บทความวิจัย

การศึกษาลักษณะวัสดุจีโอโพลิเมอร์ที่เตรียมจากวัสดุผสมของดินขาวเผากับเถ้าใยปาล์มและกากของเสียจากกระบวนการผลิตไฮโดรเจนเปอร์ออกไซด์

อาพากร พรมเพชร[1] ธนันท์ ชุบอุปการ[1] ชัยศรี สุขสาโรจน์[1]
และ พรพิมล ประยงค์พันธ์[2*]

บทคัดย่อ

งานวิจัยนี้ศึกษาลักษณะของวัสดุจีโอโพลิเมอร์ที่เตรียมจากการผสมดินขาวเผาร่วมกับเถ้าใยปาล์มและกากของเสียจากกระบวนการผลิตไฮโดรเจนเปอร์ออกไซด์และสารละลายเบส $NaOH/NaSiO_4$ โดยพบว่าวัสดุจีโอโพลิเมอร์ดังกล่าวมีความแข็งแรงในการรับแรงอัดได้ดี และความแข็งแรงของวัสดุจะลดลง 22-6% ขึ้นอยู่กับปริมาณของเถ้าใยปาล์มและกากของเสียที่ทดแทนดินขาวเผาในตัวอย่าง ในงานวิจัยนี้ได้มีการตรวจสอบลักษณะพื้นผิวของวัสดุจีโอโพลิเมอร์โดยเทคนิค SEM และจากการวิเคราะห์หมู่ฟังก์ชันที่ปรากฏในวัสดุดังกล่าวโดยเทคนิค FTIR ยังช่วยยืนยันการเปลี่ยนแปลงโครงสร้างอันเนื่องมาจากการเกิดปฏิกิริยาโพลิเมอไรเซชันได้เป็นอย่างดี

คำสำคัญ: จีโอโพลิเมอร์, ดินขาวเผา, เถ้าปาล์ม, กากของเสีย, อินฟราเรด สเปกโทรสโกปี

---

[1] ภาควิชาวิศวกรรมโยธา คณะวิศวกรรมศาสตร์ มหาวิทยาลัยสงขลานครินทร์

[2] ภาควิชาเคมี คณะวิทยาศาสตร์ มหาวิทยาลัยศรีนครินทรวิโรฒ

*ผู้นิพนธ์ประสานงาน, e-mail: pornpim@g.swu.ac.th

Characterization of Geopolymer Materials based on Metakaolin Incorporating with Palm Ash and Solid Waste of Hydrogen Peroxide Process

Arpakon Prompet[1], Tanan Chub-uppakarn[1], Chaisri Suksaroj[1] and Pornpimol Prayongpan[2*]

ABSTRACT

Palm ash and solid wastes of hydrogen peroxide process have been used to synthesize geopolymer from the combination with meakaolin and NaOH/$NaSiO_4$ base activator. The study confirmed the good strength material produced here. The compressive strength could be decreased by 22-6% depending on the amount of metakaolin replaced. The morphology of geopolymer products have been characterized by scanning scanning electron microscopy (SEM). Fourier transform infrared spectroscopy confirmed that the geopolymer structures created under ambient temperature.

Keywords: geopolymer, metakaolin, palm ash, solid waste, infrared spectroscopy

[1]Civil Engineering Department, Faculty of Engineering, Prince of Songkla University.

[2]Chemistry Department, Faculty of science, Srinakharinwirot University.

*corresponding author, e-mail: pornpim@g.swu.ac.th

Introduction

Geopolymer is an inorganic polymer which is out of interest due to their impressive compressive strength and ease to make. It can be synthesized from the combination of aluminosilicate and alkaline activator. The reaction occurs under curing at room temperature. It could produce Poly(sialate), Poly(sialate-siloxo) or Poly(sialate-disoloxo) as the product depending on the ratio of silica/alumina presented [1-6]. The previous works have shown that the compressive strength of the geopolymers could be varied from 70-100 MPa. There are various factors affecting the properties of the materials including the SiO_2 and Al_2O_3 ratio obtained from raw materials, type and amount of the alkaline activator, and curing time [7-11]. The elastic modulus, compressive strength, or material properties could also be improved by adding some additive or use different types of ash-binder [12-15].

