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AN ENVIRONMENTAL STAGE FOR IN-SITU STUDIES OF BIOPOLYMERS IN HIGH PRESSURE CO_2

A.V. Nawaby, P.S. Whitfield, and X. Liao

Institute for Chemical Process and Environmental Technology, National Research Council Canada, 1200 Montreal Road, Ottawa, Ontario, K1A 0R6, Canada

ABSTRACT

A high pressure stage for CO_2 processing has been designed, certified according to Canadian Standards Association (CSA) regulations, and built by an approved pressure-vessel manufacturer. This stage is designed to fit onto a normal laboratory powder diffractometer. Together with the use of MoKα radiation and a Bruker Våntec PSD detector, this stage will allow extensive studies on the kinetics of polymer crystallization under sub- and super-critical CO_2.

INTRODUCTION

The application of X-rays to study high pressure systems has largely been used by the mineralogical community for geologically-important structures. These studies often use diamond anvil cells (DACs) and can easily reach pressures in the GPa range. However, the behaviour of biopolymers in CO_2 makes the use of DACs very difficult if not impossible.

There are many studies in the literature reporting on sorption kinetics of CO_2 at sub and supercritical conditions in polymers [1-3]. There is however comparatively little fundamental information on the interaction of CO_2 with biopolymers such as polylactic acid (PLA) and the resultant physical changes thus induced. Preliminary investigations on the interaction of CO_2 with PLA and PLA nanocomposites indicate induction of crystallinity in the polymer as a function of gas pressure [4,5]. Fortunately the pressures required for studying polymer–CO_2 systems, even at the supercritical state are much lower (125 bar), thus allowing for the use of an environmental pressure stage in the laboratory. The design described in this paper is based on work by Koster van Groos *et al.* [6] for studying gas hydrate systems under high pressures.

The volume of gas and the stage dimensions qualifies as a Category "H" fitting under the Canadian Standard Association (CSA) B51 pressure vessel code [7]. The original design had no certification [6]; the design presented in this work has been modified and evaluated using finite element analysis to satisfy the pressure vessel regulations. In order to safely reach 125 bars and satisfy the Ontario Technical Standards and Safety Authority (TSSA), the design was modelled, modified, and certified by a professional pressure engineer. The certification allow for operation with air, nitrogen or CO_2 in the temperature range -40 to 200ºC. The use of flammable gases such as methane or hydrogen would require more checks under different parts of the regulatory code.

EXPERIMENTAL

The original design by Koster van Groos [6] was modified in order to cope with higher pressures. The window assemblies were changed to a Swagelok-type compression fitting with Viton O-rings to more easily pass TSSA certification. The materials were all required to conform to those allowable for category "H" pressure fittings. The windows were 3.175mm (0.125 inches) thick discs with anti-corrosion coatings supplied by Brush-Wellman. The grade of beryllium used was SR-200. Although this is not the optimum material for X-ray windows (nominal 2.0% impurities as opposed to 1.0% for PF-60 beryllium foil), the mechanical properties were available for finite element analysis, and could be certified on delivery.

The original design was for a Siemens D5000 θ–θ diffractometer, which uses the same goniometer fitting as the θ–θ Bruker D8 system in our laboratory. In common with the design by Koster van Groos [6]; the temperature of the sample can be varied between -40 to 200ºC by circulating a suitable fluid. A K-type thermocouple is located close to the sample position to monitor the stage temperature. The design does not use any brazing or welding, which reduces the scope for failure of the fitting. A collar screws into place to hold and seal the cover over the sample region. The accessible 2θ range is from 1 to 60º, which is lower than the 70º of Koster van Groos, but when using MoKα, this is still equivalent to a 2θ greater than 180º using CuKα.

