# THE EFFECT OF SAP AND SCM ON MICROSTRUCTURE DEVELOPMENT IN EARLY AGE FIBRE REINFORCED MORTARS

**R. Rostami (1) and A. J. Klemm (1)**

(1) School of Computing, Engineering and Built Environment, Glasgow Caledonian University, UK

**Abstract**

The use of Supplementary Cementitious Materials (SCMs) in concrete manufacture has significantly increased in the last decades mainly due to their sustainability benefits. Polymeric Fibres (PF) are commonly used in concrete in order to enhance adhesive and frictional bond with a cementitious matrix and improve mechanical properties. Despite these, early age shrinkage of cementitious materials is still a major concern and some form of internal curing is necessary, for example by Superabsorbent polymers (SAP). By providing a continuous supply of water for hydration SAPs influence long term durability and sustainability of mortars. However, the effect of different SAPs on microstructure development in fibre reinforced mortars (FRM) still remains scarce. The current study aims to address this issue. Three commercially available cements: CEM I (PC), CEM II (PC-FA) and CEM III (PC-GGBS) and three types of SAP were analysed. Microstructural features of composites were studied by MIP and SEM techniques. These were accompanied by the elastic modulus analysis of composites. The experimental results showed that application SAP E, with finer particle sizes, results in the lowest total porosities of mortars and greater number of evenly distributed smaller pores (under 20 nm). This subsequently leads to the reduced effect on elastic modulus of FRM. In summary, the smaller SAP particles and more evenly distributed the more efficient in hydration process and more homogenous internal microstructure.

Keywords: Supplementary Cementitious Materials (SCMs), Polymeric Fibres (PF), Superabsorbent polymers (SAPs), Microstructure, Elastic Modulus

## 1. INTRODUCTION

Worldwide popularity of blended cements, produced by a partial substitution of PC clinker by Supplementary Cementitious Materials (SCMs), is based on their good performance and lower environmental impact [1-2]. In early ages the contribution of SCMs to strength development is generally negligible due to slower reactions [2, 3]. Nevertheless, they have a major effect on hydration kinetics and enhancement of cementitious reactions due to physical effects (filler effect) and chemical reactions (dissolution-precipitation mechanism) during prolonged hydration [3].

However, SCMs are more sensitive to curing regimes and hence more susceptible to early cracking. This is primarily caused by slow pozzolanic reactions in fly ash (FA) [4] and by the limited degree of later reactions in ground granulated blast furnace slag (GGBS) due to a lack of space already filled by early products of PC hydration [5]. Polymeric fibres (PF) are often recommended [6] as a technique to cope with this phenomenon. Unfortunately it is often insufficient and some form of internal curing is still required to decrease self-desiccation and promote cement hydration [7]. Superabsorbent polymers (SAPs) have been proved to be a promising internal curing agent for cementitious materials, which can facilitate hydration process and control water supply in both fresh and hardened state [5, 7-10]. The most remarkable successes of SAPs have been in mitigation of autogenous shrinkage [5] and plastic shrinkage [9] in various types of mortar and concrete. Nevertheless, the effect of different SAPs on microstructure development in imature FRM containing SCM still remains unclear and deficient. Therefore, the main objective of this study is to assess this effect by application of MIP and SEM techniques. The microstructural analyses are supplemented by the analysis of elastic modulus of composites.

## 2. METHODOLOGY

### 2.2 Materials

Three types of cement have been used in this study: CEM I 52.5N (Portland cement - PC), CEM II/B-V 42.5N (PC-FA 70-30), and CEM III/A 42.5N (PC-GGBS 50-50). Their chemical and physical characteristics, as provided by manufacturers, are presented in Table 1.

