DEVELOPING A 3D PRINTABLE INORGANIC POLYMER, DERIVED FROM A Fe-RICH SLAG

Glenn BEERSAERTS[1], Yiannis PONTIKES[1]

KU Leuven, Department of Materials Engineering, 3001 Leuven, Belgium

glenn.beersaerts@kuleuven.be, yiannis.pontikes@kuleuven.be

Introduction

A rheological study was performed as a starting point towards 3D printing of an inorganic polymer (IP) paste. An IP was produced after alkali activation of an Fe-rich slag. Papers on 3D printing of Fe-rich IPs are not yet published in the open literature (to the best of our knowledge), but there are a few on geopolymers (GP). Biranchi *et al.* developed a 3D printable GP, derived from fly ash and GGBFS, by adding silica fume and sand.[1] In our case, a clay-based paste that can be printed successfully was used as a benchmark. The goal therefore was to engineer the IP paste from a standard IP formulation (reference) in a way so as to behave comparatively to the clay. Additives were introduced in the paste in order to develop a printable IP which is easily extrudable from the printer nozzle and could print distinct layers with a good adhesion to prevent cracks. The elastic and thixotropic properties were investigated on the reference IP, conventional clay and printable IP. The mechanical properties of the IP were measured as well.

Methodology

An Fe-rich slag was used as a starting material with a bulk chemistry determined by X-ray fluorescence (XRF) analysis and the amorphous content by quantitative X-ray diffraction (XRD). The slag was activated with a potassium silicate solution which consisted of 65 wt% H_2O and a SiO_2/K_2O molar ratio of 1.8. The reference IP consisted of a solution to slag ratio of 0.3 without any other additives. Based on literature, preliminary tests and the rheological behaviour of the reference IP and the clay, 1 wt% of attapulgite, 12 wt% of fine sand and 9 wt% of silica fume were added to adjust the rheological properties. The activating solution was mixed with the slag, according to an activating solution to slag and silica fume ratio of 0.3. The desired consistency of the clay ("Limoges") was achieved by adding 3 wt% of ethanol. The IP pastes and clay were manually mixed for 4 min and afterwards introduced in the measurement cup. A rheometer (Discovery HR-3, TA Instruments) was used with a four-bladed vane impeller and at a temperature of 20°C and 50% relative humidity (RH). Prior to each measurement, a preconditioning for 200 s was performed at a shear rate of 100 s^{-1}. A frequency sweep was performed in the linear regime with a frequency from 100 to 0.01 rad/s and a strain amplitude of 0.05%. A thixotropic loop

was executed when increasing the shear rate from 0.01 to 100 s^{-1} and afterwards decreasing to 0.01 s^{-1}. Once the rheological behaviour was characterised, the printable IP was 3D printed. The printable IP paste was mixed for 6 min with a high shear mixer (IKA RW20) at 800 rpm. Afterwards, the IP paste was placed in a canister. A pressure of 4 bar was applied to press the material through the extruder of a WASP 2040 3D printer. A 5 x 5 x 5 cm^3 hollow cube was printed with a wall thickness of 1 cm. A secondary electron microscope (SEM) was used to investigate the microstructure of the printed IP matrix. The IP pastes were cast in 4 x 4 x 16 cm^3 moulds, sealed and cured for 24 h at room temperature (RT). After demoulding, one batch of samples was cured in 100% RH at RT until testing, while the other batch was cured for 3 d at 60°C and 100% RH and afterwards stored at RT and 100% RH. 7 d mechanical properties of the samples were determined with an Instron 5985 according to the EN 196-1 standard.

Results and discussion

The slag has an amorphous content of 92.7 wt% whereas the bulk chemical composition is (in wt%): 40.9 FeO, 32.3 SiO_2, 11.0 Al_2O_3, 3.9 CaO, 2.2 P_2O_5, 2.0 Na_2O, 1.6 Cr_2O_3 and 6 others. SEM images of the IP surface (Figure 1a) show that some slag particles remained undissolved. Figure 1b shows that the attapulgite particles remained unreacted and are distributed throughout the matrix.

