EFFECT OF CHEMICAL COMPOSITION AND DEALKALIZATION ON WEATHERING DURABILITY OF COMMERCAIL SODA-LIME-SILICATE GLASSES

Nuntawan Pongput,[1,2] Sirithan Jiemsirilers,[1,2,]* Tepiwan Jitwatcharakomol[3,]*
[1] Research Unit of Advanced Ceramics, Department of Materials Science, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand
[2] National Center for Petroleum, Petrochemical and Advanced Material, Chulalongkorn University, Bangkok 10330, Thailand
[3] Department of Science Service, Ministry of science and Technology
Bangkok 10400, Thailand
*email: sirithan.j@chula.ac.th, tepiwan@dss.go.th

Abstract: Generally soda-lime silicate glasses are weathered in the atmospheric environment especially in the rainy season of Thailand. In this study, the glass samples were kept in weathering chamber for controlling a cycling condition of 60 % and 80 % relative humidity and a cycling temperature of 20 °C and 32 °C. The weathered glass was visually investigated by difference light intensity, optical microscopy, and by Scanning Electron Microscopy (SEM). The surfaces mechanical properties were evaluated by Vickers hardness. The reformulation by adding Zr and Zn in the glass batch and surface treatment by $NaHSO_4$ as sources of sulfur dioxide gas showed the increase of hydrolytic resistance and surface hardness. The reformulated glass and surface treatment implemented to lower amount of defects and slower the weathering process. After 28 days, the amount of haze defects decreased, comparing with ordinary glass.

Introduction: In the rainy season of Thailand, glass manufacturing still always found the problem of its process, a bloom defect occurs in a very short time. Weathering resistance is a concern for both container and float glass manufacturing. The weathering process starts with the absorption of water form the atmosphere on the glass surface.[1] Then H^+ in absorbed water diffuses into bulk glass via substation with Na^+ in the glass structure and then the leached Na+ forms crystal with the acid gases such as SO_2 and CO_2 which are high content in industrial zone. In long term cycle, this forms irremovable crystalline deposits and clouds on the glass surface. The changing of glass batch can improve the strength of glass structure that leads to decreases alkali leaching volume which is one of weathering steps. This research aimed to study glass batch changing and surface treatment that affect the improvement of weathering durability of container soda-lime silicate glass. The ZrO_2 addition, Zr^{4+} increased glass polymerization, bring about the increasing of chemical durability.[1] In term of glass modifiers (Ca, Mg and Zn), the chemical durability closely relate to bond strength between the cation and the non-bridging oxygen ion. The higher columbic force of the cation and surface treatment, could strengthen the glass structure.[2] Dealkalization is a process for reducing the alkali ions at the near surface of glass namely; the water-soluble crystalline deposits will be rinsed away. After that alkali content near the surface were reduced trends to decreasing of weathering.[3]

Methodology: Glass samples were prepared with the compositions summarized in Table 1. Materials used in the glass batch were commercial grade raw materials due to this study, based on troubleshooting of commercial glass manufacturing. The mixed glass batch was melted at 1550 ° C then annealed at 570 ° C for 1 hour. D0 is ordinary glass as used in the commercial glass manufacturing.

Table 1. The glass composition of ordinary glass and reformulated glass in weight %

Raw material	D0	D1	D2	D3	DZr1	DZr2	DZr3	DZn1	DZn2	DZn3
Sand	60.635	60.635	60.635	60.635	60.635	60.635	60.635	60.635	60.635	60.635
Soda ash	18.000	18.000	18.000	18.000	18.000	18.000	18.000	18.000	18.000	18.000
Sodium sulfate	0.700	0.700	0.700	0.700	0.700	0.700	0.700	0.700	0.700	0.700
Sodium nitrate	0.540	0.540	0.540	0.540	0.540	0.540	0.540	0.540	0.540	0.540
Lime stone	18.950	12.750	6.750	0.750	0.750	0.750	0.750	0.750	0.750	0.750
Antimony	0.055	0.055	0.055	0.055	0.055	0.055	0.055	0.055	0.055	0.055
Alumina	1.115	1.115	1.115	1.115	0.865	0.615	0.115	1.115	1.115	1.115
Dolomite	0.000	6.200	12.200	18.200	18.200	18.200	18.200	18.200	18.200	18.200
Zirconium	0.000	0.000	0.000	0.000	0.000	0.500	1.000	0.000	0.000	0.000
Zinc	0.005	0.005	0.005	0.005	0.005	0.005	0.005	1.005	2.005	3.005
Total	100	100	100	100	100	100	100	100	100	100

