Research Article

Amazonian Metakaolin Reactivity for Geopolymer Synthesis

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To determine the viability of using a local resource for geopolymer synthesis, geopolymers were synthesized using metakaolin made from clay mined in the Amazonian region of Brazil. Samples were made with mixed potassium-sodium and pure sodium metakaolin-based geopolymer. Samples were also made using commercial metakaolin (CMK) from BASF, Inc. as a comparison to the Amazonian metakaolin (AMK). Scanning electron microscopy was used to investigate the microstructure of the materials. X-ray diffraction was able to confirm the formation of geopolymer. The mechanical properties of AMK material were nearly equivalent to those based on CMK. Neither CMK nor AMK reacted completely, although samples made with CMK showed less unreacted material. By increasing the mixing intensity and duration, the amount of residual unreacted material was substantially reduced, and mechanical properties were improved.

1. Introduction

Geopolymers (GPs) are inorganic polymers which can substitute for ordinary Portland cement (OPC) as an efficient binder with a lower carbon footprint. Metakaolin-based GPs are synthesized with calcined clays (source of aluminosilicate powders) activated by an alkali silicate solution mixed with an alkali hydroxide and polycondensed into inorganic polymers. Brazil has plentiful mineral reserves as a source of aluminosilicates.

GPs are processed in a similar manner to cements and concretes by mixing, molding, and curing. They can be cured at room temperature, but an optimal curing temperature range of 40 to 65°C has been reported [1–4]. The GPs exhibit higher mechanical properties than OPC, which are highly chemically stable (having enhanced durability) and are highly fire resistant to temperatures up to 1200°C [5, 6]. The GP production can use far less energy than OPC concrete. The manufacture of 1 ton of OPC emits about 1 ton of CO_2, while the manufacture of 1 ton of GP emits no more than 0.2 ton of CO_2 [7–11]. GP compressive strength of 100 MPa can be achieved after full 28 days of curing, while 70% of this strength can be attained within 4 hours [12]. Several researchers [13–15] studied the properties of metakaolin-based GPs including the effects of composition, processing, and microstructure.

Metakaolin (MK) is used as a supplementary cementitious material for OPC. It improves the durability of the resultant binder by reacting with calcium hydroxide to form hydrated calcium aluminates and silicon aluminates. Amazonian MK GP composites have been recently tested and confirmed as a potential green construction material [16–18].
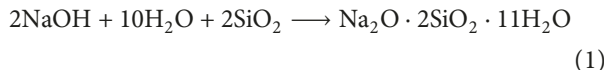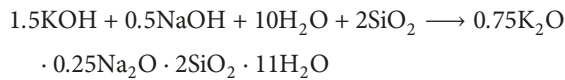
Gordon et al. [19] studied the similarities between a natural and a synthetic potassium-metakaolin-based geopolymers. While unreacted metakaolin sheets were visible in the naturally derived geopolymer, the synthetic geopolymer showed no unreacted sheet-like particles. Catauro et al. [20] concluded that a synthetic sol-gel derived aluminosilicate was more reactive than metakaolin, using particles with the same size (<80 μm). Poulesquen et al. [21] considered geopolymerization reactions by observation of the viscoelastic properties of the Na or K-metakaolin-based geopolymer, to determine the variation over time of the viscoelastic parameters, according to the geopolymer

composition. They found that sodium hydroxide accelerated the geopolymer curing kinetics compared with potassium hydroxide [21]. Sodium hydroxide activation solutions ensured better dissolution of the aluminosilicate source (MK) than did solutions of potassium hydroxide, which is nevertheless a stronger base [21–24]. Thus, the dissolution rate of the aluminosilicate source depends on the activation solution composition [21, 23].
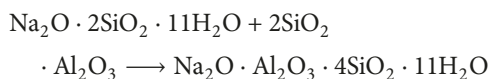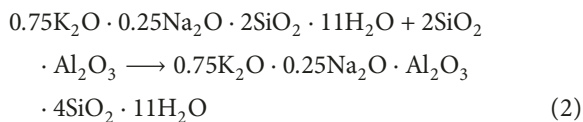
Previous work [18] on K-MK-based GPs reinforced with bamboo chopped fibers revealed a potential sustainable construction material. The present research used commercial (high-purity, high-reactivity) metakaolin (CMK) as a comparison to the Amazonian metakaolin (AMK) to determine the viability of using a local resource for geopolymer synthesis. Samples were made with mixed potassium-sodium and pure sodium metakaolin-based geopolymer at different mixing intensities and durations.

