

SOLIDIFICATION OF ORGANIC OIL WASTE IN METAKAOLIN-BASED GEOPOLYMER USING GRAPHENE OXIDE STABILISED PICKERING EMULSION

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ABSTRACT

This research focuses on incorporating and solidifying organic oil waste into metakaolin-based geopolymer using a pre-emulsification technique. Graphene oxide has been utilised as Pickering particles to stabilise the emulsion during the pre-emulsification of oil with an alkali activator solution. The prepared samples underwent various experimental procedures, and the creaming index was determined to evaluate the stability of Pickering emulsions. The results demonstrated that the graphene oxide-stabilised Pickering emulsion exhibited excellent stability, and the emulsified organic waste oil could be successfully incorporated within a metakaolin-based geopolymer.

Keywords: Organic oil waste, Solidification, Pickering emulsion, Geopolymer

1. INTRODUCTION

Solidification is employed to prevent or retard the release of hazardous contaminants from waste. This method aims to prevent harmful contaminants from leaching above a specified level rather than actively destroying the contaminants. Solidification of industrial waste in construction materials is a trending research topic, with numerous researchers focusing on incorporating organic and inorganic wastes in cementing materials [1]. The inclusion of organic liquids, particularly organic oils, in Ordinary Portland Cement (OPC) significantly impedes the hydration process of the cement, resulting in a notable reduction in the strength of the final cementitious product [2]. Therefore, selecting an appropriate material to accommodate and limit the leaching of solidified organic liquid is necessary.

Geopolymer has recently received much attention in various applications, especially cement-free concrete and radioactive waste encapsulation [3]. Geopolymer is an amorphous to semi-crystalline, inorganic aluminosilicate material. Geopolymerisation is a mechanism that occurs when aluminosilicate materials react with a high concentration of alkali-activated solutions (alkali silicate and alkali hydroxide) [4]. In addition to being a construction material, it has other advantages, such as acid/base resistance, heat resistance, high strength, and the potential to be applied in solidifying oil wastes [1,5]. Recently, extensive research has been carried out on GEOIL (GEopolymer/OIL) [6].

The characteristics and properties will vary significantly based on the selection of the raw materials for the geopolymer [7]. Metakaolin is one of the raw materials for geopolymer and is currently being extensively studied for its potential for application in different fields. Since it has been proved that the potential is to be applied in inorganic ion adsorption for

nuclear wastes [8], this research will focus on the potential of incorporating organic waste oils in metakaolin-based geopolymer.

The incorporation of organic liquids in geopolymers can be done in three ways: 1) direct incorporation, 2) pre-emulsification and 3) solid impregnation [6]. Pre-emulsification refers to emulsifying an organic liquid with an alkali activator solution before mixing it with an aluminosilicate material. In the pre-emulsification method, the composition, concentration, and type of surfactant determine long-term emulsion stability. Moreover, it is identified that amphiphilicity (Lipophilic-Hydrophilic characteristic) and critical micelle concentration also play a critical role in forming and stabilising surfactant-based emulsion systems [9].

Pickering emulsions attracted many researchers after the studies of Pickering and Ramsden on stabilising emulsion droplets using solid particles (nano or microparticles) [10] due to their advanced stability and less toxicity compared to conventional surfactant-based emulsion systems [9,11]. The morphology of nanoparticles affects the stability and performance of the Pickering emulsions [12].

Nano-sheets/2D nanostructures are one type of colloidal particle used to stabilise the Pickering emulsions [13,14] because of their multilayer tiling and high atomic efficiency [12]. Among numerous nanosheets, Graphene Oxide (GO) is currently the focus of extensive research owing to its potential applications in various areas. One notable advantage of GO is its ability to dissolve in a variety of solvents [15] and its amphiphilic (hydrophilic-lipophilic) characteristics due to its functional groups and basal plane [13,16–18].

