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XPS and FT-IR investigation of silicate polymers

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Abstract This article presents the results of an investigation of the compositional and structural features of an inorganic polymer synthesized from amorphous silica and KOH. The inorganic polymers were characterized using Fourier transformation infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and X-ray diffraction (XRD). FT-IR investigation of the inorganic polymers showed that an increase in the hydroxide concentration used in the synthesis shifts the position of the maximum absorbance of Si–O bands toward lower wave numbers, indicating the transformation of Q^4 units to Q^3 and Q^2 units. XPS investigation of the inorganic polymers showed that the total amount of oxygen and potassium present in the sample increased when higher concentrations of hydroxide were used in the synthesis. The O/Si ratio of the inorganic polymers changed from 2 to 2.6 when the KOH concentration was increased from 0.75 to 4 M. The increase in the O/Si ratio can be explained by the greater dissolution of SiO_2 particles leading to the formation of branched polymers and gelation.

Introduction

The development of inorganic polymers is a new promising technology that may be used for many applications. The synthesis of inorganic polymers is normally carried out by mixing an amorphous material for example silicium dioxide with a mineral base, such as NaOH or KOH. Depending on the preparation method, the inorganic polymers can exhibit a wide variety of properties, including high compressive strength, fire resistance, and low thermal conductivity [1, 2].

In previous work, inorganic polymers have been synthesized by a sol–gel process in which the silicate precursors were formed in situ by dissolution of amorphous silica particles (microsilica, Elkem 983 U) by an alkaline solution (0.75–4 M KOH) [3]. The dissolution of the amorphous silica in alkaline conditions can be expressed by the following reactions.

$$SiO_2 + 2H_2O \rightarrow H_4SiO_4 \quad (1)$$

$$SiO_2 + H_2O + OH^- \rightarrow H_3SiO_4{}^- \quad (2)$$

$$H_3SiO_4{}^- + OH^- \rightarrow H_2SiO_4{}^{2-} + H_2O \quad (3)$$

$$SiO_2 + 2OH^- \rightarrow H_2SiO_4{}^{2-} \quad (4)$$

These reactions suggest that H_2O and OH^- are consumed during the dissolution process resulting in a decrease in pH, which also was observed experimentally [3]. Caullet and Guth [4] have computed the distribution of the ionized forms of H_4SiO_4 versus pH, and the results showed that $H_3SiO_4{}^-$ is the dominant species around pH 11 and that the amount of $H_2SiO_4{}^{2-}$ increase with increasing pH > 11.

Applying the partial charge model (PCM) reported by Henry et al. [5] the chemical reactivity of metal ions during hydrolysis and condensation can be predicted and explained. Partial charge calculations have shown that polymerization at high pH may not be favored since the partial charge of the leaving group and the partial charge of the nucleophil are in the same order of magnitude. In

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addition, high degree of ionization of the silicate species at high pH results in repulsive interaction between the reactants hindering polymerization. As the pH drop to below 12, the mean electronegativity of the solution decreases. As a consequence, the condensation between silicate species becomes more favorable [3]. ESI-MS investigation of the reaction solution of inorganic polymers synthesized from microsilica and 4 M KOH has shown that monomers, dimers, and trimers are the most dominant species in the solution before polymerization, thus suggesting that polymerization of the silicate species in the solution is determined by the alkalinity.

The inorganic polymers are composed from Si–O tetrahedrons which are connected via corner sharing bridging oxygens. The connectivity of the tetrahedrons is specified by the number of bridging oxygens. Tetrahedrons with n bridging oxygen's are denoted Q^n ($n = 0, 1, 2, 3$, or 4). Thus, silicon in Q^3 configuration is surrounded by three bridging oxygens and one non-bridging oxygen. Amorphous SiO_2 is assumed to consist of only Q^4 species forming a continuous random network [6].

In the present work, the composition and the kinetics of the formation of the inorganic polymers synthesized from microsilica (Elkem 983 U) and different concentrations of KOH is investigated using Fourier transformation infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS).

XPS is a highly sensitive technique well suited to examining the composition and chemical states of a surface. In previous studies [7–10], XPS has been used to study the variation in the Ca/Si ratio in cement materials by comparison of the Ca 2p and Si 2p peak intensities. It was found that upon hydration of C_3S [7, 10], blast furnace slag [11], and β-C_2S [8], a shift in binding energies was observed, indicating changes in bonding structure. The shift in binding energy was ascribed to the formation of bridging oxygen (Si–O–Si) compared to the more common non-bridging oxygen (Si–O–X) found in fresh cement samples [7].

Additionally, Miyaji et al. [12] have investigated the surface of silicone substrates treated with 2, 5, and 10 M NaOH using XPS. The obtained O1s spectra of the silicone samples showed a dominant peak located at 532 eV, which was assigned to siloxane (Si–O–Si) bonds in the silicone skeleton. The samples treated with 5 and 10 M NaOH for more than 3 h showed two additional peaks located at 533 and 531 eV, which were assigned to Si–OH and Si–ONa, respectively. The amount of Si–OH and Si–ONa formed increases with increasing period of NaOH treatment [12].

The reported experimental work indicated that XPS analysis may be used to obtain detailed information of the hydrolysis and condensation reactions occurring during synthesis of the inorganic polymer.

Infrared spectroscopy is a useful analytical technique used for both qualitative and quantitative analysis of organic and inorganic materials. FT-IR has been widely used in the past to study structural evolution of geopolymers. The most important bands are located at 1088 and 1094 cm^{-1} and are assigned to asymmetric stretching of Al–O and Si–O bonds, respectively, in the geopolymer [1]. Moreover, attenuated total reflectance Fourier transform infrared (ATR FTIR) spectroscopy has been applied to study the gel formation of fly ash geopolymers [13, 14].