2. Materials and Methods

2.1. Geopolymer Composite Synthesis. Three distinct batches of mixed potassium-sodium AMK and CMK, and pure sodium AMK silicate solutions were made by mixing fumed silica (Cab-O-Sil EH-5 Cabot Corp, Tuscola, IL) with mixed K-NaOH or pure NaOH pellets (Fisher Scientific Waltham, MA, USA), respectively, dissolved in deionized water according to the reactions:

$$1.5\text{KOH} + 0.5\text{NaOH} + 10\text{H}_2\text{O} + 2\text{SiO}_2 \longrightarrow 0.75\text{K}_2\text{O}$$
$$\cdot\, 0.25\text{Na}_2\text{O} \cdot 2\text{SiO}_2 \cdot 11\text{H}_2\text{O}$$

$$2\text{NaOH} + 10\text{H}_2\text{O} + 2\text{SiO}_2 \longrightarrow \text{Na}_2\text{O} \cdot 2\text{SiO}_2 \cdot 11\text{H}_2\text{O}$$
$$(1)$$

The three batches of alkali-MK-based GPs are described in Table 1. Geopolymers K-Na-AMK67/CKM were prepared by mixing K-Na water glass and metakaolin mixed in a high-shear mixer (IKA mixer, Model RW20DZM, Germany) for 3 minutes at 600 rpm, plus 2 minutes at 1100 rpm, plus 1 minute at 1600 rpm, in order to obtain good mixing of the components. Na-AMK76 GP was prepared by mixing Na water glass and MK (Figure 1) with a high-shear mixer for 7 minutes at 2400 rpm, cooled down for 2 minutes in a freezer (at −10°C), then mixed another 7 minutes at 2400 rpm. The slurry was then put in a planetary conditioning mixer (Thinky ARE-250, Intertronics, Kidlington, Oxfordshire, UK) that further mixed and degassed the slurry for removal of fine bubbles. The geopolymerization reactions could be summarized as follows:

$$0.75\text{K}_2\text{O} \cdot 0.25\text{Na}_2\text{O} \cdot 2\text{SiO}_2 \cdot 11\text{H}_2\text{O} + 2\text{SiO}_2$$
$$\cdot\, \text{Al}_2\text{O}_3 \longrightarrow 0.75\text{K}_2\text{O} \cdot 0.25\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3$$
$$\cdot\, 4\text{SiO}_2 \cdot 11\text{H}_2\text{O} \qquad (2)$$
$$\text{Na}_2\text{O} \cdot 2\text{SiO}_2 \cdot 11\text{H}_2\text{O} + 2\text{SiO}_2$$
$$\cdot\, \text{Al}_2\text{O}_3 \longrightarrow \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 11\text{H}_2\text{O}$$

Unreinforced geopolymer slurry was poured into a high-strength Delrin® mold attached to a vibration table (FMC

Syntron vibrating table, FMC Technologies, Houston, TX) to achieve a more uniform distribution and less void formation. The filled mold was closed by a Delrin® plate and wrapped in a plastic food service film to prevent water loss during setting and curing. It was then cured for 24 hours at 50°C in a laboratory oven. Then, the samples were demolded and set to dry at room temperature until testing.

2.2. Compressive Strength. Nine cylindrical specimens for each of the three batches of 5 mm diameter and 12 mm height were tested in accordance with ASTM C1424-10 [26]. Tests were carried out on an Instron-5882 testing machine, with 2-kN load cell, located in the Ceramics Laboratory at UIUC. The test crosshead speed was 0.0001 mm·s^{-1}. Strain was calculated from crosshead displacement.

