

Anti-Bio-Fouling Effect of Water-Soluble Glass of Na₂O-ZnO-SiO₂ System

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Abstract: In this study, water-soluble glass based on an Na₂O-ZnO-SiO₂ system was fabricated and its properties related to inhibition of marine biological pollution were analyzed as a function of the amount of Na₂O in the glass. An ion dissolution test in seawater was performed for 1-14 days for glass containing 20-35 mol% ZnO. From the results of the ICP analysis, it was confirmed that the amount of dissolved ions was closely related to the composition of the water-soluble glass and the immersion time in seawater. The Na ions dissolved to 3 order ppm while the Si and Zn ions were dissolved to just a few ppm. *B. thuringiensis* strain, a gram-positive bacterium was used to measure the bactericidal ability of water-soluble glass. It was found that the bactericidal ability of the glass increased with the amount of Zn ions dissolved and the immersion time in seawater. In conclusion, water-soluble glass based on a Na₂O-ZnO-SiO₂ system could be applied to suppress marine bio-fouling pollution.

Key words: Na₂O-ZnO-SiO₂ system, water-soluble glass, microbial sterilization, marine biofouling, dissolved, time

INTRODUCTION

Large-scale red tides occur annually in Korea, causing enormous damage to marine aquaculture farms. The first occurrence of red tide was reported in Jinhae Bay in 1981 and since then the red tide phenomenon has been getting worse and the annual damage cost is more than 11 million dollars per year. In response, many studies have been carried out to remove the red tide by installing equipment such as membranes filled with porous ceramic bodies in marine cage farms (Lee *et al.*, 2014; Kim and Reddy, 2015; Shin, 2014). However, bio-fouling occurs on exposed surfaces of ceramic membranes even after a few months. The ceramic membrane then will not function properly due to the bio-fouling.

Generally, the initial stage of marine biological damage on marine structures starts when microorganisms attach to them. The amount of biodegradation increases exponentially with the deposition of microorganisms, diatoms and other types of seaweed with time (Shim and Jeong, 1987; Sung and Khan, 2015; Sujatha, 2017; Park *et al.*, 2011). The attachment of seaweed and large diatoms may cause structural safety problems by increasing the self-weight and surface resistance of ships and marine structures (Jung *et al.*, 2009; Townsin, 2003). In order to prevent biofouling in the ocean, several

antifouling paints containing various substances such as tin organic compounds have been developed. However, due to their toxicity, some of these products are prohibited worldwide (Yebra *et al.*, 2004).

Recently, many studies on ZnO as a material for inhibiting marine biological pollution have been carried out and some have showed an inhibition property against biological pollution (Seil and Webster, 2012; Sim and Ishvi, 2017; Srinidhi, 2016). Lee *et al.* (2014) found that nanometer size ZnO particles inhibit biofilm formation on marine structures. Leo *et al.* (2012) studied the inhibition of the bio-oxidation phenomenon by applying ZnO nanoparticles to polymer membranes. Sathe *et al.* (2016) developed polymer fibers containing ZnO nanoparticles and evaluated the biooxidation ability for the fibers by observing the photocatalytic reaction of ZnO. Annadurai (Malini *et al.*, 2015; Park *et al.*, 2017) assessed the biohazard of chitosan membranes containing ZnO nanoparticles. However, to date, there has been no in-depth study of the sterilization property of water-soluble glass containing ZnO.

In this study, sodium silicate glass containing ZnO that could be coated on the surface of a ceramic membrane was fabricated. The dissolution rate of Zn ions in seawater and their ability to inhibit the biofouling phenomenon was measured. The solubility and

bactericidal effect of a Na₂O-ZnO-SiO₂ glass system evaluated by varying the amount of ZnO in seawater over time. In particular by observing the microstructure of glass by a scanning electron microscope, the resistance to marine biofouling of the prepared glass specimens was evaluated.

MATERIALS AND METHODS

Experimental

Manufacture of water-soluble glass of Na₂O-ZnO-SiO₂ system: In this study, SiO₂ (99.9%), Na₂CO₃ (Duksan Pure Chemicals, Korea, 99.0%) and ZnO (High Purity Chemicals, Japan) were used as starting materials for preparing Na₂O-ZnO-SiO₂ glass. The batch powder prepared according to the molar ratio shown in Table 1 was mixed by dry ball milling at 60 rpm for 24 h using zirconia balls. The mixed powder was then melted in a vertical furnace at 1400°C for 30 min and then cast into a carbon mold. The formed glass was pulverized with an alumina mortar to control its particle size to 600–850 μm.

