- Technical Paper -

APPLICABILITY OF BIO-BASED MATERIALS TO REPAIR WATER LEAKAGE OF CONCRETE

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ABSTRACT

This paper presents applicability of bio-based materials comprising dry yeast, glucose, and calcium acetate to repair water leakage of concrete. Water permeability test is conducted to evaluate sealing efficiency. FT-IR and FE-SEM analysis show the crystal polymorph observed in the precipitation is calcium carbonate. As the result of permeability tests carried out using leakage specimens, for crack width 0.2 mm, the liquid-based repair materials could decreasing water leakage to zero after 96 hours.
Keywords: bio-based materials, repair leakage, Fourier Transformed Infra-Red spectroscopy (FT-IR), Field Emission Scanning Electron Microscopy (FE-SEM).

1. INTRODUCTION

The appearance of cracks and leakages is an inevitable phenomenon during the aging process of concrete structures upon exposure to weather changes. If left untreated, cracks tend to expand further and eventually lead to costly repair.

Resin-based materials such as epoxy resin have been applied as repairment of gap and cracks in concrete commonly [1]. Epoxy resin is known resistance to acid/alkali and does not lead to corrosion. It also has benefits which are small elastic coefficient and excellent adhesion. However, there are several disadvantages on effects of repairments because of water contamination, when the surface of the concrete is wet affects on adhesion, also there is ultraviolet deterioration concern [2]. Therefore, it appeared not compatible in repairing water leakage where lack part is not identified.

Recently, liquid-based repair materials in the field of self-healing through the use of microbial induced precipitation (MIP) have been conducted [3]–[11]. Kawasaki et al. [3] attempted to use biotechnology as repair materials for ground improvement. The bio-based repair material is comprising yeast, organic nutrient source and calcium source. Microbial metabolism produces carbon dioxide shown in Eq. 1 allows carbonate ions are leading to calcium carbonate precipitations formed by calcium source mixed in bio-based repair materials. It presents that bio-based repair materials using yeast microbial metabolism could precipitate calcium carbonate crystals. In the bio-based repair materials, the $CaCO_3$ precipitates according to the following reactions:

$$
\begin{aligned}
&C_6H_{12}O_6 \rightarrow 2CO_2 + 2C_2H_5OH \\
&CO_2 + H_2O \rightarrow CO_3^{\ 2-} + 2H^+ \\
&Ca^{2+} + CO_3^{\ 2-} \rightarrow CaCO_3 \downarrow
\end{aligned}
\qquad (1)
$$

The microbial metabolic process of bio-materials mixtures as shown in Fig. 1.

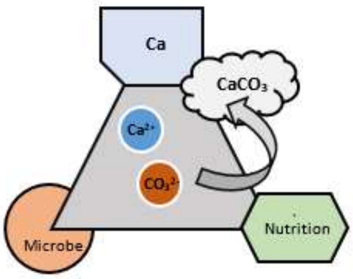

Fig. 1 Basic constituents of bio-based repair material

The materials produced through the reactions do not adversely affect concrete properties because the precipitates are mainly comprised of calcium carbonate which is one of reaction products formed by carbonation of hydration products. Thus, it is preferable if the reaction products have similarity on material properties of concrete.

Besides material properties, the bio-based material is a less viscous material. It may overcome deficiency related to the traditional repair materials. Therefore, it would be useful if the mixture penetrates into deeper zones of gaps and could effectively enhance the water tightness of concrete with the defects.

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Ujike et al. [6] and Kawaai et al. [7] have researched some considerations on precipitation rate of calcium carbonate in bio-based materials. Putri et al. [8]–[10] also investigated the temperature effects, the types of dry yeast, and concentration of Tris buffer solution on precipitation rate of calcium carbonate. This study using commercially available dry yeast as microorganism, glucose as source of organic nutrient and calcium acetate as calcium source which were selected as basic constituents of bio-based repair material.

Moreover, this study investigated the applicability of bio-based repair materials to concrete-member. Correspondingly, on this research, water permeability test was carried out to evaluate the effectiveness of the selected mixtures for sealing cracks in concrete specimens. The precipitates were also tested for Fourier-Transformed Infra-Red spectroscopy (FT-IR) and Field Emission Scanning Electron Microscopy (FE–SEM) analysis for mineral identification formed through the microbial metabolic process of bio-based materials in mixtures.

