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Characterization and reactivity of sodium aluminoborosilicate glass fiber surfaces

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ABSTRACT

Multicomponent complex oxides, such as sodium aluminoborosilicate glass fibers, are important materials used for thermal insulation in buildings and homes. Although the surface properties of single oxides, such as silica, have been extensively studied, less is known about the distribution of reactive sites at the surface of multicomponent oxides. Here, we investigated the reactivity of sodium aluminoborosilicate glass fiber surfaces for better understanding of their interface chemistry and bonding with acrylic polymers. Acetic acid (with and without a ^{13}C enrichment) was used as a probe representative of the carboxylic functional groups in many acrylic polymers and adhesives. Inverse gas chromatography coupled to a mass spectrometer (IGC–MS), and solid state nuclear magnetic resonance (NMR), were used to characterize the fiber surface reactions and surface chemical structure. In this way, we discovered that both sodium ions in the glass surface, as well as sodium carbonate salts that formed on the surface due to the intrinsic reactivity of this glass in humid air, are primary sites of interaction with the carboxylic acid. Surface analysis by X-ray photoelectron spectroscopy (XPS) confirmed the presence of sodium carbonates on these surfaces. Computer simulations of the interactions between the reactive sites on the glass fiber surface with acetic acid were performed to evaluate energetically favorable reactions. The adsorption reactions with sodium in the glass structure provide adhesive bonding sites, whereas the reaction with the sodium carbonate consumes the acid to form sodium-carboxylate, H_2O and CO_2 without any contribution to chemical bonding at the interface.

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1. Introduction

The applications of glass fibers are diverse; they are used for insulation, filtration, reinforcements and more [1]. Chemical knowledge obtained from single oxide materials is often applied to understand multicomponent oxide surfaces, even though it is widely recognized that a broad distribution of reactive sites exist at the surface of these more complex systems [2,3]. The surface atomic structure of sodium aluminoborosilicate glass fibers is heterogeneous due to its disorder and the multicomponent nature of this glass system. Thus, a wide distribution of adsorption sites can be expected. In the case of these hydrolytically reactive alkali–silica surfaces, reactions with humidity can further modify the surface. Of particular relevance here is the formation of carbonate salts on the

surface during processing and storage due to atmospheric weathering [4–8]. This can deplete the alkali through an ion exchange reaction with water to create a hydrated surface layer and sodium-carbonate reaction products [9].

Understanding the interfacial bonding of a polymer with a glass surface requires a thorough knowledge of the reactive sites at the polymer/glass interface. The specific bonds that form when multicomponent aluminoborosilicate glasses are dosed with simple organic molecules (representative of the functional groups in the polymer) is one way to understand these surface reactions and the interface they produce. In a previous study [10], the adsorption of acetic acid was determined to be very different on this sodium aluminoborosilicate glass compared to a pure silica surface. Whereas silyl–ester bonds linked the acetic acid to the pure silica surface, the formation of sodium-carboxylate was observed on the sodium-aluminoborosilicate surface. It was not clear whether the carboxylate was created as a distinct phase via leaching of sodium from the glass surface, or formed a complex with sodium

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ions within the glass surface structure. The possible effects of surface hydration and weathering were not considered, although in most industrial practices there is limited exposure of the fresh fiber surface to humidity before the coating is applied. In this study, the surface reactions and chemical structure of the reaction products on the multicomponent glass fibers are examined in more detail using a combination of inverse gas chromatography with a mass-spectrometer (IGC–MS) and solid-state nuclear magnetic resonance (NMR). We also use the deconvolution of a NMR line to refine the conclusion of previous NMR studies [10]. Geometry optimization using Gaussian 03 software package was used to study the thermodynamic favorability of different reaction complexes. Acetic acid was chosen as the probe molecule due to the prevalence of carboxylic acid groups in many commercial polymer adhesives and coatings, and their potential to form silyl ester linkages to the silicate network and carboxylates with sodium (and other alkali or alkaline earth species in glass).

The term IGC unifies several chromatographic techniques that, in contrast with conventional chromatography, are used not for the study of a mobile phase but for the study of a stationary phase, which in this case is a bundle of glass fibers. IGC is mainly used for measuring surface energies (IGC at infinite dilution), adsorption isotherms (IGC at finite concentrations) and diffusion in polymers among others [11]. However, in this study IGC–MS is used to study chemical reactions on glass fiber surfaces.

2. Experimental

2.1. Materials

Sodium aluminoborosilicate glass fibers were drawn using a lab-scale single-tip fiber drawing system. Bulk glass marbles (a commercial glass wool insulation composition, courtesy of Johns–Manville) were re-melted at 1000 °C in a single tip platinum–rhodium crucible and allowed to equilibrate for 1 h before drawing fiber. The melted glass was drawn through a 2 mm diameter tip at 4.6 m/s onto a rotating Teflon cylinder. Fibers were drawn for 15 min under standard laboratory conditions (25 °C and less than 25% relative humidity) and either analyzed immediately or stored under vacuum for future analyzes. Fibers had an average diameter of approximately 24 μm.