Evaluation of elution and microbial sterilization ability of glass: To analyze the long-term microbiocidal ability in seawater of the water-soluble glass produced in this study, the glass was immersed in seawater and ion dissolution was observed for 1, 7 and 14 days by replacing seawater every week. An ICP analysis was performed on the seawater in which the water-soluble glass was dipped by use of an elemental analyzer (Flash EA 1112, Thermo Scientific, Netherlands). The elution rate of each element in the glass was analyzed according to the elution time and composition of glass specimens. In addition, a scanning electron microscope (S-4800, HITACHI, Japan) was used to observe the disintegration process of the glass specimens dipped in the seawater with time.

The germ, positive bacteria, *B. thuringiensis* was inoculated aseptically into a pre-culture medium to be pre-cultured for 12 h. Tests were carried out in a tube in which the water-soluble glass and 5 ml of distilled water was inoculated at 5 vol.% and the time was set at 0, 5, 12 and 24 h. 0.1 mL of solution in each tube was diluted to the appropriate volume and 0.1 mL of the diluted solution was aseptically applied to a previously prepared solid nutrient agar.

The tube containing the dilute solution and solid then incubated at 30°C for 24 h in an incubator. The sterility was evaluated by counting the colonies generated in the solid medium and multiplying the dilution factor by CFU (Colony Forming Unit, viable cell count/mL).

Table 1: Chemical composition of glass (unit: mol %)

Specimen ID	Na ₂ O	ZnO	SiO ₂
15N-35Z	15	35	50
20N-30Z	20	30	50
25N-25Z	25	25	50
30N-20Z	30	20	50

RESULTS AND DISCUSSION

Elution characteristics of water-soluble glass: The amount of elution of Na, Zn and Si ions from the Na₂O-ZnO-SiO₂ glass immersed in the seawater according to exposure time was measured and the results are shown in Fig. 1. Na, Si and Zn ions were present in the pure seawater without glass and the amounts were 6230.20, 1.07 and 0.26 ppm, respectively. In all seawater experiments with glass, the amount of ions detected was higher than the amount of ions present in pure seawater.

Regardless of the period of immersion in seawater, the amount of eluted Na ions which act as a modifier in the glass structure, was the highest at a 3 order ppm level and the amount of eluted Si ions and Zn ions was very low at a several ppm level.

No significant difference in the amount of elution between Si and Zn ions was observed in the case of 1 day. The amount of eluted Si ions, however was about 1.4 to 4.1 times larger than that of Zn ions in the specimens immersed for 7 and 14 days. In the experiment in which the glass was immersed in seawater for 1 or 7 days, the amount of eluted Na increased with increasing Na₂O content in the glass but the amount of Zn and Si ions released decreased with increasing Na₂O content.

In the experiment in which the glass was immersed in seawater for 14 days, the amount of eluted Na increased with increasing Na₂O content in the glass but the amount of Zn and Si ions released showed no significant difference with increasing Na₂O content.

Microbial sterilization ability of water-soluble glass:

The sterilizing ability of glass immersed in the seawater according to exposure time was measured and the results are shown in Fig. 2. This test was done as follows: the bacteria were placed in a container filled with Na₂O-ZnO-SiO₂ glass. For most tests, the bacterial population decreased very rapidly and after 24 h, the number of bacteria decreased by about 98% from the initial number. This trend was also shown when bacteria were added to pure seawater without adding glass.

As the molar ratio of ZnO contained in the glass increased, the sterilization rate tended to increase, suggesting that the role of Zn ions in sterilization was dominant. For the 1 day test, the specimen with the smallest amount of ZnO, the 30N-20Z specimen showed