2. MATERIAL AND METHOD

2.1 Basic constituents of mixtures

Based on the result of past experiments carried out by Putri et. al [10], the highest calcium carbonate precipitates were found to the concentration of tris buffer solution in the range of 0.5 to 0.75 (mol/L) for initial pH adjusted to 9.0. The concentration of dry yeast were specified as 27 g/L, which were mixed with glucose and calcium acetate with concentrations of 0.3 mol/L and 0.15 mol/L respectively. The basic constituents of selected mixture for bio-based materials as shown in Table 1.

Table 1 Basic constituents of bio-based materials

Dry yeast (g/L)	Glucose (mol/L)	Calcium acetate (mol/L)
27	0.3	0.15

2.2 Testing procedure for determining the amount of precipitates in mixtures

In order to measure the concentration of calcium ions present and the pH in mixtures after the reaction had started, each mixture was prepared in a test tube. First, each material, based on the mix proportion specified as shown in Table 1, was prepared and they were mixed with Tris buffer solution in a beaker. The mixture in the beaker was subsequently stirred (800 rpm in 5 minutes) or until each material was visually dissolved into the solution. And then further Tris buffer solution was added to make the solution 60 mL totally. The test tubes were placed in a room controlled at 20ºC for the measurement.

The concentrations of calcium ions and pH were measured in mixtures using commercially available meters (pH/mv meter model SK-620PH and calcium ion electrode model CA-2031). Each test was carried out using two test tubes to confirm the consistency of results obtained. The precipitated calcium carbonate calculated using the following formula:

$$CaCO_3 = Q\left(\frac{mol}{L}\right)\times m(L)\times M\left(\frac{g}{mol}\right)\times\frac{C_0 - C_a}{C_0} \qquad (2)$$

Where $CaCO_3$: the amount of precipitates (g), Q: concentration of calcium acetate (mol/L), m: the amount of solution (L), M: molar mass of calcium carbonate (100.09), C_0: Initial concentration of calcium ion and Ca: concentration of calcium ion measured.

2.3 Application of bio-based repair materials and water permeability test

In this work, the leakage (permeability) test has designed and developed taking into account the characteristic of the bio-based materials. The idea is rather simple and can be described as follows. If water flows through the leakage in concrete, it will end up flowing out from the other end. Water will leak out from the gaps of concrete.

The mix proportion of the concrete is shown in Table 2. Fine aggregate, has a dry density of 2.65 g/cm^2 and water absorption rate 1.68%. For coarse aggregate G1 and coarse aggregate G2 were crushed stone No. 5 (sizes are from 25.0 to 12.5 mm) and No. 6 (sizes are from 19.0 to 9.5 mm) respectively, with density 2.70 g/cm^2 and water absorption rate of 0.66%. The maximum size of the coarse aggregate is 20 mm. All material was produced by Kagi-o, Shirokawa-cho, Seiyo City, Ehime prefecture. This specimen using Ordinary Portland Cement (OPC), and put in room temperature controlled at 20ºC.

Table 2 Mix proportion of concrete specimen

w/c (%)	Slump	Air volume (%)	Admixture
55	8.5	4.5	2.86

Amount (kg/m^3)				
Water	Cement	Sand	G1	G2
175	318	864	383	572

The concrete specimen is propped horizontally. The dimension of the specimen is 400x150x50 mm (bottom side), and 280x150x50 mm (upper side) placed parallel and made crack subsequently. These specimens were sealed with waterproof tape to prevent repair mixtures from leaking through the right and left side of specimens as shown in Fig. 2. Three type of water permeability test are shown in Table 3. Test type A is the main test. The result of water permeability test obtained from the test type A was compared with flow rate result obtained from test type B and C. The effectiveness of bio-based repair materials was evaluated based on consecutive measurements once per 24 hours for the reduction of water leakage in the concrete specimens.