This article presents the results of an investigation of the compositional and structural features of an inorganic polymer synthesized from amorphous silica using different concentrations of potassium hydroxide. The inorganic polymers were characterized using FT-IR, XPS, scanning electron microscopy (SEM), and X-ray diffraction (XRD). Moreover, the evolution of the inorganic polymer during gel formation is investigated by FT-IR and XPS analyses.

Materials and methods

The inorganic polymers were prepared by mixing amorphous silica (Microsilica U 983, Elkem) with a highly concentrated solution of potassium hydroxide in distilled water. In this investigation, the molar concentration of potassium hydroxide was varied from 0.75 to 4 M. In standard experiments, equal amounts (w/w%) of silica and potassium hydroxide solution were used. In the investigation of the formation of the inorganic polymer, thin films were prepared at different times after mixing. The films were rapidly dried in an air stream in order to remove water from the system and as a result stop the reaction. This procedure provided samples at different stages in the gel formation.

Characterization

XPS analysis was carried out in a UHV chamber on a SX700 at the synchrotron source at the Institute for Storage Ring Facilities in Aarhus, employing a Zeiss SX700 plane grating monochromator. The chamber was equipped with a VG CLAM2 electron spectrometer running with a pass energy of 50 eV and a slit width of 2 mm. The base pressure was around 8×10^{-10} mbar. The inorganic polymer was cleaved prior to the investigation in order to obtain a surface representing the bulk polymer. The samples were placed in the sample holder and placed in the UHV chamber. The obtained XPS spectra were fitted using XPS Peak software [15].

Reflection XRD was used to determine the presence of crystal phases in the inorganic polymers. The XRD spectra were obtained using Co radiation ($\lambda = 1.7889$ Å) with a Philips X'pert MPD reflection diffractometer.

SEM images of the inorganic polymer and EDS mapping were obtained using a LEO electron microscope 1500 with GEMINI column.

FTIR investigations of the inorganic polymers were made on a Perkin Elmer Paragon 1000 Spectrometer. The inorganic polymers were crushed and grained into fine powders. The powders were mixed with KBr in a 1% (w/w) mixture and pressed into tablets at 10 ton for 3 min. The transparent tablet was inserted in the spectrometer and a spectrum was recorded from 4000 to 400 cm^{-1} with a resolution on 4 cm^{-1}.

Results and discussion

FT-IR investigation

FT-IR spectroscopy allows differentiation of various types of bonds in a material on a molecular level. In the present work, the FT-IR absorption spectra of the inorganic polymer were compared to known absorption lines in literature.

As mentioned earlier, amorphous SiO_2 is normally assumed to consist of Q^4 species forming a continuous random network. The position of the main Si–O–X stretching band (X = Si, K, or H) gives an indication of the length and angle of the bonds in a silicate network. For amorphous silica, this peak occurs at approximately 1100 cm^{-1} [13]. A shift of the Si–O–X stretching band to lower wave numbers indicates a lengthening of the Si–O–X bond, a reduction in the bond angle, and thus a decrease of the molecular vibrational force constant [16]. This shift can be attributed to an increase in the proportion of silicon sites with non-bonding oxygens (NBO) [13].

The FT-IR spectra of the inorganic polymers synthesized using different KOH concentrations are shown in Fig. 1. In Fig. 1, the IR bands are identified as follows: Si–O stretching is located in the range 1000–1200 cm^{-1}, Si–O bending is found at 800 cm^{-1} and between 890 and 975 cm^{-1}. The band at approximately 1100 cm^{-1} is assigned to the Si–O stretching of Q^4 units and the band at 1050 cm^{-1} is assigned to Q^3 units with one non-bridging oxygen (Si–O–NBO) per SiO_4 tetrahedron [17].

From Fig. 1 it is seen that an increase in the hydroxide concentration shifts the position of the maximum absorbance of Si–O bands toward lower wave numbers, indicating the transformation of Q^4 units to Q^3 units. Moreover, the emerging of a new band centered around 900 cm^{-1} is observed, which is assigned to Si–O stretching of Q^2 unit with two non-bridging oxygen per SiO_4 tetrahedron [18]. The observed increase in the signal at 2380 cm^{-1} can be assigned to CO_2 which have reacted with increasing amounts of KOH leading to the formation of HCO_3^-.

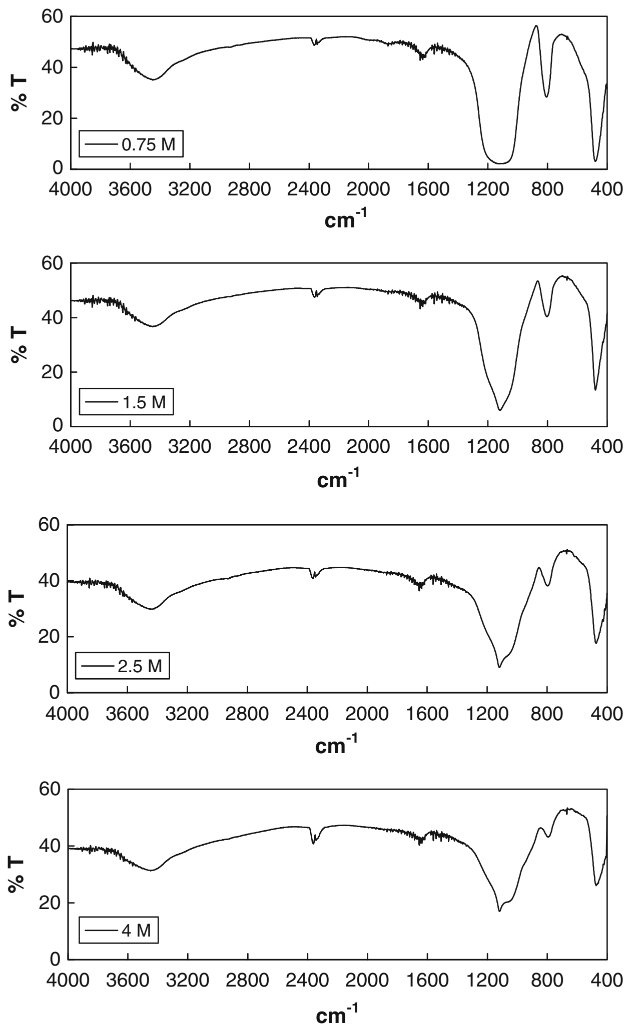

Fig. 1 FT-IR spectra of the inorganic polymers synthesized using different KOH concentrations