2.3. Flexural Strength. Seven Na-AMK76 geopolymer specimens $(55 \times 10 \times 10\,\text{mm})$ were tested in three-point bending to obtain their flexural strength, based on ASTM standard C1341-13 [27]. Tests were carried out in an Instron-5882 testing machine, equipped with a 2-kN load cell, located in the Ceramics Laboratory at UIUC. The test span-to-depth ratio was 4:1, and the crosshead displacement rate was 0.010 mm·s^{-1}. Strain was measured by crosshead displacement, as was done in previous work [18].

2.4. Materials Characterization. Materials characterization followed the procedures described by SáRibeiro et al. [18] and is reproduced below.

Imaging and fractography of posttested geopolymer matrix were qualitatively analyzed by scanning electron microscopy (SEM) (JSM-6060LV JEOL USA, Inc., Peabody, MA). The geopolymer samples were put in a dessicator connected to a vacuum pump under a 30 in Hg vacuum for at least 24 hours in order to avoid outgassing in the SEM. After that, samples were Au/Pd sputter-coated before analysis to avoid any charging in the SEM.

X-ray diffraction (XRD) was used for phase characterization of pure geopolymers. XRD was performed on a Siemens/Bruker D-5000 Model with a copper K-alpha radiation wavelength of 0.15418 nm using an aluminum holder. XRD was carried out according to the following parameters: scan speed 1 deg·min^{-1} with 0.05° increments and the scan type was locked in a coupled configuration.

3. Results and Discussion

Compressive and flexural strength results for the present work are shown in Tables 2 and 3. The Weibull probability plots (Figure 2) of the compressive and flexural strength test data resulted in a straight line with high coefficients of determination of 92.6% and 89.9%, respectively, which denoted that Weibull statistics could be used to analyze the data. The average Weibull value of the compressive (σ_c) and three-point flexural strengths (σ_f) for the Na-AMK76 geopolymer tested specimens were 83.37 MPa and 10.49 MPa, respectively, as shown in Tables 2 and 3. A plot of

TABLE 1: Geopolymer batches compositions.

GP batches	Descriptions	Compositions wt% [25]				
		Na_2O	K_2O	Al_2O_3	SiO_2	H_2O
K-Na-AMK67	76% pure AMK/24% quartz; 75% K, 25% Na	2.1	9.6	20.7	40.7	26.9
K-Na-CMK	Metamax® MK, $Al_2O_3 \cdot 2SiO_2$, particle size 1.3 μm; 75% K, 25% Na	2.5	11.3	16.3	38.4	31.6
Na-AMK76	76% pure AMK/24% quartz, particle size 4.7 μm; 100% Na	9.2		19.9	41.4	29.5

FIGURE 1: Amazonian metakaolin composed of 76% MK and 24% quartz.

TABLE 2: Compressive strength test results and Weibull parameters.

GP	Modulus β shape	Scale σ_o (MPa)	$\sigma_{c\text{-avg}}$ (MPa)	SD (MPa)	L95% (MPa)	U95% (MPa)
KNa-AMK67	9.50	60.90	57.81	7.30	53.63	62.42
KNa-CMK	6.63	75.32	70.25	12.42	64.26	77.68
Na-AMK76	5.02	90.78	83.37	19.04	73.13	95.51

TABLE 3: Three-point flexural strength test results and Weibull parameters.

GP	Modulus β shape	Scale σ_o (MPa)	$\sigma_{f\text{-avg}}$ (MPa)	Std. dev. (MPa)
Na-AMK76	10.29	11.02	10.49	1.23

the Weibull average values of the compressive strength for the three batches is presented in Figure 3. Na-AMK76 GP compressive strength was 19% and 44% stronger than KNa-CMK and KNa-AMK67 GPs, respectively. The flexural strength result was considered to be high for a pure brittle GP, while it was much less variable, and the Weibull modulus was high.