Before the selected mixtures were poured into the crack, water permeability tests were carried out as benchmarks. The quantity of water flowing through the crack were measured for 5 minutes. And then, selected mixtures were poured into the crack. A container is placed underneath the specimen to collect the water drained out through the leakage. The digital scale with a maximum capacity of 2000 g and resolution 0.1 gr is used to measure the weight over time of the water outflow from the leakage. It was removed prior to the water permeability tests which were finally carried out using the specimens in which cracks were supposed to be sealed with precipitated calcium carbonate. In case there is no leakage in the main body or the cracks is sealed already, the water will be no flow at all. A manual stopwatch was used to monitor this time interval.

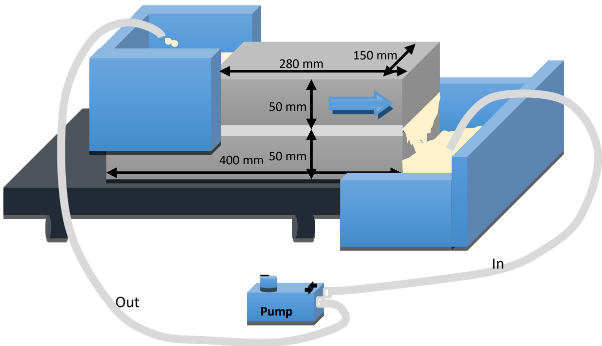

Fig. 2 Experimental set-up for bio-based repair materials and water permeability test

Table 3 Three types of water permeability test

Type	Crack width (mm)	Mixture constituents
A	0.2	Dry yeast + glucose + calcium acetate
B	0.2	Dry yeast + glucose
C	0.6	Dry yeast + glucose + calcium acetate

The application of the selected mixture to cracked concrete specimens was carried out from the back side of concrete specimen via ponding. First, 540 mL of the mixture was poured into the specimen in each application. Using the hand pump, the mixture was cycling in and out through the leakage. And it was carried out once two days for four days, before the water permeability test was conducted.

It is noted that the right and left side of specimen sealed. Thus, the less viscous mixture essentially flowed out through the cracked specimen unless bonding between cracked surface and precipitates was formed immediately after they flowed. 24 hours after leak was stopped, surface of the concrete specimens were observed using a portable digital microscope. Result of surface observation as shown in Fig. 6.

2.4 Evaluation techniques of calcite precipitation by FT-IR and FE-SEM

The test type A was first observed under portable digital microscope to analyze and locate the expected bio-minerals deposition. It was planned the observation would be carried out in five different points throughout the surface of the specimen as sketched in Fig. 3; in the inflow area, slightly below the inflow area, two points in the mid-section, and slightly near to the outflow area. This was intended to obtain higher likelihood to collect evidence of bio-based material activity and identify mineral characteristics.

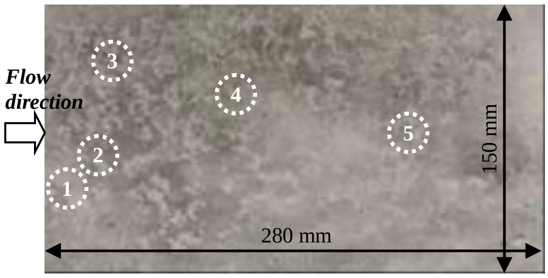

Fig. 3 Surface of concrete specimen (test type A) before pouring bio-based repair materials. Section marked with points where FT-IR observation will be spotted

The calcium carbonate precipitation deposited in the specimens is formed with the aid of a pincer by gentle scrapping the surface of the concrete were analyzed using Fourier-Transformed Infra-Red spectroscopy (FT-IR). Infrared spectroscopy is a technique based on the vibrations of the atoms of a molecule. It is used for the determination of molecular structure or the identification of chemical species. A vibration will be infrared active if a change in the dipole moment of the molecule occurs during the vibration. An infrared spectrum consists of a series of bands or peaks which result from the absorption by a part of the molecule of the incident radiation at a particular energy [12]. FT-IR spectroscopy is especially favored due to its versatility and non-destructiveness. It is a fast and cost-effective technique, as it does not require a sample preparation step [13]. This analysis requires a tiny amount of sample (<5 mg), and furthermore, no preparation or dilution of the sample is needed [14].