The observed change in the FT-IR spectra from mainly consisting of Q^4 units to Q^3 and Q^2 units with increasing concentration of KOH can be applied to investigate the change in composition during preparation. In Fig. 2, the FT-IR spectra of an inorganic polymer synthesized using 4 M KOH recorded at 0.5, 1, 3, 6, and 10 h after mixing are shown. From Fig. 2 it is seen that the intensity of the Q^4 peak located at 1120 cm^{-1} decreases significantly during the reaction, which also is consistent with the dissolution model. In Fig. 3, the intensity of the Q^4 peak located at 1120 cm^{-1} is plotted as a function of reaction time together with the evolution in hydroxide concentration. From Fig. 3 it is seen that the two curves nearly overlap, indicating that the change in intensity of the peak assigned to Q^4 units can be used to describe the dissolution process occurring during synthesis of the inorganic polymer. The small increase in

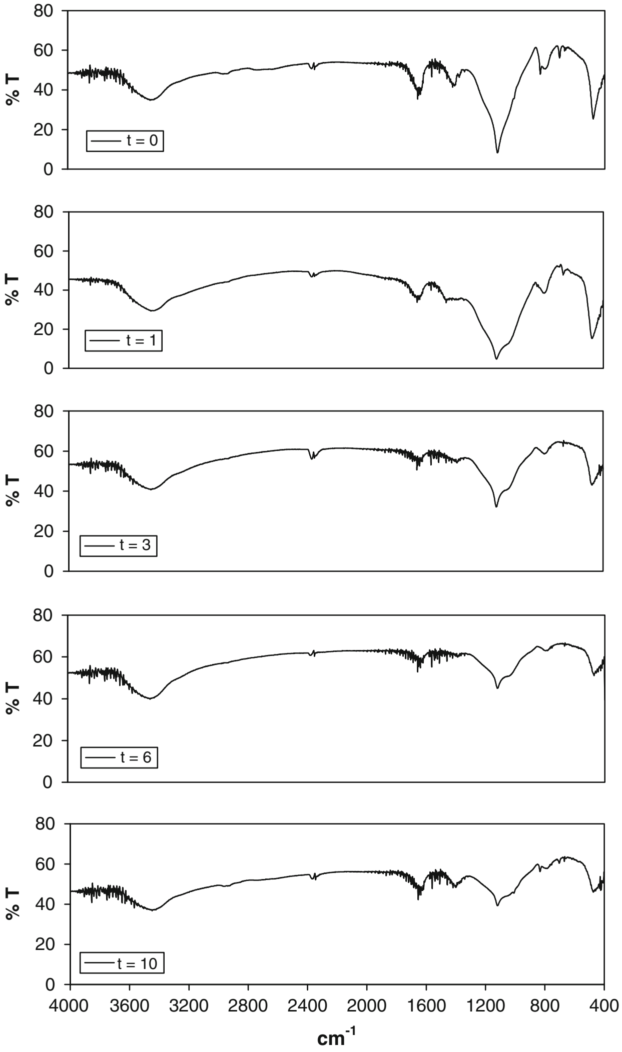

Fig. 2 FT-IR spectra of an inorganic polymer synthesized using 4 M KOH recorded at 0.5, 1, 3, 6, and 10 h after mixing

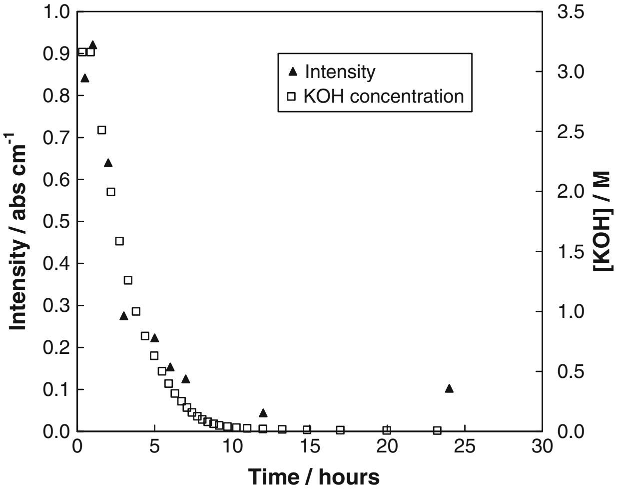

Fig. 3 Intensity of the peak located at 1120 cm^{-1} as a function of the reaction time compared to the evolution in hydroxide concentration

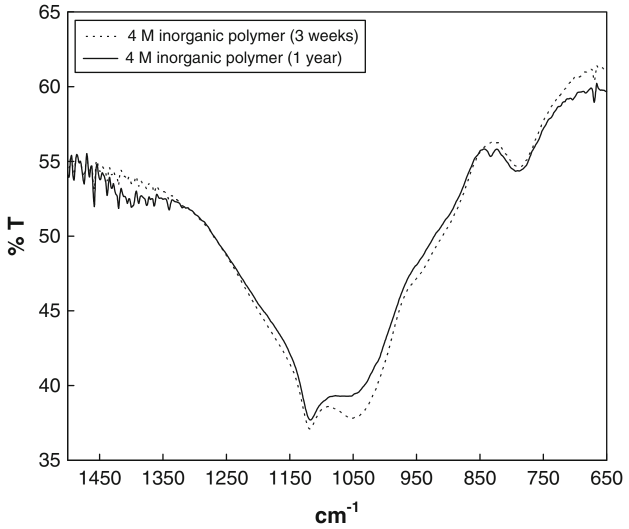

Fig. 4 FT-IR spectra of the inorganic polymer recorded after 3 weeks compared to a spectra recorded after 1 year

the intensity of the Q^4 peak after 24 h may be due to formation of Q^4 units during the polymerization process leading to gelation. FT-IR investigation of inorganic polymer 3 weeks after preparation has shown that the peak increases further to ~0.4. In comparison, the FT-IR spectra of the inorganic polymers were not found to change further after the 3 weeks. FT-IR spectra of the inorganic polymer recorded after 3 weeks and after 1 year are shown in Fig. 4.

