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P. RISDANARENI[1*], B.S. UMNIATI[1], R. KAROLINA[2], K. ZAI[3], A.A.M.B. HASTUTI[4,7], I. MUSTAFA[5], M.M.A.B. ABDULLAH[6]

THE APPLICATION OF SUPER ABSORBENT POLYMER IN SELF-HEALING MORTAR: THE EFFECT ON MECHANICAL PROPERTIES

Super Absorbent Polymer (SAP) were used in various application, including in mortar production. The ability of SAP to absorb a high amount of water made this material become a promising water reservoir in the mortar that can later mitigate micro-cracks in concrete. Besides SAP, a nutrient must be embedded into self-healing mortar to support metabolism in bacteria-based self-healing mortar. However, adding SAP and nutrient was reported to decrease the mechanical properties of the resulting self-healing mortar. Thus, in this research, the modification in the mix design of mortar containing SAP and nutrient were observed. The water to cement ratio was decreased up to 0.3. The amount of SAP and entrained water added is based on its swelling capacity. The swelling capacity of SAP, the workability of fresh mortar, and the compressive strength of mortar were examined. The results show that the swelling capacity of SAP was affected by the pH and the presence of calcium ions in the solution. The higher the pH and the calcium ion in the solution, the lower SAP's swelling capacity. Applying the modified mortar mix design containing SAP and nutrient proofed to mitigate the reduction in workability and compressive strength of the resulting self-healing mortar.

Keywords: super absorbent polymer; self-healing mortar; nutrient; swelling capacity; mechanical properties

1. Introduction

The usage of super absorbent polymer (SAP) has found its way to be applied in concrete production [1-6]. The ability of this 'smart' additive to swell up to 100 times its weight after it has contact with water made this material become promising internal curing for concrete production. Besides being employed as an internal curing agent, the ability of SAP to retain a high number of waters was used to stimulate the autogenous healing mechanism [7]. When microcracks were present in young concrete, the remaining water inside the SAP was released and slowly reacted with the un-hydrated cement in the concrete or mortar matrix [8]. However, adding SAP tends to decrease the mechanical properties of the resulting mortar or concrete[1]. During the hydration process, some of the water taken by SAP will evaporate and leave holes in the concrete that could decrease the concrete's strength.

On the other hand, research on developing autogenous and autonomous healing has risen in the last decade [6]. Autogenous healing depends on the continuous hydration of un-reacted cement, while autonomous healing stimulates the healing mechanism by adding a healing agent [9]. Although autogenous healing seems simpler than autonomous healing, the width of crack that an autogenous healing system could heal was limited [6]. It is reported that the maximum early age cracks width that could be healed with the addition of commercial SAP was 0.2 mm [10]. On the other hand, bacteria-based-self healing, an autonomous healing system that employed urease positive bacteria to heal the cracks, was reported to heal cracks with widths up to 0.5 mm [11,12]. In the bacteria-based self-healing system, nutrients such as yeast extract (YE), urea, and calcium nitrate tetrahydrate were needed to support the metabolism activity of bacteria in a concrete environment. However, adding nutrients, especially yeast extract in the concrete matrix, tends to decrease the strength, while calcium nitrate accelerates the setting time of fresh mortar or concrete [13].

Several reports on optimizing the number of nutrients needed in bacteria-based self-healing recommend a composition

1 UNIVERSITAS NEGERI MALANG. FACULTY OF ENGINEERING, DEPARTMENT OF CIVIL ENGINEERING, JALAN SEMARANG NO 5 MALANG, EAST JAVA 65145, INDONESIA
2 UNIVERSITAS SUMATERA FACULTY OF ENGINEERING UTARA, DEPARTMENT OF CIVIL ENGINEERING, MEDAN, NORTH SUMATRA 20222, INDONESIA
3 UNIVERSITAS GADJAH MADA, FACULTY OF PHARMACY, DEPARTMENT OF PHARMACEUTICS, YOGYAKARTA 55281, INDONESIA
4 UNIVERSITAS GADJAH MADA, FACULTY OF PHARMACY, DEPARTMENT OF PHARMACEUTICAL CHEMISTRY, YOGYAKARTA 55281, INDONESIA
5 UNIVERSITAS BRAWIJAYA, FACULTY OF MATHEMATICS AND NATURAL SCIENCES, DEPARTMENT OF BIOLOGY, MALANG 65145, INDONESIA
6 UNIVERSITI MALAYSIA PERLIS, CENTER OF EXCELLENCE GEOPOLYMER AND GREEN TECHNOLOGY (CEGEOGTECH), 01000 KANGAR, PERLIS, MALAYSIA.
7 UNIVERSITAS GADJAH MADA, CENTER OF EXCELLENCE INSTITUTE FOR HALAL INDUSTRY AND SYSTEMS (PUI-PT IHIS), YOGYAKARTA 55281, INDONESIA

