Capillary rise properties of porous geopolymers prepared by an extrusion method using polylactic acid (PLA) fibers as the pore formers

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Abstract

The geopolymers were prepared from sodium silicate, metakaolinite, NaOH and H_2O at SiO_2:Al_2O_3:Na_2O:H_2O of 3.66:1:1:x, where $x = 8$–17, and curing temperatures of 70–110 °C. Since the bending strength of the geopolymers was highest (36 MPa) where $H_2O/Al_2O_3 = 9$ and the curing temperature = 90 °C, these conditions were adopted. The porous geopolymers were prepared by kneading PLA fibers of 12, 20 and 29 μm diameter into the geopolymer paste, at fiber volumes of 13–28 vol%. The resulting paste was extruded using a domestic extruder, cured at 90 °C for 2 days then dried at the same temperature. The PLA fibers in the composites were removed by alkali treatment and/or heating. The highest capillary rise was achieved in the porous geopolymers containing 28 vol% of 29 μm fibers. The capillary rise of this sample, estimated by the equation of Fries and Dryer[1] was 1125 mm.
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1. Introduction

We have previously produced porous ceramics with controlled pore size and orientation by an extrusion method, using flammable fibers as the pore formers.[2–4] These materials are called "lotus ceramics" because of their microstructure.[2–4] By controlling their porous properties, lotus ceramics show much higher permeability and mechanical strength than conventional porous ceramics.[4] We also found that lotus ceramics show excellent capillary rise (about 1300 mm) not equalled by conventional porous ceramics.[5] The high surface temperature of building materials in summer sunshine can efficiently be lowered by wetting these porous materials to exploit their capillary rise of water which then evaporates.[5,6] The effectiveness of this passive cooling has been confirmed by observation of cool areas in the vicinity of many lotus ceramics, suggesting that these materials are good candidates for counteracting heat island effects.[7]

Although the lotus ceramics developed by our group show high water retention and good cooling effects due to their excellent capillary rise of water, it would be of greater advantage if these porous ceramics could be prepared by a more environmentally friendly process without the need for firing at high temperatures, e.g. at 1600 °C required for the present lotus ceramics. The most widely used building material is Portland cement which hydrates and solidifies at ambient temperatures, but high temperatures are required to produce the cement clinker. By contrast, geopolymers are really green materials which solidify at ambient temperatures by the formation of a framework structure of alkali aluminosilicate gel.[8] In the present geopolymer, we only need to fire kaolinite for converting to metakaolinite at 600 °C much lower than the temperature for Portland cement. Geopolymers can be formed in the Na_2O–Al_2O_3–SiO_2–H_2O system, with no CaO or MgO present to cause efflorescence[9] which blocks the pores by absorbing atmospheric CO_2 and forming carbonates. This makes our geopolymer material much better for our purpose, by comparison with Portland cement, which contains compounds in the CaO–Al_2O_3–Fe_2O_3–SiO_2–H_2O system. In our previous paper we reported a qualitative enhancement of the capillary rise properties of porous geopolymers produced using flammable fibers

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as the pore formers which were then removed by heat treatment at several hundreds of °C.[10]

In the present work, geopolymers were prepared by reaction of sodium silicate and metakaolinite at various H_2O/Al_2O_3 ratios in alkaline solution at 70–110 °C. Following the procedure developed previously, composites of geopolymer with PLA fibers were prepared by an extrusion method and the fibers were then removed by alkali and/or heat treatments to obtain porous geopolymers. The porous properties and capillary rise properties of these materials were determined to assess their suitability as materials for counteracting heat island effects.