XPS investigation

XPS is a highly sensitive technique well suited to examining the composition and chemical states of a surface. When a material is bombarded with X-rays, photoelectrons may be emitted from the topmost surfaces (typically 1–10 nm). All elements yield photoelectrons of a specific binding energy, enabling elemental analysis. Furthermore, small changes in the chemical bonding environments result in small shifts in the photoelectron energy, thus allowing chemical information to be obtained. Among the chemical properties which may be evaluated from the binding energies are oxidation state, nearest neighbor atoms and type of bonding [7]. In the present investigation, the Si 2p, O1s, and K 2p spectra of the inorganic polymers are recorded in order to obtain information of the elemental and chemical composition.

Si 2p binding energies

The energy difference between the Si 2p 3/2 and Si 2p 1/2 levels is ~0.5 eV, causing the two peaks to overlap [19]. The ratio ([2p 1/2]/[2p 3/2]) of the Si 2p 1/2 and Si 2p 3/2 peak intensities has been determined experimentally to 0.52 in a high-resolution XPS investigation of the metallic component of a clean silicon wafer compared to a theoretical ratio of 0.5 [19]. Comparison of the metallic and oxidized silicon species has shown that the Si–O–Si composite peak is broadened and does not show a resolved structure. The broadening of the Si–O–Si peaks is caused by differences in the chemical environments changing the electron density at the silicon atom and hence induces small chemical shifts broadening the Si 2p spectra. The overlap of the Si 2p 1/2 and Si 2p 3/2 peaks and the fact that the Si–OH groups are only observed as a broadening of the Si 2p peak makes it difficult to separate the Si–OH from the Si–O–Si bonds of the bulk silica network. By use of X-rays from a synchrotron source, the presence of Si–OH groups has been observed in a high-resolution Si 2p spectrum of a silicon wafer at ca. 105.2 eV, while Si–O–Si bonds were found at 103.8 eV [20, 21]. Conventional XPS studies are not suitable to determine the presence of those surface groups [19, 20].

In the present work, a synchrotron source was used in the investigation of the inorganic polymers; however, the experimental settings used in our investigation did not show significant changes in the Si 2p spectra of the different inorganic polymers which could be related to changes in the Si–OH amount. Contrary to this the amount of Si–OH and Si–OK in the inorganic polymer is believed to increase considerably as the KOH concentration used in the synthesis is increased from 0.75 to 4 M. Moreover, charging effects and the non-uniform morphology (SEM images in Fig. 7) of especially the inorganic polymers synthesized at low KOH concentration also contributed to the broadening of the Si 2p spectra.

The Si 2p spectra of the inorganic polymer shown in Fig. 5 were deconvoluted into two peaks representing the Si 2p 3/2 and Si 2p 1/2 levels. The area of the Si 2p 3/2 peak is used in the following calculations to determine the atomic composition of the inorganic polymers.

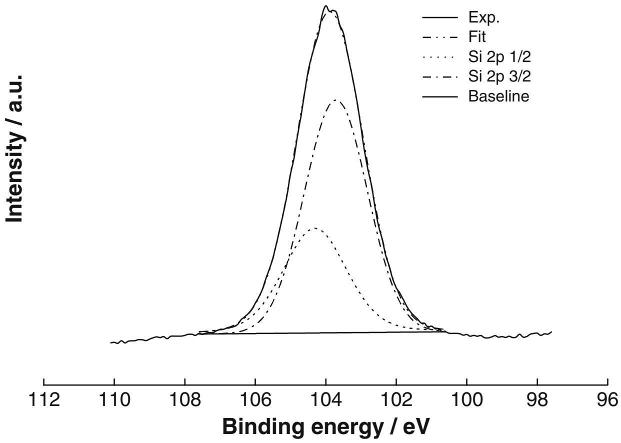

Fig. 5 Si 2p spectra of an inorganic polymer synthesized using 4 M KOH. The peak Si 2p is deconvoluted into two peaks representing the Si 2p 3/2 and Si 2p 1/2 levels

O1s binding energies

Figure 6 shows the O1s XPS spectra of a freshly cleaved inorganic polymer synthesized from 0.75, 1.5, 2.5, and 4 M KOH, respectively. From the XPS spectra it is seen that the oxygen peak is asymmetric, indicating that at least two different chemical states of oxygen are present. In the literature, the O1s peak has been proposed to consist of at least 3–4 contributors such as oxygen in siloxane bonds (Si–O–Si), silanol bonds (Si–OH), and non-bridging oxygen Si–O–X (X = Ca, Na) and water [7, 12]. Although H_2O is easily adsorbed on the surface of the inorganic polymer samples, physically absorbed H_2O are easily desorbed under the ultrahigh vacuum condition of the XPS system [22]. Therefore, the hydroxyl on the surface of the cleaved samples can be attributed to the silanol groups in the inorganic polymer.

Normally the peak ascribed to siloxane (Si–O–Si) bonds corresponding to the silicon skeleton in microsilica and the peak ascribed to silanol (Si–OH) bonds are reported to be located at 532 and 533 eV, respectively [7, 12, 20]. The peak corresponding to non-bridging oxygen is reported to be located at lower binding energies. In the present work, non-bridging oxygen in the form of Si–OK bonds are included in the fit, instead of X = Ca or Na as these elements are only present in negligible amounts. In comparison, the amount of potassium is considerable as the mineral base used in the synthesis is potassium hydroxide. The existence of these groups in the inorganic polymers has also been observed by using electro spray ionization mass spectroscopy (ESI-MS) (work not published).

