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Fragment-based simulation study of interactions between sodium polyacrylate, styrene-butadiene latex and calcite surface

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Abstract. *Binding and interactions of sodium polyacrylate (PA) (dispersing agent) with styrene-butadiene latex (SB-latex) (binder) and calcite (pigment) surface were investigated by molecular dynamics simulations. In order to keep the size of simulated components manageable, a fragment-based approach was adapted. PA was described as a set of tetrameric polyacrylate fragments and SB latex as monomeric units of styrene and butadiene. Calcite was present as a single layer of calcium and carbonate ions and the system was filled with water molecules. During the simulation, the fragments were free to move and interact with other components in the system. PA fragments were found to bind to calcite with about half of the acid groups available. The unbound acid groups created a negatively charged and hydrophilic surface over the calcite. This surface inhibits the aggregation of the calcite particles, thus providing an effective dispersion. However, contacts between PA and SB-latex were not observed. The hydrophilic and negatively charged calcite surface was well solvated and did not favor latex binding. The fragment-based approach proved to be applicable for the above interaction studies; it is recommended that it be tested also in the simulation of other high molecular weight surface treatment polymers.*

Keywords: *molecular modelling, fragment-based molecular dynamic, calcite surface, sodium polyacrylate polymer, adsorption, styrene-butadiene latex*

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I. Introduction

1.1. Paper coating

Pigments, binders and dispersing agents are important paper coating components. The goal of this coating process is to improve the optical and printing properties of the paper. Pigment is a major ingredient of coating color and it is used for improving the quality of the paper. Binders are used in pigment coated paper to bind the pigment particles together and onto the paper. The function of dispersing agents is to produce the dispersion where only the primary particles, but no agglomerates or aggregates, are present. In the coating process, pigment and dispersing agents are added before the binder and therefore they can interact with each other before the binder [1]. Thus, when modelling the coating system (pigment-binder-dispersing agent), it is expected that the calcite surface first interacts with the dispersing polymers and after that with the latex. In addition, molecular water must be included in the simulations, because the paper coating process takes place in an aqueous environment.

Calcium carbonate, available both as ground and precipitated mineral, is one of the most commonly used pigments in paper coating. The average particle size of PCC (synthetically precipitated calcium carbonate) in an aqueous environment is 0.4-2.0 µm [1]. The positive Ca^{2+} ions on the calcite surface are known to have a Lewis acid character [2]. The calcite surface is able to bind to various basic organic groups, mostly by those acidic Ca^{2+} sites [3, 4].

Styrene-butadiene latex (SB-latex) is a long-chain macromolecular substance which is commonly used as a binder in the paper coating process. It consists of styrene and butadiene monomers with widely variable proportions (from 40/60 to 80/20) [5]. In a water environment, SB-latex forms spherical particles with a diameter of 0.1-0.2 µm, which are electrostatically stabilized through carboxylic groups introduced into the polymer during the emulsion polymerization. The adsorption of latex binder onto the dispersed pigment particles has been studied by several authors [6, 7]. It seems evident that latex particles can be adsorbed either directly onto the dispersing agent layer or on the pigment surface by partially replacing the dispersing agent.

The direct adsorption of the binder on sodium polyacrylate has been found to be preferred instead of the binder displacing the dispersant layer [8] sodium polyacrylate, SB-latex and calcite surface.

Sodium polyacrylate (PA) polymers are widely used as dispersing agents; they can also prevent the agglomeration of particles and reduce the viscosity of the slurry. Electrostatic interactions between PA polymers and coated nano-sized $CaCO_3$ particles are the main factors contributing to the dispersion of nano-sized $CaCO_3$ in water [9]. PA polymers have been found to attach on calcite surface and act as chelating agents at the calcite surface enhancing the dissolution [10].Calcite suspensions can be efficiently stabilized with PA by electrostatic forces. According to experimental data [10] PA polymers are also able to change the surface charge of calcite from positive to negative.