All flexural strength tested samples showed the initial vertical crack located at the high tensile central point (Figure 4(a)). The samples exhibited sudden failure, characteristic of pure geopolymers and ceramics which fail suddenly without any warning (Figure 4(b)).

Test results demonstrated the great effect of highly reactive Amazonian metakaolin on geopolymer strength. SEM micrographs of the structure of the tested geopolymer matrices are seen in Figure 5. Characteristic drying cracks are present in all three matrices. Na-AMK76 geopolymer matrix showed much higher reactivity than did the other K-Na-AMK matrices, with much less unreacted MK. This higher Na-AMK reactivity was influenced by the higher GP synthesis mixing time (14 min) and speed (2500 rpm). Consistent with this finding, several researchers also reported faster GP setting times with sodium hydroxide solutions and better dissolution of metakaolin than with solutions of potassium hydroxide [21–24].

An X-ray diffractogram for K-Na-AMK67-based geopolymer is presented in Figure 6. The XRD pattern shows the geopolymer to be 81.9% X-ray amorphous with a pronounced hump at 28° 2θ, which confirmed geopolymer formation plus 18.1% quartz crystalline phases at room temperature. The quartz was present in the native kaolinite sample.
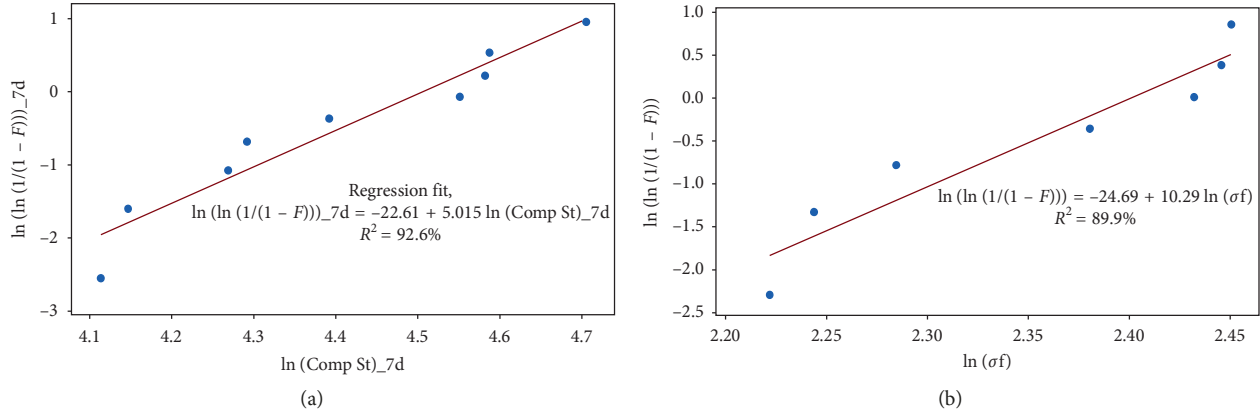
(a)

(b)

FIGURE 2: Weibull plot for (a) compressive and (b) 3-point flexural strength data for Na-AMK76 geopolymer.
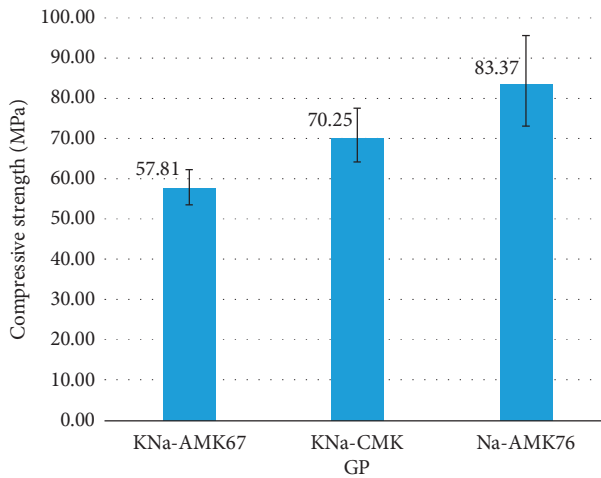

