Improvement of Hydrolytic Resistance of Inner Surfaces of Glass Containers for Energy Drinks

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Nowadays, the market of the energy drinks has been expanding substantially. From the safety point of view, the contamination of elements which might be leached from their glass containers is concerned. The glass possessing a higher hydrolytic and chemical resistance can consequently decrease the leaching. The objective of this study is to improve the hydrolytic resistance of the energy drink glass containers by means of treating the inner surfaces with 0, 1, 2, 3 and 5% of acetic acid. Hydrolytic tests were conducted in accordance with ISO 4802-1. The leached elements, i.e., Na, K, Ca, Pb, Cd, Cr, Hg Se As and Sb of treated and untreated glass surfaces were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) at pH 3.5 (close to the pH of energy drinks) in specified time periods.

Introduction

Among materials, it is known that the chemical resistance of glass is superior. This makes glass very popular for packaging food, beverages, cosmetics and for pharmacy. Most of glass is soda-lime-silicate system which is low stable than other types of glass in term of the hydrolytic resistance.

The chemical reactions of soda-lime glass surfaces when attacks with water are as following [1]

$$(Si-O-Na)_{glass} + H_2O \rightarrow (Si-O-H)_{glass} + Na^{+}_{solution} + OH^{-}_{solution} \quad (1)$$

$$2(Si-O-H)_{silanol} \rightarrow (Si-O-Si)_{gel} + H_2O \quad (2)$$

$$(Si-O-Si) + OH^{-} \rightarrow (Si-O-H) + (Si-O^{-}) \quad (3)$$

$$Si-O^{-}) + H_2O \rightarrow (Si-O-H) + OH^{-} \quad (4)$$

Normally, energy drinks are filled in amber soda-lime glass bottles in order to prevent light reactions that may effect to some ingredients. More chemical reactions on glass surfaces could happen from many driving parameters i.e., high temperature, high pressure, acid-base and concentration of solutions, long time storage before consumption, exposure to sunlight during transport and high sodium concentration of glass composition. In addition, it is said that Cr, Th, La, Zr, Nd, Ce, Pr, Nb, Ti, Fe, Co and Er elements could be leached from color glass bottles higher than clear glass bottles. [2].

Objective

The aim of the study is to improve the hydrolytic resistance of inner glass surfaces of energy drinks bottles by a treatment which affects on Na leaching.

Procedure

Energy drink containers

→ Chemical composition analysis pH measurement of energy drinks

→ Untreated / Treated with 1, 2, 3 and 5% acetic acid at 30, 60 and 120 Sec.

→ Hydrolytic resistance testing according to ISO 4802-1

→ Suitable condition of treated containers

→ Filled with citric acid at pH 3.5

→ Leached element analyzed by ICP-MS at 7, 14, 21 and 28 days

Result and Discussion

Table 1. Chemical Composition of glass containers

Chemical Composition, %	Clear Glass Bottles	Energy drinks bottles		
		Sample A	Sample B	Sample C
Na_2O	11.64	14.01	13.77	13.51
MgO	1.07	1.67	1.51	2.79
Al_2O_3	1.67	1.82	1.81	2.02
SiO_2	71.50	71.06	71.49	70.42
P_2O_5	0.02	0.02	0.02	0.02
SO_3	0.18	0.04	0.05	0.04
K_2O	0.27	0.17	0.26	0.21
CaO	13.27	10.75	10.66	10.52
TiO_2	0.08	0.09	0.08	0.07
Fe_2O_3	0.14	0.28	0.26	0.30
SrO	0.07	0.01	0.01	0.01
ZrO_2	0.03	0.02	0.02	0.02
BaO	0.04	-	-	-
Cr_2O_3	-	100 ppm	84 ppm	89 ppm
MnO	-	49 ppm	45 ppm	37 ppm
PbO	100 ppm	70 ppm	77 ppm	75 ppm

Three brands of energy drink bottles in Thailand were used in this study. From the chemical concentration analysis (see table 1.), it was found that chemical compositions of three were similar and Na_2O contents were higher than clear glass bottles obviously. Clear glass contained more PbO meanwhile the contents of Cr_2O_3 and MnO were found only in these three energy drink bottles.