2. Experimental procedure

2.1. Preparation of the samples

The starting materials were sodium silicate solution ($Na_2O/SiO_2 = 0.5$, Kanto Chemicals, Japan) and metakaolinite ($Al_2Si_2O_7$, prepared from Georgia Kaolinite, Inagaki Corp., Japan, dehydroxylated at 600 °C for 24 h). These reagents were mixed with NaOH solution (Wako Chemicals, Japan) using a planetary homogenizer (ARE-250, THINKY, Japan) operated at 2000 rpm for 30 s. The molar ratios $SiO_2:Al_2O_3:Na_2O:H_2O$ were 3.66:1:1:x, where x was varied from 8 to 17. The homogenized slurry was cast into an airtight container (34 mm × 34 mm × 100 mm) which was half-filled with sample and cured at 70–110 °C for 2 days. Higher curing temperatures than reported previously[10] were used to enhance the mechanical strength.[11] The geopolymer samples were then dried at the curing temperature for 4 days.

The preliminary experiments on the influence of the water content and curing temperature on the preparation of the geopolymers suggested that the composites with PLA fibers should be optimal where $x = 9$ and a curing temperature of 90 °C is used. The geopolymer slurry was mixed with PLA fibers and two dispersants (0.02 mass% of Serna D-305, Chubu Pile Ind., Japan and 0.02 mass% of oleic acid, Wako Chemicals, Japan), and extruded using a hand extruder. The PLA fibers (Terramac, UNITIKA, Japan) were of 12, 20 and 29 μm diameter and 500 μm in length, supplied in this form by Chubu Pile Ind. The amount of PLA fibers in the composites was 13–22 vol% of the 12 μm fiber, 23 and 26 vol% of the 20 μm fiber and 28 vol% of the 29 μm fiber.

The PLA fibers in the composites were removed by alkali, hydrothermal and/or heat treatments to introduce porosity into the geopolymers. Alkali treatment[12] was performed at ambient temperature by immersing the composites in NaOH solutions at pH values of 12, 13 and 14 for 1–2 days. Treatment with 10 M NaOH was also tried. Hydrothermal treatment was performed by placing the sample and solution separately in an autoclave at 180 °C for 1 day to react the composite with water vapor. Heat treatment was carried out in an electric furnace at 180 °C or 330 °C for 1 days in flowing air to thermally decompose the fibers. These heating temperatures were based on the melting point (~170 °C) and thermal decomposition temperature (~350 °C)[13] of PLA. Combinations of alkali and heat treatments were also used, i.e. treatment in alkali solution at

pH = 13 at 90 °C for 1 day followed by heating at 330 °C for 1 day in flowing air.

2.2. Characterization

The bulk densities of the samples were determined by the Archimedes' Principle and the pore size distribution and pore volume was measured by mercury intrusion porosimetry (Pascal 140 and 240, Mountech Co., Japan) at a maximum injection pressure of 200 MPa. The contact angle and surface tension used for the calculation was 130° and 0.485 N/m, respectively. X-ray measurements were performed using monochromated Cu Kα radiation (XRD-6100, Shimadzu, Japan) to identify the phases formed. The DTA/TG curves were recorded up to 600 °C at a heating rate of 10 °C/min using a sample weight of about 10 mg (Thermoplus TG8120, Rigaku, Japan). The four-point bending strengths of the geopolymer samples were measured on unpolished testpieces (4 mm × 3 mm × 40 mm) using a domestic testing machine. The average bending strength was obtained from measurements of 10 samples. The microstructures of the porous geopolymer samples after sputtering with Pt were observed using a SEM (JSM-5310, JEOL, Japan) at an accelerating voltage of 20 kV.

2.3. Capillary rise properties

The capillary rise of the samples (ϕ 10 mm × 140 mm) was measured by immersing the one side (10 mm) in water at room temperature. The capillary rise height was measured at various time intervals using a video camera. The measurements were performed under ambient conditions (between 20–25 °C and 30–40% relative humidity).