* Corresponding author: puput.risdanareni.ft@um.ac.id

that minimizes the decreasing strength of the resulting mortar [14-16]. Similar optimization on the amount of SAP in concrete has also been performed. The RILEM technical committee recommends that the amount of SAP added into concrete should be calculated based on its 10 minutes of swelling capacity in cement filtrate [17].

Although the research on employing SAP or bacteria to heal the micro-crack in concrete was widely reported, the effect of using both SAP and bacteria nutrients on the mechanical properties of the resulting mortar was limited. Thus, in this fundamental research, the effects of adding SAP and nutrient designed for self-healing mortar were conducted. By performing this fundamental investigation, the researched gap in the coupling mechanism of SAP and bacteria nutrient addition will be filled.

2. Materials and methods

Portland Pozzolana Cement (PPC) from *Tiga Roda*, equal to cement II 42.5N with a specific density of 3.43 g/cm^3, was used as a binder in mortar production. River sand with a maximum particle size of 20 mm and a specific density of 2.4 g/cm^3 was used as fine aggregate. Commercial super absorbent polymer (SAP) sodium polyacrylate-based ($C_3H_3NaO_2$) from Aqua keeper was used as a healing agent in this research. The morphology of SAP observed with a scanning electron microscope (SEM) is presented in Fig. 1. As the bacteria will later be embedded in

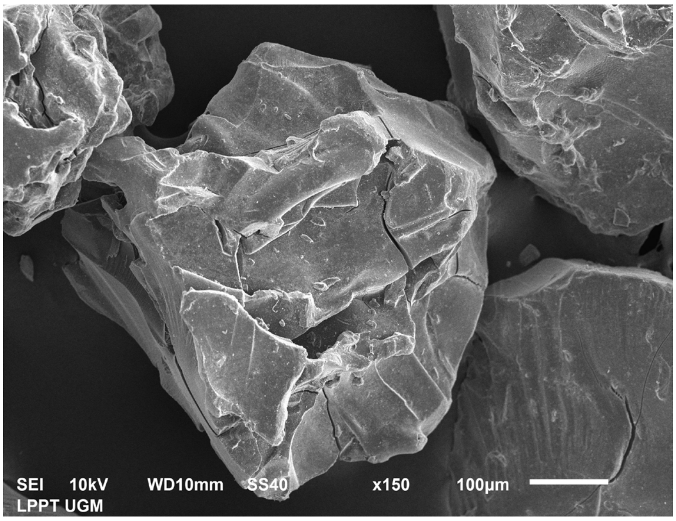

Fig. 1. Morphology of super absorbent polymer

this mortar, nutrients needed for bacteria metabolism activity were added. Yeast extract, urea, and calcium nitrate tetrahydrate (purity of 99%) from Merck were added to the mixture. A superplasticizer MasterGlenium from BASF with a dose of 0.3% from cement weight was used to improve the workability of fresh mortar.

The mortar was produced according to EN NBN 196 standard with a water/cement ratio of 0.3. In the mixture containing calcium nitrate tetrahydrate, the required water was reduced to accommodate the excess water that came from calcium nitrate tetrahydrate ($4H_2O$). The amount of SAP needed was calculated based on its swelling capacity measured at 10 minutes, following equation (1) [17]. The water/cement ratio of a sample with SAP was adjusted to 0.354 [4]. The mix design to produce one batch mortar containing six mortar cubes with a dimension of 5×5×5 cm was presented in TABLE 1.

$$M_{SAP} = \frac{{}^{w}\!/\!{}_{b_{SAP}} \times W_{binder}}{SC} \tag{1}$$

While M_{SAP} was the mass of SAP needed, w/b_{SAP} was set to 0.054, W_{binder} was the mass of cement, and SC was the sorption capacity of SAP in cement filtrate (10 minutes).

