Fracture parameters of fly ash geopolymer mortars with carbon black and graphite filler

H Simonova[1], C Mizerova[1], P Rovnanik[1], M Lipowczan[1] and P Schmid[1]

[1] Brno University of Technology, Faculty of Civil Engineering, Veveří 331/95, 602 00 Brno, Czech Republic

Email: simonova.h@vutbr.cz

Abstract. In this study, the effect of carbon black and graphite filler on the crack initiation and fracture parameters of fly ash geopolymer mortar is investigated. The carbon black was added in the amount of 0.5 and 1.0% and graphite powder in the amount of 5 and 10% relative to the fly ash mass. The reference mixture without any filler was also prepared. The fracture characteristics were determined based on the results of the three-point bending test of prismatic specimens provided with an initial central edge notch. The fracture experiments were conducted at the age of 48 days. The vertical force (F), the displacement measured in the middle of the span length (d), and the crack mouth opening displacement ($CMOD$) were continuously recorded during the test. The records of fracture tests were subsequently evaluated using the effective crack model, work-of-fracture method, and double-K fracture model. The addition of both fine fillers led to a decrease in monitored mechanical fracture parameters in comparison with reference mortar.

1. Introduction

The incorporation of novel additives and functional fillers into cement-based composites has been frequently studied in recent decades and especially materials with increased electrical conductivity represent a potential for advanced smart applications. Since the variation of external ambience conditions (temperature, humidity, stress due to mechanical loading etc.) can be detected via alteration of electrical resistivity, the development of self-sensing or self-heating structures is now in the scope of investigations [1]. Hence, the traditional cement-based composites are considered an electrical insulator and the applicability of plain binder for such purposes is low, various admixtures are used to establish a functional conductive network within the composite and improve its self-sensing performance. The most common conductive fillers include carbon or metal materials, e.g. carbon fibres, carbon nanotubes, graphite powder, carbon black, steel fibres or nickel powder [1–3]. Graphite powder and carbon black are fine carbon materials that have been widely used in asphalt or polymeric conductive composites, carbon black as a colloidal form of carbon with a high specific surface is also an inexpensive filler [4].

Geopolymers are a group of alternative alkaline activated binders manufactured from solid aluminosilicate precursors and alkaline activator [5]. Apart from favourable mechanical and durability performance, research of their electrical properties has shown that increased availability of mobile hydrated cations in the pores of the geopolymeric structure contributes to improved piezoelectric behaviour in comparison to cementitious binders [6, 7]. This phenomenon makes alkaline activated matrix a promising material for the above mentioned self-sensing structural components. Since

the addition of alternative and not commonly used fillers can alter the mechanical properties of these composites, it is necessary to study their mechanical performance. Therefore, the determination of mechanical fracture parameters is an important issue for the practical application of such conductive composite materials. In this study, the effect of carbon black and graphite filler on the crack initiation and fracture parameters of fly ash geopolymer mortar is investigated.

2. Experimental part

2.1. Materials

The basic aluminosilicate precursor for the preparation of the geopolymer mortars was fly ash from the high-temperature combustion of coal (Dětmarovice power plant, ČEZ). Sodium silicate solution with the SiO_2/Na_2O ratio of 1.6 was used as an alkaline activator and quartz sand with the maximum grain size of 2.5 mm was used to prepare the reference geopolymer. The chemical composition of fly ash and activator solution is given in table 1. The geopolymer mortar was modified by graphite powder or carbon black as fine conductive fillers. Graphite (PMM 11) was supplied by Graphite Týn (CZ) having a particle mean size of 11 μm. Carbon black (Vulcan 7H) was supplied by CS Cabot (CZ). Since carbon particles are hydrophobic, Triton X-100 (Sigma-Aldrich) in the form of a 2% aqueous solution was used as a dispersing agent and 1% solution of Lukosan S (Lučební závody, CZ) was added as an air detraining agent to avoid foaming and increased porosity.

Table 1. Chemical composition of raw materials.

	Composition (%)								
Material	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	MnO	TiO_2
Fly ash	51.67	23.31	7.08	4.45	0.36	2.95	0.77	1.14	1.00
Sodium silicate	26.43	–	–	–	–	–	16.61	–	–

2.2. Specimens preparation and curing

The composition of geopolymer mixtures is presented in table 2. The carbon black was added in the amount of 0.5 and 1.0% (CB0.5 and CB1.0, respectively) and graphite powder in the amount of 5 and 10% (G5 and G10, respectively) relative to the fly ash mass. The reference mixture (REF) without any filler was also prepared.

