Commercial glasses: structure, chemical durability and surface treatments in acidic medium

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Abstract

Glass chemical durability is at the cross section of industrial issues and scientific knowledge. Glassmaking industries are submitted to increasing regulations, through the framework of Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) in Europe and the food contact material directives, setting standards for the leaching of glass constituents from containers to edible contents over time. Understanding the mechanisms of glass alteration is now required to guarantee the safe use of daily glassware over their lifetime. A major comprehensive study of a wide range of commercial glass compositions has been pursued for four years under the project Behavior of Industrial Glasses During Aqueous Dissolution (BIGDAD) funded by the French Agency for Research (ANR). Five types of silicate glass from four major French glass manufacturers have been investigated: lead crystal glass (fine glassware), soda lime glass (containers for food and cosmetic industries), borosilicate glass (cooking dishes), barium glass (tableware) and opal crystallized glass (tableware). Glass articles made from these compositions are all bestseller products widely available, and yet no comparative study of their structure and durability has been undertaken using the same experimental procedure.

Glass alteration experiments were carried out for three years in acetic acid (4% vol.), which has been established by the International Standard Organization as the reference medium.
for food contact replication. A temperature of 70°C was applied to accelerate the alteration mechanisms. From the analyses of the leachates by ICP-AES, the behavior of each glass constituent in the course of alteration and the kinetics of each glass composition were determined. In parallel, solid-state Nuclear Magnetic Resonance (NMR) spectroscopy was operated on pristine and altered glasses to compare the local environments of the main glass elements and the evolution of the crystalline phases in the opal glass. In complement to the global picture of alteration depicted by kinetics and NMR spectroscopy, surface characterization techniques of high precision were used after alteration to examine the remaining altered layers. SEM images were acquired for altered layer above 1 µm thick and ToF-SIMS confirmed by Spectroscopic Ellipsometry were performed on all samples to allow the most precise measurement of nanometric alteration layers and to access the distribution of elements in the altered layer. In the case of opal crystallized glass, TEM was also engaged to observe the peculiar changes induced by the presence of heterogeneous crystalline phases in this glass. The confrontation of results from local and global scales allowed establishing a referential for the alteration of commercial glasses in acidic medium and unfolding the links between structure and alteration for these compositions.

Industrial glass production may use surface treatments to enhance the properties of their glasses. Consequently, real case glass items found on shelves in our stores and homes have been already processed with surface treatments but the impact of these surface treatments on glass durability is poorly documented. Therefore the second part of this study focused on the impact of these treatments on glass alteration based on alteration tests carried out in the same experimental conditions, as stated previously (acetic acid 4% vol., 70°C). Five surface treatments were selected, all developed by glass manufacturers to address specific needs of their production such as resistance to mechanical abrasion (SnO, TiO), esthetics (TiO, acid polishing), surface tension modification (SiO) or Pb leaching reduction (SO dealkalization treatment). Each of the three coatings (SiO, TiO and SnO) and two acidic attacks (SO dealkalization and acid polishing) was performed on each of the five investigated glass compositions. Glass samples were characterized by ToF-SIMS and SEM before and after alteration showing changes in the surface of the glass which impacted the alteration behavior observed for 1.3 years and recorded through ICP-MS analyses of alteration solution samplings over time. The unique data collected gives access to quantitative information on glass and coating constituents leached in solution over time yielding a broad view of alteration mechanisms. Significant reduction of long-term lead leaching, especially in the case of SO dealkalized lead crystal glass, is obtained as well as beneficial effects towards the retention of Ba in Ba-containing glassy matrices but shows poor interest for borosilicate glass.

Finally, the impact of chromium added as a colorant in lead crystal glass has been investigated because of the high toxicity of hexavalent chromium for human health. The same conditions of alteration were applied (acetic acid 4% vol., 70°C) and uncovered major changes induced by the presence of Cr, even at very low concentrations on the leaching of lead crystal glass. The differences noticed in alteration derived from the structural modifications caused by the presence of Cr. These changes were unraveled by combining NMR spectroscopy and XANES demonstrating that chromium is never found under its hexavalent form in the pristine and altered glasses under experimental uncertainties, nor available in the altered solution. Furthermore, increasing Cr concentrations demonstrated a dual benefit effect on lead crystal chemical durability by reducing the leaching of Pb and increasing the repolymerization of the silicate network. Both observations were rationalized by the specific insertion of Cr in certain glass domains. Overall the extraordinary resistance of these materials to long and tough alteration conditions can be underlined and their endless recyclability make glass containers highly suitable candidates for sustainable product consumption and packaging.

Keywords: Alteration, Food contact, Surface Treatment, Chromium