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Stability of Poly(methyl methacrylate) on Super-critical CO2: A Molecular Dynamics Study Toward the Re-usability of PMMA Artefacts

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PURPOSE OF THE ABSTRACT

Poly(methyl methacrylate) (PMMA) is a transparent thermoplastic used in a multitude of applications as a lightweight alternative to glass that is safer on impact. It is also a more economic and environmentally friendly alternative to polycarbonates, since it does not contain nor emits bisphenol-A [1]. Moreover, one of the most common degradation paths for PMMA is anionic de polymerisation, yielding the original monomer (methyl methacrylate) and thus allowing for full recyclability under relatively mild conditions. In later years, PMMA has seen extensive usage not only in everyday objects, but also on a number of protective gear items implemented in an attempt to mitigate the propagation of coronavirus. Deep cleaning and disinfection of PMMA artifacts has since become a pivotal matter to prevent discarding these items after a single use. Unfortunately, PMMA has lower chemical and heat resistance than other popular transparent materials such as polycarbonates and silica glass.

In this work, we explore the possibility of using supercritical CO2 as an alternative solvent for the deep cleaning and disinfection of PMMA artifacts, using Molecular Dynamics studies simulating PMMA slabs in CO2 around its critical point. The PMMA slab contains 100 molecules with approximately 10 kDa each, topped by a region of varying height occupied by 1000 CO2 molecules. All calculations were carried out using the LAMMPS software [2]. Force field parameters for PMMA were obtained from Behbahani and co-workers [3] and CO2 parameters are those from the TraPPE forcefield [4]. The PMMA slab was generated by randomising the conformation of each PMMA molecule, followed by geometry optimisation, heating, and annealing of the slab to minimise tensions within the polymeric medium. Each system of PMMA plus CO2 was equilibrated at 280 K before data acquisition for 10 ns. Following this initial stage, each system was then heated to 290 K, 300 K, 310 K, 320 K and 340 K, with a 5 ns equilibration run at each temperature, followed by a 10 ns production run. All simulations were carried out using the canonical ensemble (NVT), with the CO2 pressure being evaluated from the mean kinetic energy of CO2 molecules per unit volume of the CO2 region in the simulation cell.

Preliminary results show that CO2 has a strong affinity for the PMMA surface, even in the gas and vapour phases. Two processes were identified when heating the PMMA plus CO2 system: desorption and penetration of CO2 into the PMMA moiety. The former of these phenomena was mainly observed in the low-pressure systems. On the other hand, the latter phenomenon is rarely observed in all systems, making the possibility of PMMA solubilisation in supercritical CO2 highly unlikely. These results were then quantified and confirmed by assessing the mobility of CO2 molecules inside the PMMA matrix. Nevertheless, the increase in pressure leads to a deformation of the PMMA surface, which was quantified by the changes in the fractal dimension of the PMMA/CO2 boundary. These changes of the PMMA surface appear to be partially favoured by the increase in the adsorption/desorption rate at high temperature and pressure. In order to shed some light on this phenomenon, a detailed evaluation of the relative orientation of CO2 at the PMMA surface was carried out, highlighting the preferential points of contact between the two compounds, and the variation of such preferences with increasing pressure and temperature. Finally, an overview of the effect of CO2 on the PMMA surface is carried out, enumerating potential problems involved in the use of supercritical CO2 as an alternative cleaning solvent for PMMA objects.

FIGURES

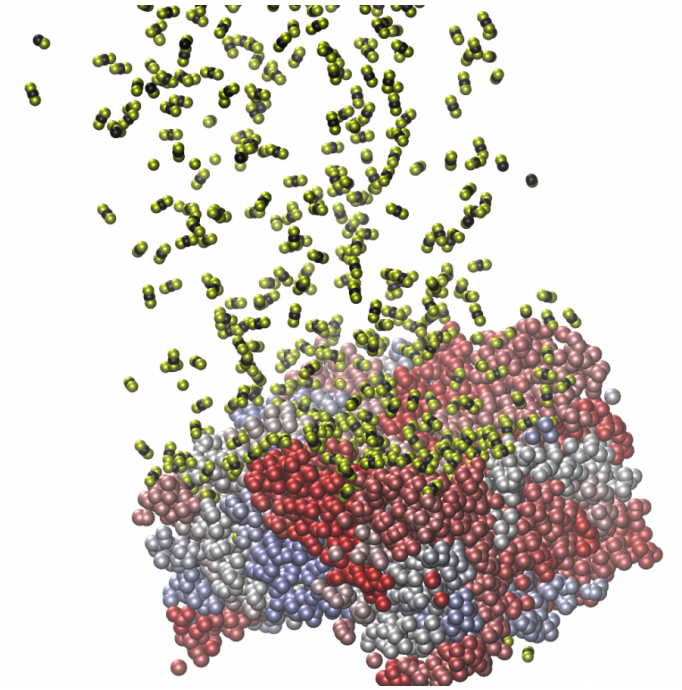

FIGURE 1

Figure

Snapshot of the PMMA plus CO2 system at 340 K and low pressure (high volume cell).

FIGURE 2

KEYWORDS

Supercritical CO2 | PMMA | Molecular Dynamics Simulations | Re-usability of artefacts

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