Table 2. Mixing proportions of geopolymer mortars.

	Mortar				
Component	REF	CB0.5	CB1.0	G5	G10
Fly ash (g)	350	350	350	350	350
Sodium silicate (g)	280	280	280	280	280
Graphite (g)	–	–	–	17.5	35
Carbon black (g)	–	1.75	3.5	–	–
Sand (g)	1050	1050	1050	1050	1050
Dispersing agent (ml)	–	1.75	3.5	17.5	35
Air detraining agent (ml)	–	–	–	7.5	7.5
Water (ml)	35	32	32	35	35

Geopolymer mortars were prepared in the Hobart planetary mixer according to the following procedure. At first, graphite powder/carbon black was dispersed in the sodium silicate and Triton X-100 solution. Then, fly ash and quartz sand together with additional mixing water were added and stirred for at least 5 minutes to prepare a fresh slurry. Finally, an air detraining agent was added and the prepared geopolymer mixture was cast into prismatic moulds with dimension 40 × 40 × 160 mm. After 2 hours at laboratory temperature, the moulds with fresh mixtures were cured at 40°C for 24 hours to accelerate the geopolymerization reaction. Hardened specimens were wrapped in plastic bags and stored under laboratory conditions until fracture testing. Three specimens made of each mortar were used for the fracture tests.

2.3. Fracture tests

The fracture experiments in the three-point bending configuration were conducted at the age of 48 days. The above-mentioned prismatic specimens were provided with an initial central edge notch one day before testing. The notch length was approximately one-third of the specimen's height. The span length was set to 120 mm. The stiff multi-purpose mechanical testing machine LabTest 6.250 with a load range of 0−250 kN was used for fracture tests. The loading process was controlled by a constant increment of displacement of 0.02 mm/min in the whole course of the experiment.

The vertical force (F), the vertical displacement (d) measured in the middle of the span length using the inductive sensor, and the crack mouth opening displacement ($CMOD$) measured using a strain gauge mounted between blades fixed on the bottom surface of the specimen were recorded during the experiment. In this way, the continual records of the fracture tests in the form of $F–d$ and $F−CMOD$ diagrams were obtained. The raw data were further processed to obtain the correct input values for diagrams evaluation using the selected fracture models described below. The modification of diagrams consisted of the removal of duplicate points, the shifting of the origin of the coordinate system, the smoothing of the diagram, and the decrease of the number of points. The adjustment of raw data was performed in GTDiPS software [8] which is based on advanced transformation methods used for the processing of extensive point sequences.

2.4. Microstructural characterization

Pore distribution was evaluated utilizing mercury intrusion porosimetry analysis that was conducted on samples using Micromeritics Poresizer 9310 porosimeter that can generate a maximum pressure of 207 MPa and can evaluate a theoretical pore diameter of 0.006 μm. Micrographs of the geopolymer composites were taken on a TESCAN MIRA3 XMU scanning electron microscope in secondary electron imaging mode. The micrographs were taken on samples that were sputtered with gold.

3. Assessment of fracture parameters

The mechanical fracture parameters were determined based on the direct evaluation of the $F–d$ and $F−CMOD$ diagrams using the chosen fracture models. The modulus of elasticity was assessed from the initial parts of $F–d$ diagrams according to Karihaloo [9]. The effective fracture toughness was determined from $F–d$ diagrams using the effective crack model introduced by Karihaloo [9]. This approximative model combines the linear elastic fracture mechanics and crack length approaches.

The $F–d$ diagrams were further used for the calculation of work of fracture according to the RILEM method [10]. Then, the specific fracture energy is assessed by dividing the work of fracture by the ligament area (i.e. the projection of the original uncracked area).

The double-K fracture model [11] was chosen for the evaluation of $F–CMOD$ diagrams. The double-K fracture model works on the combination of the concept of the cohesive forces on the fictitious crack with a criterion based on the stress intensity factor. The different stages of the fracture process in materials with the brittle matrix can be predicted using this model. The two parameters are used for this purpose, namely initial cracking toughness and unstable fracture toughness which are given in terms of stress intensity factor. The unstable fracture toughness is defined as the critical stress intensity factor, which is similar to effective fracture toughness used in the effective crack model by Karihaloo [9].