**Table 1: Chemical and physical characteristics of PC, PC-FA and PC-GGBS**

| | $SiO_2$ (%) | $Al_2O_3$ (%) | $Fe_2O_3$ (%) | CaO (%) | MgO (%) | $SO_3$ (%) | $K_2O$ (%) | $TiO_2$ (%) | ZnO (%) | LOI (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| PC | 20.1 | 4.9 | 2.57 | 64.3 | 2.2 | 3.2 | 0.27 | 0.0 | 0.0 | 2.39 |
| PC-FA | 32.69 | 13.13 | 3.29 | 43.48 | 1.33 | 0.4 | 1.26 | 0.56 | 0.02 | 0.16 |
| PC-GGBS | 24.50 | 8.99 | 1.76 | 57.13 | 5.33 | 0.0 | 0.0 | 0.58 | 0.0 | 1.19 |

The micro polypropylene fibres used in this study had the following characteristics: length of 6-mm, diameter 18μm and density 0.91 $kg/m^3$. Three types of cross-linked Superabsorbent polymers were used in the experiments; SAP A-copolymer of acrylamide and acrylic acid, SAP C and E-modified polyacrylamide.

### 2.3 Characterisation of SAPs

Table 2 summarises properties of SAPs, including particle size distribution, their chemical and sorption characteristics. Water absorption capacities have been determined in deionised water and different binder solutions. It should be noted that SAP E has a similar molecular structure to SAP C (modified polyacrylamide) but different particle grading. Predominant particles sizes and mode values for SAP A are 102.51± 0.43 μm, for SAP C 95.19± 0.44 μm and for SAP E 76.74 ± 0.22 μm.

**Table 2: Characterisation of SAPs**

| SAP | Type | Particles size (µm) | WAC[1] Deionized water | WAC PC Solutions | WAC PC-FA Solutions | WAC PC-GGBS Solutions |
|---|---|---|---|---|---|---|
| SAP A | copolymer of acrylamide and acrylic acid | 30-140 | 340 g/g | 34 g/g | 33 g/g | 25 g/g |
| SAP C | modified polyacrylamide | 30-140 | 290 g/g | 36 g/g | 37 g/g | 33 g/g |
| SAP E | modified polyacrylamide | 20-130 | 340 g/g | 40 g/g | 46 g/g | 40 g/g |

[1] WAC : water absorption capacity

Shapes and size of SAPs have been characterised by SEM image analysis (Figure 1).

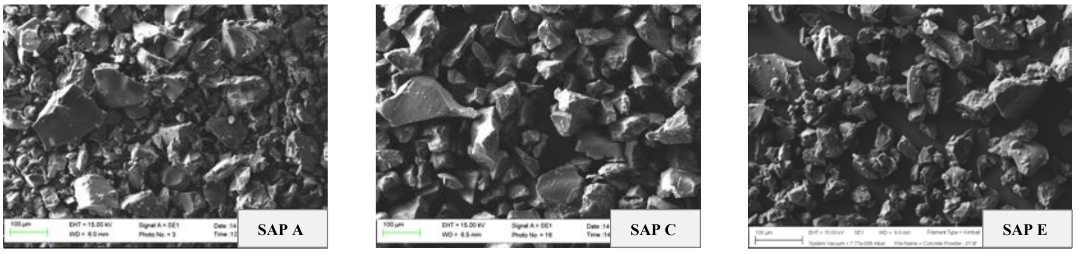


**Figure 1: The SEM micrographs of SAP A, C, and E**

## 2.4 Mix Compositions

Fifteen different compositions of FRMs were designed to carry out this study with different water/binder ratios as shown in Table 3. In SAP modified mortars, the water-to-binder ratio (w/b) was increased, in order to compensate for water absorbed by polymer [10].

**Table 3: Mix proportion of mortars and water/binder ratios**

| Cement | Sample Name | SAP type | SAP Content | Fibre Content | W/B ratio |
|---|---|---|---|---|---|
| | I | - | - | - | 0.48 |
| | I1 | - | - | 0.50% | 0.52 |
| **CEM I** | I1A | A | 0.25% | 0.50% | 0.58 |
| **(PC)** | I1C | C | 0.25% | 0.50% | 0.58 |
| | I1E | E | 0.25% | 0.50% | 0.58 |
| | II | - | - | - | 0.45 |
| | II1 | - | - | 0.50% | 0.50 |
| **CEM II** | II1A | A | 0.25% | 0.50% | 0.56 |
| **(FA)** | II1C | C | 0.25% | 0.50% | 0.56 |
| | II1E | E | 0.25% | 0.50% | 0.57 |
| | | | | | |
| | III | - | 420 | - | 0.48 |
| | III1 | - | - | 0.50% | 0.52 |
| **CEM III** | III1A | A | 0.25% | 0.50% | 0.58 |
| **(GGBS)** | III1C | C | 0.25% | 0.50% | 0.58 |
| | III1E | E | 0.25% | 0.50% | 0.58 |

All studied mortars were prepared with the proportion of binder to fine sand of 1:2 (by weight). Three types of SAPs were added to mixtures in the proportion of 0.25% by mass of binder. The amount of fibre used was 0.50% by mass of binder. Fine sand had 90% of particles smaller than 0.425mm.