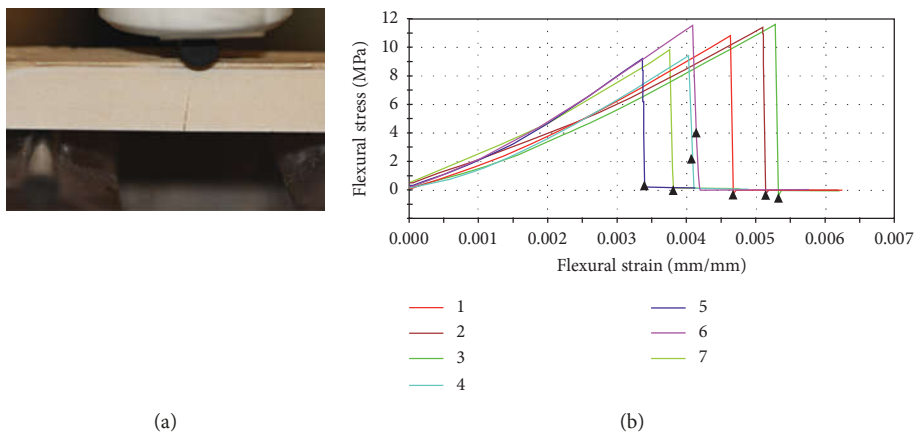FIGURE 3: Weibull plot for average compressive strengths of tested geopolymer batches.

(a)

(b)

FIGURE 4: Na-AMK76 geopolymer tested in three-point bending (a) failure mode and (b) stress-strain curves.

4. Conclusions

This investigation on the viability of using an indigenous resource for geopolymer synthesis resulted in the following findings:

(1) SEM micrographs revealed that is better to use sodium hydroxide solutions for AMK-based geopolymer matrix. NaOH solutions offered better rheological behavior (faster setting time) and were less expensive than KOH solutions.
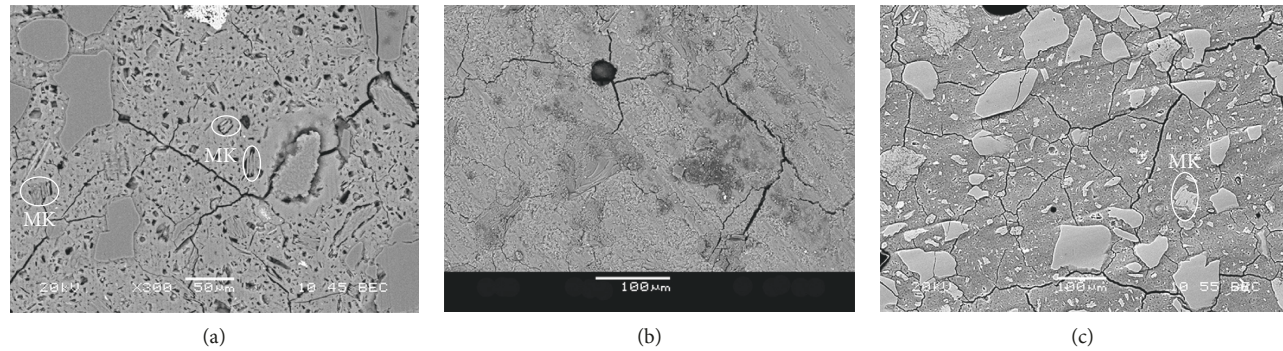
FIGURE 5: SEM micrographs of geopolymer specimens, showing unreacted MK (encircled) (a) K-Na-AMK67, (b) K-Na-AMK76, (c) Na-AMK76.
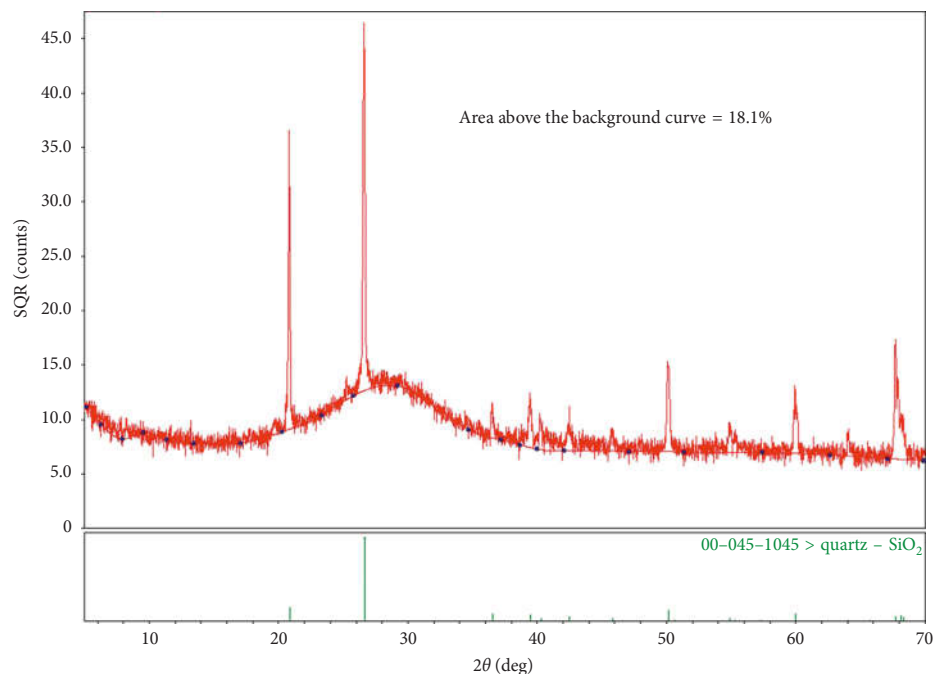

