First Year Report (2023/2024)

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Research Activity Development

Project title: Computational Design of Superplasticising Polymers for Low Environmental Impact Ceramics

1- Aim of the Project Research

The ceramics market is booming in many fields (building, medicine, ICT, energy...). However, rising energy costs threaten the competitiveness of this sector. These costs are due to the heat treatments required to dry and consolidate the parts. Thus, for reducing energy consumption, one solution is to minimize the water present in the compositions.

The aim of the project is to identify the ideal superplasticizer polymeric (SP) additive for this

water reduction while ensuring the rheological properties necessary for the manufacture of parts.

My goal is to exploit molecular models of both ceramics and SP to shed light on the molecular factors that control the interaction between polymers and the oxide surfaces, and to build a Martini 3 CG models which will allow us to simulate oxides/polymers suspensions at large scale.

2- Description of the Activity Research, and Preliminary Results

First, I run NPT molecular dynamics simulations at an atomistic level (AA) of planar surfaces of amorphous silica and alpha alumina (α-Al2O3), which are the main components of ceramics, to:

- set up computationally efficient protocols for AA simulations of such systems

- investigate the atomistic structure of the substrates at the water/surface interface with different degrees of surface ionization.

Silica protocol: 1) energy minimization in vacuum; 2) NVT equilibration in vacuum for 10 ns; 3) solvation and energy minimization; 4) NPT anisotropic equilibration for 200 ns; 5) production run

Alumina protocol: 1) solvation and energy minimization; 2)) NPT anisotropic equilibration for 45 ns; 3) NPT anisotropic equilibration for 100 ns; 5) production run.

Second, I implemented an atomistic model of the SP methacrylate-based polycarboxylate ethers (PCEs).[3] As a test model, we investigated the behavior of 10-mers of poly(methacrylate) (PMA) in the iso- and syndio-tactic forms, both in diluted aqueous solution and in presence of an Al-terminated (non-ionized) Al2O3 surface. As a notable result, the two model polymers interact very differently with the surface: while the isotactic interacts only mildly with the alumina, the syndiotactic shows a marked tendency to adsorb on the substrate. This difference in behavior suggests that tacticity may have an important role in the design of novel methacrylate-based SPs.

Third, we investigated the behavior of the same model (PMA)in the iso- and syndio-tactic forms, both in diluted aqueous solution and in presence of a silica surface. As a notable result. The two model polymers also interact differently with the surface: while the syndiotactic interacts only mildly with the alumina, the isotactic shows a marked tendency to adsorb on the surface

To summarize, I designed an efficient protocol for building structures of (i) amorphous silica and alpha alumina planar surfaces with various degrees of ionizations, and (ii) PMA with different tacticity. Then, I investigated the interaction between alpha alumina and PMA, amorphous silica and PMA,showing that different tacticity leads to different adsorption.

3 – Methods

For silica surfaces, I implemented the model proposed in Ref 1. For alpha alumina surfaces, I implemented the (*non-bonded*) model proposed in Ref 2. Notably, the advantage of having a non-bonded model, besides having a simple energy expression and fewer parameters, is that it confers a certain degree of restructuring capability to the surface. For the PMA, I implemented the model proposed in Ref 4.

AA simulations have been performed with Gromacs. All models use the CHARMM forcefield.

4 - Outlines:

- Simulate the interaction between PMA and both alumina and silica as a function of the surface ionization degree; this will require the implementation of enhanced sampling techniques (e.g., metadynamics) to estimate the free energy of adsorption.

- Build the Martini 3 CG model for all the species involved

5 – References:

(1) Fateme S. Emami, Valeria Puddu, Rajiv J. Berry, Vikas Varshney, Siddharth V. Patwardhan, Carole C. Perry, and Hendrik Heinz Chemistry of Materials 2014 26 (8), 2647-2658 DOI: 10.1021/cm500365c

(2) Krishan Kanhaiya, Michael Nathanson, Pieter J. in ’t Veld, Cheng Zhu, Ilia Nikiforov, Ellad B. Tadmor, Yeol Kyo Choi, Wonpil Im, Ratan K. Mishra, and Hendrik Heinz

Journal of Chemical Theory and Computation 2023 19 (22), 8293-8322 DOI: 10.1021/acs.jctc.3c00750

(3) ACS Sustainable Chem. Eng. 2021, 9, 8354−8371

(4) *J. Chem. Theory Comput.* 2021, 17, 4, 2431–2443

6 - Other activities:

This year I attended two courses, the first course was about Microscopic and Spectroscopic Techniques for the Analysis of Surfaces and Interfaces and the second course was about computational physics. I have also attended the “XXVII Congresso Nazionale SIBPA 2024” in Genova that lasted from 16 to 20 juin.