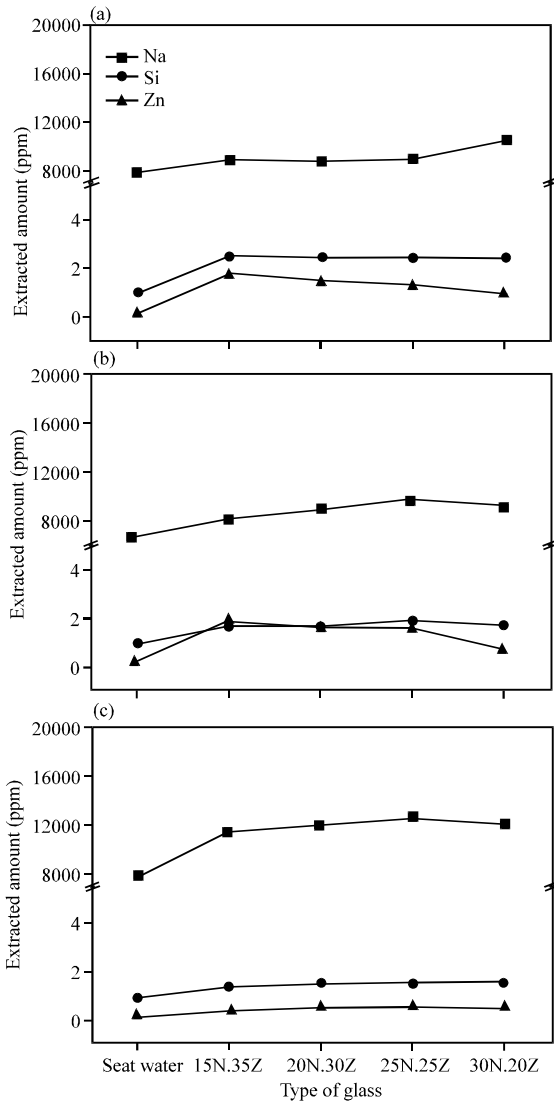


Fig. 1: Dissolution rate of Na, Si and Zn ions from the glass immersed in the seawater with time: a) 1 day; b) 7 days and c) 14 days

the lowest microbial sterilization ability due to having the smallest amount of eluted Zn ions as shown in Fig. 1a-c. For the 7 days test, the 25N-25Z and 30N-20Z specimens showed the lowest microbial sterilization ability. For the 14 days test, however, all specimens showed a similar microbial sterilization effect, indicating that all specimens eluted enough Zn ions for microbial sterilization.

Furthermore, in the 14 days test, the number of bacteria was reduced to almost zero within 12 h: about 96-99% of the initial number of bacteria was sterilized in most of the tests.

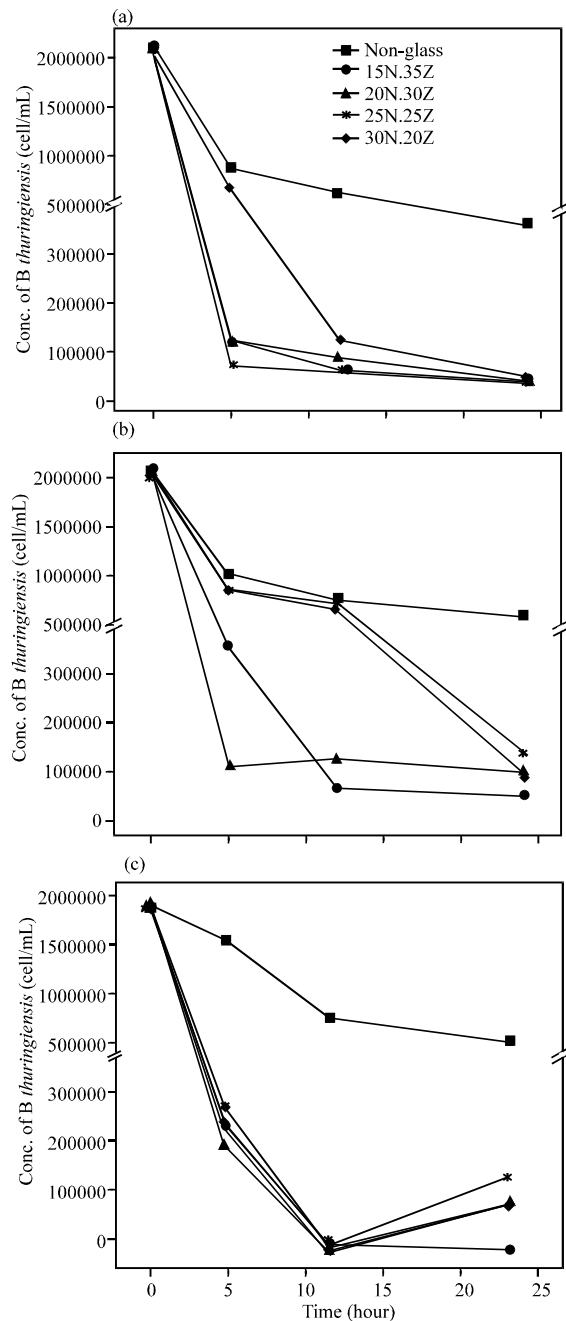


Fig. 2: Microbial sterilization ability of the glass immersed in the seawater with time: a) 1 day; b) 7 days and c) 14 days