The resulting capillary rise curves were fitted using an Eq. (1) reported by Fries and Dreyer[1] for viscous and gravitational time stages. The effective pore radius (r) and contact angle between water and the pore wall (θ) required for this calculation were fitted by a trial and error method:

$$t = -\left(\frac{8\eta}{\rho \cdot g \cdot r^2}\right) h - \left(\frac{16\eta \cdot \sigma \cdot \cos\theta}{\rho^2 \cdot g^2 \cdot r^3}\right) \ln\left(1 - \left(\frac{\rho \cdot g \cdot r}{2\sigma \cdot \cos\theta}\right) h\right) \quad (1)$$

$$h_{eq} = \frac{2\sigma \cdot \cos\theta}{\rho \cdot g \cdot r} \quad (2)$$

where t is the time, η is the viscosity of water (9.11×10^{-4} kg/m s), ρ is the density of water (1×10^3 kg/m^3), g is gravitational acceleration (9.8 m/s^2), h is the capillary rise height and σ is the surface tension of water (73 mN/m). The equilibrium capillary rise height (h_{eq}) was evaluated by Eq. (2) based on the r and θ values obtained from Eq. (1).

3. Results and discussion

3.1. Geopolymers

All the geopolymer products set and hardened without apparent shrinkage, forming pale yellow-brown slabs with smooth
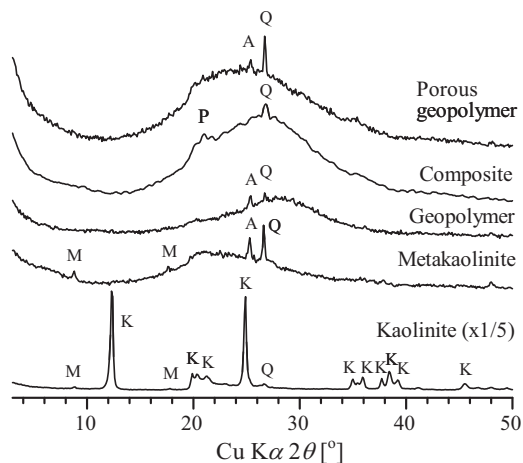
Fig. 1. XRD patterns of kaolinite, metakaolinite, geopolymer ($H_2O/Al_2O_3 = 9$ cured at 90 °C), geopolymer/PLA composite (16 vol % of 12 μm diameter fibers) and the porous geopolymer derived from this composite. A, anatase; K, kaolinite; M, mica; P, PLA; and Q, quartz.

surfaces. The XRD patterns of all the samples showed a halo at 25–30° 2θ corresponding to typical X-ray amorphous Al_2O_3–SiO_2 gel structures,[14] shown in Fig. 1 together with the XRD patterns of kaolinite and metakaolinite. The measured bulk densities and bending strengths of the samples are shown in Fig. 2 as functions of the H_2O/Al_2O_3 ratio and curing temperature. The density values and range from 1.00 to 1.60 g/cm³ with a clear tendency to decrease with increasing H_2O/Al_2O_3 ratio but relatively independent of the curing temperature. This suggests that excess H_2O in the synthesis is not included in the framework structure of the geopolymer and causes the bulk density of the porous matrix to decrease. This trend is similar to previous results,[10] suggesting that the pore size similarly increases with increasing H_2O/Al_2O_3 ratio.

The relationship between bending strength and the H_2O/Al_2O_3 ratio and curing temperature (Fig. 2(b)) shows a good correlation with the bulk density (Fig. 2(a)), namely, samples with higher bulk density show higher strengths. The highest bending strength (35.8 ± 5 MPa) was obtained for a sample prepared with $H_2O/Al_2O_3 = 9$ and a curing temperature of 90 °C. These preparation conditions were therefore adopted for the preparation of the porous geopolymer samples.