The difference in binding energy of Si–OH, Si–O–Si, and Si–OK can be understood in terms of simple electrostatic interactions. There are on average fewer electrons at the oxygen atom in Si–OH than in Si–O–Si, due to the fact that the hydrogen atom has larger electronegativity than the silicon atom. Thus, the electron–electron repulsion at the oxygen atom decreases and hence the binding energy of the electrons increases.

The fitted peak information for the three types of bonds is shown in Table 1. From the table it is seen that the percentage amount of Si–OH and Si–OK bonds increase with increasing hydroxide concentration used in the synthesis of the inorganic polymer.

The fitted parameters of the O1s XPS spectra of the inorganic polymers synthesized using 0.75–4 M KOH and microsilica showed that the total amount of oxygen present in the sample increased when higher concentrations of hydroxide were used in the synthesis. The calculated O/Si

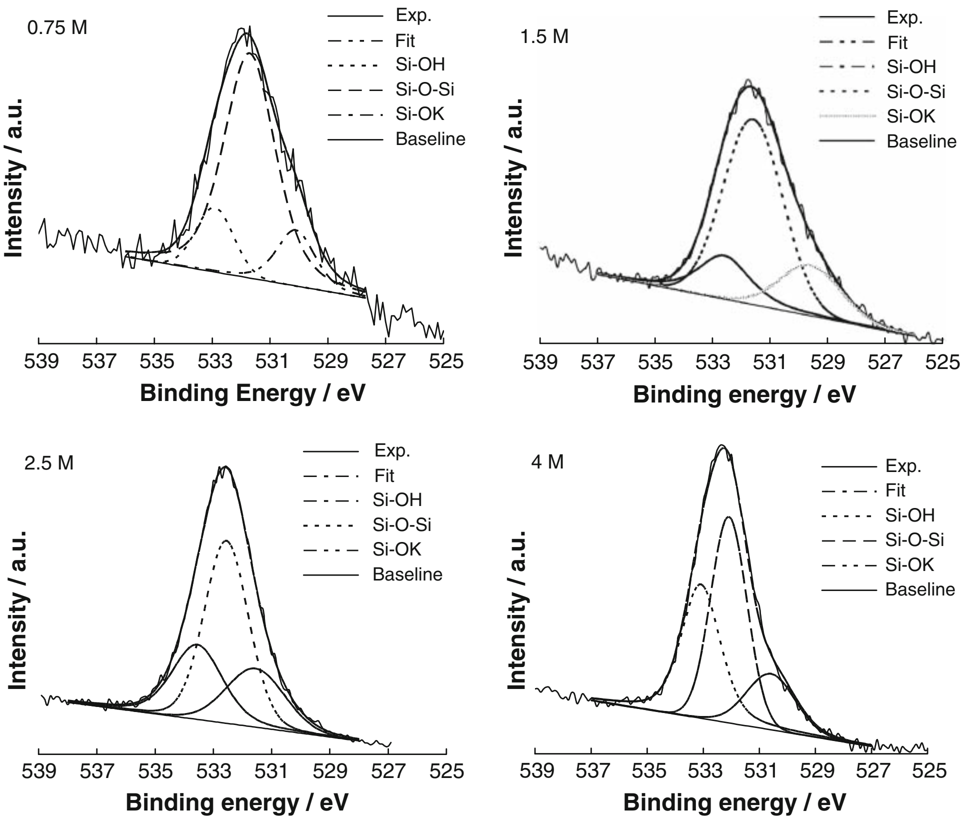

Fig. 6 O1s XPS spectra of freshly cleaved inorganic polymers synthesized using 0.75, 1.5, 2.5, and 4 M KOH, respectively

Table 1 Fitted peak information for the three types of bonds (Si–OH, Si–O–Si, and Si–OK)

KOH (M)	$\text{Area}_{\text{Si–OH}}$ (%)	$\text{Area}_{\text{Si–O–Si}}$ (%)	$\text{Area}_{\text{Si–OK}}$ (%)
0.75	13.5	73.6	12.9
1.5	16.5	64.8	18.7
2.5	26.4	52.1	21.5
4	37.8	45.3	16.9

Table 2 Calculated O/Si ratio from the total fitted area of the O1s peak and the Si 2p 3/2 peak using the atomic sensitivity factors for the instrument and microsilica as a standard

KOH (M)	Atomic ratio of O_{total}/Si	Atomic ratio of $\text{O}_{\text{Si–O–Si}}$/ Si ratio	Atomic ratio of $(\text{O}_{\text{Si–OH}} + \text{O}_{\text{Si–OK}})$/Si
0.75	1.99	1.48	0.51
1.5	2.20	1.43	0.77
2.5	2.48	1.29	1.19
4	2.61	1.18	1.43

ratios from the total fitted area of the O1s peak and the Si 2p 3/2 peak using the atomic sensitivity factors for the instrument settings and microsilica as a standard are shown in Table 2. From the table it is seen that the O/Si ratio of the inorganic polymers increases significantly as the concentration of KOH used in the synthesis increases. Microsilica is normally reported to consist of Q^4 units when examined by ^{29}Si NMR corresponding to a network of siloxane bonds, resulting in an average formula of SiO_2 equivalent to a O/Si ratio of 2 (results not shown).