1.2. Molecular modelling of the coating system

When modelling the above coating system (involving calcite, PA polymer and SB-latex particles) it is reasonable to assume that the dispersing agent polymers first adsorb on the calcite surface. Hence, a dispersing agent polymer layer is formed first and after that the SB-latex will bind on that layer. Thus, calcite and SB-latex mostly adhere with each other via a dispersing agent polymer layer. This process takes place in water, and an aqueous environment is essential to the function of the dispersing agent. Therefore, the simulations should be carried out in a periodic box filled with water molecules. This corresponds to the conditions where the system is completely immersed with water.

Molecular dynamics studies of adsorption and deformation behaviour of polyacrylic acid (PAA) have been published earlier by Liu et al. [11]. Their results show that most of the carboxylic groups in PAA molecules tend to settle close to the calcite surface. There are also indications of the formation of a Ca-O bond between PAA and the calcite surface, and the formation of hydrogen bonds between the oxygen atom of a CO_3^{2-} ion and hydrogen atoms of the carboxylic acid group of PAA [11]. On the other hand, up to now only a limited amount of work has been reported on molecular simulation between calcite and polymers due to the complex structures of polymers and the complex interactions between the polymers and calcite [12]. Thus, to our knowledge, detailed interactions between calcite and different coating polymers are still unclear at the molecular level.

MD simulations can give detailed information of binding modes and atomic level interactions in the SB-latex-calcite-PA system [13]. However, the real sizes of the elements included in this model are larger than those routinely described with MD simulations. Building and running simulation systems for full size particles require excessive computational resources and still cannot avoid certain problems. Performing computer simulations for large polymeric systems is not straightforward if atomic level information is of interest. Large scale simulation systems with atomic resolution are extremely resource intensive. Mesoscale simulations partly solve the problem, but they require parameterization of the compounds in question to correctly describe the chemical interactions of the system. This time-consuming process is not always possible, if the main motivation for the simulations is to support experimental work. For this purpose, a fragment-based approach would be applicable, and this approach has been successfully used e.g. in drug design [14, 15]. To our knowledge, however, a fragment-based approach has not been applied to simulating paper coating systems.

In continuation of our previous molecular modelling studies of paper coating components [13, 16, 17], this study was undertaken in an attempt to use a fragment-based approach to obtain information about atom level interactions of macromolecular coating components. At the same time, our aim was to make such an analysis fast and less resource intensive to be routinely applicable. These goals can be achieved by breaking the system (molecules) into a set of smaller fragments that represent the different chemical entities of the system. A fragment-based approach can be used e.g. to compare different paper coating polymer types in terms of atom level interactions and relative binding affinity.

1.3. Experimental

A one-layer calcite model surface was constructed with 100 Ca^{+2} and 100 CO_3^{2-} ions using charges calculated by Catti et al. [18]. The experimental crystalline atomic coordinates by Effenberger et al. [19] were used in the calcite model surface. The crystal face(10.4) (the $10\bar{1}4$ face in the hexagonal notation) of calcite was used in this study since it has been found to be the most stable morphology of calcium carbonate [20, 21, 22].

PA was described as tetrameric fragments. Eight PA fragments were placed close to the calcite surface using Maestro molecular modelling software [23]. The energy of the system was minimized and equilibrated, and then a 10 ns MD simulation was performed to allow the fragments to freely find their preferred binding mode on the calcite surface. The calcite surface was kept frozen in space during the simulations. The purpose of this simulation was to create a starting structure for the simulation with water.

After the vacuum simulation the system was solvated. In addition, SB-latex was added to the simulation system. Latex was described as a group of monomeric latex units: 24 styrene units and 24 butadiene units were placed as a layer above the calcite surface with PA fragments. Finally, the system was neutralized with randomly positioned Ca^{2+} ions.