The initial cracking toughness stands for the capability to withstand an external load before the origin of crack propagation. The difference between these two parameters is the equivalent stress intensity factor caused by the cohesive forces on the fictitious crack called cohesive fracture toughness [12]. In this paper, the unstable fracture toughness and the cohesive fracture toughness were assessed first, and afterwards, the initial cracking toughness was calculated.

The cohesive softening function which characterizes the relationship between cohesive stress and effective crack opening displacement needs to be defined for calculation of the cohesive fracture toughness. In this paper, the nonlinear softening function according to Reinhardt [13] was chosen. The tensile strength as an input parameter of softening function was determined based on the identification process using the artificial neural network (ANN) [14]. The trained ANN is used to transfer the input data – a measured response in the form of an *F–d* diagram obtained from the fracture test – to the desired material parameters. Besides the tensile strength, the modulus of elasticity and fracture energy were also determined by the identification process. The details about the procedure of parameters identification can be found in [15].

The informative compressive strength was determined to complement material characteristics. The two parts of the specimen left after the fracture experiments were used for this purpose.

4. Results

The selected mechanical fracture characteristics of geopolymer mortars modified by graphite powder or carbon black as fine conductive fillers obtained by the above-mentioned fracture models are introduced in figures 1 and 2. The average value (determined based on 3 independent measurements) and standard deviation represented by error bars are presented.

The compressive strength of reference geopolymer mortar was about 50 MPa. The addition of carbon black did not have any effect on compressive strength in comparison with reference mortar. Contrarily, the addition of graphite powder did have a significant effect. While the addition of graphite in an amount of 5% caused an increase of compressive strength of about 24%, on the contrary, the addition of 10% of graphite powder caused a decrease of compressive strength of about 42%.

The modulus of elasticity of reference geopolymer mortar was about 6 GPa. The addition of both fine conductive fillers caused a decrease in modulus of elasticity by more than 30%. The modulus of elasticity determined by identification was about 0.5 GPa higher when the variability of the results is taken into the account for all investigated geopolymer mortars in comparison with the direct evaluation of the *F–d* diagrams, see table 3.

The effective fracture toughness of reference geopolymer mortar was about 0.3 $MPa \cdot m^{1/2}$. The addition of 1% of carbon black caused the decrease of fracture toughness by 15%. In the case of graphite, the decrease of fracture toughness was higher about 25 and 30% for filler amounts of 5 or 10%, respectively. Similar values of fracture toughness were obtained also from *F–CMOD* diagrams using the double-*K* fracture model, see figure 2.

The specific fracture energy was about 47 $J \cdot m^{-2}$. The addition of both fillers caused the decrease of fracture energy. This decrease was more significant in the case of the addition of graphite. The decrease of fracture energy is independent of filler amounts when the variability of the results is taken into account. Table 3 introduces the fracture energy obtained by identification. The differences in average values of fracture energy imply from their different physical sense – the values obtained by the identification process are primarily related to the material point, whereas the values obtained from the work of fracture method are related to the tested specimen and represent the average fracture energy.

Table 3 introduces also the tensile strength of investigated geopolymers mortars. The highest value was obtained for mortar with the addition of 0.5% of carbon black, which is in agreement with the maximum force obtained during the fracture experiments. These values were used together with fracture energy as input parameters of the nonlinear softening function used in the double-*K* fracture model.