3.2. Composite samples

Composites of geopolymer and PLA fibers were prepared using three different fiber diameters (12, 20 and 29 μm). The maximum vol% of fibers which could be mixed into the paste increased with the fiber diameter, reflecting the lower numbers of fibers (Table 1), making them easier to mix with less tangling and lower aspect ratios. The DTA and TG curves of the geopolymer, PLA fibers and composite are shown in Fig. 3(a) and (b), respectively. The DTA curve of the composite contains a small broad endotherm at 85 °C, a sharp exotherm at 285 °C and a broader exotherm at 410 °C. The TG curve shows a three-stage weight loss at about 20–100 °C, 250–270 °C and 330–420 °C. Comparison of the thermal behavior of the geopolymer and PLA
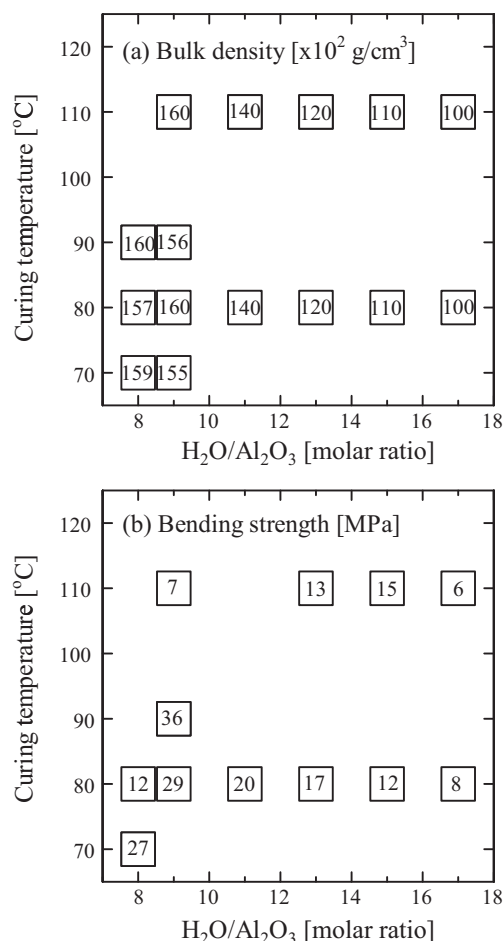

Fig. 2. Bulk density (a) and bending strength (b) of the geopolymer samples as functions of their H_2O/Al_2O_3 ratio and curing temperature.

fibers suggests that the endotherm and weight loss at 100 °C is due to the dehydration of geopolymer, while the exotherm and weight loss at 250–285 °C arises from the thermal decomposition of the PLA fibers. The reason for the exotherm and weight loss at ~400 °C is not clear, but may be due to the thermal decomposition of the PLA fibers deep inside the composite.

3.3. Porous geopolymers

Porous geopolymers were prepared by removing the fiber pore formers from the composites. Strongly alkaline treatment in 10 M solution collapsed the composite. Some of the fibers still remained in the pores after alkali treatment at pH = 12 and 13, but were completely dissolved in a solution of pH = 14. The weight loss after this treatment was however much greater than expected, suggesting that some of the geopolymer is also dissolved in this solution. It is therefore difficult to completely remove the PLA fibers from the composites by alkali treatment alone without significantly influencing the geopolymer matrix.

The composites were therefore treated under hydrothermal conditions at a slightly higher temperature than melting point of PLA. Since no residual fibers were observed in the microstructure, this treatment appears to effectively remove the fibers, but the geopolymer matrix became very porous, with a total pore

Table 1
Calculated parameters on capillary rising.

Sample	Relative fiber numbers[a]	Pore size [μm]	Contact angle [°]	h_{eq} [mm]	$t(h_{eq})$ [h]	$t(h_{eq})_{90\%}$ [h]
Geopolymer	0	0.52	89.6	198	1765.9	212.5
12 μm-13%	1	1.9	88	271	183.1	21.8
12 μm-16%	1.23	3	87.8	189	48	6.09
12 μm-19%	1.46	2.5	83.5	667	224.1	32.7
12 μm-22%	1.69	2.5	81	922	400	42.9
20 μm-23%	0.64	2.5	82	820	350.3	38.1
29 μm-28%	0.37	2.5	79	1125	510	52.3
Ref. 5	–	4	69.5	1290	136.1	23.4

[a] (Number of fibers in a sample)/(Number of fibers in sample 12 μm-13%).

volume of almost 0.8 ml/g. This may mean that the geopolymer reacted with the steam in the autoclave and was partially dissolved.