The swelling capacity of SAP was measured at 10 minutes in de-ionized water pH 7, cement filtrate pH 13, and de-ionized water pH 13 according to TC 260-RSC recommendation [17]. Around 0.1gram (M_d) SAP were immersed to desired 50 ml solution (M_s). After 10 minutes immersion, the solution containing SAP were filtered with filter paper (12-15 µm mesh size). The total liquid that went through the filter paper were then weight (M_f) The swelling capacity was calculated using equation (2).

$$SC = \left(M_s - M_f\right) / M_d \tag{2}$$

SC was the sorption capacity at a specific time, M_s was the liquid mass, M_f was the liquid remaining after filtration and M_d was the mass of dry SAP.

The setting time of paste was performed according to ASTM C191. The workability of fresh mortar was performed by following NBN EN 1015-3 standard. The fresh mortar was casted into cubes mold with dimension of 5×5×5 cm. After 24 hours, the mortar cubes were demolded, wrapped with plastic and cured in room temperature (28±5°C) for 28 days. The 28 days old mortar were then tested for its compressive strength and bulk density following the guidelines from ASTM C 109.

TABLE 1

Mix Design of Mortar for Six Mortar Cubes 5×5×5 cm

Type	SAP (g)	Sand (g)	Cement (g)	Water (g)	Glenium (g)	YE (g)	Urea (g)	Cal* (g)
Ref	0.00	1350	450	135	1.35	0	0	0
N	0.00	1350	450	124	1.35	1.53	18	36
SAP R 0.12	0.52	1350	450	159.30	1.35	0	0	0
SAP N 0.12	0.52	1350	450	148.30	1.35	1.53	18	36

* Cal: Calcium Nitrate Tetrahydrate

3. Results and discussions

3.1. Swelling Capacity of SAP

The swelling capacity of SAP measured after 10 minutes in contact with water was displayed in Fig. 2. The swelling capacity of SAP was affected by the pH and mineral content of the solution [2,18]. The higher the pH, the lower the swelling capacity of SAP observed. This result agrees well with the previous finding by Mignon et al., stating that the ionic charge of SAP at specific pH could cause an increase or decrease in swelling capacity [2]. The lowest swelling capacity was observed in SAP immersed in cement filtrate. As SAP is sensitive to the existence of calcium ions, a reaction between the polymers and calcium ions in cement filtrate could also inhibit the swelling of SAP. Similar behavior was also reported by Lee et al., stated that the calcium ion in cement filtrate induces a high ion charge in the system that could decrease the swelling capacity of SAP [19].

3.2. Setting Time of Paste

The setting time of paste containing nutrients and SAP is presented in Fig. 3. The addition of SAP tends to delay the resulting paste's initial and final setting time. On the other hand, adding nutrients accelerates the initial setting time due to the presence of calcium nitrate tetrahydrate. Still, no significant effect on the final setting was observed compared to the reference sample. A significant delay in the final setting time was observed in the sample containing both SAP and nutrient compared to the reference sample. In several research, yeast extract was reported to significantly delay the cement paste setting time due to the carbohydrate (sugar) consisted in the yeast extract [13,20,21]. On the other hand, the present of calcium source proofed to accelerate the hydration rate [22-24].

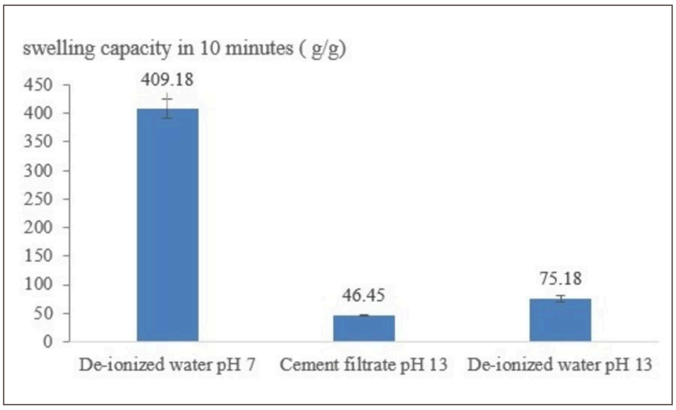

Fig. 2. Swelling Capacity of SAP measured after 10 minutes. Error bars represent standard deviation (n = 3)