Some research groups have focus on producing geopolymer containing the industrial wastes [16-17]. These works are of interest recently because it is a way to add value to the unwanted materials. Ash is an agriculture waste material commonly found in South East Asia. Palm ash is the waste produced from the palm fields or palm oil industry. The agricultures are trying to get rid of the palm tree by burning once they are out of age to produce palm oil. Most of the wastes have been deposited to the ground and produced the bad impact to the environment. Some studies have tried to add-value to the ash by using them in many applications [18-20].

Palm ash is an interesting material in term of the chemical composition which is rich in Si. It might be best to combine with metakaolin which is rich Si and Al to act as starting substances in geopolymer material. It has been draw our attention to identify the best ratio of palm ash to metakaolin which could produce a desirable strength geopolymer [21]. The present study is attempted to investigate the physical and chemical properties of the geopolymer materials synthesized from the combination of palm ash and solid waste of hydrogen peroxide process incorporating with metakaolin and alkaline activator. The surface morphology of the materials would be identified by Scanning electron microscopy (SEM). The chemical compositions were characterized by Fourier transform infrared spectroscopy (FTIR).

Materials and Methods

Metakaolin and palm ash were provided from Naratiwat province and Suratthanee province, Thailand. Before using as the source materials, metakaolin was heated to the temperature of 750°C for 3 hours and both of the metakaolin and palm ash were ground with abrasive machine to bring the average particle size to 13.97 μm, 54.01 μm, respectively. The solid waste of hydrogen peroxide process has been characterized before used which found that the waste were rich in alumina. The particle size of the alumina waste is less than 637.20 μm. The chemical compositions of the metakaolin, palm ash and alumina waste have been characterized by XRF as the results shown in Table 1.

The geopolymer materials were synthesized with different composition of the Si-Al based mixture of metakaolin, palm ash, and/or alumina waste (Si-Al based materials) and alkaline liquid. The ratio of metakaolin: palm ash: alumina waste were chosen in 5 different mass ratios from 100:0:0 to 60:20:20 (Table 2). The alkaline solutions were prepared from the mixture of sodium hydroxide aqueous solution (concentration range from 5-15 molar) with solid sodium silicate, $NaSiO_4$ (purchase from Sigma-Aldish) at a certain amount. Then the mixture of the alkaline solutions was added to the Si-Al based materials. The paste was stirred to obtain homogeneous mixture and purred into 5 cm × 5 cm × 5 cm plastic mold. They were pressed and vibrated to avoid the air bubbles. The cube samples were left at room temperature for 1 hour before curing at 70°C in the oven for 24 hours. The samples were stored at room temperature under dry condition before determined the physical and chemical properties.

The surface morphologies of the geopolymer samples were classified by Scanning electron microscope (SEM) with FEI Quanta 400. The structural studies of the geopolymer were characterized by the Fourier transform infrared spectroscopy (FTIR) which performed in a range of 400-4000 cm^{-1}. The samples were suspended in KBr disks (1% wt). FTIR spectra were obtained using a Perkin-Elmer 2000 spectrometer.

Results

The chemical compositions of the metakaolin, palm ash and alumina waste were determined using XRF as shown in Table 1. The metakaolin used in this study has 48.08% SiO_2 and 37.20% Al_2O_3. Palm ash has 45.88% SiO_2 and alumina waste has 77.93% Al_2O_3 as the main compositions.