Then, D1, D2, and D3 were compositions that limestone was replaced by dolomite. The hydrolytic resistance of D0, D1, D2, and D3 glasses was analyzed at 98 ° C for 1 hour in accordance with ISO 719.[4] The lowest leached alkali formula shown in D3. So that was chosen for adding Zr and Zn in second step. DS was prepared by exposing to SO_2 gas from burning Sodium hydrogen sulfate ($NaHSO_4$) at 570 °C for 5 minutes.[5] The glass samples were kept in cycling atmospheric condition of 60 % and 80 % relative humidity and a cycling temperature of 20°C and 32 °C for 28 days. The weathered glasses were monitored for identify amount of defects by naked eye under the artificial daylight lamp (500 lux) and intense beam light lamp (1000 lux). [6] The surface glasses were inspected by optical microscope and Scanning Electron Microscopy (SEM). And also Energy Dispersive X-ray Spectrometer (EDS) was used to study chemical composition of deposited defects. The near surface hardness was investigated by Vickers hardness.[7]

Results, Discussion and Conclusion:

The hydrolytic resistance of the reformulated glass and surface treated glass were evaluated. The resistance results were shown in Table1. The volume of 0.01 mol/l HCl solution ere used to titrate against solution which was extracted alkali form glass powder. The hydroytic class was classified in accordace with ISO 719. D0 was highest in acid consumption namely; D0 was highest volume of extracted alkali. In group of dolomite addition, 18.20% of dolomite was added in D3, which was lowest alkali leaching formula so that D3 was selected for further experiment of Zn and Zr addition in glass batch. In the reformulated group of Zr and Zn addition, DZr3 and DZn2 were found to be lowest alkali in their group and also less than the original glass. And dealkalization method, D3 was prepared by SO_2 of D3 sample. DS was the lowest leached basic oxide formula when compared with any glass formulas and was classified as grade 2 hydrolytic resistance glass.

Table1. The result of hydrolytic resistace test in accoedace with ISO 719

Sample	0.01M HCl needed to neutralize extracted basic oxides, ml/ 1 g. of glass	Hydrolytic resistance Class
D0	0.53	HGB3
D1	0.45	HGB3
D2	0.43	HGB3
D3	0.41	HGB3
DZr1	0.34	HGB3
DZr2	0.30	HGB3
DZr3	0.26	HGB3
DZn1	0.30	HGB3
DZn2	0.24	HGB3
DZn3	0.32	HGB3
Ds	0.20	HGB2

For weathering test, the flat glass specimens were accelerated weathering under Relative humidity and temperature cycle condition for 28 days which shows in Fig 1 in weathering chamber.

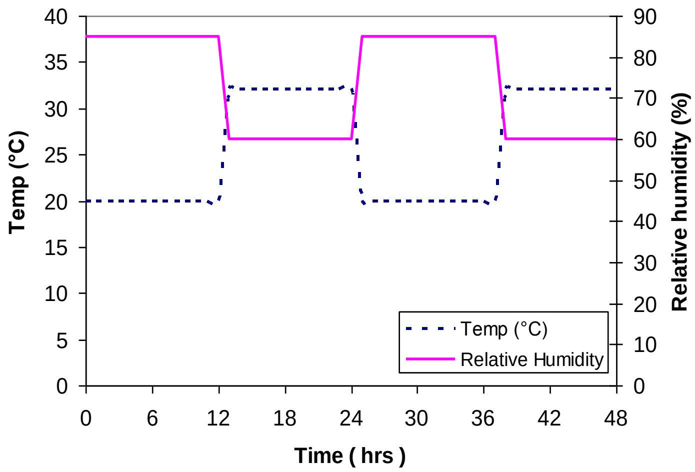


Fig 1. Relative humidity and temperature cycle demonstrated form rainy season in Thailand that used in this work.

Fig 2. Image of glass specimens after weathering.