FIGURE 6: X-ray diffraction pattern of geopolymer matrix confirming its 81.9% amorphous nature and the presence of 18.1% crystalline quartz present in the natural kaolinite sample.

(2) SEM revealed near to fully reactive Amazonian MK Na-GP matrix, resulting in high 1-day compressive strength of 83.4 MPa and flexural strength of 10.5 MPa. Test results demonstrated the great effect of highly reactive AMK on GP strength.

(3) XRD pattern of the GP matrix confirmed the 81.9% amorphous geopolymer formation with a hump at 28° 2θ and presence of 18.1% crystalline quartz in the native kaolinite.

(4) Amazonian MK was a viable precursor for geopolymer synthesis.

The utilization of regional and indigenous materials in the production of geopolymeric composites may reduce environmental impacts and raise their practicality.

Data Availability

The materials composition and compressive and flexural strength results data used to support the findings of this study are included within the article. The data of compressive and flexural strengths for all three batches used to support the findings of this study are available from the corresponding author upon request.

Disclosure

Part of this work was presented at the American Ceramic Society 41st International Conference and Exposition on Advanced Ceramics and Composites.

Conflicts of Interest

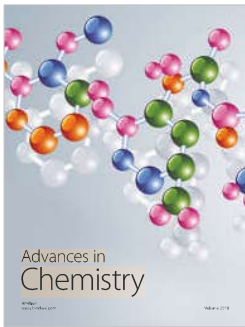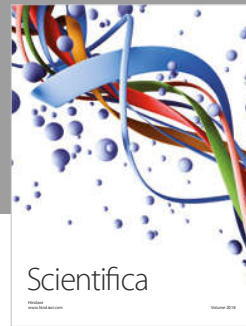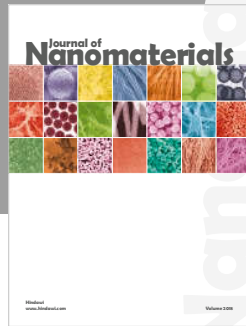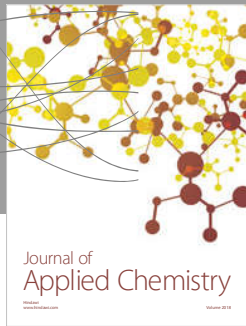The authors declare that they have no conflicts of interest.