Table 1 The chemical compositions of metakaolin, palm ash and alumina waste.

reactant	Concentration (%wt)						
	SiO_2	Al_2O_3	MgO	P_2O_5	Fe_2O_3	K_2O	CaO
Metakaolin	48.08	37.20	-	-	1.19	1.97	-
Palm ash	45.88	0.64	2.92	6.13	1.90	10.34	14.78
Alumina waste	0.09	77.93	-	0.34	-	-	-

The compressive strengths for all geopolymer samples were tested at the period of 1, 7, 14, and 28 days after curing (the results are not shown here). The compressive strength is increasing dramatically as the time of curing increase and produced the high strength at the curing time 7 day (Table 2). Then it has small increasing after left the samples for 14 and 28 days. The increase strength is very close to hardening process of cement. However, product of cement is $CaCO_3$ while geopolymer is aluminosilicate. The study showed that the samples produced by using 15 M NaOH have highest compressive strengths for all composition. A higher concentration of NaOH favors the better compressive strength. The sample with 100%w metakaolin has the best strength at 98.75 MPa.

Table 2 The compressive strength at 7 days of curing time for geopolymer materials synthesized from different percent composition. The Si-Al based mixtures were mixed with base solution with the ratio of $Na_2Si_2O_3$/NaOH equal to 2.5%wt.

Composition (%)			**Compressive strength (MPa)**		
Metakaolin	**Palm ash**	**Alumina waste**	**5 M NaOH(aq)**	**10 M NaOH(aq)**	**15 M NaOH(aq)**
100	-	-	47.14	77.00	98.75
80	20	0	36.75	46.6	61.81
80	10	10	30.65	43.87	53.71
60	40	0	15.96	18.00	23.12
60	20	20	15.27	19.39	31.59

When adding the palm ash into the sample the strength is decreasing. The chemical compositions of Al_2O_3 presented in the metakaolin and palm ash are 37.20, and 0.64% respectively. The greater the percentage of Al_2O_3 present, the better the reactants to produce geopolymer. The studies have also shown that the compressive strength is decreasing once adding alumina waste instead of the palm ash into the sample. It might be the particle size (as shown in Table 1) of the alumina waste used here are much greater than those of the metakaolin and palm ash. Thus the strength of the samples would depend on the chemical composition of the silica and alumina, and particle size of the raw materials.

The microstructures of the geopolymer surface were determined from SEM study. Figure 1 represent the morphology of the three geopolymer materials which prepared from the ratios of metakaolin: palm ash: alumina wastes are 100:0:0, 80:20:0 and 80:10:10. The texture of the samples at 80:20:0 and 80:10:10 ratios were denser than at 100:0:0. With regard to the addition of palm ash or alumina wastes, the dense matrices are produced.