The primary aim of this research is to immobilise organic waste oil within construction materials. Considering the inherent drawbacks linked to the

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hydration process of the widely employed Portland cement when exposed to oil, an investigation into alternative materials has been initiated. Geopolymers have emerged as a viable substitute for OPC in this study. However, to successfully incorporate waste oil into the geopolymer, it is crucial to achieve stability in the emulsion phase during the mixing process. Therefore, the establishment of a stable emulsification process becomes imperative. In this regard, the research explores the application of Pickering emulsion, focusing on utilising graphene oxide nanosheets as the selected Pickering particles to effectively stabilise the emulsion.

2. MATERIALS AND METHODS

2.1. Materials for Emulsion and Geopolymer Preparation

The metakaolin used in the geopolymer synthesis was acquired from Sobueclay in Japan [19]. Table 1 provides the chemical composition (wt. %) of the metakaolin. For the preparation of the alkali-activated solution, a potassium silicate solution (50%) was purchased from Wako Chemical Industries Ltd, KOH from Kanto Chemicals Co., and deionised water and water in GO dispersion were employed. Graphene Oxide (GO) nanosheets, obtained from Ceylon Graphene Technologies (10 g/L) in Sri Lanka, were utilised at a concentration of 0.1% of the total weight of metakaolin and alkali-activated solution.

Table 1 Chemical composition of Metakaolin [19]

Composition	Wt. %
SiO ₂	48.59
Al ₂ O ₃	43.11
Fe ₂ O ₃	0.54
CaO	0.21
MgO	3.66
Na ₂ O	2.25
K ₂ O	0.13
TiO ₂	1.27
P ₂ O ₅	1.08
L.O.I*	1.74

L.O.I* - Loss on ignition at 1100 °C for 12h

For the representation of organic waste oil, FBK Turbine 46 oil was used, and it was bought from ENEOS corporation, Japan. The density at 15 °C is 0.85 g/mL, the viscosity index is 124, and the acid number is 0.07 mg KOH/g.

2.2. Sample preparation

The alkali-activated solution was prepared using potassium silicate solution, KOH, and water a day before the geopolymer casting and sealed to obtain the chemical equilibrium at 20 °C. A 150 mL GO water dispersion (10 g/L) (20 °C) was added to the alkali-activated solution

for the Pickering emulsion formation. Then, the oil was added and shear mixed at 10000 rpm for 5 minutes to form the Pickering emulsion at the same environmental condition. The oil was added in 10,20,30,40, and 50% of the volume of alkaline solution. Fig. 1 shows the stable emulsion of the oil-alkali activator and GO. Creaming Index (CI) analysis was done in a 25 mL sample of the indicated emulsion types.



Fig.1 Prepared oil in alkali activator solution emulsion with GO as Pickering particles

The geopolymer was synthesised at a molar ratio of 1:1:13 of K₂O, SiO₂ and H₂O respectively [19]. The mix proportion details of each sample type are summarised in Table 2. 567.7 g of Metakaolin and prepared Pickering emulsion were added and hand-mixed in a container for a minute and then, mixed in the Kitchen Aid (KSM5ER) at 60 rpm for 30 minutes to achieve a homogenised mixture of the paste at 20°C environment. Then, the paste was moulded into 50 mm diameter and 100 mm height plastic moulds, packed air tightly, and placed in 20 °C and 98% RH chamber for 28 days for curing.

Table 2 Mix design for geopolymer casting

Mix type	Potassium Silicate (g)	KOH (g)	Water (g)	GO (g)	Oil (mL)
GP10	495.60	164.80	271.95	1.5	66.60
GP20	495.60	164.80	271.95	1.5	133.20
GP30	495.60	164.80	271.95	1.5	199.80
GP40	495.60	164.80	271.95	1.5	266.40
GP50	495.60	164.80	271.95	1.5	333.00

2.3. Experimental procedures

The creaming index (CI) is a method of evaluation to obtain the details of the aggregation of oil droplets in an emulsion system. This is an indicator of the shelf life of the emulsions. The less the value of the CI, higher the stability of emulsion. This indicates that the emulsion is evenly distributed throughout the solution, resulting in reduced aggregation. Such aggregation can lead to the separation of oil droplets from the emulsion system. CI analysis was done as per the method indicated by Anvari et al [20]. The CI can be calculated from the following equation for an emulsion [21].

