FACILE SYNTHESIS OF ORGANOSILOXANE-MODIFIED HYDROPHOBIC GEOPOLYMER THROUGH PEPTIZATION OF POLYDIMETHYLSILOXANE

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Abstract

We report a scalable, facile synthetic process for hydrophobic geopolymer containing organosilane. Using polydimethylsiloxane (PDMS) as an organic precursor, the surface of sodium and potassium geopolymers of varying precursor composition was functionalized with degraded PDMS oligomers by first partially hydrolyzing PDMS in a hot, concentrated NaOH or KOH solution and subsequently by undergoing geopolymer synthesis with metakaolin. Both types of geopolymer yielded nonporous hydrophobic materials with external surface areas of 0.6475 and 4.342 m^2/g for sodium and potassium geopolymer, respectively. The materials showed an oil capacity of 75 and 134 wt%, respectively. X-ray diffraction patterns of the samples indicate that the PDMS functionalized sodium geopolymers contain zeolite A and sodalite, while the potassium geopolymers were amorphous with two overlapping broad humps in contrast to the typical geopolymers.

Keywords: metakaolin, geopolymers, synthesis, surface modification, zeolites, amorphous structure

Introduction

The production of organic/inorganic hybrid materials, such as organically modified silicates (ORMOSILs), is a major emerging field within materials chemistry [1]. The possibility of creating such materials within geopolymer research has been relatively less explored. Geopolymers are inorganic nanomaterials that consist of highly porous amorphous aluminosilicate frameworks with smaller aluminosilicate clusters on the nanometer scale [2-5]. Given that the geopolymer synthesis closely resembles the sol-gel chemistry of silica, we suspect that it would be possible to create a new type of geopolymer-based organic/inorganic hybrid materials. Indeed, the production of such materials has been reported by using various crosslinking silanes [6, 7], as well as oligomeric polysiloxanes [8].

In contrast to the readily crosslinking silanes, the incorporation of chemical-resistant siloxanes into geopolymer network structure is more challenging but would provide a new way of utilizing used silicone oil, polydimethylsiloxane (PDMS). Approximately a half million tones of silicone oils were produced in 2018 [9], but silicone oils have a low recycling rate because it does not meet the same refining and performance standards as unused oil. Disposal to landfills is not ideal as it does not decompose in the natural environment, and its high thermal stability makes it inefficient to depolymerize and upcycle [10]. The production of geopolymer is highly scalable and the ability to incorporate potentially used silicone oil gives these materials potential for sustainable large-scale application. Using recycled silicon oil in the proposed geopolymer materials would increase the recycling rate of the oil while also providing the material its hydrophobic character.

Our specific synthetic approach for geopolymer/PDMS hybrid material involves first heating and stirring PDMS in a strong alkali solution. Under such conditions, PDMS can be hydrolyzed into smaller oligomers with anionic ends [11]. Metakaolin (a calcined kaolin clay) powder is added to the PDMS/alkali solution and homogenized using a high-shear mixer. After homogenization, the mixture is heated in a closed container at 90 °C to form the PDMS-functionalized geopolymer product. Finally, the product is filter-washed with water, ethanol, and toluene to remove any excess organics and then dried for further characterization.

Experimentals
Synthesis

For the potassium geopolymer, samples were prepared by dissolving the precursor potassium hydroxide (Sigma-Aldrich; ACS reagent, ≥85%) in 200 mL of ethanol (Sigma-Aldrich; ACS reagent, ≥99.5%). The solution was added to the PDMS (Sigma-Aldrich; poly(dimethylsiloxane), hydroxy terminated: viscosity ~65 cSt) in a sealable bottle and stirred at 80 °C for 24 hours. The solution was then placed in the rotary evaporator with an 80 °C bath and 120 rpm rate to remove the ethanol. After evaporation, the PDMS and potassium hydroxide were added to a beaker containing the precursor water. The shear mixer was used to stir the solution at 200 rpm while the metakaolin powder (BASF, MetaMax®) was slowly added until homogenous. Once all the metakaolin was added, the mixing rate was increased to 600 rpm and allowed to continue for 40 minutes. Equal parts of the mixture were then put into two centrifuge tubes and placed in a 90 °C oven. One half of the total mixture was heated for 24 hours and the other 72 hours. After heating, each sample was filter washed with water, ethanol, and toluene to remove excess alkali and organic chemicals. The same procedure was repeated for the sodium geopolymer samples, replacing the potassium hydroxide with sodium hydroxide

(Sigma-Aldrich; ACS reagent, ≥97%). **Table 1** shows the nominal compositions of every prepared sample in addition to the silicon source ratios.