A Field Emission Scanning Electron Microscope (FE-SEM, JEOL JSM-7001FA) element were employed to analyze in depth the surface feature of the polished section. Fig. 5 exhibits the FE-SEM image taken at point 1 and 3 from the specimen. The JSM-7001F is a versatile high-performance FE SEM. The electron produces the maximum 200nA probe current with the patented in-lens thermal FEG and small probe diameter even at the large probe current with the patented aperture angle optimizing lens[15].

3. RESULTS AND DISCUSSION

3.1 Water Permeability Test

A water permeability test was carried out before and after the mixture was poured into the cracked specimen to evaluate the effectiveness of the liquid-based repair mixture for leakage in concrete. Table 4 shown measuring water permeability time for concrete specimen. The rate of water flowing through the cracks in the concrete specimens was measured at predetermined intervals up to 300 s as shown in Fig. 4. As can be seen, the water flowing through the cracked section was substantially decreased, which was prominent in the case of mixture poured into the specimens after the mixture was left in room conditions.

Table 4 Measuring water permeability time

Case	Application time
0	Before repaired
1	Immediately after repaired
2	After 24 hours
3	After 48 hours
4	After 72 hours
5	After 96 hours

Fig. 4(a) shows the result of water leakage test for test type A. Flow rate is the slope of the straight line between amount of flow (cm^3) and time (s). As can be seen, 0.73 cm^3/s water flowing through the gaps before the bio-based material was poured into the cracked specimen. After the mixture poured, it was decreased to 0.26 cm^3/s after 24 h and to 0.03 cm^3/s after 72 h. The flow rate is zero after 96 h. In this time, post-repairing permeability test revealed a zero slope which can be interpreted there was no water flow out from the crack.

Based on Eqs. 2, amount of precipitates is mainly comprising calcium carbonate up to 48 h after they were mixed which seemed to reach about 0.388 g in the 30 ml test tube. The volume of the gap is 22.764 cm^3 and based on the calculation, required 1761.5 mL of bio-based materials to fill the leakage for 0.2 mm crack width. Furthermore, it will be possible to fill the cracks by flowing four times of 540 mL of bio-based materials. However, in this experiment, the water leakage was stopped after pouring twice of 540 mL bio-based material. In fact, not all the gaps were filled with calcium carbonate, but because the cracks were partially filled with calcium carbonate, flow rate of water leakage became zero.

This result compares to the water leakage test on test type B and C as shown in Fig. 4(b) and (c). On the other hand, for test type B, there was no significant difference of water leakage from 24 h up to 96 h. It was clear that no precipitation of calcium carbonate after 96 h because the mixture has not contained calcium acetate. Decreasing of water leakage caused by sedimentation of yeast and glucose on the surface of the cracks. This result confirmed by visual observation.

For test type C, the leakage with crack width 0.6 mm was too large to close on 96 h elapsed time. Until 96 h after pouring the mixture, the flow rate in the specimen about 0.38 cm^3/s. In this case, the test continue until water leakage decreasing to zero. The flow rate is zero after 9-days (216 h) pouring of the bio-based materials.

Fig. 5 displays the surface of concrete specimens after the water permeability test were carried out. Formation of suspected newly Ca-based materials is visually seen by comparing to Fig. 3. Mostly, the calcium carbonate precipitated in the inflow area of the specimen. The widespread precipitates in the specimens led to the significant decrease in the water permeability. Furthermore, the results suggested that precipitated calcium carbonate in cracked part concomitant with seeping into deeper zones of concrete specimens was crucial to decrease water leakage effectively.