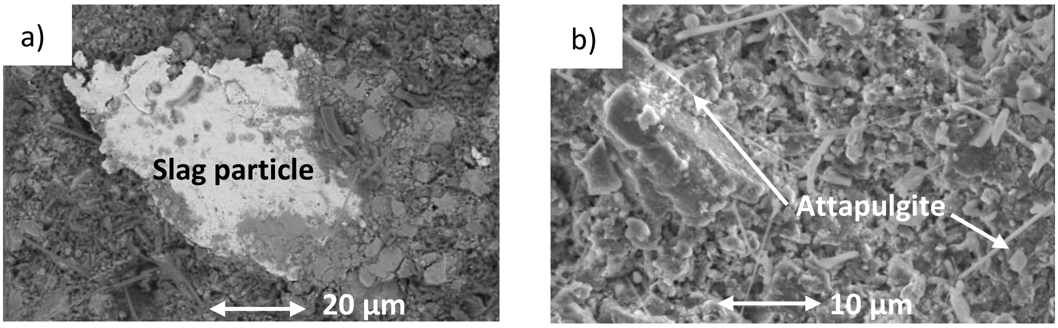

Figure 1: SEM image a) of an undissolved slag particle in the printable IP matrix, b) is a SEM image of the printable IP matrix

Frequency sweeps are conducted to investigate the viscoelastic behaviour in the linear regime and the network structure of the paste. Clay has a higher storage modulus G’, followed by the printable IP and the reference IP (Figure 2). A high G’ or elasticity is the result of a large number of crosslinks in the paste, indicating a stronger network structure.[2] Higher elastic properties in the paste are important for 3D printing, as the paste needs to retain its shape after extrusion. G’ is dominant over the loss modulus G” for most frequencies, indicating that the paste has a more solid-like behaviour. The cross-over point of G’ and G” are exhibited at higher frequencies for the reference IP, indicating a decreasing relaxation time and weaker attraction

forces among the particles.[2] G' of the clay and reference IP are frequency independent from a frequency larger than 10 rad/s, indicating that these pastes have a higher local network density.[3] The clay and printable IP seem to have a more connected or cross-linked network in the paste, as a result of the clay minerals and the additives, compared to the reference IP.

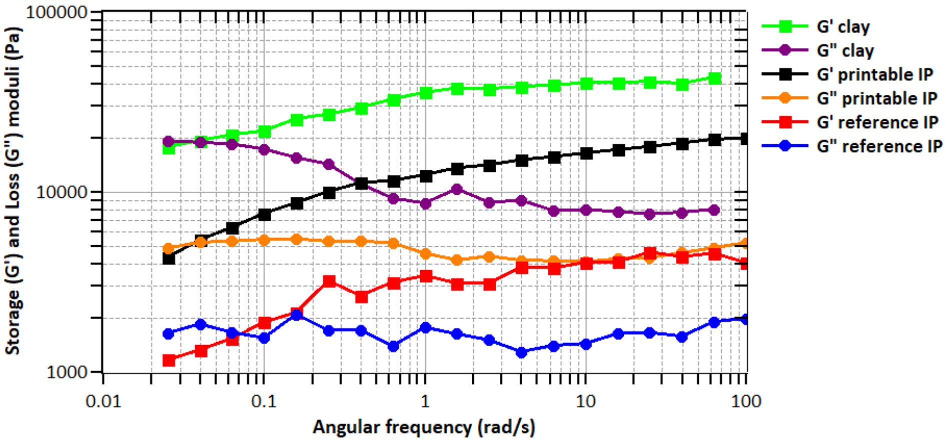

Figure 2: A frequency sweep to measure the storage and loss modulus of the clay, reference IP and printable IP