Table 1. Nominal molar ratios of precursor mixtures with respect to aluminum and the molar ratios of the silicon sources, metakaolin and PDMS.

Molar Composition				Si Source Ratio (metakaolin:PDMS)
Na/K	Al	Si	H_2O	
4	1	3	22	1:2
4	1	2	28	1:1
3	1	2	24	1:1
3	1	4	32	1:3
3	1	2.7	15	1:1.7
2.5	1	2	22	1:1
2	1	2	20	1:1

Characterization

      The geopolymer powders were created into disk-shaped pellets using a hydraulic press pelletizer. As pellets, water drops were placed upon their surface to observe the hydrophobicity of each sample. The samples that absorbed the least amount of water were selected for further analysis. Gas sorption analysis was conducted on the most hydrophobic composition to determine the porosity and surface area of the materials. SEM images of those samples were taken in tandem with EDX analysis to analyze the microstructures of each sample. The oil capacity of these samples was measured using dibutyl phthalate as the oil. Droplets of oil were slowly added to a known mass of geopolymer powder by using spatula rub-out test (ASTM D281-12(2021)). The powder was mixed with the oil after every droplet, and the addition stopped when no more oil was being absorbed by the sample. XRD analysis was conducted on the materials to determine if they had any crystal structure. This allowed for a comparison of the effects nominal molar composition and reaction time had on the final structure of the materials.

Results and Discussion

      Success at functionalizing the surface of geopolymer with organic silane saw its first indication with the hydrophobic nature of the powder product created from the new synthesis procedure. Forming the powders into pellets allowed for more consistent and reliable observation and comparison to determine which molar compositions created the most promising products. By creating pellets out of the PDMS-modified geopolymer, the hydrophobicity of each composition could be observed. It was found that the 3:1:4:32 nominal composition produced the most hydrophobic material. The sodium-containing sample of the most hydrophobic composition is shown in **Figure 1**. The oil capacity measurement was conducted on the most hydrophobic composition for the 24-hour reaction time samples. The

materials showed an oil capacity of 75 and 134 wt%, respectively, for the sodium and potassium geopolymers.
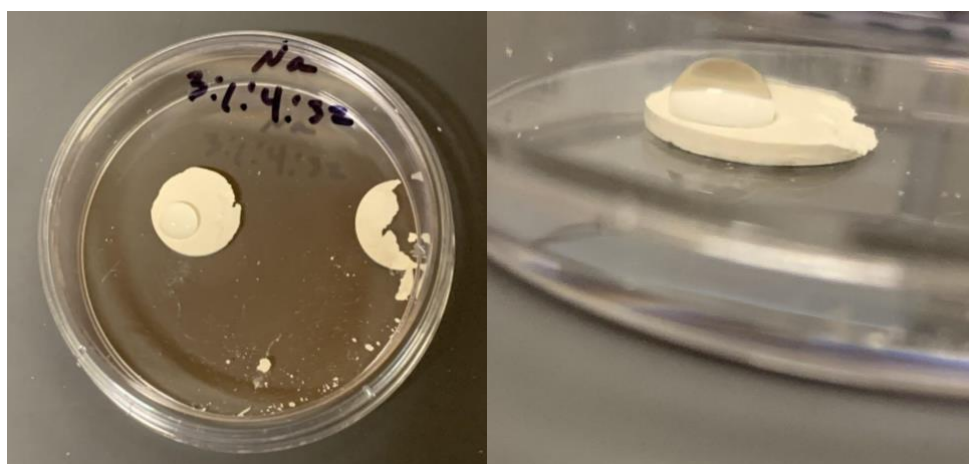

Fig. 1. Image from above and from the side of a PDMS-modified sodium geopolymer pellet with nominal molar composition 3:1:4:32 that was cured for 24 hours.