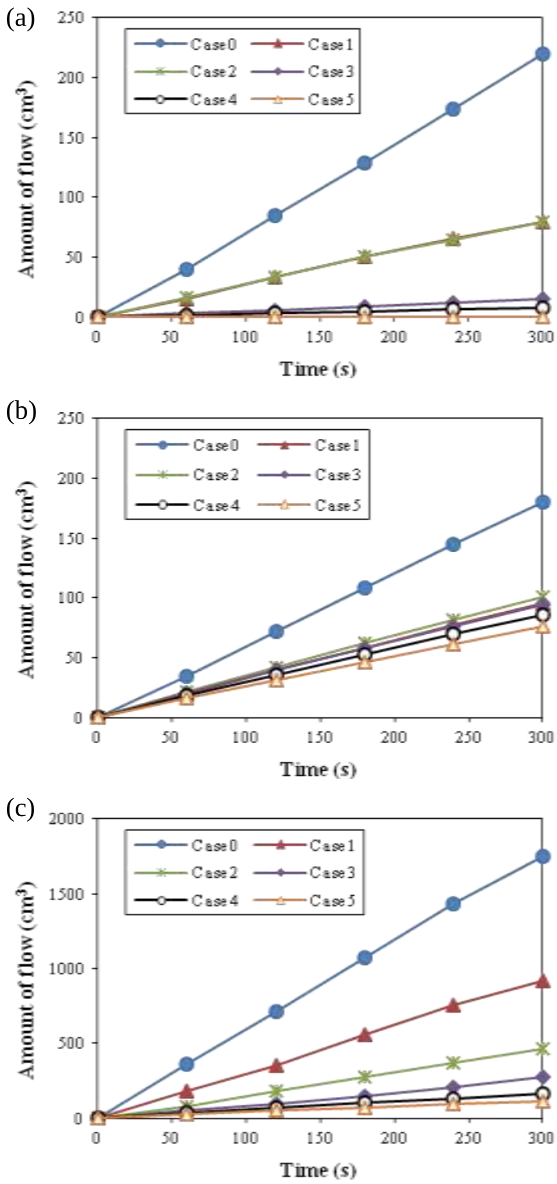

Fig. 4 Result of water permeability test for (a) test type A; (b) test type B and (c) test type C

Precipitation comprising calcium carbonate was visually confirmed in the area surrounding the cracked surface after 4-day pouring of the mixture, some of which was observed using a portable digital microscope as shown in Fig. 6. Fig. 6a and b were after 60x magnifications, and Fig. 6c and d were for 200x magnifications. It is worth noting that the precipitated calcium carbonate would be present in the cracked parts even the bio-based materials mixture is flowing through the cracks. Following the visual observation, the image analysis was carried out for the FT-IR and FE-SEM test.

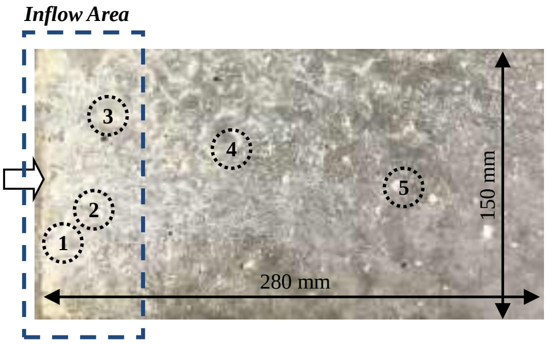

Fig. 5 Surface of concrete specimen after 96 hours pouring of bio-based materials (test type A)

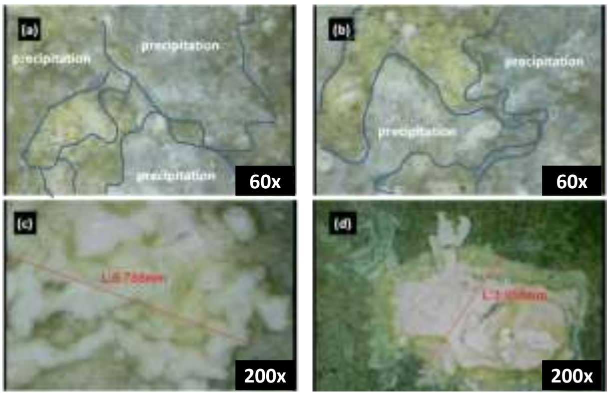

Fig. 6 Images of the post-repairing specimen were taken by 3R Anyty microscope showing the newly formed materials suspected as Ca-based minerals (test type A).

3.3 FT-IR and FE-SEM Analysis

Fig. 7 and 8 present the images of FT-IR and FE-SEM observation. The images were taken from the precipitation on the surface of the test type A. Observation revealed Ca-based surface layer which may be attributed due to carbonation.