Based on the result on setting time, it seems that the role of calcium nitrate that should be act as accelerator did not become strong enough to alter the delay in setting time due to the presence of yeast extract and SAP. The carbohydrate in yeast extract was reported to hinder the hydration process in cement paste, while the high water up taken by SAP also contributes to slowing down the hydration reaction [1,13,14,25].

3.3. Workability of Fresh Mortar

The workability of fresh mortar was presented by the flow value (Fig.4). The modification of the mortar mix design regarding the addition of SAP recommended by Jensen et al. proved to maintain the workability of mortar containing SAP [4]. The result on the workability of fresh mortar is also in line with the setting time result. A slight decrease in the flow value compared to the reference sample was observed in the sample with nutrients. However, when SAP presence together with the nutrients, an

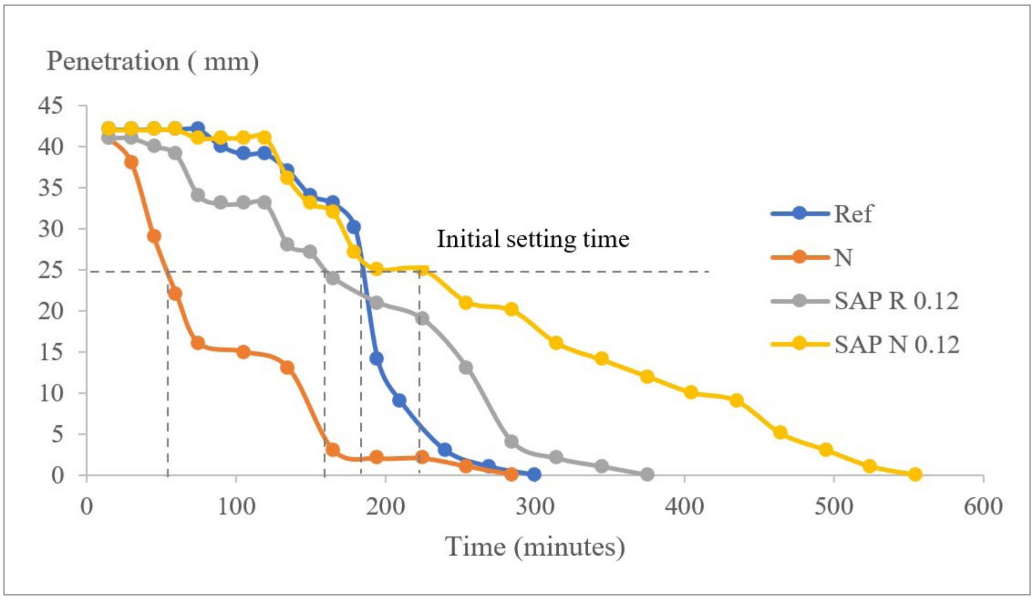

Fig. 3. Setting Time of Cement Paste

increasing in workability was observed. This mechanism might be due to the multi reaction between calcium nitrate, SAP, and yeast extract in the mortar matrix [14].

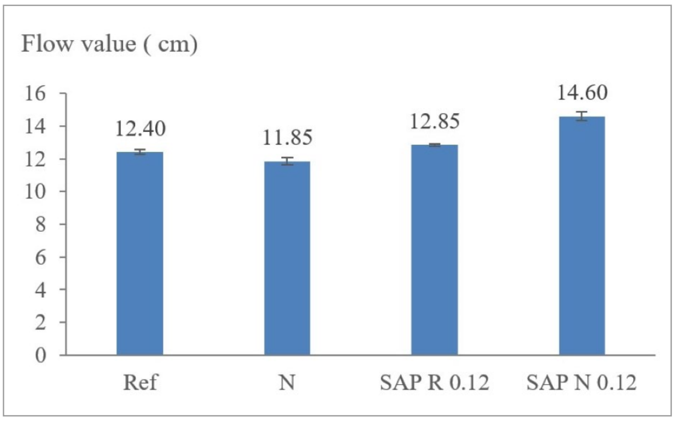

Fig. 4. The workability of fresh mortar. The error bar represents the standard deviation (n = 3)