The flow behaviour was investigated by monitoring the stress and viscosity evolution at different shear rates, which is closely related to the paste behaviour at the moment of extrusion. The viscosity decrease with shear rate is the result of physical bonds being broken and is more pronounced for the clay and printable IP (Figure 3a). The viscosity of the reference IP is lower for the backward shear rate curve, where the paste remained more fluid, compared to the viscosity in the upward shear rate curve. This difference in viscosity is called a thixotropic loop and is related to a slow recovery of the paste after shearing and is therefore not desirable for 3D printing. No thixotropic behaviour is visible for the clay and printable IP; the viscosity and stress values adapted instantaneously to a lower shear rate and are similar to the upward shear rate curve, which is desirable for 3D printing. The clay and printable IP viscosity decrease with increasing shear rate while the stress stayed constant, which is typical for materials exhibiting a yield stress (Figure 3b).[4] The clay has a low yield stress of 72 Pa but could maintain its yield at higher shear rates, up to 2.5 s^{-1}, compared to the printable IP. A double yield can be noticed, one at 0.025 s^{-1} and the other at 0.4 s^{-1}, for the reference IP but this cannot be maintained for a long range of shear rates. The viscosity and stress value of the printable IP are one order of magnitude higher compared to clay. However, the viscosity and stress value should be as low as possible at higher shear rate, to have a beneficial flow behaviour during extrusion. Further optimisation is required to obtain an easier extrusion of the printable IP.

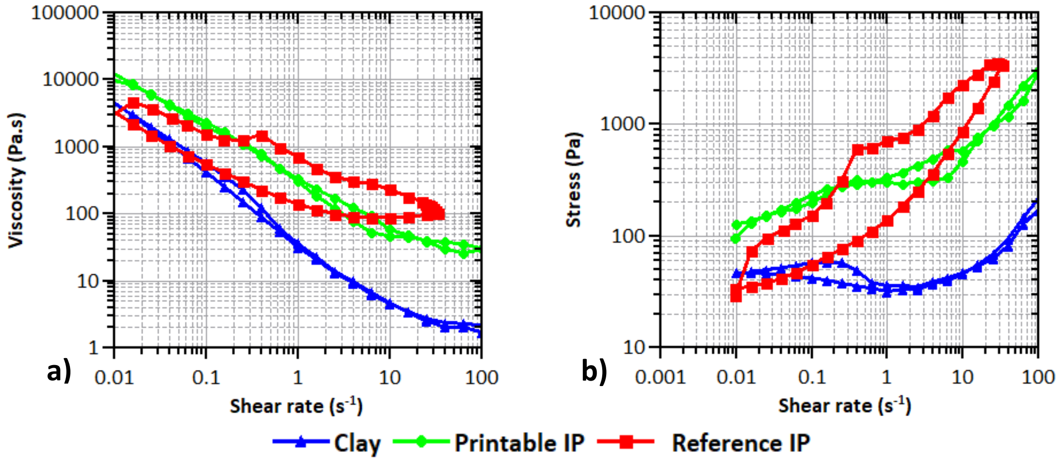

Figure 3: The results from the thixotropic loop with the a) viscosity and b) stress development of the clay, reference IP and printable IP

The ambient-cured paste samples exhibited ductile failure and had a 7 d compressive strength of 15 ± 4 MPa. The ductile failure can be the result of the excess of silicates in the solution, creating a silica-saturated binder. This could also account for the partial solubility of the samples, when submerged in water for a long time period. The heat-cured IP samples showed brittle failure and achieved a compressive strength of 25 ± 2 MPa. These samples did not dissolve in water, suggesting that an IP binder was indeed formed.

Conclusion

A printable IP was developed as a proof-of-concept. The rheological behaviour was compared to a benchmark clay. Fine sand, silica fume and attapulgite were added to the reference IP to comply with the rheological behaviour of the clay and to obtain a printable IP. The use of these admixtures resulted in higher elasticity and no thixotropic behaviour. The printable IP was easily extrudable and did not deform once printed. In order to develop an insoluble binder of 25 MPa heat curing was needed after printing.

References

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