$$CI = \frac{H_1}{H_2} \times 100 \quad (1)$$

Where,

H₁ : height of the separated alkali-activated solution phase

H₂ : initial height of the emulsion

After preparing emulsion systems for the CI measurement, each emulsion system was placed in 40 mL plastic tubes at room temperature (20° C) and then with the time the heights of the emulsion layer and separated alkali activator region have been measured. CI was measured for 0, 5, 10, 15, 30 minutes, 1, 2, 3 hours and 1 and 3 days.

The workability of the geopolymer can be assessed by conducting a flow table test similar to previous studies [8] with mould dimensions of 50 mm diameter and 51 mm height. For the prepared geopolymer paste, 0, 20 and 60-minute flow table tests were performed. The spread diameters were measured four times, and the average was taken. Due to the zero flow at 120 minutes, the flow test could not be done after 120 minutes.

The assessment of compressive strengths for distinct sample types was undertaken to scrutinise the fluctuations in the compressive strength of geopolymers subject to diverse oil encapsulations. Compressive tests adhered to the standards outlined in JIS A 1108, employing a loading speed of 0.6 N/mm² per second [22]. Each sample type underwent three individual tests, and the average strength was derived from these measurements. The pore structure analysis was conducted utilising a Scanning Electron Microscope (SEM: JSM-IT200, JEOL, Japan) with a 15 kV acceleration voltage. For the resin sample preparations, 2 mm thick samples were sliced from the cylindrically casted samples and they have immersed in epoxy resin after removal of water by dehydrating and cured in 65 °C. Then the samples were polished using diamond paste and gold dust coated for SEM observation.

A leaching test similar to ANSI/ANS 16.1:2003 was performed [23] by immersing each sample in deionised water separately. The leachate volume to surface area ratio was maintained at 10 mL/cm². During each cumulative leaching period, leachate was replaced entirely and experimented with 1, 3, 7 hours, 1, 3, 7, 14, and 28 days. Then the Total Organic Carbon (TOC) test was performed to evaluate the organic carbon activity in each leachate sample.

3. RESULTS AND DISCUSSION

In augmentation of the preconceived geopolymer samples, a reference sample devoid of the emulsion stabiliser (GO) was additionally formulated. The comparative examination between the reference sample and the GP-50 sample is depicted in Fig. 2. The observation of sample (a) in Fig. 2 elucidates the discernible separation of the oil phase, whereas in the GP-50 sample (b), no such demarcation was discerned. This robustly substantiates the efficacious integration of oil through the application of GO as Pickering particles for the pre-emulsification process.

3.1. Creaming Index

Fig. 3 shows the overall trend of CI of each

emulsion type with time up to three days. Overall, all types of emulsions have been stable for up to one day without any creaming, and later, each type starts to cream at different rates. It was observed that with the increasing percentage of oil, the creaming behaviour of the emulsion increases.

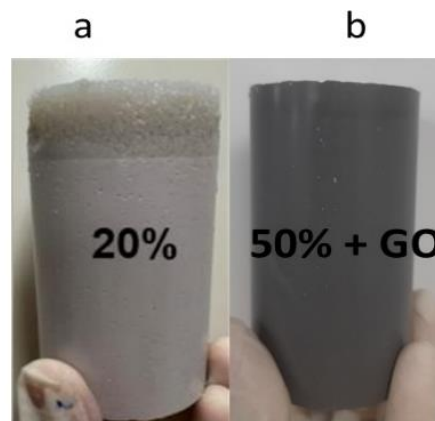


Fig. 2 Comparison of 20% oil incorporated sample without GO (a) and GP-50 sample (b)

This suggests that the increase in oil content leads to a reduction in the utilisation of GO nanoparticles in the emulsion. Notably, the emulsion of the 20% types exhibited superior stability compared to all others. An exploration of Stoke's equation about the gravitational separation of Pickering emulsions [6] may provide insights into this phenomenon by scrutinising the droplet size distribution within each emulsion system. Notably, a discernible separation of the oil phase was observed throughout continuous improvement analysis.