### 2.5 Microstructure and Elastic Modulus

Microstructural characteristics of FRMs were assessed at 7, 14 and 28 days by the Mercury Intrusion Porosimetry (MIP) and the Scanning Electron Microscopy (SEM) techniques. Porosity and pore size distributions were determined by AutoPore IV 9500 by Micrometrics (with pressure range up to 60000 psi). The elastic modulus in compression were tested on prismatic samples ($40 \times 40 \times 100$ mm$^3$) at 14, 28, 270 and 365 days from the moment of sample preparation, BS EN13412[11].

## 3. RESULTS AND DISCUSSIONS

Figure 3 shows the total porosity results from the MIP measurements. Generally, the addition of fibre and SAPs increased the total porosity. This effect was reduced over the time for the reference samples (without fibre and SAP). The samples with CEM III (PC-GGBS) had the highest total porosities followed by CEM I (PC) and CEM II (PC-FA). This can be explained by the presence of GGBS (reduction of PC content) and decrease of total volume of hydrates formed [5, 12]. This is also related to low water-to-cement ratio of FA-blended system. As it can be seen in Figure 3, after 7 days, the appearance of a peak of total porosity is closely linked to the presence of bigger pores. With the progress of hydration (at 14 days), the total porosities of SAP samples increased by approximately 8%. However, after 28 days, all total porosities have slightly decreased.

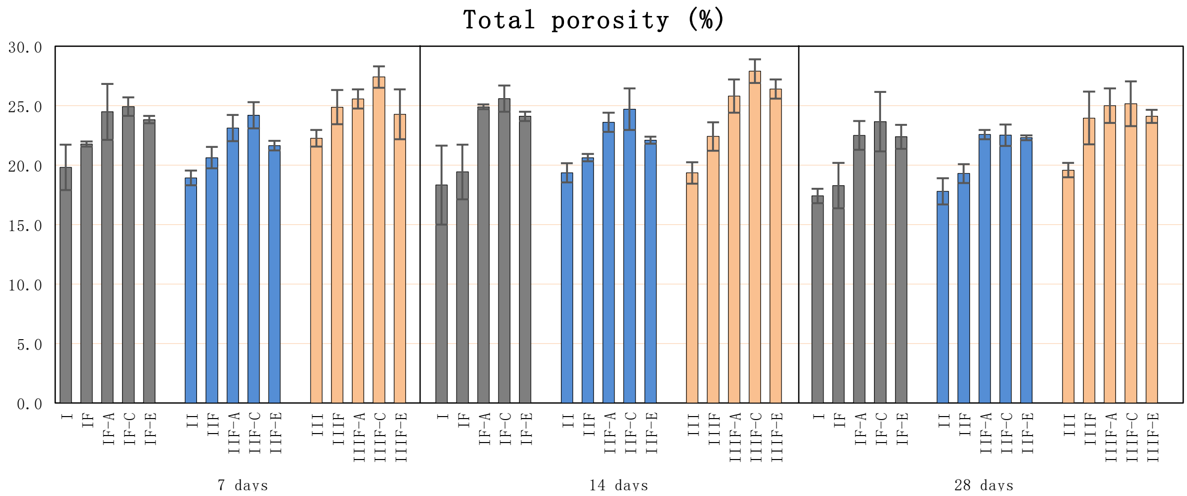


**Figure 3: Results of total porosity by MIP**

Figure 3 illustrates a clear increase in total porosities of SAP mortars in comparison with corresponding reference samples. The highest total porosity values have been recorded for samples with SAP C, due to its intermediate WAC and larger particle sizes (Table 2). It was also found that SAP E with the similar composition to SAP C, but finer particle sizes had the lowest total porosity values, especially at later age. It appears that the SAP particle sizes notably affect absorption/desorption characteristics.

