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The mechanical properties of float glass surfaces measured by nanoindentation and acoustic microscopy

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Abstract

We have combined nanoindentation with measurements of Rayleigh wave velocity to determine the elastic properties of the surfaces of a commercial soda–lime float glass and found significant differences between the mechanical behaviour of the side in contact with the air and that in contact with tin. By using two measurement methods we have obtained the two independent elastic constants of glass (assuming surface isotropy and homogeneity). The air-side has a Young's modulus $E = 81.3 \pm 0.5$ GPa and Poisson's ratio $\nu = 0.22 \pm 0.01$, which is significantly different from the tin-side values of $E = 79.6 \pm 1.0$ GPa and $\nu = 0.187 \pm 0.015$. The Young's modulus of both surfaces is significantly greater than the bulk value reported by the manufacturer of 73 GPa and Poisson's ratio smaller than the reported value of 0.23. The tin-side, having a lower Young's modulus than the air-side, is in the opposite sense to the reported increase in stiffness of bulk float glass with increasing levels of tin doping. We critically review the possible mechanisms for the difference in mechanical properties between the tin- and air-sides of a float glass sheet and produce quantified predictions of likely changes from each mechanism. From this we conclude that no individual mechanism can account for the magnitude of the difference we have measured.

Keywords: Acoustic methods; Nanoindentation; Non-metallic glasses (silicates); Elastic behaviour

1. Introduction

1.1. Properties of float glass surfaces

Most flat soda–lime glass is manufactured using the float glass process. Molten glass is poured onto a liquid tin bath, on which it cools and solidifies, to produce two flat and parallel surfaces of a sheet with thickness typically in the range 2–10 mm. These two surfaces will be subsequently distinguished as the tin-side and air-side of the glass sheet. After solidification, the continuous glass sheet undergoes a carefully controlled cooling process to eliminate any residual stresses before being cut into sheets for subsequent use. The air-side of the sheet remains free of any contact throughout this process. The tin-side has been in contact with liquid tin and there is some diffusion of tin into the glass structure near the interface. The tin-side is also in contact with supporting rollers during heat treatment. Thus the two sides of the glass sheet undergo different histories during processing and it is the objective of this study to investigate whether these histories influence the mechanical properties of the glass surface.

It is well known that there is some incorporation of tin into the glass network structure during the float glass process. Depth profiling microanalysis using Rutherford backscattering (RBS) indicates that the highest concentrations of Sn occur in the top 100–200 nm of the tin-side [1,2]. Sn can penetrate up to 40 μm into the surface of float glass during processing where it exists in both stannous (Sn^{2+}) and stannic (Sn^{4+}) forms, with Sn^{2+} predominating near the surface and Sn^{4+} predominating in the subsurface region. The penetration of Sn into the glass follows a diffusion profile and significant concentrations of Sn can

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penetrate up to 40 μm into the glass sheet. With some glass compositions there is an anomalous increase or "hump" in the tin concentration profile beneath the surface. The reasons for this are not fully understood but are believed to be associated with a change in the dominant ionic species from Sn^{2+} to Sn^{4+} [3]. Sn is believed to diffuse into the glass as Sn^{2+} but is partially oxidized within the glass to Sn^{4+} and also at the surface as the glass lifts off the liquid Sn surface [4]. Krohn et al. [5] measured the elastic properties of bulk soda–lime glasses that had been doped with up to 3 mol.% tin oxide. They found a small increase in elastic modulus with increasing tin content. Ziemath et al. [6] found an increase in hardness of tin-doped float glass with increasing Sn content and also a small increase in bulk density.