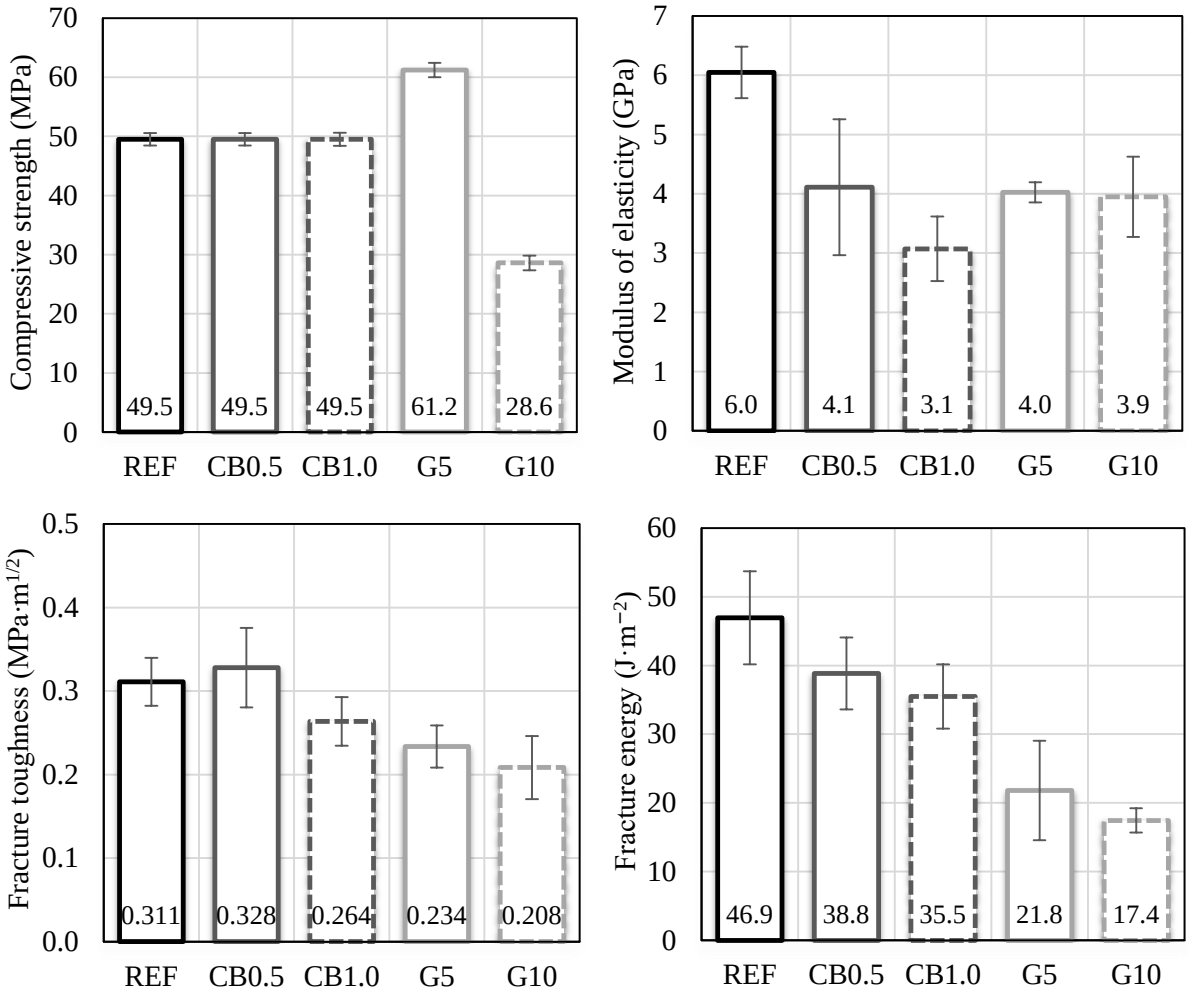

Figure 1. Compressive strength and mechanical fracture parameters obtained from *F*−*d* diagrams.