Different pore size distributions in studied FRMs are shown in Figure 4.

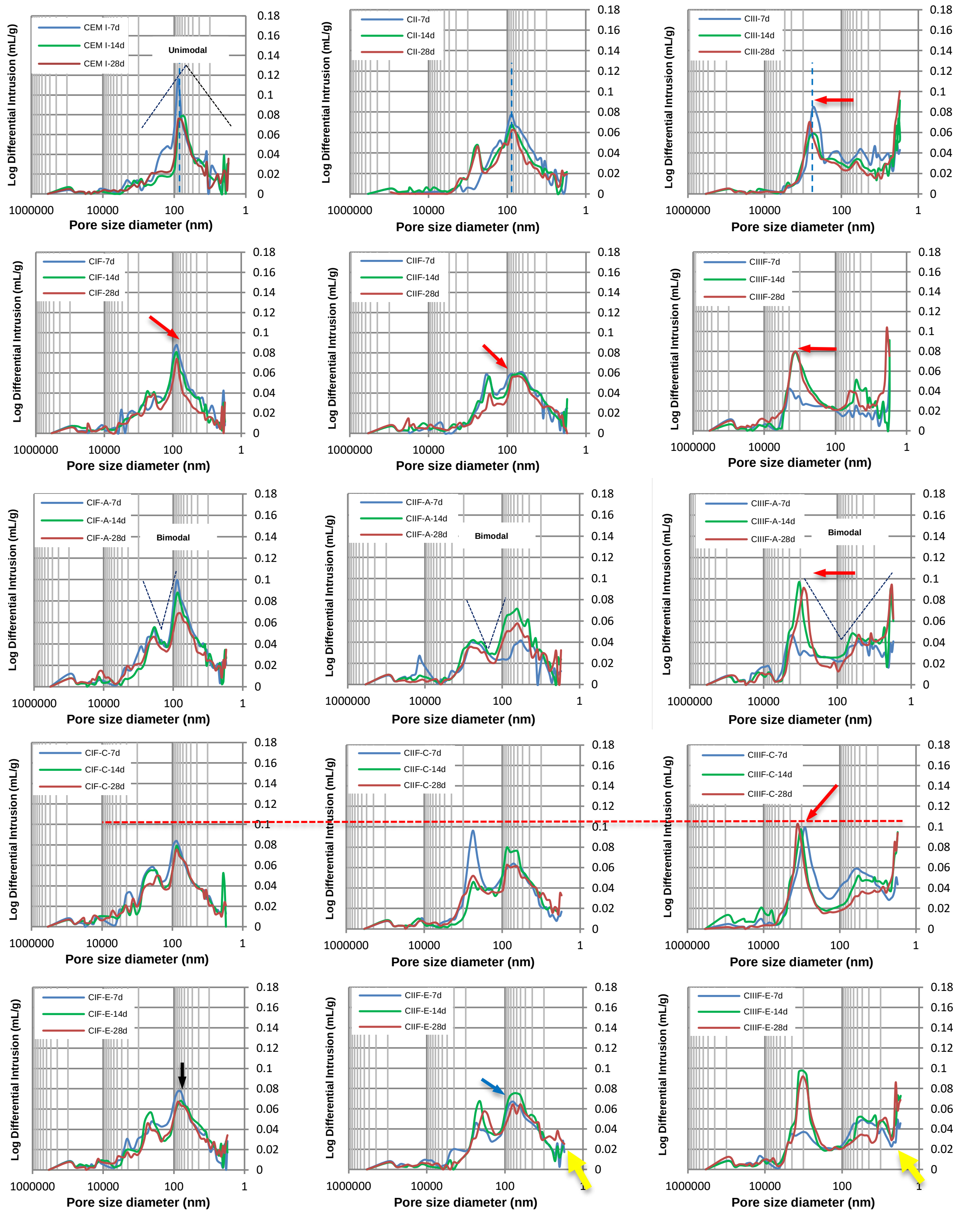


**Figure 4: Pore size distributions (by MIP) of mortars**

The effects of PF and SAPs on microstructural characteristics differ significantly. Several peaks corresponding to the predominant pore diameters can be identified (red arrows). SAP-free reference mortars had predominant sizes between 5 to 500 nm and peak around 80 nm, 90 nm and 400 nm for CEM I (PC), CEM II (PC-FA) and CEM III (PC-GGBS) respectively (blue dash line). SAP samples had pore diameters greater than 500 nm, which were formed by collapsing SAPs. The largest pores were recorded for mortars with SAP C (red square dot line).

