# POROUS MICROSTRUCTURE OF THE INTERFACIAL TRANSITION ZONE IN GEOPOLYMER COMPOSITES

#### <sup>#</sup>MICHAELA STEINEROVÁ, JANA SCHWEIGSTILLOVÁ

Institute of Rock Structure and Mechanics, ASCR, v.v.i. V Holesovickach 41, 182 00 Prague, Czech Republic

#E-mail: steinerova@irsm.cas.cz

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The study deals with a comparison of the differences in the structure, composition and micromechanical properties of a metakaolinite geopolymer composite matrix, inside and outside of the interfacial transition zone (ITZ) with quartz grains of added silica sand. The microstructure is investigated by a measurement of the mercury porosimetry, microscopy and by a measurement in SEM and AFM, completed by Raman spectroscopy. Weaker mechanical properties, micropores in the ITZ, a higher concentration of Al atoms and hydroxyl groups than in the ambient matrix were detected. The water transport is probably the reason for the micropore formation, caused by disequilibrium in the course of solid-phase building from geopolymer dispersion.

# INTRODUCTION

Geopolymers are usually inhomogeneous solid substances or composities comprised for special purposes by the addition of fillers. The resulting mechanical properties are thus determined by the texture of the nonhomogeneities, added filler and microstructure of the matrix [1]. This study is therefore aimed at determining the effect of the presence of the filler, in this case silica sand, on the matrix's microstructure of the transition zone (ITZ) between the matrix and the filler grain boundary. Like in the case of Portland cement, also the geopolymer (GP) matrix of metakaolinite does not reach as high mechanical strength values as in the case of composites with an optimal amount of a suitable filler. The factors contributing to the dramatic improvement of strength is the filler texture, such as its grain size distribution and the compaction, in addition to the filler material's intrinsic strength. Another factor is the interaction with the grain surface and matrix, to which the microstructure of the ITZ may partially provide evidence. It is obvious that the formation of a GP matrix is initiated by the present active units of Al<sup>3+</sup>, derived from the hydrolyzed metakaolinite [2], being even preferably consumed in the first moments of the solid network creation from the GP dispersion, as has been proven [3]. The matrix on the surface of the filler grains does not arise by another rule. However, the concentration of Al<sup>3+</sup> in the GP matrix layer on the grain surface is reported to be higher than in the remote GP matrix structure [4]. This conveys the idea that the structure's precursor units, oxygen atoms tetra-coordinated in  $Al^{3+}$ , should preferentially be deposited on the grain surface which could accelerate the polycondensation of the GP matrix network and produce the bonds with the surface here.

The previous work [5] showed that a measurable difference in the properties of the matrix without the filler and the matrix in the composite is particularly the noticeable change in the pore size distribution. The mesopores present, which are an integral part of the GP matrix, are formatted due to the nature of the solid phase generation from the GP precursors in water dispersion [6]. It occurs during the polycondensation of SiO<sub>4</sub> and AlO<sub>4</sub> units and depends on the concentration of water. The by-product water arising from the fusion of the hydroxyl terminals gradually increases the distance between the remaining terminal O atoms which must be overcome to produce other bridging oxygens in the integrated network chains. At the critical distance, as soon as the fusion is hindered, the nascent pore nucleates. Moreover, the excess water in the dispersion and the water originated as a by-product of polycondensation are retained in the pores and determine their size. Since this is a state of equilibrium and the distance at which the polycondensation is stopped is approximately the same, the size of the mesopores is equal [7]. There is therefore a typical picture of pore size distribution of mesopores [8] for a GP matrix of a certain water content [9] in the initial dispersion with a single signal spectrum in the pore size of 10 - 20 nm [4]. In the presence of silica sand filler, another signal of 1 - 10 mm appears in the spectrum, which indicates the presence of new, larger pores, whose origin is known in the case of Portland cement composites to be caused by the conditions different in situ in the areas jointing the filler aggregates. These ITZ pores have been found to be the carriers of the freeze resistance of GP composites. The object of this study is to explore what causes the differences in the microstructure of a geopolymer matrix occurring near the surface of quartz and in the remote matrix.

#### **EXPERIMENTAL**

# The materials used and the method of sample preparation

The samples of the GP composites were prepared from metakaolin, which was micronized kaolin Sedlec Ia fired at 750°C and a dwell of 6 h. The particle size distribution of metakaolin was characterized by a mean grain size of  $d_{50} = 8$  mm and a specific surface area of  $18 \text{ m}^2/\text{g}$ . The chemical composition of kaolin Sedlec Ia was (in wt. %): SiO<sub>2</sub> 47.5; Al<sub>2</sub>O<sub>3</sub> 36.7; Fe<sub>2</sub>O<sub>3</sub> 0.9; TiO<sub>2</sub> 0.18; Na<sub>2</sub>O 0.03; K<sub>2</sub>O 0.95; CaO 0.27; MgO 0.23; L.O.I. 12.9. The main compound was kaolinite (90 wt. %); the impurities include mica minerals and a small amount of quartz. The geopolymer was prepared from a water dispersion of sodium silicate, sodium hydroxide, and metakaolin in the ratio Si/Al = 1.5; Na/Al = 1.0; H<sub>2</sub>O/Na = = 7.14 and the water coefficient was 0.74. The filler was added silica sand Strelec ST52, characterized by a mean grain size of  $d_{50} = 0.4$  mm.