3.4. Density and Compressive Strength of Mortar

The result shows that the addition of SAP and nutrient into resulting mortar has no negative effect on the compressive strength of resulting mortar (Fig. 5). It is worth to point out that even though the addition of SAP and nutrients caused decreasing in bulk density of resulting mortar compared to reference sample, it did not lead to the decreasing of mortar's compressive strength compared to reference sample. It seems that the SAP induced the formation of closed pores that has a positive effect on the mechanical properties of the resulting mortar. The presence of calcium nitrate seems to accelerate the hydration mechanism as stated in previous finding by Vandervoort et al. [14]. Regarding the effect of SAP addition to the compressive strength of mortar, it seems that the designed amount of SAP added into the mixture was the optimum composition. Adding higher amount of SAP were reported to significantly decrease the compressive strength of resulting mortar [26].

4. Conclusions

Based on the results presented in this paper, several conclusions could be drawn as follows:

1. The swelling capacity of SAP depended on the presence of calcium ions and the pH of the solution. High pH and high calcium ion content are proven to hinder the swelling capacity of SAP.
2. The presence of combined nutrients and SAP tends to delay the initial and final setting time compared to the reference sample. The presence of calcium nitrate seems not sufficient to counterattack the delay in setting time contributed by the presence of yeast extract in the mixture.
3. The designed mix design of mortar that generates based on SAP's swelling capacity proves to stabilize the workability of fresh mortar containing SAP and nutrients.
4. The addition of nutrients and SAP tends to decrease bulk density but did not lead to the decreasing of mortar's compressive strength compared to reference sample. It seems that the SAP induced the formation of closed pores that has a positive effect on the mechanical properties of the resulting mortar.

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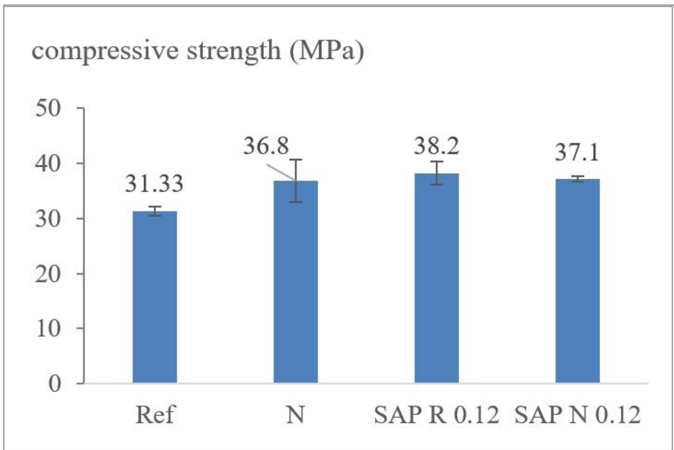
REFERENCES

[1] B. Craeye, M. Geirnaert, G. de Schutter, Constr. Build. Mater. **25**, 1 (2011).

[2] A. Mignon, G.J. Graulus, D. Snoeck, J. Martins, N. de Belie, P. Dubruel, S. van Vlierberghe, J. Mater. Sci. **50**, 970 (2014).



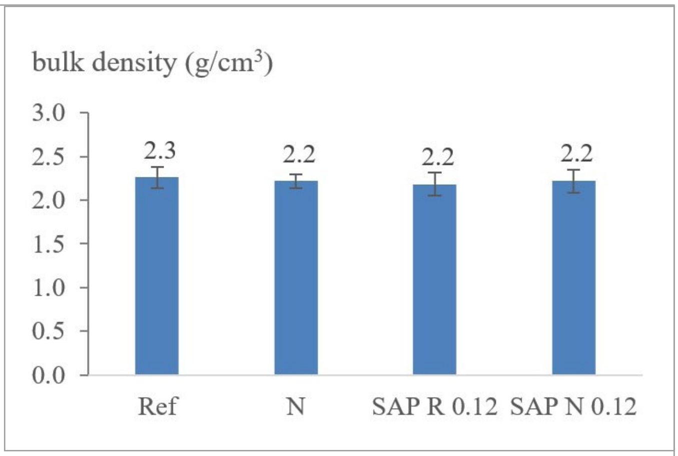


Fig. 5. The 28 days old compressive strength and the bulk density of mortar. Error bar represents the standard deviation of mean (n = 6)

[3] M. Adelaide, P. Gomes, D. Araújo, E. Mannekens, N. de Belie, D. Snoeck, Cem. Concr. Res. **159** (2022).