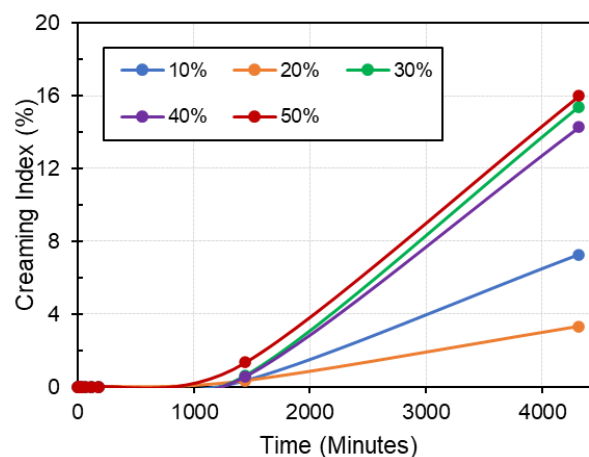


Fig. 3 Creaming Index with time for different proportions of oil

Given the unequivocally established outstanding hydrophilic and lipophilic attributes of GO nanosheets, they manifest robust oil and water absorption capabilities, resulting in the formation of a highly stable emulsion phase within the alkali activator solution.

3.2. Workability of geopolymer

The flow of the geopolymer with oil as a function of time is depicted in Fig. 3. It is evident that the inclusion of

organic oil waste did not exert a substantial impact on the workability of the geopolymer, assuming a 5% margin of error. This phenomenon could be attributed to the rapid geopolymerization process, wherein all samples exhibited a consistent trend in flow, and no cessation of flow was observed even at the 120-minute mark. Conversely, a comparable geopolymer lacking both GO and oil did not exhibit a notable alteration in flow characteristics [8]. This lends support to the proposition that the incorporation of GO into the geopolymer serves to enhance the pace of the geopolymerization mechanism. However, this limited flowability of the geopolymer could be a limitation in the application.

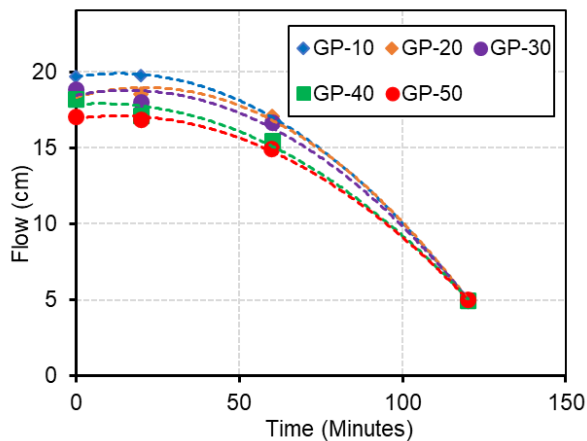


Fig. 4 Flow table results of geopolymer paste with different proportions of oil

3.3. SEM observation

Following the execution of SEM analysis on the cross-sectional perspective of the samples, Fig. 5 presents the SEM images of the cross-section of the samples. It becomes apparent that the organic waste oil has been successfully incorporated into the specimens. Fig. 5 shows the rise in pore density commensurate with the heightened oil content. This observation attests to the effective solidification of the introduced emulsion within the metakaolin geopolymer, even amid varying oil concentrations. With substantiation from Fig. 2 and Fig. 5, it can be posited that the integrated oil has been uniformly dispersed throughout the casted specimens. The SEM images corroborate the success of this incorporation.

It is noteworthy that the range of droplet sizes in the emulsion exhibits a noticeable increase as the oil content increases. Nevertheless, it is crucial to observe that the SEM images depict the existence of cracks, discernible even at a magnification of x50. Significantly, the presence of oil content contributed to a reduction in these cracks. Importantly, the cracks were not initially evident in the raw samples. It is conceivable that these cracks may have developed during the high temperature exposure in epoxy resin preparation procedures.