#### METHODS OF MEASUREMENT

To determine the pore size distribution, high-pressure mercury porosimetry was applied, using the ink-bottle computation model. The measurements were performed on a Pascal 240 device from POROTEC.

The microscopy and measurements of a polished section sample of the GP composite containing 10 wt. % of silica sand were conducted by an Optifot 100 optical microscope with the NIS Elements AR imaging system, from Lim Laboratory Imaging.

The SEM microscopy, element analyses and measurements were performed on a Quanta 450 microscope with an EDAX microprobe, from FEI.

The AFM measurements were carried out on a Veeco Dimension 3100 device, from Novascan Technologies and a XE-100TM from Park Systems.

The Raman spectra were collected on a Labram HR Raman dispersive spectrometer, from Jobin Yvon, which is equipped with an Olympus confocal microscope. The excitation source was a laser of the wavelength of 532 nm with an input power of 50 mW. The samples were measured at a power of 5 mW, measuring time of 10 s with 32 spectra accumulations in a moving step of 3 mm and a distance of rows 10 mm; the number of measured points was 72.

The determination of the micromechanical properties was performed by the nanoindentation method on a CSM Nanohardness tester device. Two surfaces were measured, the interface between the quartz grain and matrix and in the middle of the matrix area outside the influence of the filler; with a maximum power of 2 mN, respectively, and a maximum depth of 300 nm. In the first case, the area was  $140 \times 110 \mu m$  with 180 indents, a spacing of  $10 \times 10 mm$ , in the latter the area it was  $35 \times 80 mm$ , 192 indents, and a spacing of indents of  $3.5 \times 5 mm$ .



Figure 1. The pore size distribution with the marked sand content (a) and specific volume of pores decreasing with the rising sand content (b) in the composites in wt. % (for simplification, only the first additions of sand up to 40 wt. % is displayed).

### RESULTS

### High-pressure mercury porosimetry

A comparison of the results of the porosimetry measurement of GP matrix before and after the addition of sand (Figure 1a) shows a change in pore size distributions. The characteristic size of the matrix mesopores was about 6 nm in radius. In the case of the added silica sand, the composites displayed additionally microsized mesopores of a size of 0.8 to 2 mm. As is shown in Figure 1b, the specific volume of the pore system in composites decreased with their increasing sand content and thus the rising specific density. At that, the ratio of the volume occupied by the micro-sized pores (pictured as a relative volume of micropores) to specific volume (pictured as bulk pore volume) is increased (Figure 2), whereas the size of these micropores slightly decreased (Figure 1a) when there was a low sand content (30 - 50 wt. %).



Figure 2. The micro-sized mesopore volume portion increasing with the rising content of the sand filler.

#### Microscopy of ITZ

The optical microscopy and SEM shows that micropores are present preferably in close proximity to quartz grains (Figure 3) and thus they draw the ITZ obvious feature. The size detected by mercury porosimetry is confirmed by microscopic observation being estimated as 1 - 10 mm in diameter; their size and morphology is further measured by AFM.

A precise measurement of the size and morphology of micropores was acquired by AFM measurements (Figure 4a, b). The 3D imaging put the software WSxM 3.12 to advantageous use [10] computing the profiles of pores as average values of the selected places surrounding the highlighted pores (Figure 4a). In the pictures, they visualize the dimension of micro-sized pores whose width is in units of mm and a displayed depth of up to 350 nm. Of course, the depth is affected by the polishing process.



a)





Figure 3. The structure of the matrix with micropores visible, nearby quartz grains imaged: a), b) by optical microscopy, c) by SEM in secondary-electrons modus (a group of the pores is highlighted by arrow).

The next picture shows another interface between the GP matrix and quartz grain in the same polished section sample (Figure 4a, b). The group of pores is situated at a grain boundary that ITZ has shown a smooth transition between the quartz and matrix in this area of the polished section. The average pore size is similar,  $8 - 9 \mu m$  in diameter.