[4] O.M. Jensen, P.F. Hansen, Cem. Concr. Res. **31**, 647 (2001).

[5] A. Mignon, D. Snoeck, K. D'Halluin, L. Balcaen, F. Vanhaecke, P. Dubruel, S. van Vlierberghe, N. de Belie, Constr. Build. Mater. **110**, 169 (2016).

[6] N. de Belie, E. Gruyaert, A. Al-Tabbaa, P. Antonaci, C. Baera, D. Bajare, A. Darquennes, R. Davies, L. Ferrara, T. Jefferson, C. Litina, B. Miljevic, A. Otlewska, J. Ranogajec, M. Roig-Flores, K. Paine, P. Lukowski, P. Serna, J.M. Tulliani, S. Vucetic, J. Wang, H.M. Jonkers, Adv. Mater. Interfaces **5**, 1 (2018).

[7] D. Snoeck, O.M. Jensen, N. de Belie, Cem. Concr. Res. **74**, 59 (2015).

[8] D. Snoeck, N. de Belie, Journal of Materials in Civil Engineering **28**, 1 (2016).

[9] E.S.M. De Rooij, K. Van Tittelboom, N. De Belie, Self-Healing Phenomena in Cement-Based Materials (Springer Netherlands, Dordrecht, The Netherlands, 2013).

[10] Y.F. Su, C. Huang, H.G. Jeong, T. Nantung, J. Olek, P. Baah, N. Lu, Cem. Concr. Compos. **114**, (2020).

[11] V. Wiktor, H.M. Jonkers, Cem. Concr. Compos. **33**, 763 (2011).

[12] J.Y. Wang, D. Snoeck, S. van Vlierberghe, W. Verstraete, N. de Belie, Constr. Build. Mater. **68**, 110 (2014).

[13] Z. Basaran Bundur, M.J. Kirisits, R.D. Ferron, Cem. Concr. Res. **67**, 237 (2015).

[14] M. Vandervoort, Impact of Bioagents on the Cementitious Matrix, master degree thesis, Ghent University, 2019.

[15] S. Joshi, S. Goyal, M.S. Reddy, Constr. Build. Mater. **158**, 601 (2018).

[16] P. Risdanareni, J. Wang, N. de Belie, in 75th Rilem Week Conference (Merida, Mexico, 2021).

[17] D. Snoeck, C. Schröfl, V. Mechtcherine, Materials and Structures/Materiaux et Constructions **51**, (2018).

[18] E. Gruyaert, B. Debbaut, D. Snoeck, P. Díaz, A. Arizo, E. Tziviloglou, E. Schlangen, N. de Belie, Smart. Mater. Struct. **25**, (2016).

[19] N.K. Lee, H.K. Lee, Constr. Build. Mater. **81**, 303 (2015).

[20] N. L. Thomas ,J. D. Birchall, Cem. Concr. Res **13**, 830 (1983).

[21] P. Risdanareni, L. Ma, J. Wang, N. de Belie, Materiales de Construccion **72**, (2022).

[22] W. de Muynck, K. Verbeken, N. de Belie, W. Verstraete, Ecol. Eng. **36**, 99 (2010).

[23] Y. Zhang, H.X. Guo, X.H. Cheng, Constr. Build. Mater. **77**, 160 (2015).

[24] E.B. Ogunbode, I.O. Hassan, Journal of Practices and Technologies **29** (2011).

[25] A.V. Bolobova, V.I. Kondrashchenko, Applied Biochemistry and Microbiology **36**, 205 (2000).

[26] D. Shen, C. Liu, J. Jiang, J. Kang, M. Li, Constr. Build. Mater. **258**, 120068 (2020).