3.4. Mechanical strength behaviour

Fig. 6 presents the results from the compressive testing revealing that geopolymers encapsulating oil demonstrate satisfactory strength. Nevertheless, as the proportion of solidified oil increases, there is a corresponding decline in strength, attributed to the substitution of geopolymer content with oil. The accompanying figure illustrates the acquired strength data for geopolymer samples cured over 28 days.

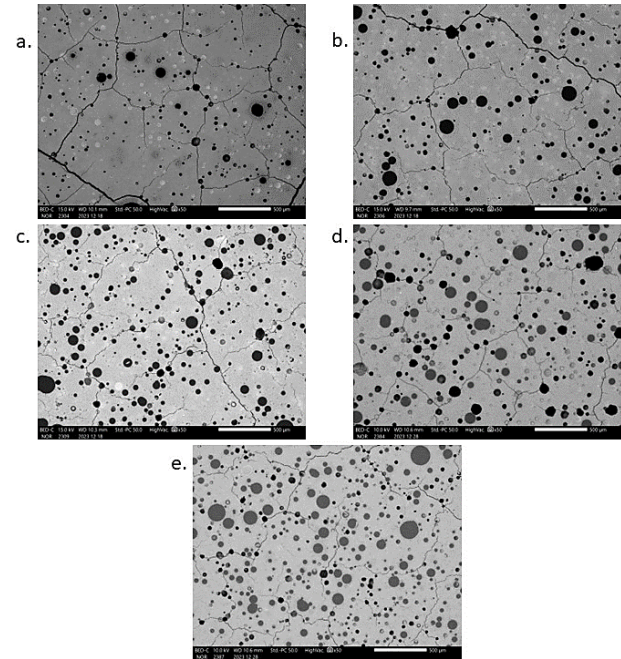


Fig. 5 SEM images of the cross-section of organic waste oil solidified geopolymers in x50 magnification factor: a. GP-10, b. GP-20, c. GP-30, d. GP-40, e. GP-50

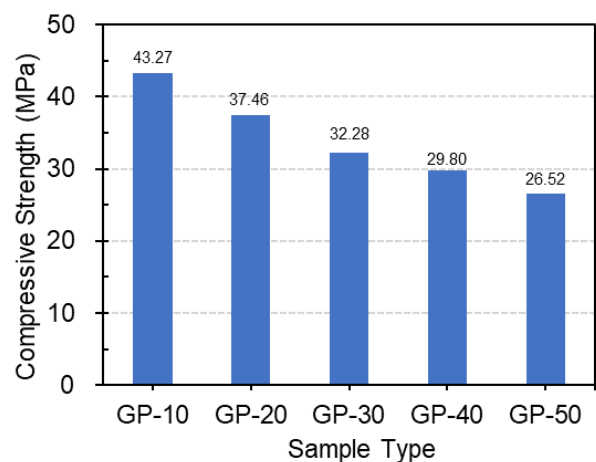


Fig. 6 Compressive strength results of geopolymer samples

Notably, the compressive strength data surpasses that reported in a comparable study conducted by Charles Reeb et al. [6]. According to their research findings, the sample with a 20 vol% of oil exhibited a strength of 22 MPa, while the sample with a 14 vol% displayed a strength of 28 MPa [6]. Also, the samples

showed highly brittle behaviour during the compressive testing.

The scanning electron microscopy (SEM) images corroborate the observation that the density of pores experiences an escalation concomitant with the incremental rise in oil content within each sample. Consequently, a discernible non-linear decline in compressive strength is noted with the increasing oil content in each sample. More precisely, the results from compressive strength testing reveal a reduction of approximately 10±2% in strength for each proportional increase in the incorporation of oil, exhibiting an approximately linear trend, wherein the geopolymer is substituted by emulsified oil. Given the absence of a substantial and abrupt drop in compressive strength associated with the integration of organic oil, it can be asserted that the process of geopolymerisation has remained largely unaffected.