These deep pores are large up to  $20 \ \mu m$ . They are placed at the nearest points at both of the quartz boundaries and actually play the stitching point of two neighboring grains. The pore formation is affected from both sides and two ITZ are overlapped here. The situation



a) 3D imaging couple of micropores



c) small elongated pore (on an average 7  $\mu$ m)

Figure 4. AFM imaging of the ITZ with profiles of the shown micro-sized pores.

characterizes the structure in the composition of a high content of sand, where the lack of a free matrix leads to mass transport formatting of micro-sized pores merging into the largest sizes (Figure 1a).

#### Raman spectroscopy measurements

The interface between the geopolymer matrix and a grain of quartz was studied in terms of the distribution of the hydroxyl groups (Figure 7a, b). The distribution of the  $OH^-$  group proved to be very inhomogeneous. Therefore, the changing concentrations of  $OH^-$  were compared regarding the location of the measured point and the distance from the surface of the quartz. The microstructures of the ITZ matrix and the matrix outside of the quartz influence differ in these two ways:

 The enclosed areas in the microstructure of ITZ with a lower and a higher concentration of OH<sup>-</sup> groups than the average concentration surrounding the area are shown (Figure 7a). However, the areas with higher OH<sup>-</sup> concentrations occur preferentially at the surface of the grain and thus display a thickness of the ITZ up to 50 µm (Figure 7a). On the contrary, the enclosed



a) 3D imaging



Figure 5. AFM imaging of the ITZ with 3D imaging (a) and averaged profiles (b) of the group of pores.

areas with a lower concentration mostly avoid the ITZ and characterize the free matrix without a quartz influence.

2. A large OH-concentration gradient is observed at the contact with the surface of the grain extending into the distance of a maximum of  $1 - 2 \mu m$ . This thin layer represents the direct boundary between the quartz and the matrix. In the interface itself, the concentration of the OH<sup>-</sup> groups is very low, while increasing in the direction towards the matrix (Figure 7b). This structural situation is described above, by the AFM measurement (Figure 7a).

The ITZ is formed by two neighboring grain boundaries whose direct influence on the matrix in the stitching site showed a very low OH<sup>-</sup> concentration. The dimension of this transition layer responds approximately to 10  $\mu$ m. In both of the Raman images, the measurement points are depicted by the dots. They prove the low OH<sup>-</sup> group concentration (Figure 7c) at the direct boundary



Figure 6. AFM imaging of the merged ITZ between two grains with 3D imaging (a) and averaged profiles (b) of the group pores up to 700 nm deep.

leading to an explanation that molecular bonds bind the quartz surface with the geopolymer matrix. The hypothesis is supported by the absence of  $OH^-$  groups indicating a high density of the matrix molecular structure.



Figure 7. The integral-intensity isoline map of the measured hydroxyl vibration bands in the range of  $3000-4000 \text{ cm}^{-1}$  measured in a singular ITZ (a), in an ITZ between two quartz grains (b) and the Raman spectra of the stretching vibration bands (c) measured separately in the two indicated points (1, 2).

# Micromechanical properties of the ITZ matrix

The following figures show the results of the elasticity modulus (*E*) measurements by nanoindentation on the identical sample cross section in the chosen areas, in the matrix far from the filler grains and in the ITZ (Figure 8). The measurement was made in the enlarged range of 0 - 20 mN (Figure 8a), due to the included quartz, whose resulting records of all the force-depth curves are shown in a slope with a rough Y-axis resolution up to 20 mN. The following figure shows recorded measurements by nanoindentation at a location outside of the influence of grains (Figure 8b), where the Y-axis resolution is more detailed, because of the matrix





Figure 8. The results on the measurements of the micromechanical properties in representative areas.

softness, when compared to the quartz. The courses of the both sets of measurements are compared graphically by fitting the densest line recording. This course is limited within the range of 0 - 4 mN (Figure 8 c), referring to GP matrix in both cases, in ITZ as well as away from the filler. The slopes indicate the differences between the two matrix structures. It is clear that the matrix outside the influence of quartz has a significantly higher value of the resulting slope representing elasticity modulus than that reported in the ITZ. This means that the ITZ matrix has worse mechanical properties than the free matrix outside the grains.

The evaluated parameters for each indent into the geopolymer matrix were plotted in a histogram of the elasticity moduli (E) (Figure 9). This is the probability density of the variable up to the value of 40 GPa. The greatest E frequency is about 11 MPa in the ITZ and up to 15 MPa in the free matrix. A higher value than approximately 30 GPa is absent, all the way to levels that correspond to quartz, which is about 80 GPa (also not shown). At the edge of the grain, there is a sharp decline of E from the values of quartz, whereas in the distance of several mm from the edge, there are matrix properties comparable with the E of the free matrix without filler aggregates. In any case, when comparing the histograms of elastic moduli of the two measuring areas, a peak shift to the lower values is evident in the case of the ITZ.



Figure 9. The histograms of the elasticity modules of matrix at an area without quartz grains, and in the ITZ between the quartz and the geopolymer matrix (gray line).