Analytical columns for the IGC experiments consisted of quartz tubing (6.3 mm outer diameter, 4 mm inner diameter, Technical Glass Products) with a length of 23 cm. The quartz tubing was cleaned using ethanol and then dried in a vacuum oven for 12 h at 125 °C. Fibers were packed into the column by tying wax-free dental floss around the center of a 52 cm long monofilament bundle. The strand of floss was then used to pull the fibers through the column ensuring alignment of the fibers along the column axis. The column was packed as densely as possible to maximize the amount of surface area available for adsorption. On average, 3 g of fibers could be packed within the 23 cm long, 4 mm internal diameter column.

Acetic acid (HPLC grade, >99%, Sigma–Aldrich) and isotopically enriched acetic acid ^{13}C (99 atom %, Sigma–Aldrich) were used for the adsorption experiments. Sodium carbonate (ACS primary standard, 99.95–100.05% (dried basis), Alfa Aesar) was used for the NMR experiments.

2.2. Characterization methods

2.2.1. IGC–MS

IGC–MS experiments were performed using a standard GC (gas chromatograph) (HP 5890 Series II GC) equipped with a 5792 mass spectrometer (GC–MS). The oven temperature was set at 100 °C and the split/splitless injector temperature was set at 60 °C. A cup liner was used with injection directly in the cup; this created a broad peak of solute concentration at the inlet of the column. The pressure drop on the packed column (a fraction of a psi) is too small for the electronic pressure control (EPC) of the HP 5890. For that reason, the deactivated guard column (6 m length, 0.25 mm internal diameter) was inserted between the injector and the packed column.

Once the column is loaded in the GC, it is conditioned under UHP (Ultra High Purity) helium (10 mL/min) at 200 °C for 30 min before any experiment begins. A typical IGC analysis consisted of an injection of 1 μL of acetic acid using a Hamilton syringe (7000 series, Hamilton Company, Reno, NV). Before injection the mass sensitive detector (MSD) is turned on and a time delay of 0.5 min precedes the actual injection.

A GC/MS chromatogram consists of separate points, each point containing the entire mass spectrum. The mass spectra were scanned in the interval of m/z values from 10 to 70. Da. There are two standard procedures the MS software allows one to carry out with those spectra: background subtraction and averaging. Both were employed in this study. The background spectrum was recorded during the first 0.5 min before injection of acetic acid and was subtracted from all the target spectra. The background spectrum included mainly the lines of $m/z = 17$, 18 (water) and $m/z = 28$, 32 (air). Averaging allows one to average spectra in a predetermined area, it is a process performed by the instrument software. In this study averaged areas are the portions within the lines marked in the spectra (Fig. 3). Averaging allows to have a better representation of the masses obtained in a certain region and it is based on time, not m/z.

Another subtraction procedure used in this work was subtraction of the pure acetic acid spectrum from the sample spectrum. The goal of this subtraction was to discover the reaction products which appear due to interaction of acetic acid with the glass surface. The pure acetic acid subtraction is performed using a special Microsoft Excel module developed for this work. First, the mass spectrum of pure acetic acid is obtained without the packed column (the guard column is connected to the MS). The three lines with highest abundance in this spectrum are selected, and then the same three lines are searched for in the target spectrum. A ratio of abundance for each of the three lines in the target and pure acetic acid spectra is made, and an average is calculated. Then, all the lines in the pure acetic acid spectra are multiplied by that averaged ratio and subtracted from the target spectrum.

There are three molecules (carbon dioxide, water and acetic acid) whose mass spectra are discussed below. Those mass spectra can be found in Ref. [12].

2.2.2. Nuclear magnetic resonance (NMR)

For NMR experiments, glass fibers and sodium carbonate powder samples were packed into 4 mm (outer diameter) zirconia rotors and fitted with a Kel-F drive cap. Sample preparation, including the packing and unpacking of rotors, was performed under an inert nitrogen atmosphere utilizing a glove bag apparatus. The NMR probe molecule was ^{13}C carbonyl enriched (99 atom%) acetic acid (Sigma–Aldrich, St. Louis, MO).

A custom built dosing apparatus was used to perform vapor dosing of NMR samples. The apparatus consisted of a roughing pump connected to a glass manifold with two separate chambers. One of the chambers, called the sample chamber, was heated using an external furnace, and the second chamber held acetic acid. The dosing experiment consist by loading about 0.5 g of sample and then heating the sample to 125 °C for 30 min under vacuum (~1 × 10^{-3} Torr). After the 30 min of heating, the vacuum valve was closed, and the dosing chamber is opened to expose the sample to the vapor of acetic acid for up to 16 h. After dosing, the sample chamber was disconnected from the apparatus and placed in a N$_2$ purged glove bag in order for the sample to be packed into NMR