The gas sorption analysis was conducted on the most hydrophobic composition for both the sodium and potassium geopolymers. Nitrogen was used to determine the BET surface area and BJH pore size and volume. The data for the 3:1:4:32 samples with 24 hour reaction time are shown below. Next steps involved determining whether the products with organics incorporated still had high surface area. The data in **Table 2** show very low surface areas for both sodium and potassium geopolymers functionalized with PDMS.

Table 2. Gas sorption data for the 3:1:4:32 PDMS modified geopolymer compositions with 24-hour reaction time.

	BET Surface Area (m^2/g)	t-Plot External Surface Area (m^2/g)	BJH Desorption cumulative pore volume (cm^3/g)	BJH Desorption average pore diameter (nm)
NaGP	0.65	0.88	0.001	9.0
KGP	4.3	6.4	0.02	15

Following the surface area analysis, SEM images of the most hydrophobic samples were taken. **Figure 2** shows images of the 3:1:4:32 compositions of sodium geopolymer and potassium geopolymer, respectively. The SEM images explained in part the observed low surface areas. Micron-sized particles were present in both types of organic modified geopolymer. In addition, thin sheet-like structures were present which indicated that there was unreacted metakaolin still present after the reaction supposedly reached a conclusion. The unreacted metakaolin was present in samples with 24-hour reaction times and 72-hour reaction times. These observations are in stark contrast to the previous reports on the production of

geopolymer nanomaterials with high surface areas in which no PDMS was used but with the same precursor compositions [12-15].
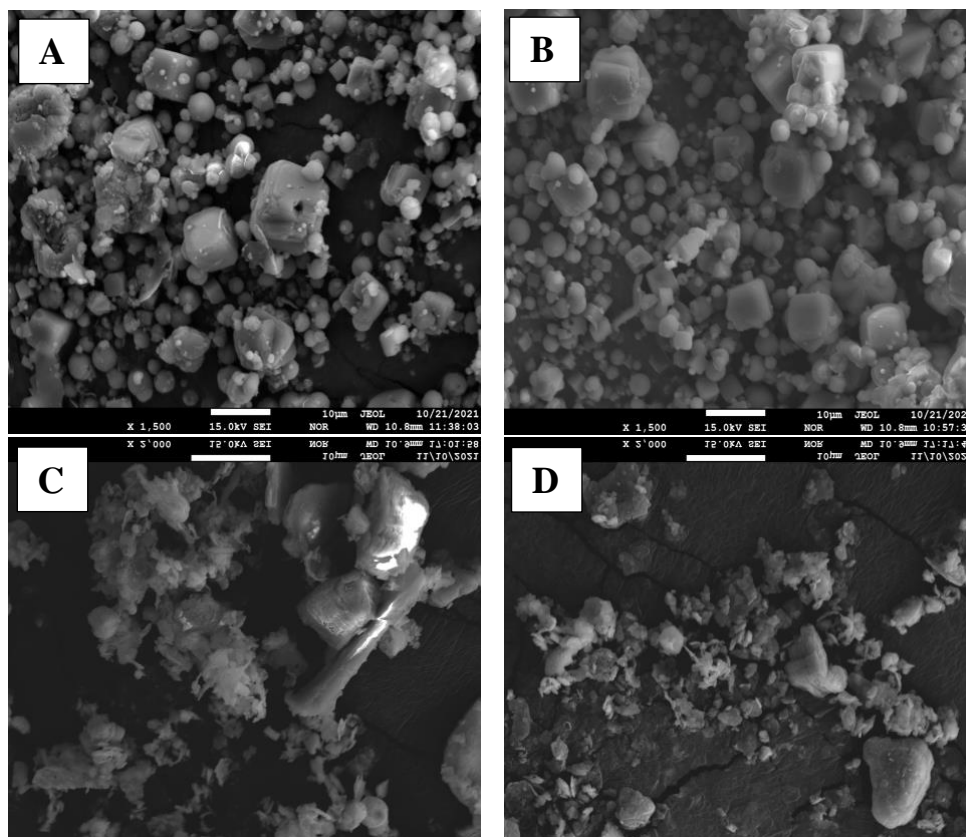

Fig. 2. SEM images of PDMS modified geopolymers with nominal molar composition Na(K):Al:Si:H$_2$O = 3:1:4:32. Pictured is sodium geopolymer with a 24-hour reaction time (A) and 72-hour reaction time (B) and potassium geopolymer with a 24-hour reaction time (C) and 72-hour reaction time (D).