In early hydration stage, SAP mortars had a similar bimodal PSD pattern compared to the free-SAP samples. However, at about 28 days, the number of smaller pores (under 20 nm) was reduced in SAP mortars; while in the reference sample, this amount has not changed over time. MIP porosity obtained for samples with GGBS is significantly larger than for FA and PC samples. However, as seen on Figure 4, the total porosity values increased during the first 14 days. With the progress of hydration (after the second week), the total porosities slightly decreased. This effect is more evident for SCM samples with SAP E (yellow arrows). Water released from SAPs facilitates formation of hydration products and filling up the existing pores spaces, which in turn results in densified microstructure at later age [5].

Figure 5 shows SEM micrographs of mortars at age of 28 days. The absorption potential of SAPs can be determined by the voids partially filled with hydration products left by the SAP. These voids displayed on the scanned sections can give an estimate of SAPs volumetric fraction. These also can have an impact on the surface roughness, which lead to higher roughness surface [5].

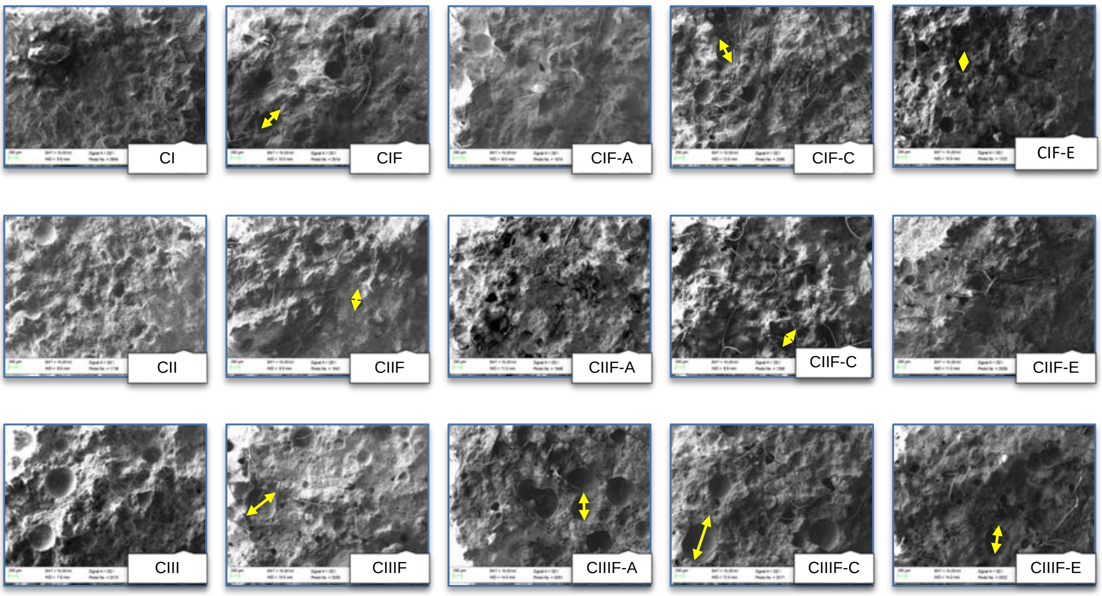


**Figure 5: SEM micrographs of mortars at 28 days (100x)**

A set of images given in Figure 5 shows clear contrast between macro pores and concaves of all samples. From the SEM analysis of samples at low magnification (100x), it is apparent that big concaves can be clearly identified in samples with CEM III (PC-GGBS) followed by CEM I (PC) and CEM II (PC-FA). The large macro pores observed in all SAP samples contributed to the increased total porosities of mortars. The samples with SAP C seem to have larger (micro and macro) pores, especially for PC-GGBS blends (yellow arrows). It is likely that the high-water absorption capacity and large particle size for this polymer has caused formation of pores of such big diameters.