The cloudy surface can be seen after 28 days of weathering. Fig 2 shows the large tracts of weathered film occurred on D3, DZr3 and DZn2 glass surfaces, while the DS glass sample treated with SO_2 was significantly less than that of reformulates glass.

The defect qualtity on glass surface was evaluated by naked eye in homemade equipment. The difference intensity of lamp were used for haze qualtity classification follow Table 2.[6]

Table2. Criterion for bloom defects quality on glass surface classification.

A	Excellent	No spot and/or haze are visible when examine with the concentrated beam light source less than 6 in. from the specimen.
B	Good	A few spots and/or a slight haze are visible with condition as for A.
C	Fair	Much haze are visible only with ligthing condition as for A.
D	Poor	Some spot are visible with artificial daylight.
E	Very poor	An expensive of defects accumulation are visible with artificial daylight.

The visual observation result shows in Fig 3. The defect appeared on glass samples after were kept in RH and temperature cycle. In first weeks, a few spots were appeared on D3, Dzr and Dzn samples. The clearness quality of D3 samples reverses variation with times. DZn2 sample was classified in class B until third week. The result of DZr3 sample resembles DZn2 except for week 3 that is less clear than DZn2. In last week, D3 Dzr and Dzn samples reveal an expensive accumulation of weathering products in 4 week. Only Ds sample shows clearness surface which was classified in A grade all 4 week.

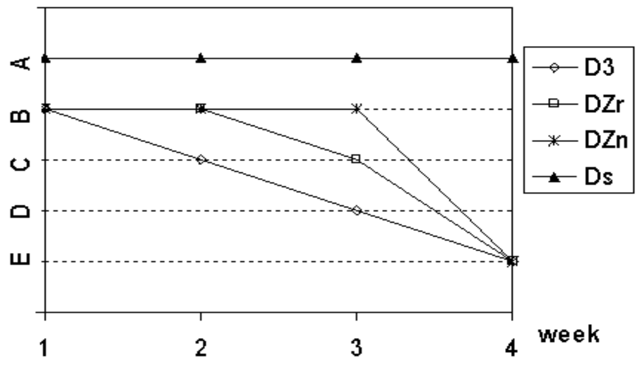
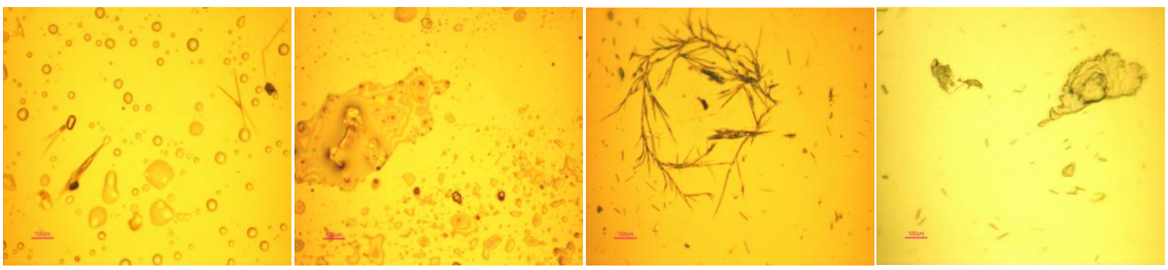


Fig 3. Visual evaluation of reformulated glass specimens after weathering in 28 days.



a b c d

Fig 4. Optical microscopy images of glass samples after weathering.

After 28 days, the weathered surface was monitored by optical microscopy, as shown in Fig 4. The weathering process start with the water in atmosphere is adsorbed on the glass surface that is shown in Fig4a. And then H^+ or $H3O^+$ from absorbed water diffuses into glass via ion-exchange reaction with alkali ions in glass.[8] Fig 4b shows evaporation of absorbed water after that the coated crystalline which was formed by reaction of acid gas with leached alkali that was shown in Fig 4c and Fig 4d.