Powder XRD patterns were obtained for all the prepared samples. Comparisons were made between different compositions and reaction times and it was found that there were few differences in diffraction patterns between different compositions and reaction times. In **Figure 3**, the patterns of the 4:1:2:28 and 2:1:2:20 samples were shown after 24 and 72 hours of heating, as representatives. The peaks of the patterns for sodium geopolymer were matched consistently to zeolite A and sodalite structures, as shown in Figure 4 for the sodium geopolymer of molar composition 4:1:2:28 after 24 hours of heating. It is noted that there is an appreciable amount of amorphous phases, judging from the uneven background, especially in the region of $2\theta = 20 - 30°$.
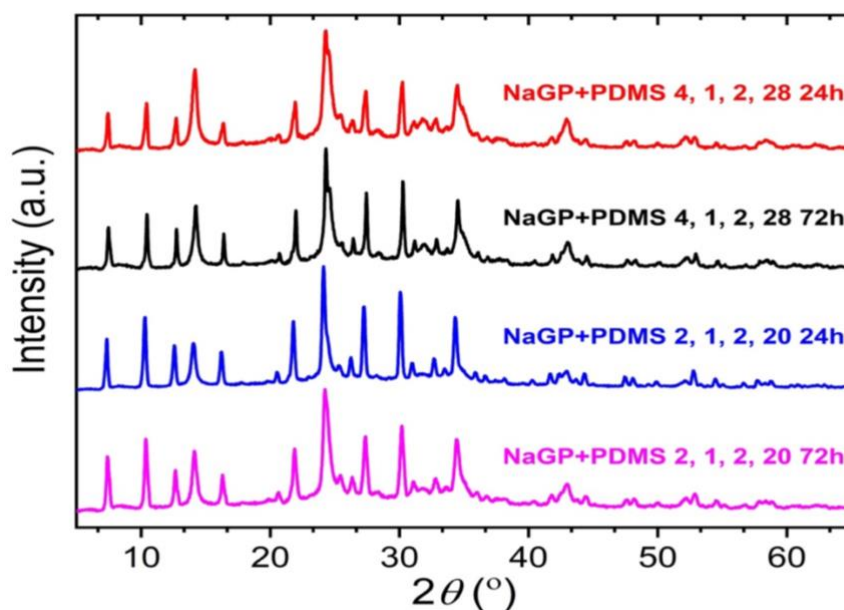
Fig. 3. Powder XRD patterns for the sodium geopolymer compositions with molar ratios 4:1:2:28 and 2:1:2:20.
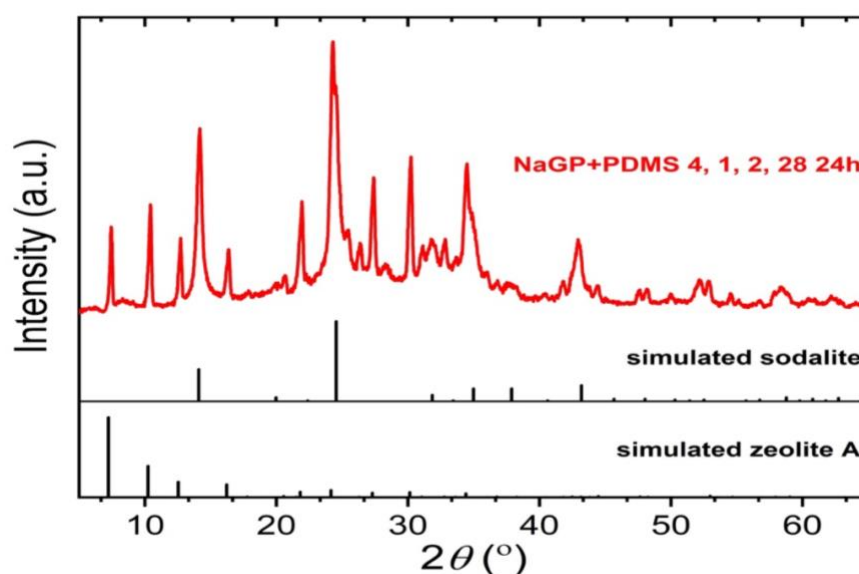

Fig. 4. Powder XRD pattern for the sodium geopolymer of molar composition 4:1:2:28 after 24 hours of heating, with reference peak positions for zeolite A (red) and sodalite (blue).

