MIDTERM REPORT: DOW CHEMICAL LATEX WATER ABSORPTION

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UNDERSTANDING THE SYNTHESIS PROCESS

Our first step was to study the latex preparation protocols, starting from a colloidal dispersion (suspension) of polymer particles, polymerized from monomer molecules in solution and stabilized via steric or Coulombic interactions, through the evaporation of water that results in Latex particles coalescing.

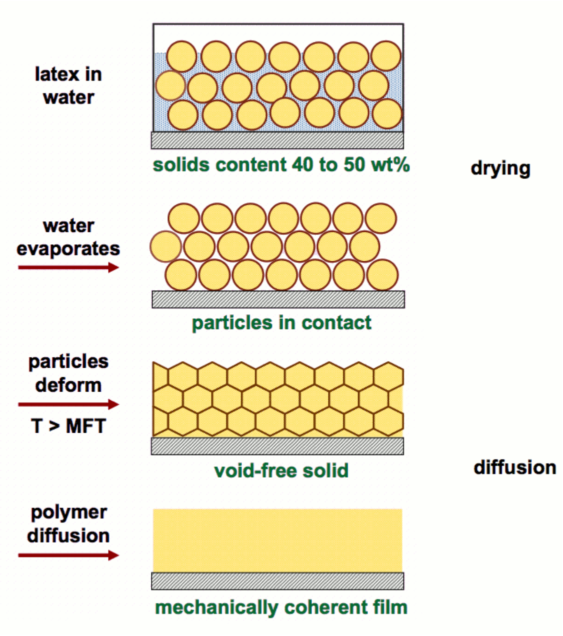


FIGURE 1 LATEX FILM FORMATION PROCESS

The emulsion polymerization proceeds as a segregation of free radicals among monomer-swollen polymer particles. Transport of monomer, free radicals, and surfactant to the growing latex particles and partition of these reagents among the continuous aqueous phase, the monomer emulsion droplets (the monomer reservoir), and the monomer-swollen polymer particles (the primary reaction loci) play a crucial role in the particle growth stage. Our objective at this point was to extract information on what influences the general properties of Latex, including water adsorption characteristics.

Among the properties of interest for determining the characteristics of the colloidal mixture and the final Latex product are: particle size and particle size distribution, particle surface charge density, particle surface area covered by stabilizers, conformation of the hydrophilic polymer adsorbed or coupled onto the particle surface, type and concentration of functional groups on the particle surface, crosslinking agents, and colloidal stability, among others. These properties regulate the response of the dry, mechanically coherent film that results after polymer diffuses into Latex (Figure 1), including how it responds to water adsorption in time.

Since our approach starts from first-principles quantum mechanics (bottom-up) we focused initially on developing an atomistic representation of the properties of the final bulk mechanically coherent film (i.e. reverse engineering), including structural, thermodynamical and mechanical. Atomically-resolved models are not able to probe the time and length scales involved in describing the synthesis process, but a bottom-up approach that starts from experimentally validated bulk and surface properties for specific systems of interest to DOW will enable scaling up with first-principles-based confidence. This will allow us to understand and optimize the structure and composition of the material to regulate its water adsorption properties.

MOLECULAR MODEL SYSTEMS

DOW Chemical opted for the following initial compositions:

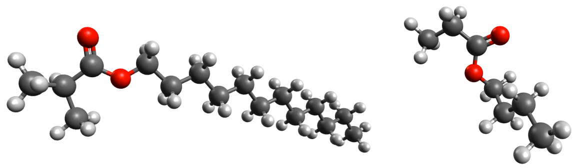
1. Hydrophobic:
    - 20% BA, 40%LMA, 39% MMA, 1%MMAA (Mass Fraction)
    - 23.4% BA, 21.3%LMA, 53.0%MMA, 2.2%MMAA (Mole Fraction)
    - Intermediate: 40% BA, 20% LMA, 39% MMA, 1% MMAA
2. Hydrophilic:
    - 60% BA, 39,36% MMA, 1,4%MMAA (Mass Fraction)
    - 56% BA, 42.2%MMA, 1.8%MMAA (Mole Fraction)

Where LMA is Lauryl methacrylate, BA is butyl acrylate, MMA* is methacrylic acid, and MMA is Methyl methacrylate.

Other components that may be included: MMAA in the range of 1% and 4%, 0.2 nDDM (competes with BA abstraction point to reduce crosslinking), Tg ~10°C, change ratio of BA(80)/MMA(19) to Tg=-20 [alters modulus]. For neutralization: NH4OH, NaOH (OH, Na+, Cl-)

AMORPHOUS POLYMER BUILDING PROCEDURE

The general building procedure involves:



Lauryl Methacrylate (LMA) Buytl Acrylate (BA)

Methyl Methylacrylate (MMA) Methacrylic Acid (MMA*)

FIGURE 2 MONOMERS USED IN BUILDING STRUCTURES

1. Preparing the atomistic monomer units model structures (Figure 2), and tagging the head tail monomeric atoms for automatic polymerization via scripting,
2. Optimizing the individual geometries using a quantum mechanics (QM) package (e.g. Jaguar),
3. Calculating from QM a Rotational Isomeric States (RIS) table and the Mulliken charge population for a trimer,
4. Using the RIS table, which provides the dihedral angle probability distribution, and charge groups

for the construction of n-mers,

5. Building an amorphous periodic system, according to the composition fractions defined in the previous section, of 4-5 chains each with 200-nmers,
6. Solvating with explicit water molecules (if necessary), according to a target wt%.