Surface of water-soluble glass immersed in seawater:

Figure 3 shows a fresh surface image of the glass specimens showing that the surface is smooth overall regardless of the composition of the glass. However, when observed at high magnification ($\times 25,000$) shown in the upper right corner of the picture, some white spherical

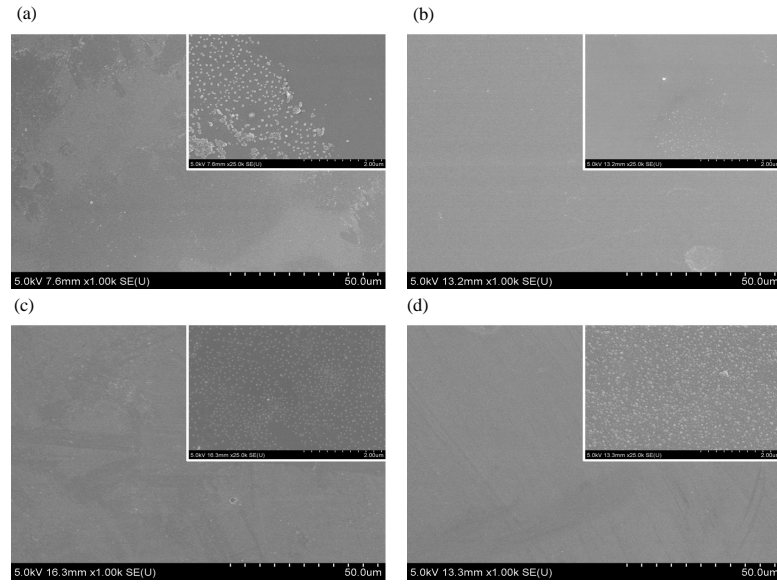


Fig. 3: SEM image of fresh surface of glass specimens not exposed to seawater: a) 15N-35Z; b) 20N-30Z; c) 25N-25Z and d) 30N-20Z

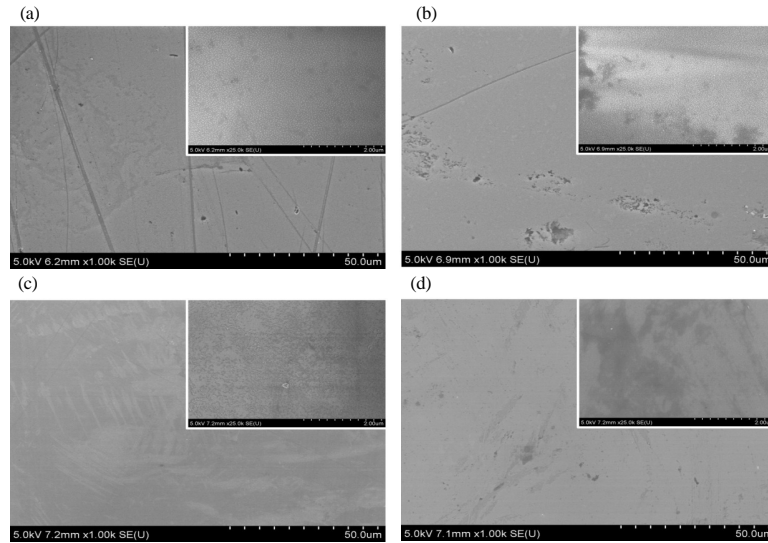


Fig. 4: SEM image of surface of glass specimens immersed in seawater for 1 day: a) 15N-35Z; b) 20N-30Z; c) 25N-25Z and d) 30N-20Z

particles were observed. In addition with a greater amount Na_2O content in glass, more white particles appeared.

Figure 4 presents a surface image of the glass that was immersed for 1 day in seawater. It can be seen that there is no obvious change with the composition of glass showing a relatively smooth surface similar to fresh glass. It is believed that white particles were washed out in the seawater during the 1st day.

Overall, the surface peeled off and some white particles which were not seen in the 1 day test were observed again. In addition as the amount of Na_2O in the glass increased, the surface became rough.