1.4. The MD simulations

After adding the latex fragments and water, the system energy was minimized to remove close contacts. The system was briefly equilibrated and re-solvated to fill vacuum bubbles. The energy of the system was again minimized and it was equilibrated immediately before a production run of 10 ns. All the simulations were performed using a Gromacs 3.3 software package and Gromos ffG53a6 force field in a constant volume. The missing parameters for PA and SB-latex fragments were derived in analogy to amino acid parameters in the GROMOS force field. LINCS [24] was used to constrain the bond lengths in the fragments and the SETTLE algorithm [25] was used for the bond lengths and angles of the water molecules. The time step was set to 2 fs. The temperature was controlled with the Berendsen weak coupling algorithm [26] with coupling constants of 100 fs. Coordinates were stored every 10 ps. The trajectory was used to analyze the preferred binding mode of PA fragments on the calcite surface and to determine the number of contacts with calcite and SB-latex fragments.

II. Results

2.1 Fragment-based approach

The aim of our fragment-based method is to obtain information about atomic level interactions of large polymeric systems, and at the same time to make such an analysis sufficiently fast and less resource intensive to be routinely applicable. These goals can be achieved by breaking the system (molecules) into a set of smaller fragments that represent the different chemical entities of the system. However, it should be noted that calculations of binding affinities from the fragment-based simulations must be analyzed carefully because the fragmentation is likely to have an effect on binding due to entropic reasons. It must be noted that a fragment-based method is most suitable for a comparison of building blocks of polymers. The real size of the polymers has a remarkable effect on the binding affinity, for example for sodium polyacrylate polymers on calcite surface [27].

The fragment-based approach (Fig. 1) relies on the fact that the system consists of repeating units, and all of them are not needed to capture the characteristics of the system. Calcite is a crystal of calcium and carbonate ions that can be described as a surface which can have similar interactions as an actual calcite crystal. SB-Latex is formed by a branched chain of styrene and butadiene units and it appears in water as an aggregate with no specific well defined structure or folding. A set of individual styrene and butadiene units can interact with the other components of the system in a way similar to real latex.

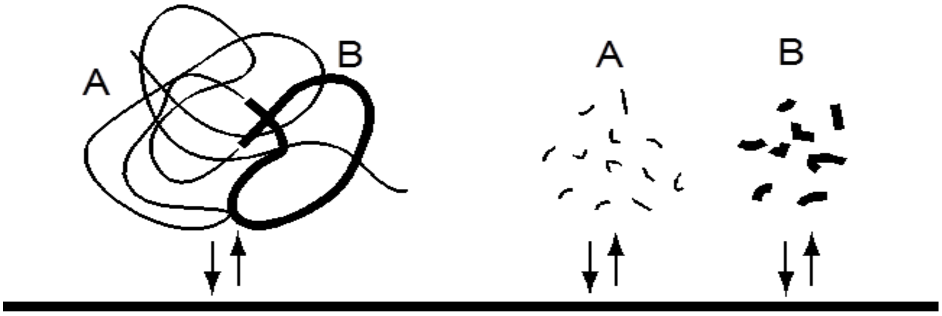
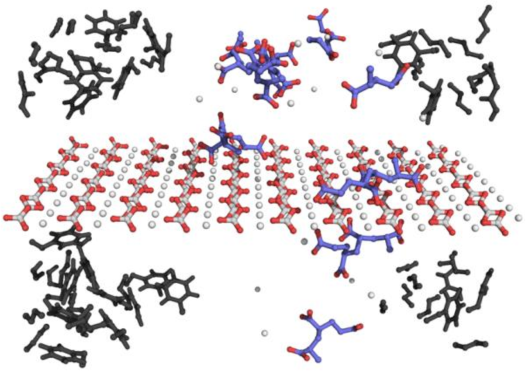


Figure 1. The principle of fragment-based approach: a polymer consisting of two different structural types (A and B) is described as a set of fragments of types A and B. The interactions and binding of these polymer types with some other part of the system are analysed separately.



For PA, a slightly more complicated approach is needed. PA binds on the surface of the calcite particles (Fig. 2). The possible binding modes are determined by the features of the acrylate unit itself and the strain and other limitations caused by the connection to the other units of the chain. To correctly model the binding mode of PA, the model has to include the information of the effects of the connection between the acrylate units in addition to the acrylate units itself. For this purpose, a chain of a few acrylate units is needed. The chain does not have to be long, because the back bone of the polymer consists of repeating sp3-sp3 carbon bonds that rotate easily, making the chain flexible. A change in the conformation of an acrylate unit is not likely to have an effect on a distant unit of the chain.