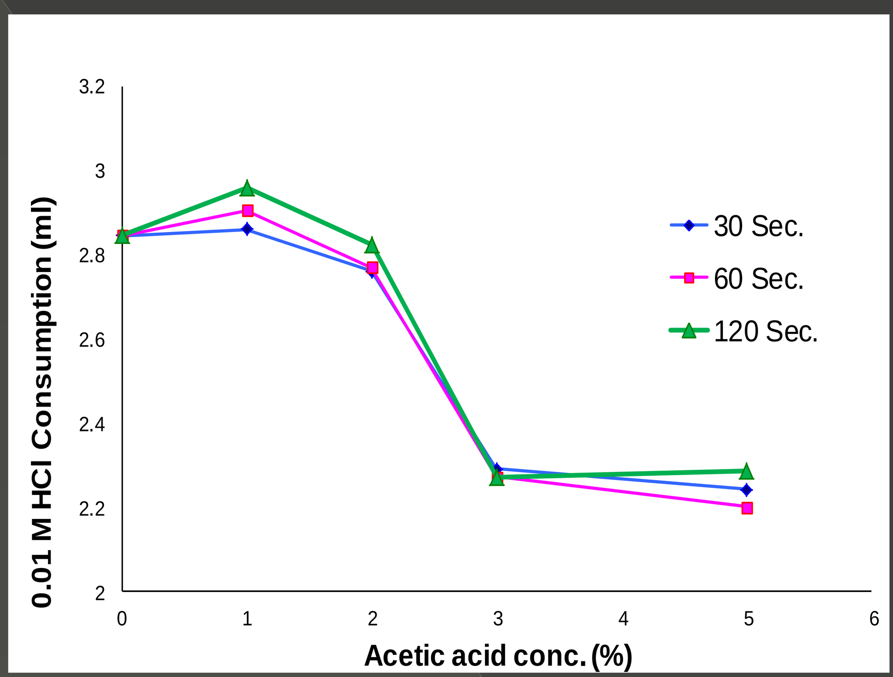

Fig. 1 Hydrolytic resistance of inner surface of company A bottles testing according to ISO 4802-1: titration method.

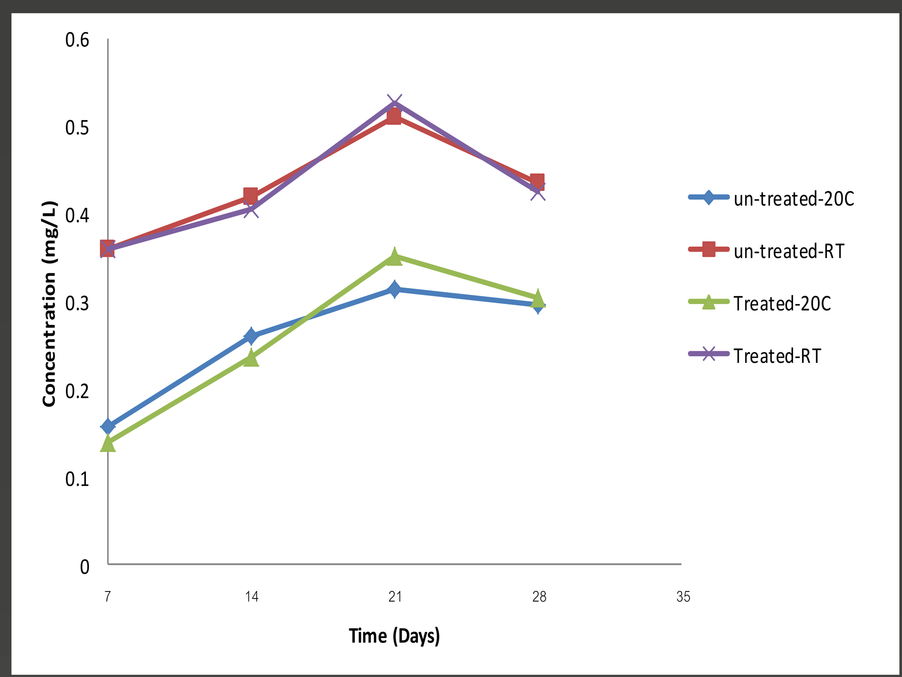

Fig. 2 Leached Na from surfaces of energy drinks bottles after 7, 14, 21 and 28 days in citric acid, pH 3.5

Bottles from company A were treated by acetic acid with various time and concentrations. After treatments, hydrolytic resistances were conducted in accordance with ISO 4802-1. The results in Fig. 1 illustrated Na leached from glass surfaces decreasing with the increasing concentration of acetic acid. But Na leached by 3 – 5% acetic acid showed the stability. This means glass surfaces reactions were already saturated. Hence, 3% acetic acid with 30 seconds was chosen as the selected condition for further glass treatments.

Fig. 2 showed results of leached Na of treated and un-treated bottles after filling with citric acid at pH 3.5 in the room temperature and 20°C with varied durations. The tested were done by ICP-MS technique. The samples kept at the room temperature showed higher Na concentration in solutions than the other one. At the same temperature, there were no significant different between treated and un-treated bottles. However all of them showed the highest leached Na concentrations at 21 days.

Conclusions

In the case of energy drinks (pH 3.5), those which were kept in 20 °C showed lower the leaching of Na. Hence it is recommended to keep the energy drinks in refrigerators all the time and should be consumed as soon as possible. Because of longer storage time at any temperatures over 2 weeks (especially at 21 days) induces higher leached Na which might cause changing of order, color and flavor . However no leached heavy metals found in any case in this study.

Acknowledgement

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