The FT-IR analysis confirms the chemical element of calcium carbonate in the crystal which is essentially associated with calcium carbonate precipitated mediated by bio-based repair materials. The IR Spectra were recorded using Thermo Scientific Nicolet iS5 Spectrometer and stores using spectroscopic software (Omnic software)[14]. Fig. 7 is the spectra of FT-IR analysis on precipitate scrapped from the specimen after 4 days. At point 1, the peaks at 1392.35, 1031.73 and 871.667 indicated the presence of calcium carbonate. For precipitation at point 2 and 3, the signals at 1403.924, 1033.658 and 871.67 show the presence of calcium carbonate respectively. Correspondingly, a similar tendency was observed as shown in spectra at point 4. It shows peaks 1392.35, 1031.73 and 871.667. Moreover, precipitation at point 5 also indicates the presence of $CaCO_3$, the peaks at 1394.281, 1029.801 and 871.67. These spectra were compared to the standard spectrum of calcium carbonate from NIST Standard Reference Database[16]. As a result, this spectrum shows that the precipitate is composed in majority of calcium carbonate. This result combined with the FE-SEM observation strongly indicates that bio-based involve at 4 days. This result leads to the implication that bio-based materials can successfully as crack repairing materials.

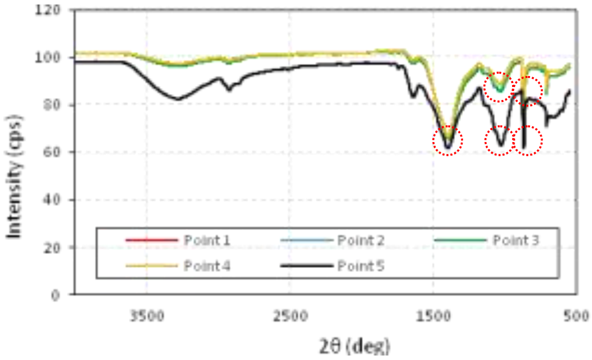

Fig. 7 Spectra of FTIR Analysis in five different points

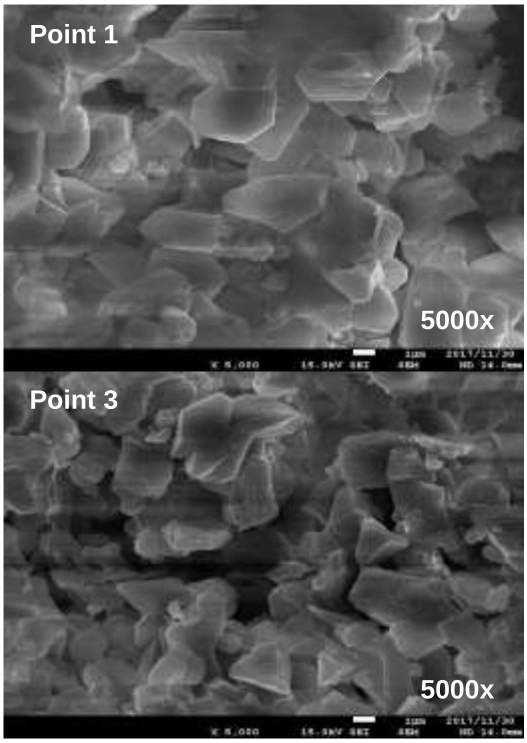

Fig. 8 FE-SEM Analysis of precipitation in point 1 and 3 (5000x magnification)

In the event of calcium acetate was used as the calcium source, rhombohedral carbonate crystals were obtained as shown in Fig. 8. Scanning electron microscopy of rhombohedral $CaCO_3$ crystals on the surface of mortar specimens treated with bio-based materials and a nutrient of glucose and calcium acetate.

4. CONCLUSIONS

The investigation obtained via water permeability tests carried out using leakage specimens, for crack width 0.2 mm, the liquid-based repair materials could decrease water leakage to zero after 96 hours by continously pouring bio-based repair materials. It shows the effectiveness of bio-based repair materials in decreasing water leakage of concrete. FT-IR and FE-SEM analysis also confirm that element of calcium carbonate in the crystal which is essentially associated with calcium carbonate precipitated mediated by bio-based repair materials. As a future investigation, a filling method will be examined in which precipitation by bio-based repair material fill the whole area inside the gap.

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