Figure 2. Overall image of the simulation system at 10 ns. Ca^{2+} ions are shown in white, CO_3^{2-} ions as red three-pointed stars. The PA fragments are coloured with blue (carbons) and red (oxygens). The SB-latex fragments (black) have gathered into one group that is seen as four separate groups in this image because of the periodicity of the system, i.e. atoms at left are in contact with atoms at right, and atoms above in contact with atoms below.

Breaking the system into small units gives several advantages. First, the size of the required system is smaller, and the amount of water needed to be included is also smaller. Limiting the number of atoms in the simulation system efficiently reduces the computational resources needed, mainly owing to the smaller number of non-bonded interactions to be calculated. Next, smaller fragments diffuse faster and rotate easier. This has the effect of decreasing the required length of the simulations needed to sufficiently sample the conformational space. The simulation will find the stable state or converge faster. It also makes the simulation less dependent on the starting structure. This is especially important for simulations of this kind of systems that have no clear minimum energy structure or other obvious starting point. A longer polymer chain could be more easily trapped into a local minimum and all parts of the conformational space could not be sampled. An earlier fragment based approach has been successfully used e.g. in drug design [14, 15]. However, for that purpose, a large number of different fragments are used and screened to find binders for a specified binding pocket, instead of simulating multiple copies of similar fragments to find their preferred mode of binding. A common approach used to study polymers and their behaviour is called coarse grained molecular dynamics simulations [28, 29, 30]. These methods describe the system at a less detailed level and gain increased simulation speed. Unfortunately, at the same time, atomic level interactions are lost.

The error that results from the fragment-based approach arises partly from the entropic contribution on binding. The binding of a larger molecule is entropically favoured compared to a smaller one owing to fewer degrees of freedom in the free-state, i.e. a smaller binder suffers a higher loss of entropy upon binding. Another entropy-related error with smaller fragments is seen when a part of the polymer is unbound. The polymer can now dissociate totally, or the unbound part can bind again. The longer the polymer and the bound part, the more likely the unbound part will bind again. This means that the smaller the polymer, the easier it will dissociate. As a result, when a polymer is described as a small fragment, its binding affinity is likely to be underestimated.

An overall image of the simulation system for the compounds studied is presented in Figure 2 as a snapshot structure of the endpoint of the simulation at 10 ns. During the simulation, five PA fragments had dissociated from the calcite surface on which they were originally bound. Three of the fragments are still bound on the calcite surface, one with four acid groups bound, one with three and one with only two of acid groups bound, while the others are pointing towards the solvent. The dissociated PA fragments form a loose group in the middle of the box with the free calcite ions that were included to neutralize the system. SB-latex fragments are gathered as one group thus minimizing their contacts with water. The group of latex fragments does not mix with the PA fragments.

2.2 The binding mode

In binding on the calcite, the fragments utilize the negatively charged carboxylic acid oxygen atoms, which interact electrostatically with the positively charged calcium ions of the calcite. All the acid groups (Fig. 3) of the fragments are not bound to calcite at the same time. To get an overview of the binding modes of the fragments, the number of bound acid groups of each fragment was determined from the snapshots of the simulation trajectory. The number of bound acid groups was calculated for every 500 ps for the first 5 ns and for each 10 ns by visually inspecting the corresponding snapshots.

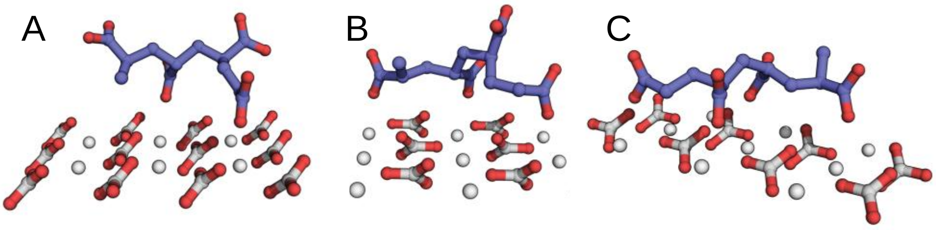


Figure 3. PA fragment bound to calcite by A: two acid groups. B: three acid groups C: four acid groups. For color coding see Fig. 2.