The reaction mechanism for the preparation of the inorganic polymer is thought to be a result of dissolution of the surface of the microsilica particles by hydroxide, resulting in formation of soluble silica monomers in the solution. Dependent on the pH, different monomers will be present in the solution after dissolution (H_4SiO_4, $H_3SiO_4^{-}$, and $H_2SiO_4^{2-}$) [23, 24]. The O/Si ratio of the monomers is equal to 4. The silica species are assumed to polymerize through condensation reactions, resulting in formation of oligomers (dimers, trimers). The size and number of oligomers in the system increase until they extent throughout the solution, resulting in formation of a gel. As the polymerization of the monomeric species continues, the O/Si ratio will decrease. A fully condensed polymer will have a O/Si ratio of 2 corresponding to that of microsilica. The O/Si ratio of the inorganic polymers prepared in this work changes from 2 to 2.6 as the KOH concentration is increased from 0.75 to 4 M. The increase in the O/Si ratio can be explained by the greater dissolution of SiO_2 particles, leading to the formation of branched polymers. Depending on the nature of these polymers, the O/Si ratio will be between 2 and 4. SEM images of the inorganic polymers show that undissolved particles remain bonded in

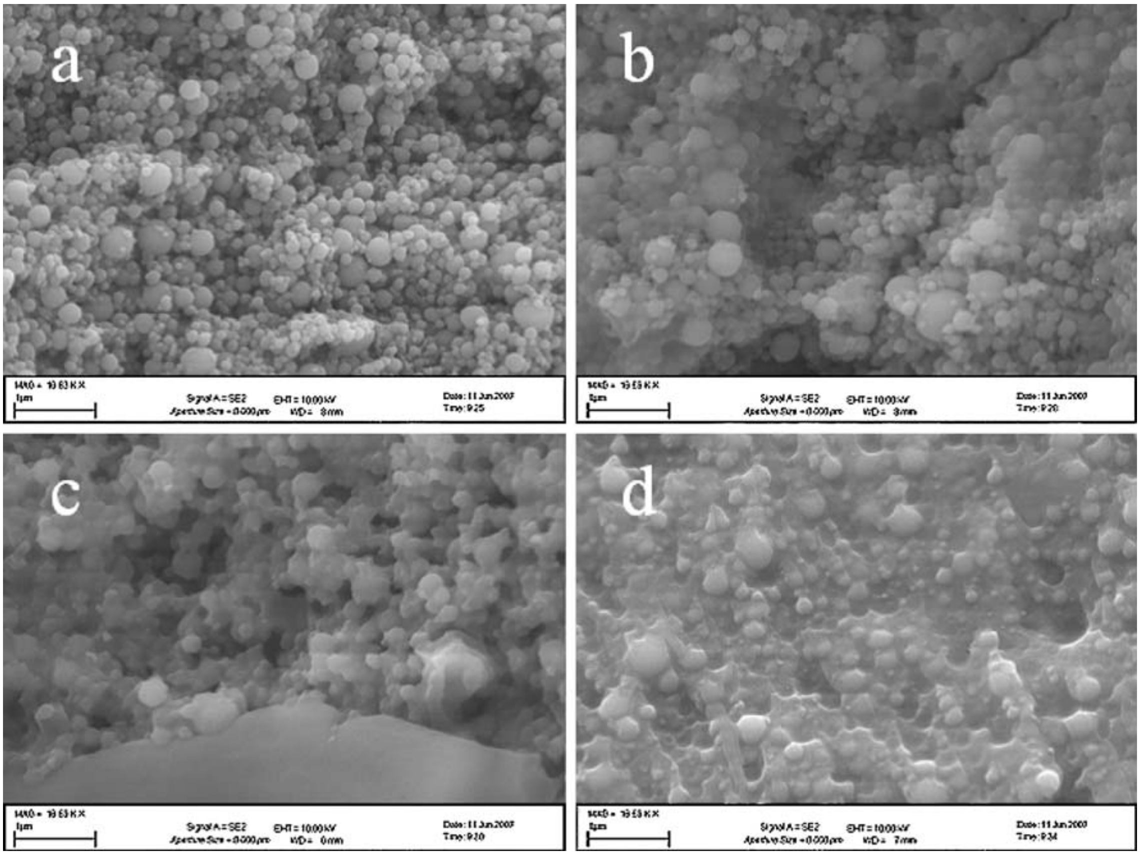

Fig. 7 SEM images of inorganic polymers synthesized using different KOH concentrations. **a** 0.75 M, **b** 1.5 M, **c** 2.5 M, and **d** 4 M

the matrix, so the obtained overall O/Si ratio of the inorganic polymer will be an average of the O/Si ratio for the remaining microsilica particles (O/Si ratio = 2) and the polymer binding the system together (O/Si ratio = 2–4). Hence, higher amount of polymer will lead to an increase in the overall O/Si ratio.

SEM images of the inorganic polymers (Fig. 7) support the discussed dissolution model. From the SEM images it is seen that the amount of polymer between the microsilica particle increases as a result of increasing KOH concentration. The increase in the amount of polymer/binder between the microsilica particles leads to a higher density of the material. Moreover, an Ostward ripening effect is shown as the smallest particles are dissolved, resulting in the formation of gel.

K 2p binding energies

Investigation of the K 2p peak was performed in order to calculate the percentage atomic content of the most abundant elements (Si, O, and K) present in the inorganic polymer. The energy difference between the K 2p 3/2 and K 2p 1/2 levels is ~2.8 eV [25], resulting in overlapping of the two peaks. The appearance of the K 2p peak did not change even for the inorganic polymers synthesized using high KOH concentrations. The atomic content of K was determined using the area of the K 2p 3/2 peak divided by the atomic sensitivity factor for the instrument.

Table 3 Percentage atomic content of the elements

KOH (M)	Si content (%)	O content (%)	K content (%)
0.75	31.5	62.7	5.9
1.5	27.1	59.6	13.3
2.5	24.7	61.4	13.8
4.0	24.5	63.9	11.7

The percentage atomic content of the elements is shown in Table 3. From the table it is seen that the Si content of the inorganic polymer decreases as the KOH concentration used in the synthesis increases, resulting in a higher O/Si ratio. Additionally, the K content also increases with the increase in KOH, with the exception of the inorganic polymer synthesized using 4 M KOH.