Acknowledgments

References

[1] J. Davidovits, "Geopolymers," *Journal of Thermal Analysis*, vol. 37, no. 8, pp. 1633–1656, 1991.

[2] J. Davidovits, "30 years of success and failures in geopolymer applications–market trends and potential breakthroughs," in *Proceedings of Geopolymer 2002 Conference Keynotes*, pp. 1–15, Melbourne, Australia, October 2002.

[3] W. M. Kriven, "Inorganic polysialates or "geopolymers"," *American Ceramic Society Bulletin*, vol. 89, no. 4, pp. 31–34, 2010.

[4] J. Davidovits, "Carbon-dioxide greenhouse-warming: what future for Portland cement," in *Proceedings of Emerging Technologies Symposium on Cements and Concretes in the Global Environment*, p. 21, March 1993.

[5] J. Davidovits, "Geopolymer cement to minimize carbon-dioxide greenhouse-warming," in *Cement-Based Materials: Present, Future and Environmental Aspects, Ceramic Transactions*, vol. 37, pp. 165–182, American Ceramic Society, Westerville, OH, USA, 1993.

[6] P. Duxson, J. L. Provis, G. C. Lukey, and J. S. J. van Deventer, "The role of inorganic polymer technology in the development of "green concrete"," *Cement and Concrete Research*, vol. 37, no. 12, pp. 1590–1597, 2007.

[7] J. S. J. van Deventer, J. L. Provis, P. Duxson, and D. G. Brice, "Chemical research and climate change as drivers in the commercial adoption of alkali activated materials," *Waste and Biomass Valorization*, vol. 1, no. 1, pp. 145–155, 2010.

[8] J. Davidovits, *Geopolymer Cement, A Review*, Institut Géopolymère, St. Quentin, France, 2013, http://www.geopolymer.org/fichiers_pdf/GPCement2013.pdf.

[9] V. F. F. Barbosa and K. J. D. MacKenzie, "Thermal behaviour of inorganic geopolymers and composites derived from sodium polysialate," *Materials Research Bulletin*, vol. 38, no. 2, pp. 319–331, 2003.

[10] P. Duxson, J. L. Provis, G. C. Lukey, S. W. Mallicoat, W. M. Kriven, and J. S. J. van Deventer, "Understanding the relationship between geopolymer composition, microstructure and mechanical properties," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 269, no. 1–3, pp. 47–58, 2005.

[11] P. Duxson, S. W. Mallicoat, G. C. Lukey, W. M. Kriven, and J. S. J. van Deventer, "The effect of alkali and Si/Al ratio on the development of mechanical properties of metakaolin-based geopolymers," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 292, no. 1, pp. 8–20, 2007.

[12] P. Duxson, A. Fernández-Jiménez, J. L. Provis, G. C. Lukey, A. Palomo, and J. S. J. van Deventer, "Geopolymer technology: the current state of the art," *Journal of Materials Science*, vol. 42, no. 9, pp. 2917–2933, 2006.

[13] E. Rill, D. R. Lowry, and W. M. Kriven, "Properties of basalt fiber reinforced geopolymer composites," in *Strategic Materials and Computational Design*, W. M. Kriven, Y. Zhou, and M. Radovic, Eds., vol. 31 of Ceramic Engineering and Science Proceedings, pp. 57–69, John Wiley & Sons, Hoboken, NJ, USA, 2010.

[14] W. M. Kriven, "Geopolymer-based composites," in *Ceramics and Carbon Matrix Composites*, M. Rugles-Wrenn, P. W. R. Beaumont, and C. H. Zweben, Eds., vol. 5 of Comprehensive Composite Materials II, Elsevier, Oxford Academic Press, London, UK, 2018.