3.5. Organic carbon leaching

Physical mechanisms like hardening and porosity predominantly govern the leaching characteristics of the solidified wastes within the geopolymer. Table 3 outlines the specific Total Organic Carbon (TOC) results and the corresponding ratios of incorporated oil for each sample. All samples demonstrated comparable leaching performance when examining the cumulative leaching outcomes irrespective of the oil content. This suggests that the leaching behaviour is consistent across the samples, with physical factors such as hardening and porosity playing crucial roles in the process of encapsulating organic oil. Since all the sample types are demonstrating similar performance in leaching behaviour, the influence of the physical properties of geopolymer plays a crucial role in the encapsulation.

Table 3 Cumulative leaching of organic carbon from geopolymer

Sample type		GP-10	GP-20	GP-30	GP-40	GP-50
The volume ratio of oil		0.06	0.12	0.17	0.21	0.25
Time (Days)	0.04	1.2	0.7	0.8	0.7	0.7
	0.13	1.9	1.2	1.3	1.1	1.2
	0.25	2.4	1.7	1.8	1.5	1.7
	1	3.7	2.8	3.0	2.6	3.2
	3	5.1	4.2	4.6	4.0	4.9
	7	6.4	5.5	6.1	5.7	6.5
	14	8.2	7.0	7.7	7.2	8.3
	28	9.8	8.9	10.1	9.9	10.7

The illustrated phenomenon is evident upon examining Fig. 7. Considering the TOC testing results suggests that any potential leaching is minimal and primarily restricted to the outer layer of the samples. And it showcases the variation in leaching of organic

components in each sample type is insignificant.

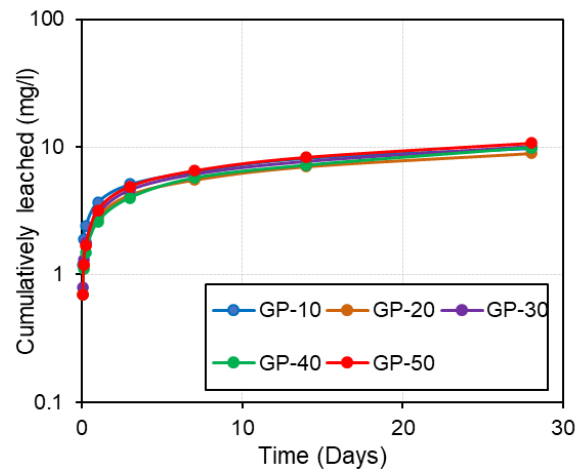


Fig. 7 Cumulatively leached organic carbon with time for each type of sample

Nonetheless, it is essential to acknowledge that GO is employed in the casting process, and being an organic particle itself, a more in-depth analysis is warranted to investigate the particles that may have leached out from the samples. A comprehensive examination of the leaching results for a geopolymer and GO mixture devoid of any oil content will be pursued in the future to delve into this aspect further.

4. CONCLUSIONS

Based on the experimental results and analysis, the organic oil has been successfully encapsulated within the metakaolin-based geopolymer using GO nanosheets as Pickering particles for the emulsion. The outcomes of the research can be summarised as follows.

1. With GO nanosheets as Pickering particles, an alkali activator solution will give a highly stable emulsion. This method helps to entrap the organic waste oil into an alkali activator solution in an excellently stable emulsion.
2. GO stabilised alkali activator emulsion helped to solidify the organic oil within the geopolymer matrix. The SEM images and the visual inspections have shown excellent incorporation results. Incorporated oil did not affect the geopolymerisation mechanism even with the different ratios of oil. However, it has been identified that the addition of GO has influenced the flow table results and the flow of the geopolymer has decreased significantly compared to prior research.
3. The mechanical strength behaviour of the examined geopolymer samples exhibited excellent results. This suggests that the geopolymer matrix developed without any disruption caused by the presence of oil. With an increase in the oil ratio, the porosity ratio also increased, leading to a corresponding decrease in mechanical strength. Nevertheless, the strength properties remain significantly superior to the acceptable standards.

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