# The composition of elements in the ITZ

The results of the linear analyzes of the elements Si, Al, Na are displayed in the following graphs (Figure 10). The relative concentration measurements at the interface up to the distance of about 7 - 8  $\mu$ m from the quartz show that the matrix composition at the surface is different from the ambient by its lower content of Si. Thus, as the matrix is slightly richer in Al, its curve points in this area show a slight mound. Similar results were obtained in other transition zones.



Figure 10. The composition of matrix in dependence on the distance from the quartz grain boundary in the case of large grain with  $200 \times 500 \ \mu\text{m}$  in diameter.

#### DISCUSSION

The measured properties indicate differences of the microstructures of the two present GP matrixes, in the transition zone with the filler and in the surrounding area outside the influence of the filler. It is obvious that the transition zone has a lower mechanical strength, a different composition and texture than the matrix beyond the influence of the filler. These differences can be seen in the matrix layer at a distance from the grain surface up to 50  $\mu$ m, which is probably related to the size of the grain, surrounded by the matrix.

#### Composition and strength of the ITZ

The ratio of Si and Al, as the core elements forming the matrix GP, favors the interface by a somewhat higher proportion of Al. This corresponds to the published findings and provides an explanation of why less micromechanical strength was measured in this area, expressed in terms of elasticity modulus. It is true that the matrix achieves higher strength when formed by a network with a higher Si content which, in the initial conditions of the experiment, is the ratio of Si/Al 1.6. Since the Al-content is slightly higher in the ITZ, even the strength of the matrix here is probably therefore lower. The lower strength at the ITZ also led to the creation of a surface profile of the polished section, where the AFM images noticed a step and a quartz grain rise slightly above the surroundings. The ITZ lower strength, however, may not apply to the intrinsic boundary, where a large gradient of the measured values was detected. The mechanical properties of this interface with a thickness of less than 1-2 µm could not be conclusively measured by the nanoindentation method with a resolution of 3.5 μm.

#### Micro-sized pore formatting

The lower strength of the matrix might be the reason for the micropore formatting in this area. Because

of the emerging solid phase with a lower strength, it may be prone to condensed water penetration which is pushing into the formatting mesopores under the otherwise equilibrium conditions of polycondensation. This hypothesis is in agreement with the finding that the ITZ contains areas with a higher concentration of hydroxyl groups than in the remote areas. It points to a weak structure with lower density, i.e. with a higher number of non-bridging oxygens (NBOs) if compared to the structure in the distant free matrix, supposing that the NBO concentration is detected by the concentration of  $OH^{-}$  groups. The size of these weak areas is about 10 - $30 \,\mu\text{m}$ ; therefore the micro-sized mesopores might easily be involved. The moment the dilution of the starting material arises, the resulting matrix is even more greatly disadvantaged, as compared to the surroundings. Nothing more can prevent the enlargement of the mesopores, and the ITZ matrix is increasingly filled by condensed water. This could lead to an enormous increase of the pore size, from the original nano- to the final micro-dimensions, when their growth process stops with the hardening of the matrix. Thus, water transport occurs probably in the direction from the inner matrix to the ITZ and continues to the matter surface. Here the excess condensing water, which does not fit into the pores, is accumulated or evaporated. Therefore, this is an open porosity of the micropores.

With the increasing content of sand in the composite, the proportion of the micro-sized pore volume to the total porosity increases, although the concentration of water in the starting precursor dispersion is constant. This is probably because the filler surface area increases and equivalently also the interaction area with the starting geopolymer mixture creating the ITZ with the properties described above. The proportion of micro-sized pores grows at the expense of the mesopores, according to the pore size distribution.

#### CONCLUSION

The properties of the geopolymer (GP) matrix at the interface (ITZ) between the aggregates of silica sand and in the surrounding matrix without the influence of the filler grains were studied.

The ITZ microstructure up to a distance of 50  $\mu$ m from the grain surface is different from the surrounding matrix. The ITZ differs by the presence of micropores. Their proportion on the total porosity depends on the filler content in the composite and increases up to 30 % in the case of the filler content of about 70 wt. %.

The micromechanical properties of ITZ suggest a lower strength than that of the surrounding matrix. The ITZ lower strength is probably due to a higher content of Al in the molecular network matrix

The ITZ contains areas with a higher concentration of OH<sup>-</sup> groups, indicating a network of a lower molecular

density and a higher amount of NBOs, which make mesopores tend to increase in size up to micro-sized pores.

The formatting of micropores in the ITZ is probably caused by the transport of water that arose as a byproduct of polycondensation beside the excess water in dispersion. It is caused by a disequilibrium, which occurs in the formation of a GP matrix of different properties in ITZ and without interaction with the filler.

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