Meanwhile, all the powder XRD patterns of the potassium geopolymer samples showed that the products were amorphous. In **Figure 5**, the patterns of 3:1:4:32, 4:1:2:28, and 2:1:2:20 samples were shown after 24 hours of heating, as representatives. They show a broad hump with a maximum intensity at $2\theta \sim 29°$ and a small shoulder around $26°$. The maximum intensity position is slightly higher than the typical position ($28°$) found for a typical potassium geopolymer, while the shoulder corroborates the presence of unreacted metakaolin observed in the SEM studies (**Figure 2**).
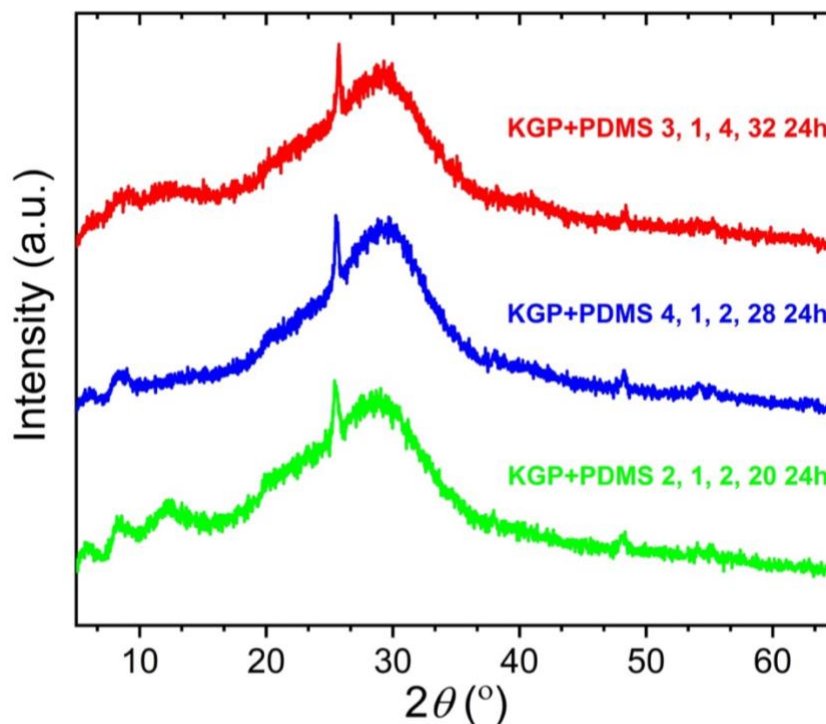
Fig. 5. Powder XRD patterns of the PDMS-modified potassium geopolymers with 24-hour reaction times and molar ratios of 3:1:4:32 (top), 4:1:2:28 (middle), and 2:1:2:20 (bottom).

Conclusion

We have shown that poly(dimethylsiloxane) (PDMS) polymer can be incorporated in geopolymer, imparting a hydrophobicity to the geopolymer, through a new scalable synthetic procedure. While the PDMS is highly stable against decomposition or hydrolysis, the pretreatment of the PDMS in ethanol at 80 °C allowed the production of reactive PDMS oligomers which subsequently blended with other geopolymer precursors. The products were in the form of powder particles that were highly hydrophobic, showing significant oil absorption capacity, although their external surface area is very small. The changes in the tested precursor compositions did not affect the nature of the products. The sodium geopolymer products were mainly zeolite A and sodalite, while the potassium geopolymers were all amorphous. The results are promising in the utilization of PDMS, including recycled PDMS, in the production of functional geopolymer materials.

Acknowledgments

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