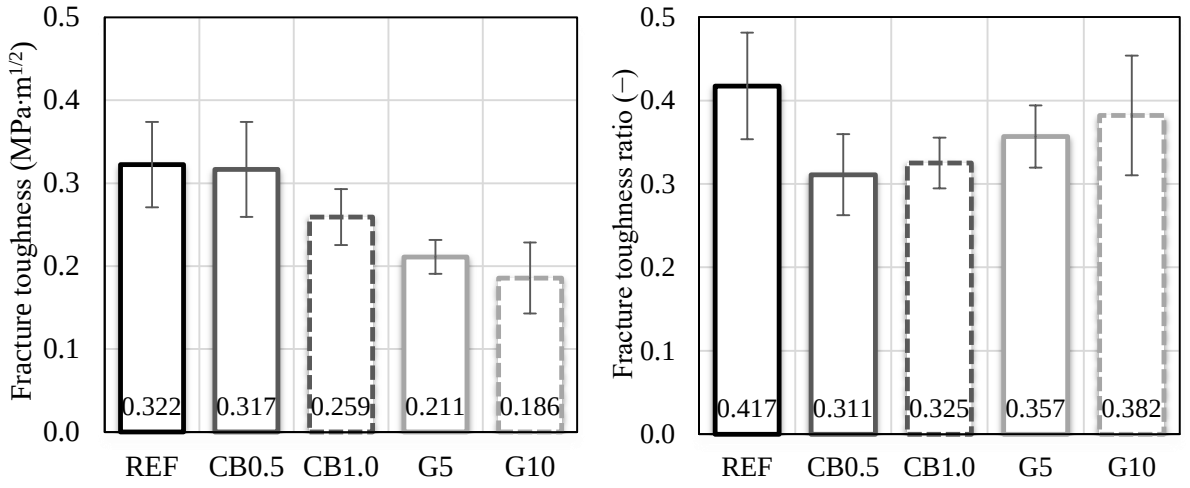

Figure 2. Fracture parameters obtained from *F*−*CMOD* diagrams.

Table 3. Mechanical fracture parameters obtained by identification – mean values (CoV in %).

Parameter	Mortar				
	REF	CB0.5	CB1.0	G5	G10
Modulus of elasticity (GPa)	6.5 (11.1)	4.9 (31.5)	3.6 (16.1)	4.7 (5.0)	4.4 (21.7)
Fracture energy ($J \cdot m^{-2}$)	41.3 (32.7)	47.8 (12.7)	45.2 (7.5)	27.4 (37.7)	21.1 (8.7)
Tensile strength (MPa)	1.49 (1.0)	2.14 (8.6)	1.45 (20.6)	1.41 (22.4)	1.31 (1.1)

On the contrary to other fracture parameters, the resistance to stable crack propagation more decreased with the addition of carbon black than with the addition of graphite, see figure 2. The resistance to stable crack propagation is expressed by fracture toughness ratio, i.e. ratio of the initial cracking toughness to the unstable fracture toughness.

Microstructural characterization of tested geopolymer samples was provided by mercury intrusion porosimetry and scanning electron microscopy. Figure 3 shows a comparison of cumulative pore curves. Data show that the lowest porosity was observed for the reference sample. When carbon black was added the porosity only slightly increased but the amount of the admixture has practically no effect on the pore distribution. On the other hand, the addition of graphite powder significantly increased the total intruded volume which can be attributed to an increase in the number of pores larger than 1 μm.

The total porosity of the samples corresponds quite well to the trends in compressive strength of the specimens with carbon fillers compared to the reference geopolymer mortar. It is also in good correlation with the fracture toughness and fracture energy as these parameters decreased while the total porosity increased. The highest drop in the values of fracture parameters determined for the geopolymer mortars with graphite powder can be attributed to the morphology of graphite particles, which have a lamellar structure (figure 4). These particles can act as stress concentrators and allow easier crack propagation.

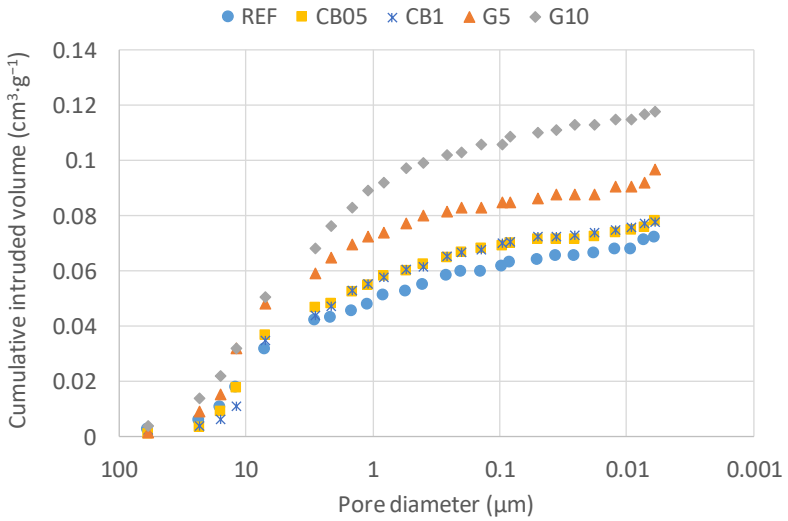

Figure 3. Pore distribution of tested composites provided as cumulative intruded volume.