Figure 5 presents a surface image of the glass that was immersed for 14 days in seawater. The surfaces were smooth for all glass specimens. When observed at a high magnification ($\times 25,000$) as presented in the upper right corner of the picture, the 15N-35Z and 20N-30Z glass

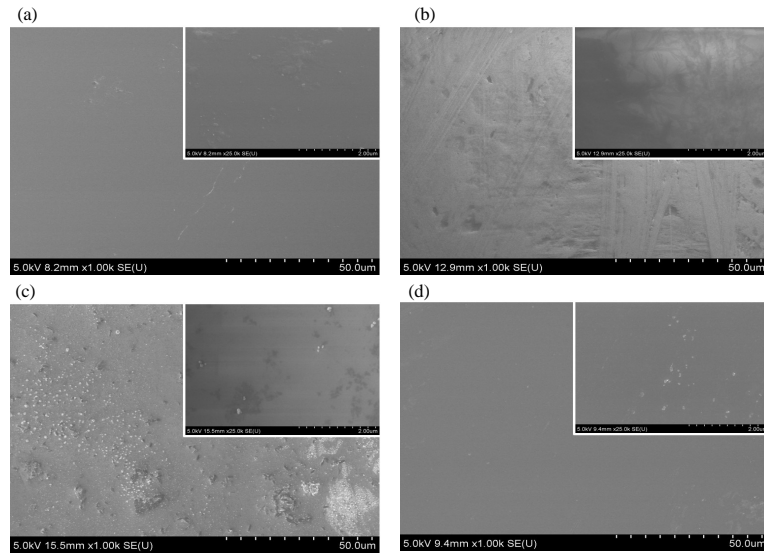


Fig. 5: SEM image of surface of glass specimens immersed for 7 days in seawater: a) 15N-35Z; b) 20N-30Z; c) 25N-25Z and d) 30N-20Z

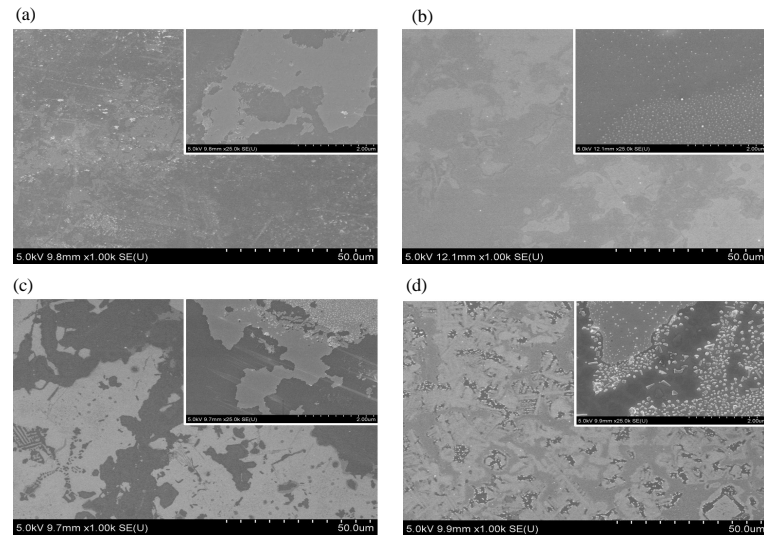


Fig. 6: SEM image of surface of glass specimens immersed for 14 days in seawater: a) 15N-35Z; b) 20N-30Z; c) 25N-25Z and d) 30N-20Z

specimens had many white particles and the 30N-20Z specimen showed no white particles on the surface. It was though that the rough surface shown in the specimen immersed for 7 days collapsed and washed out and the surface became smooth again (Fig. 6).

CONCLUSION

The microbial sterilization ability of waster-soluble glasses according to their composition was evaluated by measuring dissolution characteristics and the following results were obtained.

As the amount of ZnO in the glass increased, the sterilizing ability of water-soluble glass increased, indicating that Zn ions exhibit bactericidal ability. Despite that the amount of Zn ions eluted for the glass immersed in seawater for 14 days decreased, the bactericidal ability increased, indicating that the Na ions also affected the bactericidal ability. The surface disintegration of $\text{Na}_2\text{O-ZnO-SiO}_2$ glass immersed in seawater depends on the composition of the glass and the immersion time in the seawater: the surface is roughly peeled off as the amount of Na_2O in glass increases.

RECOMMENDATIONS

This study confirmed the long-term bactericidal effect of water-soluble glass based on a Na₂O-ZnO-SiO₂ system and furthermore, it is expected that this glass could be applied to various marine fields and therefore, contribute to reducing the damage to marine aquaculture caused by biofouling that occurs in summer.

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