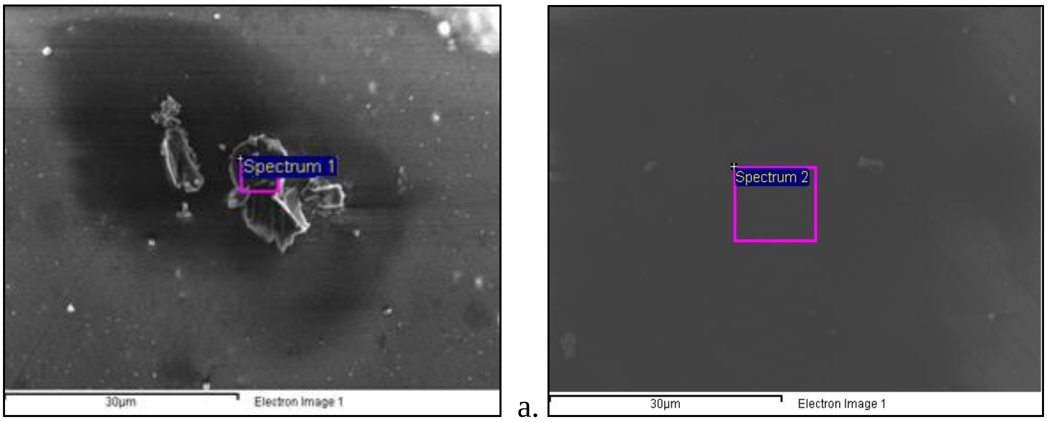


Fig 5. SEM image of ordinary glass after weathering.

Table 3. Chemical composition of weathered surface by EDS.

Element	Weight%	
	spectrum 1	spectrum 2
Si	17.21	9.43
Al	1.14	0.88
Na	9.10	8.83
Ca	2.94	0.09
C	13.63	7.19
O	55.98	73.59
Totals	100	100

Fig5 shows the morphology of glass surfaces after kept in RH and Temperature control condition for 28 days. The crystalline deposits on a weathered glass surface are shown. The chemical composition of weathered surface was monitored by EDS. Table3 shows the chemical composition of deposited crystal which was evidenced the presence of Na and Ca content on coated crystal more than the zones outside the crystals of glass surface. So that if Na leached volume decrease may lead to reduction of weathering.

Mechanical property of all glass samples were compared with before and after weathering. Vickers hardness was shown in Fig 6.

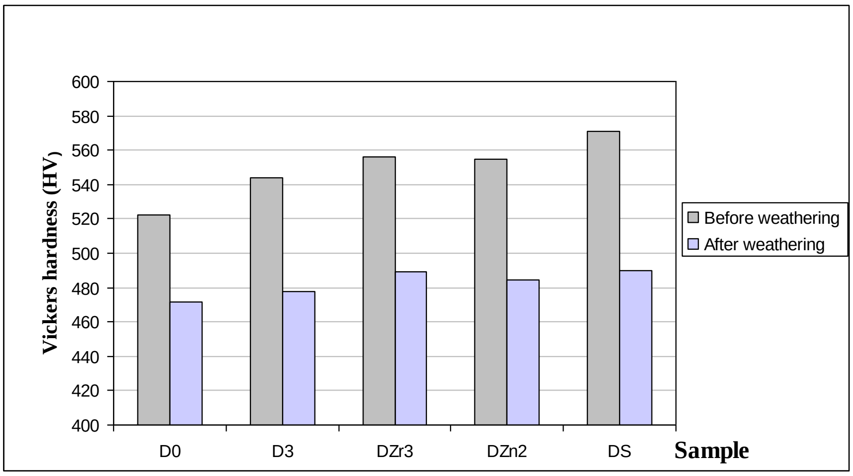


Fig 6. Hardness of as-prepared and weathered glass samples

Structural strength of glass and surface harness are closely related with chemical durability.[8] The Vickers hardness results show that Zr and Zn addition in glass batch increased hardness in DZr3 and DZn2 compares to the ordinary glass. The increase in hardness of reformulated glass brings about decreasing of extracted alkali ions in water as solution which were consisted of deposited crystal and also reduces defect quality after weathering. Ds sample was prepared by dealkalization process, the alkali ions or glass modifier were removed form glass surface result in the least of alkali leaching and showed still clear surface all 4 weeks. In this study, reduction of glass modifier content in near surface leads to decreasing of weatherability which this process shows weathering durability better than the improvement of structural strength by Zr and Zn additions.

Acknowledgments

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