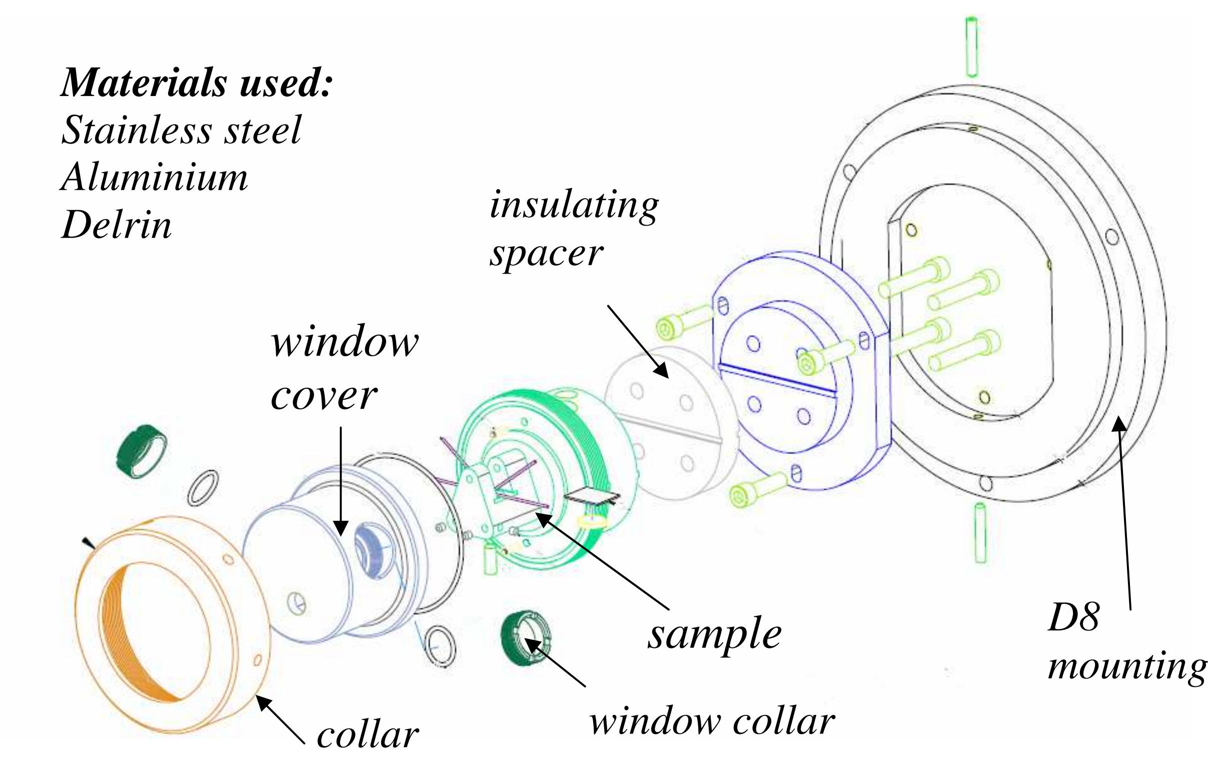

Figure 1. Exploded view of the construction of the high pressure stage.

RESULTS AND DISCUSSION

Although Koster van Groos [6] used 6.35mm thick beryllium windows for its design, the finite element analysis showed that 3.17mm windows would be sufficient even for the higher pressures. This is desirable due to the reduced attenuation and material costs.

The body of the pressure vessel itself is made of stainless steel (Figure 1), with the mounting to the goniometer constructed of aluminium. A spacer made of Delrin polymer is used to thermally insulate the stage from the goniometer. When assembled (Figure 2) the stage is very compact and weights about 2.5 kg. The vertical adjustment on the goniometer adapter plate allows for easy sample height changes for optimum alignment.

A Bruker D8 θ–θ diffractometer with variable slits will be equipped with a molybdenum X-ray tube to reduce attenuation by the windows and high pressure gas. A Bruker Våntec PSD detector will be used in 10º static snapshot mode. The use of the shorter wavelength has the added benefit of fitting a larger d-spacing range in the 10º PSD window. Samples will be 25.4mm square compression moulded polymer. The samples will be evacuated inside the stage for 1 day in order to simulate the conditions of sorption measurements. After this high purity CO_2 will be applied at a controlled pressure. The polymers will absorb some of the gas, so a reservoir will be used to stabilise the pressure.

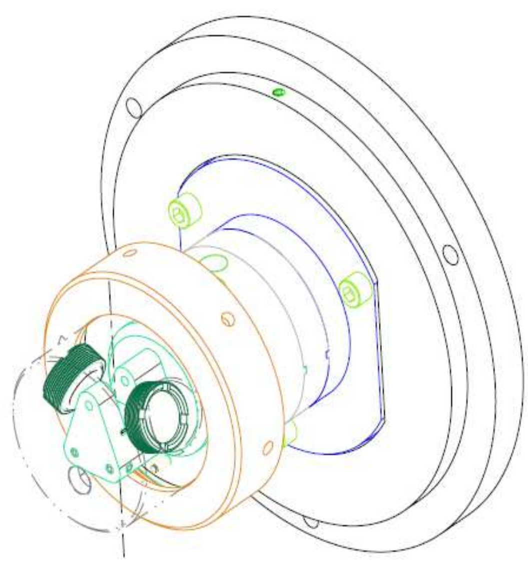

Figure 2. Schematic diagram of the assembled high pressure stage.

CONCLUSIONS

A pressure vessel has been designed, certified and constructed to study the behaviour of biopolymers in contact with high pressure CO_2. The design meets the B51 pressure vessel code of the Canadian Standards Association (CSA). Given the similarities between CSA B51 and

American Society of Mechanical Engineers (ASME) BPVC requirements [8], we believe that the design would easily pass certification under the US regulations. A simple change in the goniometer adapter plate would allow the stage to be mounted onto θ–θ diffractometers from any manufacturer. However, use of the stage with flammable or toxic gases would probably have to meet additional regulations.

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