^{(VI)}$. It was found

that with an increasing curing temperature, the peak of 50 - 80 ppm, corresponding to $Al^{(IV)}$, increased as well. However, traces of $Al^{(VI)}$ still remain. The corresponding signal for ^{29}Si indicates the initial representation of Q^4 (3/4Al), Q^4(2Al) and Q^4 (1Al). The system transformed into the prevailing representation of Q^4(2Al) depending on the increasing temperature. It means that the system underwent a structural change consisting of the involvement of $Al^{(IV)}$ tetrahedra in the structure; the structure of Q^4(2Al) is mostly represented at the maximum degree of curing.

Table 5. Curing process of the geopolymer samples for NMR.

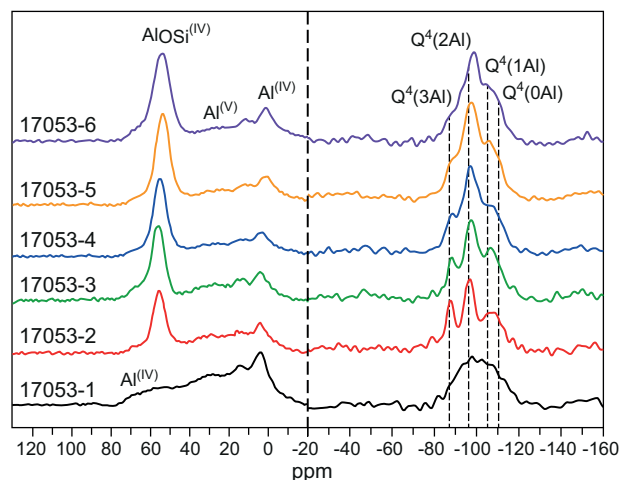| Sample	Stage 1	Stage 2	Stage 3
17053-1	Mefisto L05		
17053-2	23°C/14 days*		
17053-3	23°C/24 h*	60°C/24 h	
17053-4	23°C/24 h*	80°C/24 h	
17053-5	23°C/24 h*	80°C/24 h	100°C/24 h
17053-6	23°C/24 h*	80°C/24 h	80-90-100-110--120-130-140--150-160-170°C every 2 h

* Kept in sealed plastic packaging

Figure 7. Chemical shift for ^{29}Si and ^{27}Al in the NMR spectra of the samples cured acc. to Table 5.
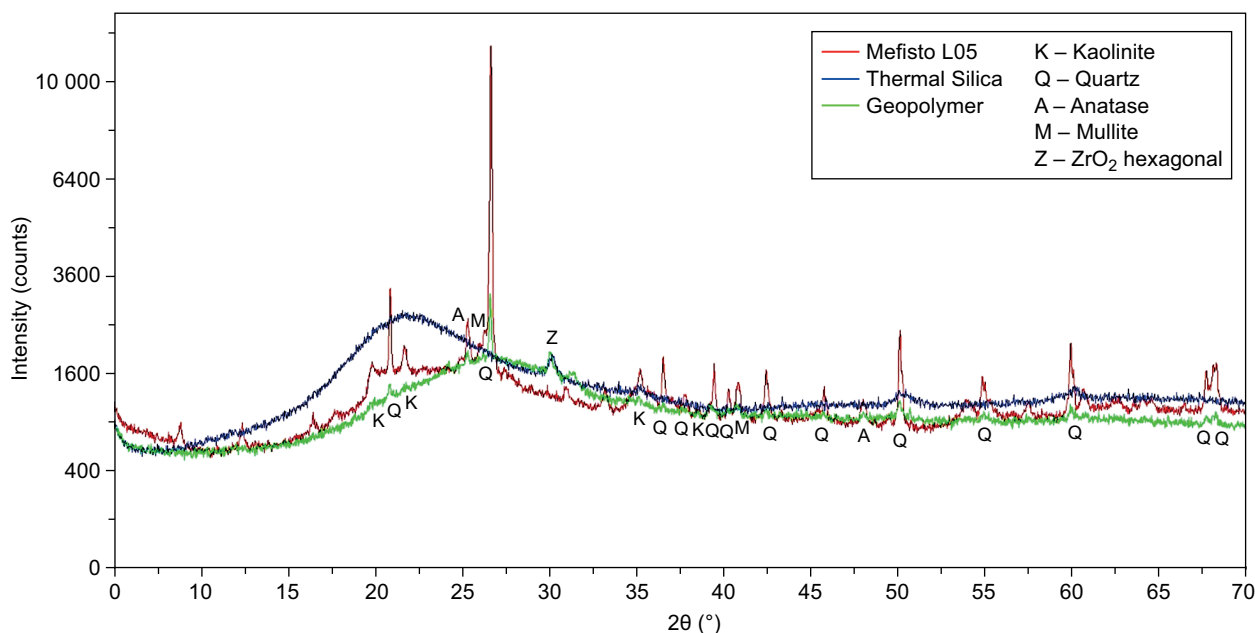

Figure 6. X-ray powder diffraction patterns of the geopolymer cured at 80°C – the green curve with markers of identified minerals; compared with the raw materials of the Mefisto L05 and the Thermal Silica as the source of mineral impurities. The matching peaks marked with capital letters.

CONCLUSIONS

Our results show that increasing the curing temperature changes the strength properties and the geopolymer structure. It was determined by NMR that aluminium octahedra $Al^{(VI)}$ are transformed to $Al^{(IV)}$ tetrahedra and that the coordination of the silicon tetrahedra changes as well. After the initial insignificant distribution of the $Q^4(4Al)$, $Q^4(3Al)$, $Q^4(2Al)$ and $Q^4(1Al)$ structures, the increase in temperature supported the $Q^4(2Al)$ structure, while the $Q^4(4Al)$ and $Q^4(3Al)$ structures were receding and the $Q^4(0Al)$ structure was virtually not present. This evolution of the structure was accompanied by the increasing resistance to the corrosive effects of hot distilled water. The maximum resistance of the composite was achieved by exposure to a temperature ramp terminated at 170°C; the weight loss was only 6 % and the storage modulus decreased by 41 %, which was the smallest decrement. The predominance of the $Q^4(2Al)$ structures was confirmed. This is consistent with the idea that aluminium and silicon tetrahedra are interconnected in a functional polymer network. The highest storage modulus, i.e., the highest stiffness, was achieved by primary curing at 80°C. Curing at higher temperatures caused a small decrease in the storage modulus. X-ray diffraction confirmed that the synthesised geopolymer is an amorphous substance with a minor crystalline phase that originates in the mineral impurities contained in the Burnt Clay Shale raw material. Scanning electron microscopy proved that the geopolymer composite cured at 170°C showed a greater tendency to separate the matrix from the fibres compared to the composite cured at 80°C.

In summary, we have determined two curing temperature modes which provide CF/geopolymer composites for two types of conditions of use. A geopolymer composite cured at 80°C for 18 hours is suitable for use in heat stressed applications, where the use of a common epoxy resin is not possible. The second type of curing proceeds at 80°C for 18 hours followed by a two-hour dwell at each temperature, 100, 110, 120, 130, 140, 150, 160 and 170°C; the resulting geopolymer composite is promising for use in a humid environment.

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