The overall trend of elastic modulus up to 360 days is shown on Figure 6. In general, the elastic modulus of mortars increases over time due to the progress of hydration reactions.

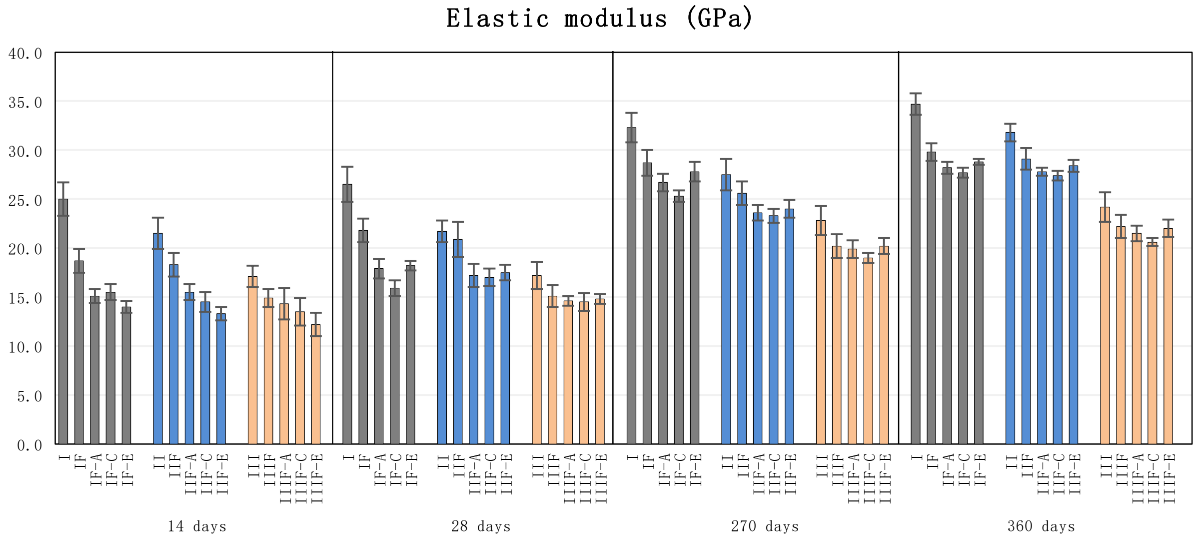


**Figure 6: Results of elastic modulus**

The results show that elastic moduli for SAP-modified samples are always lower than for the reference mixtures. However, the negative effect of SAP addition is more marked at early age (up to 14 days) and is slightly decreased at 28 days. However, this effect is reduced later due to further hydration facilitated by internal curing of SAP. The decrease in SAP mortars can be related to their higher total porosity at early ages; pores may act as weak spots and influence mechanical behaviour. When comparing mortars containing different binders, it is clear that the higher values were recorded for the CEM I (PC) samples, followed by CEM II (PC-FA) and CEM III (PC-GGBS). Figure 6 also demonstrates that the addition of PF results in a decrease in elastic modulus by comparison with the reference samples. It should be noted that this reduction is more pronounced in matrices with CEM I (PC) cement due to increased porosity of these samples. In majority of samples, SAP A with the lowest water absorption capacity (WAC) had the highest elastic modulus values at early age (up to 14 days). It should be also considered that SAP E with smaller particle sizes had the lowest influence on elastic modulus behavior as smaller particles leave behind smaller voids. Further enhancements (after the second week) were observed in blended cements due to reaction of SCM with portlandite from PC hydration. These new products of the secondary hydration have subsequently filled smaller pores under than 20 nm (Figure 4).

## 4. CONCLUSIONS

Based on experimental results, the following can be concluded:

- Both MIP and SEM analysis confirm positive effect of finer particle sizes on absorption/desorption characteristics (SAP E).

- After the second week, the number of smaller pores (under 20 nm) was reduced in SAP mortars and this effect is more evident for SCM samples with SAP E.
- SAP E had the lowest influence on elastic modulus as smaller particles left behind smaller voids. Further enhancements (after the second week) were observed in blended cements due to reaction of SCM with portlandite from PC hydration.

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