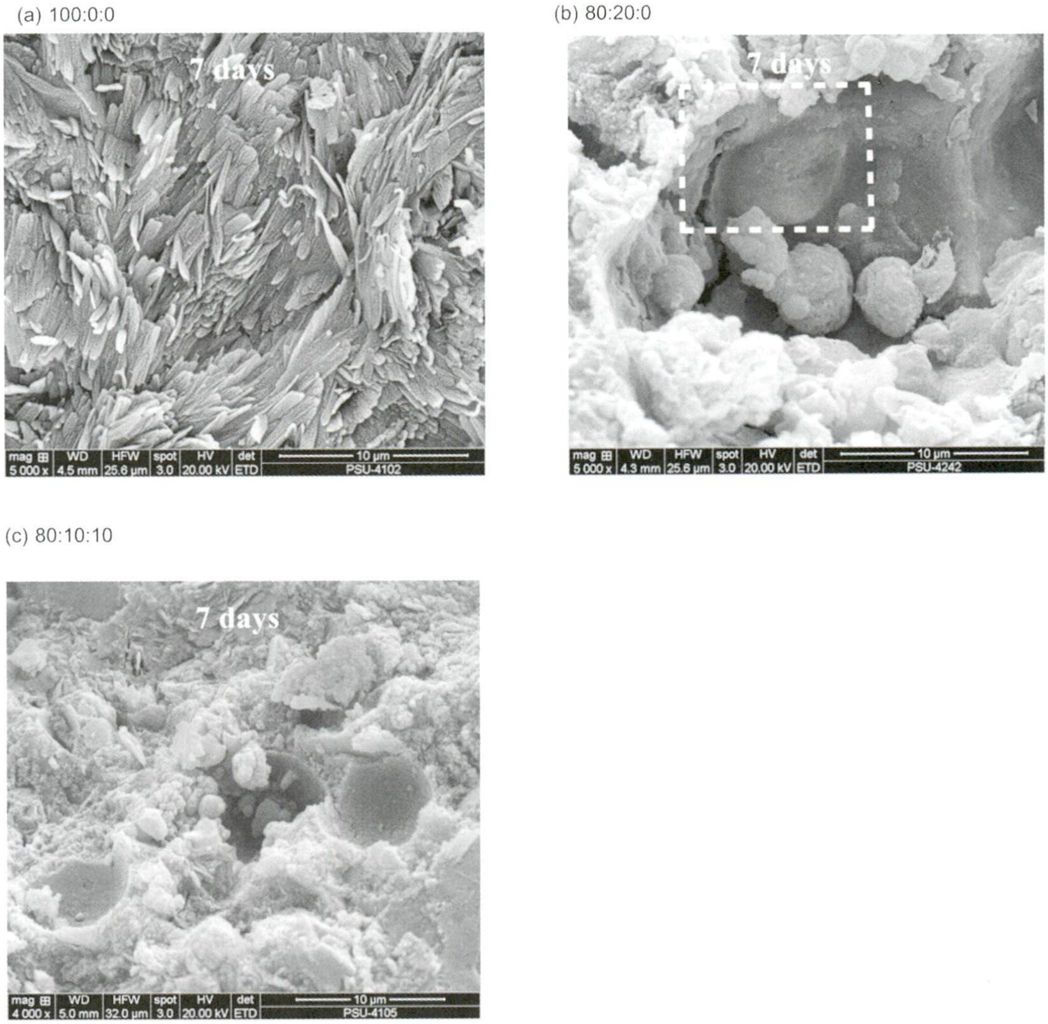

Figure 1 Morphology of the geopolymer samples produced from (a) 100% metakaolin (100:0:0); (b) 80% metakaolin and 20% palm ash (80:20:0); and (c) 80% metakaolin, 10% palm ash and 10% alumina waste (80:10:10) with $Na_2Si_2O_3$/NaOH (15 M) after curing for 7 days.

The IR spectra of original material (metakaolin) and geopolymer samples were represented in Figure 2. FTIR spectra of the samples adding palm ash or alumina waste are similar. The IR results indicated that the geopolymer formations are occurred in all compositions. The appearances of a small band at 704 cm^{-1} are observed. Here is the behavior of the Al and Si on polymerization. The band is absent in the metakaolin raw material. These changes of the geopolymer IR bands are similar to the previous studies [22-23]. The metakaolin starting material represents the IR bands at 1136 cm^{-1} due to Si-O stretching vibration has been shifted to smaller wave number (990-1050 cm^{-1}) compared to the geopolymer IR spectra. The weaker bands at 3464 cm^{-1} and 1652 cm^{-1} refer to the adsorbed moisture presented in the geopolymer samples. The presence of CO_3^{2-} due to the atmospheric carbonation during drying is indicated at the wave number 1428 cm^{-1} [24].