The thermal history of glass is known to influence its mechanical behaviour. The fictive temperature of a glass, T_f, is defined as the effective glass transition temperature of a glass for its particular thermal history. Glasses of identical composition, but with different T_f, can have significantly different physical properties. Vacher et al. [7] studied the properties of crown glass as a function of T_f using Brillouin scattering and found a longitudinal sound velocity $c_l = 5400\ \mathrm{m\ s^{-1}}$ at $T_f = 740\ ^\circ\mathrm{C}$ and $c_l = 5600\ \mathrm{m\ s^{-1}}$ at $T_f = 590\ ^\circ\mathrm{C}$. In another study [8], the influence of fictive temperature on specimen density was measured and the elastic modulus computed at two fictive temperatures for silica glass, with $c_l = 5960\ \mathrm{m\ s^{-1}}$ and $E = 78\ \mathrm{GPa}$ at $T_f = 1200\ ^\circ\mathrm{C}$ and, $c_l = 5980\ \mathrm{m\ s^{-1}}$ and $E = 79\ \mathrm{GPa}$ at $T_f = 1500\ ^\circ\mathrm{C}$. Thus if the air- and tin-sides of the glass have different values of T_f, they could have a measurable difference in their mechanical properties.

In addition, the tin-side of the glass sheet passes over a number of solid roller surfaces during the manufacture of float glass. The surface of a brittle material is readily damaged through contact, introducing a population of subcritical cracks. It is well known that the presence of a population of cracks within a body results in a reduction in its elastic stiffness. Warren et al. [9] published results on the mechanical properties of glass surfaces using acoustic microscopy and Brillouin scattering. They found that the tin-side shows a lower stiffness than the air-side and they hypothesized that this was because the tin-side showed an increased level of damage. This was supported by a further study [10] using Hertzian indentation that measured a significantly greater defect density on the tin-side when compared with the air-side.

Howell et al. [11] studied the tin- and air-sides of glass sheets using nanoindentation. They reported small differences in the mechanical properties between the air- and tin-sides but concluded that these differences were not significant. They found a significant increase in elastic modulus and hardness when the top 150 nm of the glass surface was probed and suggested that this was caused by chemical differences between the near surface region and the interior of the glass. A more recent study by Kolluru et al. [12] reviewed the available literature on the mechanical properties of the tin- and air-sides of float glass and concluded that there was little consistency among the published data. They varied the local environment through using cleaning procedures in acidic, neutral or alkali solutions prior to measuring the near surface elastic properties using nanoindentation. They found that the tin-side of the glass was more resistant to chemical attack than the air-side and they hence proposed that the poor agreement seen between published data is caused by poorly defined and documented experimental conditions, with environmental effects probably accounting for the differences in glass surface properties reported in the literature.

Thus we can see that the mechanical properties of the tin- and air-sides of float glass may be different because of their environment and history of processing; however, prior studies have not conclusively determined whether this is so. It is the objective of this study to accurately quantify the elastic properties of the tin-side and air-side of float glass samples using two independent measures of near surface mechanical properties, nanoindentation and *z*-contrast acoustic microscopy (which measures the Rayleigh wave velocity on a surface), and thus determine whether there is any significant difference between them.

1.2. Nanoindentation

Nanoindentation can be used to measure the mechanical properties of the near surface regions of materials through recording and interpreting the force–displacement relation that occurs when a well-defined indenter is driven into a surface. Oliver and Pharr [13] demonstrated that it is possible to analyse the force–displacement data to derive an expression for the contact stiffness and hence the plane strain elastic modulus:

$$E^* = \frac{E}{(1-\nu^2)} \tag{1}$$

where E and ν are the elastic modulus and Poisson's ratio of the bulk material. Nanoindentation is now an accepted tool for the characterization of the elastic properties of materials and its use in practice is now described by an international standard [14]. When nanoindentation is used to characterize the elastic properties of a material, it has become common practice to assume a value for Poisson's ratio in Eq. (1) and to quote a calculated Young's modulus that is based on this assumption.

1.3. z-Contrast acoustic microscopy

In an acoustic microscope, a piezoelectric transducer transmits high-frequency acoustic waves through a sapphire lens. The lens is acoustically coupled to the surface through a drop of water. At the lens/water interface, acoustic waves are focussed to a spot at the water/material interface. Here two wave paths are important. One travels to the interface and is reflected straight back to the lens because of the mismatch in acoustic impedance between