In comparison, the percentage elemental composition of the inorganic polymers was determined semi-quantitative using a SEM/EDS method and the results are listed in Table 4. The percentage element composition of the

Table 4 Semi-quantitative determination of the percentage atomic content of the elements using EDS

KOH (M)	Si content (%)	O content (%)	K content (%)
0.75	43.2	55.2	1.6
1.5	37.4	56.6	6.0
2.5	34.4	59.0	6.6
4.0	32.9	59.4	7.7

inorganic polymer determined using EDS follow the same trend as the element composition determined by XPS. However, the oxygen/silicon ratio is considerably lower.

XPS investigation of the evolution of the gel formation

The XPS investigation of the inorganic polymers synthesized using different concentrations of KOH solutions showed that XPS analysis in fact could be used to characterize the prepared inorganic polymers. Hence, an initial investigation of the evolution of the gel formation using XPS analysis was performed.

In Fig. 8, the Si 2p spectra of the inorganic polymer recorded 0–24 h after mixing are shown. From the figure it is seen that the peak tends to shift to higher binding energies which may be ascribed to an increase in the amount of silanol groups. Attempts of quantification were, however, not successful and more work is required in this area to distinguish the contributions from Si–O–Si, Si–OK, and Si–OH due to the overlap of the Si 2p 3/2 and Si 2p 1/2 levels.

In Fig. 9, a set of spectra of the O1s peak recorded at different times after mixing is shown. From the spectra it is seen that the O1s peaks are broadened and are shifted to higher binding energies, indicating that the amounts of Si–OH and Si–OK are increased during the reaction, which also is consistent with the dissolution model. In Table 5, the fitted peak data for the Si–O–Si, Si–OK, and Si–OH bonds are shown. It is seen from the table that the percentage of siloxane bonds decreases as a function of time, which is consistent with the dissolution model.

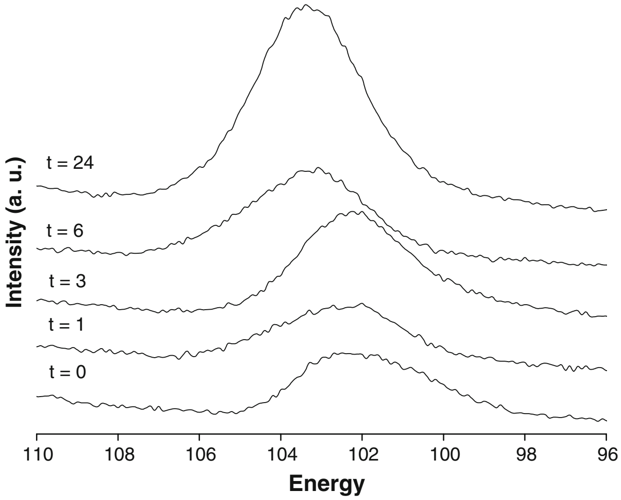

Fig. 8 Si 2p spectra of the inorganic polymer recorded 0–24 h after mixing

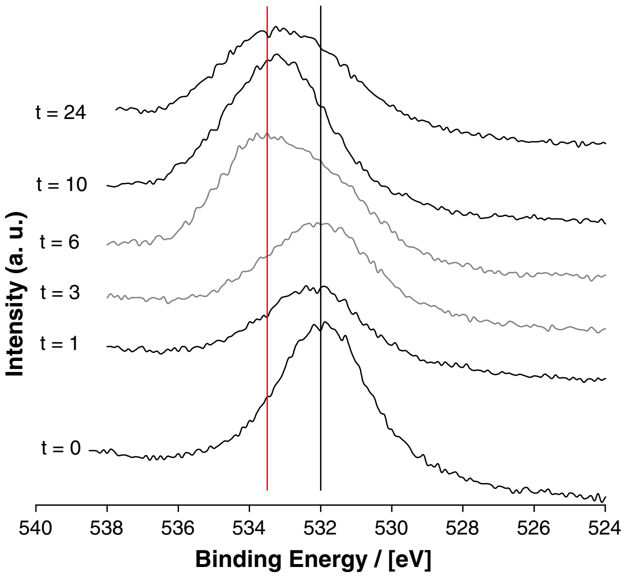

Fig. 9 O1s spectra of the inorganic polymer recorded at 0–24 h after mixing

Table 5 Fitted peak data for the O1s spectra recorded at different times after mixing

Time (h)	Area$_{Si\text{–}OH}$ (%)	Area$_{Si\text{–}O\text{–}Si}$ (%)	Area$_{Si\text{–}OK}$ (%)
0.5	8.9	83.8	7.3
1	12.9	74.2	12.9
3	15.3	72.4	12.3
6	27.4	56.0	16.6
10	25.8	49.2	25.0
24	28.0	39.9	32.0

EDS mapping

The EDS images of Si, O, and K of the surface of the inorganic polymer synthesized using 4 M KOH solution are shown in Fig. 10. From the figure it is seen that potassium is present in the inorganic polymer; however, excess potassium has been pushed out from the bulk of the sample onto the surface forming clusters which could also be seen from the SEM image. Silicon is evenly distributed in the inorganic polymer, except in the clusters containing excess amounts of potassium. Oxygen, on the other hand, is uniformly distributed in the inorganic polymer and appears also to be present in the potassium clusters. From the