Initially, during the preliminary vacuum simulation, the fragments were bound to calcite with binding conformations using two to four of the total four acid groups. Two of the fragments used two acid groups (Fig. 3A) for binding, whereas three of the fragments were using three (Fig. 3B) or all four (Fig. 3C). None of the fragments showed a binding mode with one or no acid groups bound.

The binding mode with three acid groups bound disappeared during the first 1 ns (Fig. 4, orange bars). At the same time, two of the fragments completely dissociated from the calcite surface (Fig. 4, blue) and one fragment bound with only one acid group (Fig. 4, green) before dissociating at 1.5 ns. After the initial loss of one fragment with all four acid groups bound, the remaining two fragments remained in the all-acid-groups bound conformation until 3.5 ns (Fig. 4, purple). The part of the simulation between 1.5 and 3.0 ns was stable and no changes occurred in the binding. At 4 ns, the simulation reached another stable state and binding modes with two to four bound acid groups were maintained until the end of the simulation.

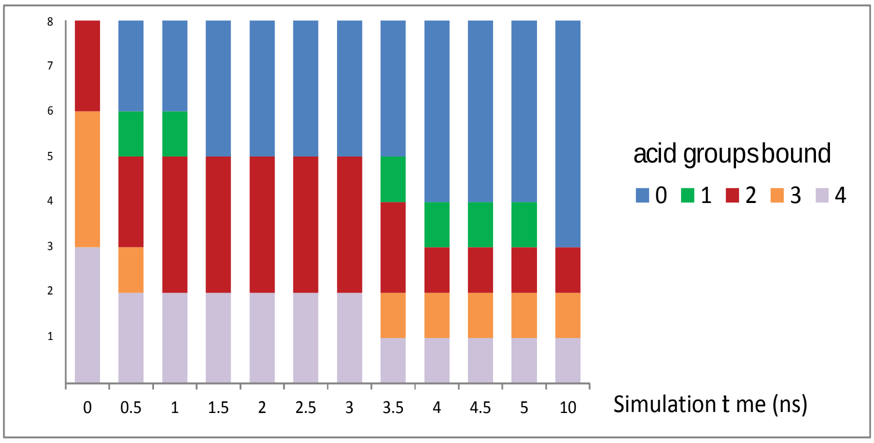


Figure 4. The number of PA fragments bound to calcite with one to four acid groups. The total eight fragments were initially bound with two to four acid groups (0 ns: red, orange, purple). During the first 1 ns, the binding mode with three bound acid groups (orange) disappeared and all bound fragments used two or four acid groups for binding.

Summing up the total number of fragments bound to a certain conformation reveals that the most common way of binding to calcite is to use all four or only two of the acid groups capable of binding (Fig. 4). The conformation with three acid groups bound is less common and occurs mostly during the equilibrium in the beginning of the simulation. The binding mode with only one acid group bound is equally common as the mode with three acid groups bound.

2.3 Contacts with calcite and latex

The number of contacts that the PA fragments made with the calcite surface was assumed from the simulation trajectories (Fig. 5). The atoms of a fragment and the calcite surface were determined to be in contact when the distance between them was below 3 Å. The contacts are mostly attractive interactions between the positively charged calcium ions of the calcite surface and negatively charged oxygen atoms of the PA acid groups. The number of contacts also contains contacts between other atoms of the calcite surface and PA fragments that are at a distance closer than 3 Å from each other.

The development of the binding modes of PA fragments observed in the snapshot structures (Fig. 4) are confirmed by the analysis of contacts between the calcite and the PA. During the first 500 ps the number of contacts drops from the level of 40 to about half, after which the number remains stable for the next 3 ns. After a decrease between 3-4 ns, the number is stable at the level of 10 contacts until the end of the simulation at 10 ns.