[15] S. S. Musil, P. F. Keane, and W. M. Kriven, "Green composite: sodium-based geopolymer reinforced with chemically extracted corn husk fibers," in *Developments in Strategic Materials and Computational Design IV*, W. M. Kriven, J. Wang, Y. Zhou, and A. L. Gyekenyesi, Eds., vol. 34 of Ceramic Engineering and Science Proceedings, pp. 123–133, John Wiley & Sons, Hoboken, NJ, USA, 2014.

[16] R. A. Sá Ribeiro, M. G. Sá Ribeiro, K. Sankar, and W. M. Kriven, "Geopolymer-bamboo composite - a novel sustainable construction material," *Construction and Building Materials*, vol. 123, pp. 501–507, 2016.

[17] R. A. Sá Ribeiro, M. G. Sá Ribeiro, K. Sankar, G. P. Kutyla, and W. M. Kriven, "Mixed alkali regional metakaolin-based geopolymer," in *Developments in Strategic Ceramic Materials II*, pp. 123–133, vol. 37 of Ceramic Engineering and Science Proceedings, pp. 123–133, John Wiley & Sons, Hoboken, NJ, USA, 2017.

[18] R. A. Sá Ribeiro, M. G. Sá Ribeiro, K. Sankar, and W. M. Kriven, "Bamboo-geopolymer composite: a preliminary study," in *Developments in Strategic Ceramic Materials II*, vol. 37, no. 7, pp. 135–143, John Wiley & Sons, Hoboken, NJ, USA, 2017.

[19] M. Gordon, J. Bell, and W. M. Kriven, "Comparison of naturally and synthetically-derived potassium-based geopolymers," in *Ceramic Transactions Series*, Vol. 165, pp. 95–106, American Ceramic Society, Westerville, OH, USA, 2005.

[20] M. Catauro, F. Bollino, A. Dell'Era, and S. V. Ciprioti, "Pure $Al_2O_3 \cdot 2SiO_2$ synthesized via a sol-gel technique as a raw material to replace metakaolin: chemical and structural characterization and thermal behavior," *Ceramics International*, vol. 42, no. 14, pp. 16303–16309, 2016.

[21] A. Poulesquen, F. Frizon, and D. Lambertin, "Rheological behavior of alkali-activated metakaolin during geopolymerization," *Journal of Non-Crystalline Solids*, vol. 357, no. 21, pp. 3565–3571, 2011.

[22] A. Hajimohammadi, J. L. Provis, and J. S. J. van Deventer, "Effect of alumina release rate on the mechanism of geopolymer gel formation," *Chemistry of Materials*, vol. 22, no. 18, pp. 5199–5208, 2010.

[23] C. Li, H. Sun, and L. Li, "A review: the comparison between alkali-activated slag (Si+Ca) and metakaolin (Si+Al) cements," *Cement and Concrete Research*, vol. 40, pp. 1341–1349, 2010.

[24] H. Xu and J. S. J. van Deventer, "The effect of alkali metals on the formation of geopolymeric gels from alkali-feldspars," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 216, no. 1–3, pp. 27–44, 2003.

[25] R. A. Sá Ribeiro, M. G. Sá Ribeiro, and W. M. Kriven, "A review of particle- and fiber-reinforced metakaolin-based geopolymer composites," *Journal of Ceramic Science and Technology*, vol. 48, no. 3, pp. 307–322, 2017.

[26] American Society for Testing and Materials (ASTM), *Standard Test Method for Monotonic Compressive Strength of Advanced Ceramics at Ambient Temperature*, ASTM Designation C1424 – 10, ASTM, West Conshohocken, PA, USA, 2015.

[27] American Society for Testing and Materials (ASTM), *Standard Test Method for Flexural Properties of Continuous Fiber-Reinforced Advanced Ceramic Composites*, ASTM C1341–13, ASTM, West Conshohocken, PA, USA, 2013.

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