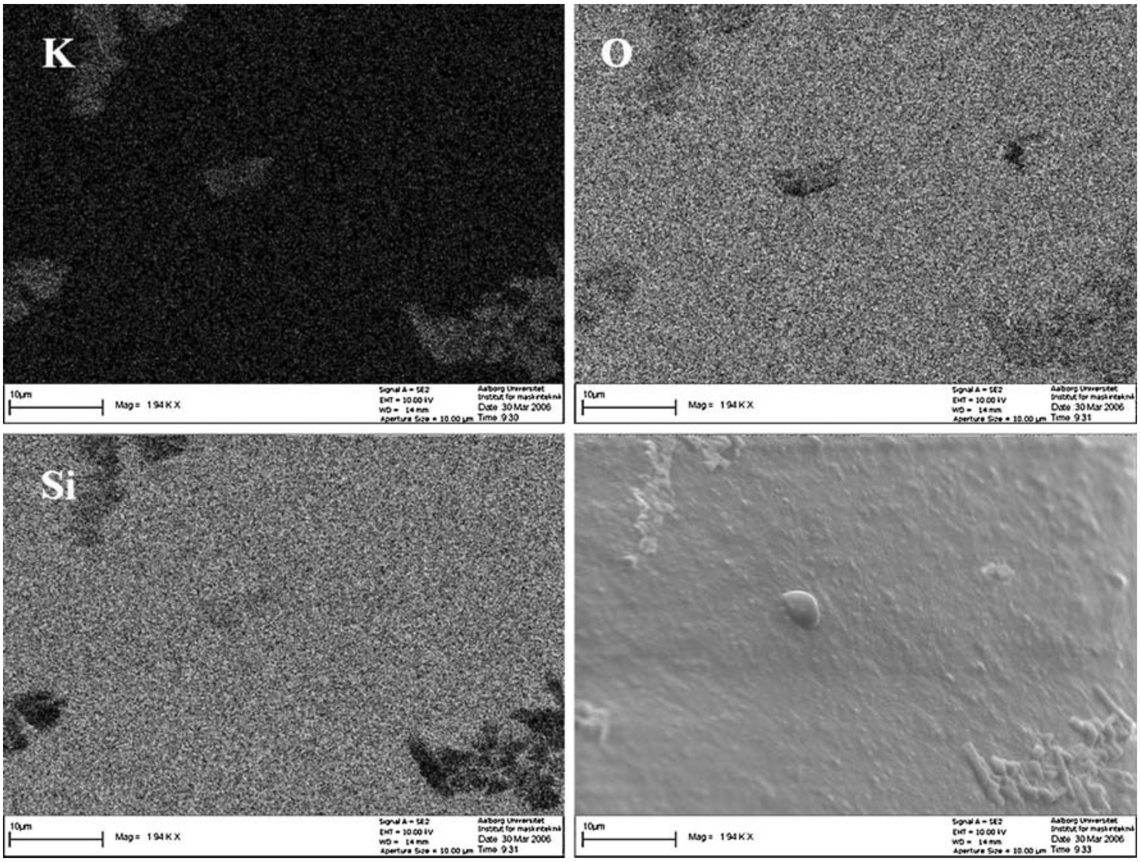

Fig. 10 EDS mapping of the surface of a newly prepared inorganic binder. The *white dots* denote potassium, oxygen, and silicon, respectively. In comparison, the SEM image of the surface is shown

obtained result it is suggested that the clusters may consist of precipitated KOH. This suggestion is supported by TGA investigation of similar inorganic polymer reported elsewhere (paper submitted). The TGA results showed that the loss in weight after heating correlated with the amount of KOH used in the synthesis of the inorganic polymer. It was also found that the primary weight loss was observed at a temperature of 300 °C corresponding to sublimation of KOH [26]. It should be noted that blank experiments of amorphous SiO_2 without the addition of potassium hydroxide did not show evidence of a decrease in the weight.

XRD analysis

Inorganic polymers including geopolymers are often described as X-ray amorphous [2], since the main characteristic of the XRD spectra is a featureless bump centred at ~20–30° 2θ. A typical XRD spectrum of the inorganic polymers prepared in this work is shown in Fig. 11. The XRD spectra of many amorphous materials appear almost identical. The similarities of these XRD spectra are related to the characteristic bond length of inorganic oxide frameworks [2]. The Si–OK bonding of potassium to the monomers and oligomers during the polymerization may lead to steric hindrance resulting in no long-range ordering.

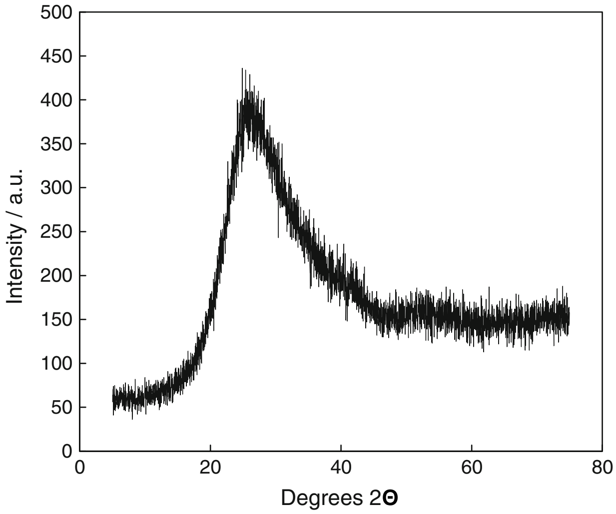

Fig. 11 Typical XRD spectrum of the inorganic polymer

Variation in the preparation temperature from 25 to 70 °C did not reveal any changes in the XRD spectrum of the inorganic polymer, suggesting that higher processing temperature will lead to formation of crystalline material.

Conclusion

The FT-IR investigation of the inorganic polymers synthesized using different KOH concentration has shown that an increase in the hydroxide concentration shifts the position of the maximum absorbance of Si–O bands toward lower wave numbers, indicating the transformation of Q^4 units to Q^3 and Q^2 units. Furthermore, comparison of the change in the hydroxide concentration during synthesis and the change in intensity of the peak assigned to Q^4 units show that the change in the Q^4 peak can be used to describe the dissolution process occurring during synthesis of the inorganic polymer.

The XPS investigation of the inorganic polymers showed that the total amount of oxygen and potassium present in the sample increased when higher concentrations of hydroxide were used in the synthesis. The O/Si ratio of the inorganic polymers changed from 2 to 2.6 when the KOH concentration was increased from 0.75 to 4 M. The increase in the O/Si ratio can be explained by the greater dissolution of SiO_2 particles leading to the formation of branched polymers.

Initial investigations of the development of the inorganic polymer as a function of time using XPS analysis showed that the O1s peaks were broadened and shifted to higher binding energies, indicating that the amounts of Si–OH and Si–OK were increased in the reaction, which is consistent with the dissolution model.

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