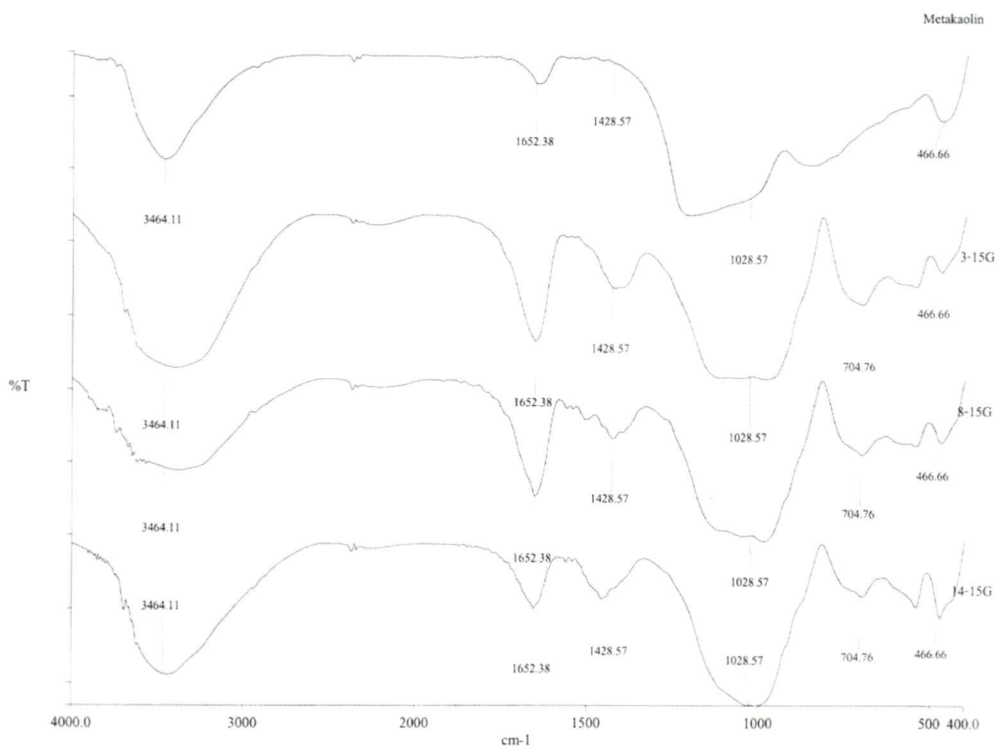

Figure 2 FTIR spectra of (a) metakaolin and three different composition geopolymers: (b) 100% metakaolin (3-15G) (c) 80% metakaolin and 20% palm ash (8-15G); and (d) 80% metakaolin, 10% palm ash and 10% alumina waste geopolymers (14-15G).

Conclusion and Discussion

The mixture of meakaolin, palm ash and alumina waste with alkaline activator could produce geopolymer materials. FTIR spectra showed the formation a network of Si-Al in geopolymer structure. The compressive strengths were decreased by 22-76% depending on the amount of metakaolin replaced. More palm ash and alumina waste in the mixture lead to lower strength. However the addition of palm ash or alumina wastes would produce the dense matrices.

Acknowledgements

This study was funded by Prince of Songkla University (PSU) under contract number ENG 550053S-011162 and ENV 550381S. The authors gratefully acknowledge Srinakharinwirot University for FTIR facility.

References

1. Davidovits, J. 1991. Geopolymers: Inorganic Polymeric New Materials. *Journal of thermal analysis* 37, 1633-1656.
2. Davidovits, J. 1999. Chemistry of Geopolymetric Systems, Terminology. *Proceeding: 2nd International Conference on Geopolymer.* France, Paris: 9-40.
3. Hardjito, D., Wallah, S. E., Sumajouw, D. M. J., and Rangan, B. V. 2004. On the Development of Fly Ash Based Geopolymer Concrete. *Aci Materials Journal,* 101(6): 467-472.
4. Duxson, P., Fernández-Jiménez, A., Provis, J. L., Lukey, G. C., Palomo, A., Van Deventer, J. S. J. 2007. Geopolymer Technology: The Current State of the Art. *Journal of Materials Science* 42, 2917-2933.
5. Duxson, P. and Provis, J. L. 2008. Designing Precursors for Geopolymer Cements. *Journal of American Ceramic Society.* 91 (12): 3864-3869.
6. Li, C., Sun, H., and Li, L. 2010. A review: The Comparison Between Alkali-Activated Slag (Si+Ca) and Metakaolin (Si+Al) Cements. *Cement and Concrete Research* 40:1341-1349.
7. Barbosa, V., MacKenzie, K., and Thaumaturgo, C. 2000. Synthesis and Characterization of Materials Based on Inorganic Polymers of Alumina and Silica: Sodium Polysialate Polymers. *International Journal of Inorganic Materials* 2: 309-317.
8. De-Guang, C., and Da-Gen, S. 2005. Structure Characterization for the Geopolymer of Sodium Silicate and Metakaolin. *Material Science & Applied Chemistry.* 4 (2): 70-73.
9. Sanawong, C., Somna, K. and Chalee, W. 2010. Compressive and Bond Strengths of Fly Ash Based Geopolymer Concrete. *Burapha Sci. J.*: 13-22.