The contacts between PA and SB-latex fragments were similarly studied, but the distance below which the atoms were defined to be in contact was 4.0 Å. The longer distance for these contacts was selected because the united atomic force field used in these simulations does not include all the non-polar hydrogen atoms and the contact distance is measured between the carbon atoms. The distance of 4.0 Å was selected by measuring distances between atoms of the latex fragments in the simulation snapshots, where the closest distances were 3.5-4.0 Å. The contacts between the PA and SB-latex are mainly lost in the first 2 ns of the simulation, and after that only random, short term contacts are observed (Fig. 5). The end structure of the simulation revealed that the SB-latex fragments were gathered in one corner of the simulation box, avoiding contacts with the PA fragments and the calcite surface.

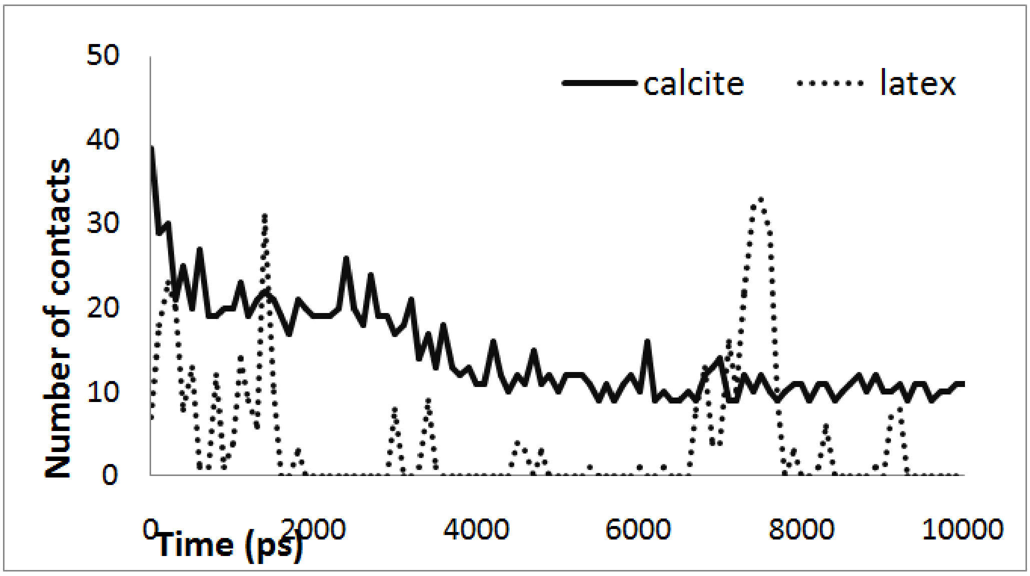


Figure 5. Contacts between PA fragments and calcite surface (solid line) and SB-latex fragments (dashed line) determined from the simulation trajectory. The contacts with calcite stabilize between 20 and 10

III. Discussion

Prior to the simulations, the PA polymers were simulated in vacuum with the calcite surface to let them find their preferred binding orientations on the calcite. During this preliminary vacuum simulation the PA fragments bound to the calcite using two to four of the total four acid groups. After the solvent was added to the system, the binding modes with three groups bound disappeared and the mode with two acid groups bound became more common. This result reflects the fact that in vacuum the electrostatic interactions are strong and may overcome other forces that contribute to the binding orientation, such as strain of the polymer backbone. Binding with all four acid groups seems possible, but is probably not entropically favoured due to the narrow conformational space of this binding mode. Extending the side chains of the polymer by adding carbons between the backbone and the acid group might favour the binding mode with all the acid groups bound by increasing the flexibility and conformational freedom of the polymer. This might also help the polymer to adapt on the surface of the real calcite particle, which probably is not as even as the model surface used in this work. In addition, it might lead to better SB-latex binding because of a larger hydrophobic binding surface.