After heat treatment at 180 °C, residual fibers were still present in the composite; although the fibers should have melted, the resulting liquid remained in the composite. By contrast, most of the fibers had disappeared from the composite upon heating at 330 °C, although prolonged heating at this temperature was required for the complete removal of the fibers.
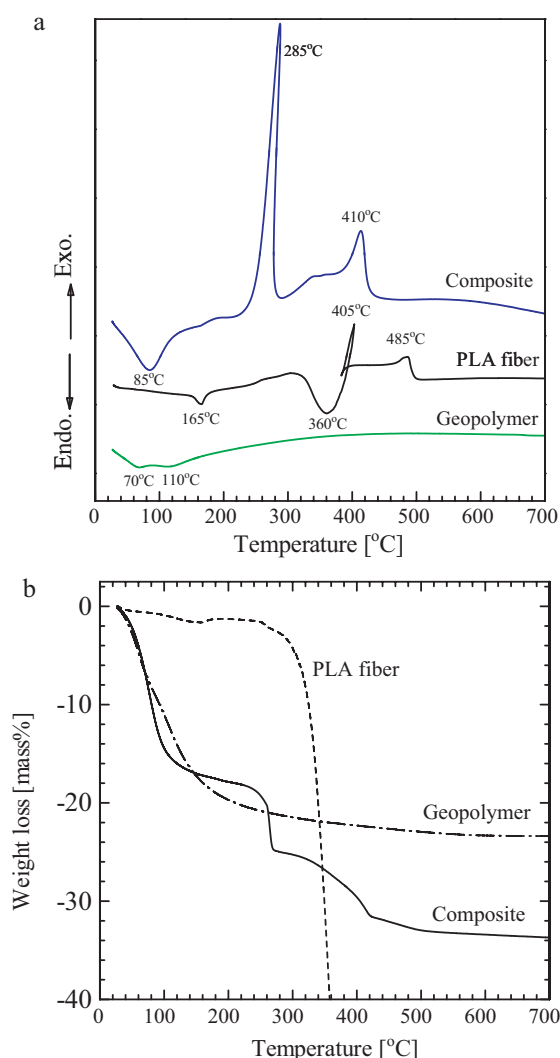

Fig. 3. DTA (a) and TG (b) curves of geopolymer, PLA fibers and composite.

The results of the alkali, hydrothermal and heat treatments suggest that none of these treatments alone is suitable for removing the fibers without damaging the resulting products. Therefore, a combination of alkali and heat treatment is considered more suitable for this purpose. The SEM micrographs of the porous geopolymers containing different volumes of 12 μm fibers and samples containing fibers of different diameters parallel and perpendicular to the extruded directions are shown in Fig. 4(a) and (b), respectively. All the micrographs show cylindrical pores formed by thermal decomposition of the fiber pore formers. The pore diameters are seen to be very similar to those of the fibers. The cylindrical pores are closely aligned with the direction in the micrographs of the parallel cross section corresponding to the extrusion direction. The cylindrical pore orientations differ slightly between samples, the degree of orientation being less in the samples with a higher volume of added 12 μm fibers (Fig. 4(a)) and with thinner fiber diameters (Fig. 4(b)). It is suggested that these trends may be related to the numbers of fibers in the various composites (Table 1).