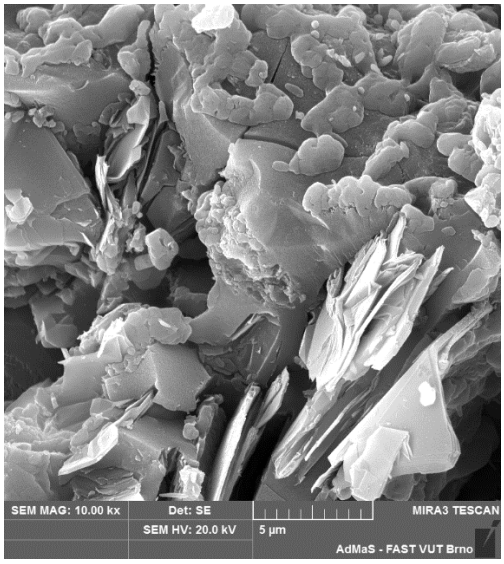

Figure 4. Morphology of geopolymer matrix with lamellar graphite particles.

4. Conclusions

This study aimed to quantify the effect of the addition of carbon black and graphite powder on the mechanical fracture behaviour of fly ash geopolymer mortar. Despite both alternative and not commonly used fine fillers were primarily added to enhance the electrical properties of the investigated geopolymer mortar, their addition should not deteriorate other material properties depending on its prospective practical application. It is obvious from the presented results, that monitoring not only the compressive strength but also the other mechanical fracture parameters is necessary to obtain complex information about material behaviour, which is considerably affected by the addition of fine fillers. The addition of carbon fillers leads to the increase of porosity which can be attributed to an increase in the number of pores larger than 1 μm. It is in good agreement with the monitored fracture parameters which decreased while the total porosity increased.

Acknowledgement

This outcome has been achieved with the financial support of the Czech Science Foundation under project No. 19-11516S.

References

[1] Han B, Zhang L and Ou J 2017 Smart and multifunctional concrete toward sustainable infrastructures (Singapore: Springer)
[2] Han B, Yu X and Ou J 2014 Self-Sensing Concrete in Smart Structures (London: Butterworth Heinemann)
[3] Chung D D L 2012 Carbon materials for structural self-sensing, electromagnetic shielding and thermal interfacing *Carbon* **50**(9) pp 3342–3353
[4] Donnet J B, Bansal R C and Wang M J ed 1993 Carbon black: science and technology (New York: CRC Press)
[5] Provis J L and Van Deventer J S J ed 2009 Geopolymers: Structure, processing, properties and industrial applications (Cambridge: Woodhead Publishing Limited)
[6] Lamuta C, Candamano S, Crea F and Pagnotta L 2016 Direct piezoelectric effect in geopolymeric mortars *Materials & Design* **107** pp 57–64
[7] Hanjitsuwan S, Chindaprasirt P and Pimraksa K 2011 Electrical conductivity and dielectric property of fly ash geopolymer pastes *International Journal of Minerals, Metallurgy, and Materials* **18**(1) pp 94–99

[8] Frantik P and Masek J 2015 GTDiPS software (*Online* http://gtdips.kitnarf.cz/)
[9] Karihaloo B L 1995 Fracture Mechanics and Structural Concrete (New York: Longman Scientific & Technical)
[10] RILEM TC – 50 FMC 1985 Determination of the fracture energy of mortar and concrete by means of three-point bend test on notched beams *Materials and Structures* **18**(4) pp 287–290
[11] Kumar S and Barai SV 2011 Concrete Fracture Models and Applications (Berlin: Springer)
[12] Xu S and Reinhardt H W 1999 Determination of double-*K* criterion for crack propagation in quasi-brittle fracture, Part II: Analytical evaluating and practical measuring methods for three-point bending notched beams *International Journal of Fracture* **98** pp 151–177
[13] Reinhardt H W, Cornelissen H A W and Hordijk D A 1986 Tensile tests and failure analysis of concrete *Journal of Structural Engineering* **112** pp 2462–2477
[14] Novak D and Lehky D 2006 ANN Inverse Analysis Based on Stochastic Small-Sample Training Set Simulation *Engineering Application of Artificial Intelligence* **19** pp 731–740
[15] Lehky D, Lipowczan M, Simonova H and Kersner Z 2019 A neural network ensemble for the identification of mechanical fracture parameters of fine-grained brittle matrix composites *FraMCoS-X 10th International Conference on Fracture Mechanics of Concrete and Concrete Structures* ed G Pijaudier-Cabot, P Grasll and C La Borderie (France: IA-FraMCoS) pp 1−9