In an aquatic environment the water molecules compete with the calcite surface in binding to the acid groups of the PA. Ca^{2+} ions have been found to bind strongly to SB-latex and thus reduce its effectiveness as a dispersing agent [10], which is in good agreement with our findings. In addition, there are free calcium ions in the solvent forming ion-ion interactions with un-bound acid groups [31]. As a result, bound acid groups are lost during the simulation. In the case of a full length PA polymer this would probably lead to a binding mode where a part of the acid groups are bound to calcite and the rest are unbound, but instead form hydrogen bonds with the solvent. In this work the polymers were seen to dissociate from the calcite surface towards the end of the simulation. With a full length PA polymer the situation may be different. The length of PA polymers has been found to have a large effect on the binding, and it has been observed that sodium polyacrylate chains with a molecular mass below 1500 g/mol do not adsorb on the calcite surface [27]. This result is in good agreement with our present observations. Because there are more acid groups bound to the calcite, the unbound acid groups can bind again and not all the contacts are lost at the same time. This effect of rebinding acid groups was not observed in this work due to the relatively short PA fragments; this can be considered a limitation of our fragment-based method. However, it is not clear that rebinding would be observed if a longer PA polymer were used, because the time scale of the phenomena might be long.

The partial binding of the PA polymers to the calcite seen in this work has the consequence of un-bound acid groups pointing towards the solvent. This result supports earlier findings [10] that PA forms a negatively charged layer on the calcite particles. This layer effectively inhibits the flocculation of the coated particles because of repulsive forces of the negative charges, thus resulting in a good dispersing effect.

Contacts of PA fragments with SB-latex were also determined from the simulation trajectories. During the simulation the latex fragments form a separate group that does not contact the calcite surface. The contacts with PA fragments were more common in the beginning of the simulation, but became rare towards the end. This progress is explained by the hydrophobic nature of SB-latex fragments, and it is well known that latexes form spherical colloids in an aqueous environment [32]. Latex fragments tend to gather into one spherical group to minimize the surface in contact with water, or actually the water molecules maximize their hydrogen bonding with other water molecules and this is achieved when the latex forms a tight spherical group. Contacts of SB-latex with PA are more common at the beginning of the simulation, because the latex fragments are more widely distributed in the solvent. The simulation suggests that in an aquatic environment the binding of latex to PA may be weak. PA is very hydrophilic due to its negative charges and it is surrounded by water. Thus, the same feature of PA that makes it a good dispersant weakens its binding affinity to SB-latex.

The change in the binding mode when water was added to the system clearly indicated that water strongly affects the binding modes of the dispersing agents. This is especially true for dispersing agents such as PA which can have strong interactions also with water. Including water in the simulation makes it more realistic compared to vacuum simulations, although at the expense of considerably higher computational costs. To make the simulations with water feasible, the size of the system must be kept as small as possible and the simulation time as short as possible. For this purpose, the fragment approach might be a good choice.

IV. Conclusions

The fragment-based approach was found to be suitable for obtaining new information about the behavior of macromolecules on a pigment (calcite) surface. Several binding conformations of PA fragments were observed and it was seen that binding was mainly caused by the acid groups of PA, using two of the four acid groups of the fragment. The contacts between PA fragments and calcite surface were stabilized during the simulation time and were mostly due to attractive electrostatic interactions between positively charged calcium ions of the surface and negatively charged oxygen atoms of the PA acid groups. During the simulation time, SB-latex fragments avoided contacts with the PA fragments and the calcite surface, which indicates their low binding affinity on those materials in an aquatic environment. Consequently, fragment simulations proved to be efficient for studying the overall behavior of polymers. We suppose that our modelling results could be valuable for practical papermaking, for example in generating useful ideas for new potential surface treatment chemicals, facilitating the optimization of suitable printing conditions and selecting the most suitable printing chemicals for various printing processes. In addition, molecular modelling experiments facilitate the understanding of possible problems in the printing process and the chemical behavior of the printing chemicals, and illustrate the interactions between coating components. Simulation data can also be of great importance for comparison with the results obtained in laboratory, pilot-scale and mill operations. However, more modelling experiments, comparisons of simulation results with experimental results and pilot-scale testing are needed to verify the present results.

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