The pore size distributions (PSDs) of the porous geopolymers in the samples containing varying volumes of 12 μm fibers and samples containing fibers of varying diameter are shown in Fig. 5(a) and (b), respectively. Fig. 5(a) shows that the PSD of the sample containing 13% fiber shows a bimodal distribution at about 0.1–0.4 and 2–4 μm. The PSD of the sample containing 16% fiber shows a similar bimodal distribution but the second peak is shifted to larger pore sizes in the range 5–10 μm. This further increases to 10–20 μm in the sample containing 22% fiber. The peaks corresponding to the larger pores become more distinct with greater volume of added fibers, and are thought to be related to the cylindrical pores. As previously reported by us,[4] these pores are formed by contact of the fibers ($P_{Contact}$) whereas the smaller pores ≤sub μm are those formed in the geopolymer matrix. The differences in the size and volume of the $P_{Contact}$ pores in the different samples are attributed to degree of connectivity of the fibers.

3.4. Capillary rise properties

The capillary rise heights of the base geopolymer and the porous geopolymers are shown in Fig. 6 as a function of time. The lines in the figure are calculated from Eq. (1) using the pore radii and contact angles listed in Table 1, together with the times
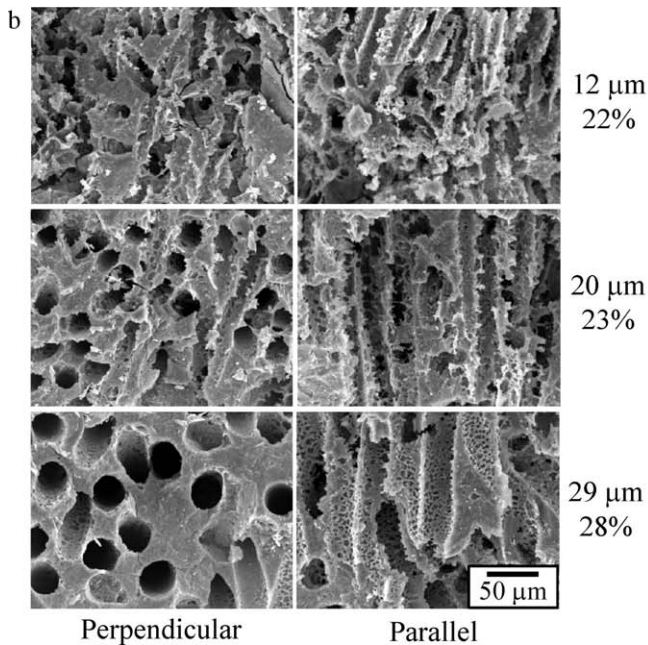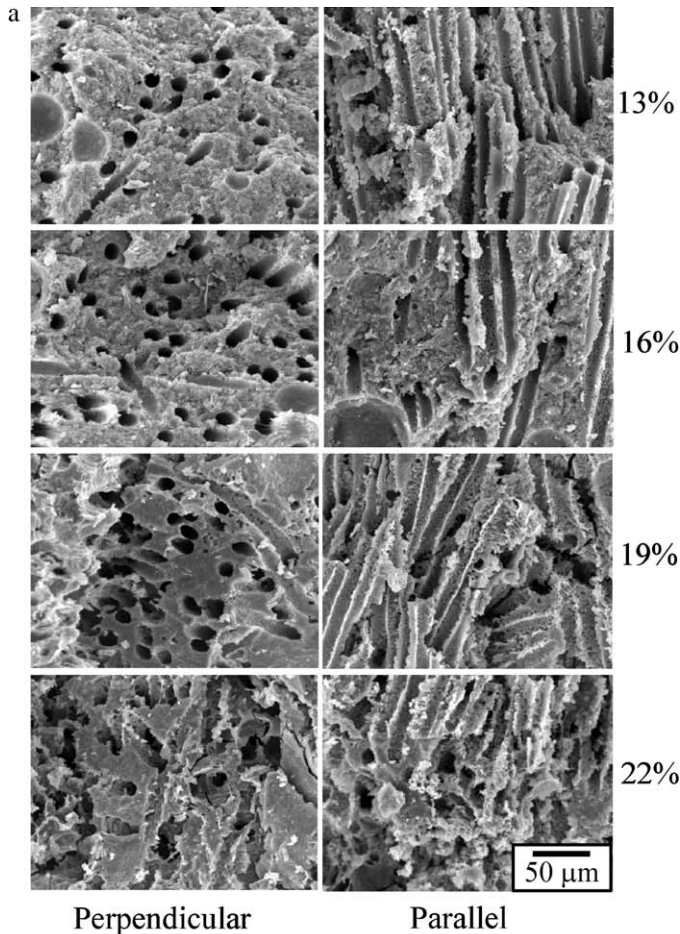
Fig. 4. SEM micrographs of fractured surfaces of samples perpendicular and parallel to the extrusion direction in geopolymers containing varying volumes of 12 μm fibers (a) and different fiber diameters (b).
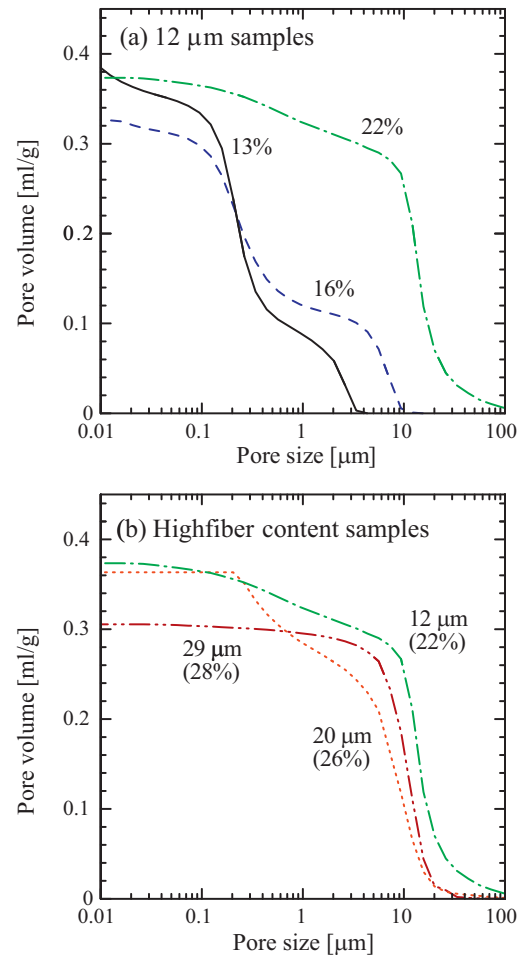