10. Kani, E. N., Allahverdi, A., and Provis, J.L. 2012. Efflorescence Control in Geopolymer Binders Based on Natural Pozzolan. *Cement & Concrete Composites.* 34: 25-33.

11. Arioz, E., Arioz, O. and Kockar, O. M. 2013. The Effect of Curing Conditions on the Properties of Geopolymer Samples. *International Journal of Chemical Engineering and Applications,* 4 (6): 423-426.

12. Yunsheng, Z., Wei S., and Zongjin, L. 2010. Composition Design and Microstructure Characterization of Calcined Kaolin-Based Geopolymer Cement. *Applied Clay Science* 47, 271-275.

13. Boonserm, K., Sata., V., Pimraksa., K., and Chindaprasirt, P. 2012. Microstructure and Strength of Blended FBC-PCC Fly Ash Geopolymer Containing Gypsum as an Additive. *Science Asia* 38: 175-181.

14. Gao, X., Yu, Q. L., and Brouwers, H. J. H., 2015. Reaction Kinetics, Gel Character and Strength of Ambient Temperature Cured Alkali Activated Slag-Fly Ash Blends. *Construction and Building Materials* 80:105-115.

15. Aughenbaugh, K. L., Williamson, T., and Juenger, M. C. 2015. Critical Evolution of Strength Prediction Methods for Alkali-Activated Fly Ash. *Materials and Structures* 48: 607-620.

16. Komnitsas, K., Zaharaki, D., and Bartzas, G. 2013. Effect of Sulphate and Nitrate Anions on Heavy Metal Immobilisation in Ferronickel Slag Geopolymers. *Applied Clay Science* 73: 103-109.

17. Sata, V., Wongsa, A., Somna, K., and Chindaprasert, P. 2016. Interfacial Transition Zone of Previous Cement and Geopolymer Concrete Containing Crushed Clay Brick. *Chiang Mai Journal of Science* 43(2):402-408.

18. Foo, K. Y., Hameed, B. H. 2009. Value-Added Utilization of Oil Palm Ash: A Superior Recycling of the Industrial Agricultural Waste. *Journal of Hazardous Materials* 172: 523-531.

19. Johnson, D. V. (2011) Palm Ash: A Humble Product of Many Uses. Palms 55(3): 117-121.

20. Ooi, Z. X., Ismail, H., Bakar, A. A., and Teoh, Y. P. 2014. A Review on Recycling Ash Derived from *Elaeis guineensis* by-product. *Bioresources* 9(4): 7926-7940.

21. Zarina, Y., Mustafa Al Bakri, A. M., Kamarudin, H., Khairul Nizar I. and Rafiza, A. R. 2013. Review on the Various Ash from Palm Oil Waste as Geopolymer Material. *Review Advanced Material science* 34: 37-43.

22. De-Guang, C., and Da-Gen, S. 2005. Structure Characterization for the Geopolymer of Sodium Silicate and Metakaolin. *Material Science and Applied Chemistry* 4(2), 70-73.

23. Yunsheng, Z., Wei S., and Zongjin, L. 2010. Composition Design and Microstructure Characterization of Calcined Kaolin-Based Geopolymer Cement. *Applied Clay Science* 47: 271-275.

24. Barbosa, V., MacKenzie, K., and Thaumaturgo, C. 2000. Synthesis and Characterization of Materials Based on Inorganic Polymers of Alumina and Silica: Sodium Polysialate Polymers. *International Journal of Inorganic Materials* 2(4): 309-31.

ได้รับบทความวันที่ 2 พฤษภาคม 2559
ยอมรับตีพิมพ์วันที่ 15 มิถุนายน 2559