Fig. 5. Pore size distributions of the porous geopolymer samples containing 12 μm fibers (a) and samples with high fiber contents of different fiber diameters (b).

required to reach h_{eq} and 90% of h_{eq}. The capillary rise rate of the base geopolymer without introduced pores is very slow, with an estimated time to reach a value of $h_{eq} = 198$ mm of >1700 h. This poor capillary rise can be attributed to the contact angle, calculated from the data of Table 1 to be very close to 90°. This high contact angle may be due to the small pore size and also very rough surface of the pore surfaces. By contrast, the capillary rise of the porous geopolymers is higher, increasing with increasing volume of added fibers in the samples containing 12 μm fibers. This increase is thought to reflect the increased connectivity of the cylindrical pores. The effect of the cylindrical pore size in the porous geopolymers is less clear, but the capillary rise tends to increase with increasing fiber diameter. The calculated contact angles (θ) showed a certain tendency to decrease with increasing of capillary rise height (h_{eq}), which means lowering of the surface roughness but no reasonable explanation for this can be made in the moment. The geopolymer prepared using 28 vol% of 29 μm fibers showed the highest capillary rise, with an estimated h_{eq} of 1125 mm. This h_{eq} value is only slightly less than that found for lotus ceramics ($h_{eq} = 1290$ mm).[5] There are, however, differences in the capillary rise rates between the various porous geopolymers, the rate being much slower in the geopoly-
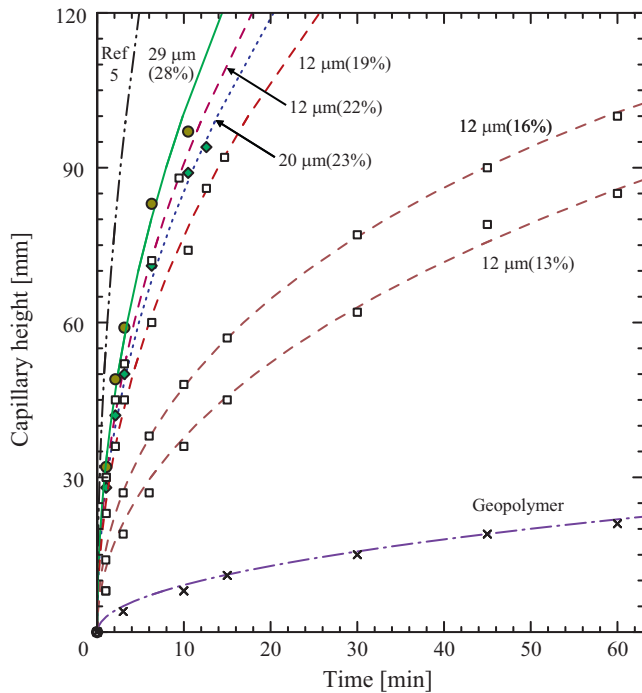
Fig. 6. Relationship between capillary rise height and rise time for the base geopolymer, various porous geopolymers and lotus ceramics.[5]

mer containing 28% of 29 μm fibers. This is due to the calculated effective pore radius (r) which is smaller in the geopolymer containing 28% of 29 μm fibers than in the lotus ceramics. The resulting r value in this geopolymer (2.5 μm) is at variance with the PSD data (5–10 μm radius), Fig. 5(b). We suggest that the smaller effective pore radius obtained from Eq. (1) is due to the effect of longer than ideal pathway lengths in the geopolymer. Since the fiber diameter used in the geopolymer containing 28% of 29 μm fibers is thinner than in the lotus ceramics (20 μm),[5] the degree of fiber orientation of the present sample is thought to be lower than in the lotus ceramics. This poor alignment of the cylindrical pores may however be improved by the use of an improved extruder similar to that used in the preparation of the lotus ceramics.

4. Conclusion

Geopolymers were prepared with varying H_2O/Al_2O_3 ratios and curing temperatures, and the effect of these variables on the bulk density and bending strength was investigated. Composites of geopolymers with PLA fibers were prepared using different sizes and volumes of fibers. Porous geopolymers were prepared by alkali and/or heat treatment of the resulting composites and their capillary rise properties were investigated, with the following results:

(1) The H_2O/Al_2O_3 ratio exerts a major effect on the physical properties; lower ratios produce increased bulk densities and bending strengths. The highest bending strength (35.8 ± 5 MPa) was achieved in a sample prepared with

$H_2O/Al_2O_3 = 9$ and cured at 90 °C. These conditions were therefore adopted for the preparation of composites of geopolymers with PLA fibers.
(2) The volume content of PLA fibers that can be introduced into the composites becomes greater with fibers of thicker diameter. The greatest possible fiber loading was 22, 26 and 28 vol% of fibers of 12, 20 and 29 μm diameter, respectively, but the numbers of fibers that could be mixed decreased with increasing fiber diameters.
(3) Removal of the fibers for pore formation was carried out by alkali, hydrothermal and/or heat treatments. A combination of alkali treatment at pH = 13 and heat treatment at 330 °C proved to be best for complete removal of the fibers with the least degradation of the microstructure of the resulting porous geopolymer.
(4) The capillary rise rates increased with increasing fiber volume and thicker fiber diameters. The estimated equilibrium capillary rise height (h_{eq}) of the sample containing 28 vol% of 29 μm diameter fibers was 1125 mm, and was the highest of the present porous geopolymers This rise height is only slightly lower than found for lotus ceramics.[5]

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