Once the 0K structure is finalized, we use the Dreiding force field[1] to re-optimize the structure with a conjugate gradient method with convergence set to 1e-5 RMS force or 1e-5 energy difference, and apply a variant of the cohesive energy density (CED) approach[2] using Dreiding to obtain a more realistic conformation of the amorphous system. This involves:

1. Gradual heating from 0-300K using an NVE[1] ensemble and a Langevin (or Nose-Hoover) thermostat over 50ps (integration timestep of 1fs)
2. 100ps NVE equilibration (confirmed via Energy conservation and normal particle velocity distribution)
3. Ramp heating from 300-1200K over 50ps, using an NVT[2] or NPT[3] @ 1 atm ensemble, simultaneously and isotropically doubling the volume (half the start density). NPT requires checking volume convergence at the desired target density
4. Equilibrate at 1200K for 50-100ps
5. Anneal to 300K over 1ns, simultaneously compressing to 1/4th the volume (twice the start density)
6. Repeat 1-5 five times, i.e. expansion (heating)/compression(cooling) cycles
7. 100ps equilibration with NPT@300K/1atm until volume converges
8. 50ps equilibration with NVT@300K, at average volume from 7

The result should be an amorphous fully periodic system, with a density comparable to the experimental value. These procedures have involved developing new compiled and scripted stand-alone code, for pre-processing and post-processing, as well as preparing structures and simulation scripts for the QM and molecular dynamics (MD) packages used, Jaguar and LAMMPS[3], respectively. So far, the Dreiding force field is used for the polymer, and the F3C model[4] for water. This will change as we move to a coarse-grain description.

MODEL CHARACTERIZATION

General bulk properties: An important step in validating the prepared models is confirming basic properties on the bulk dry and solvated systems, because these should enable direct comparison to experimental results. The calculated properties that serve to perform preliminary validation are:

1. Density
2. Radial distribution functions (RDFs) between all paired interactions of interest
3. Mean Square Displacement (MSDs) for computing diffusion coefficients in solvated systems
4. Void analysis in dry systems and water distribution in solvated systems, for determining water percolation thresholds, surface interactions between solute-solvent in large voids, among others
5. Degree of entanglement, to determine the minimum degree of polymerization required
6. Radius of gyration and dihedral angle analysis, to determine conformer states
7. Elastic constants and general stress-strain characteristics

We have developed procedures for calculating these properties within the LAMMPS runs or through independent stand-alone post processing codes. For example, the degree of entanglement analyzes

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[1] NVE: constant number of particles (N), constant volume (V), and constant energy (E)

[2] NVT: constant number of particles (N), constant volume (V), and constant temperature (T)

[3] NPT: constant number of particles (N), constant pressure (P), and constant temperature (T)

dihedral angle distribution during uniaxial strain deformation in each orthorhombic direction. Neighboring dihedral angles that decrease with strain will serve to detect the level of entanglement. The elastic constant procedures we have developed include both infinitesimal static and dynamic strain deformation procedures (see slides from our June report in Progress-6-27-2011.pdf).

Thermodynamics properties: In addition to these, we have been characterizing the thermodynamic properties of each model, by computing entropies, enthalpies and free energies. For this we have used our 2PT method[5]. This approach uses the Fourier transform of the velocity autocorrelation function from 20ps molecular dynamics runs with frequently dumped trajectories for each system, to obtain a the power spectrum DoS(υ) which is then used to calculate the thermodynamic properties by applying quantum statistics. An implementation of the 2PT method is available from our group to post process LAMMPS trajectory dump files.

The procedure applied to determine the thermodynamic properties for each of the NPT equilibrated solvated models involves taking five "snapshots" of each the system, *i.e.*, the coordinates of each atom were stored, equilibrating each snapshot for an additional 20ps in the NVT ensemble (here volume is fixed while pressure is allowed to fluctuate), and using velocities from each NVT equilibration run to calculate thermodynamic properties using the 2PT method (see June report).

Water distribution: Two different strategies will be employed to produce quantitative measurements of the distribution of water molecules in the solvated systems. In the first, a void analysis program that divides space into grids of a specified radius will be employed to calculate the void (or "water channel") volume. We have already written and tested this code (see slide 61 of Progress report 2). The second strategy involves the use of a program designed to find fragments by grouping all atoms within a certain distance of each other. With this program, we can plot the number of water clusters of a certain size as a function of water content. At the percolation threshold, a drastic drop in the number of independent clusters should be observed. We are currently developing and testing this software.

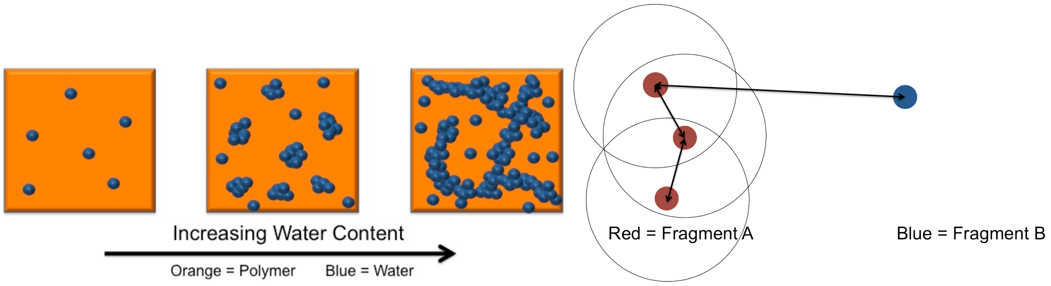

FIGURE 3 LEFT FIGURE SHOWS A WATER PERCOLATION PROCESS AND THE RIGHT FIGURE THE FRAGMENT ANALYSIS BASED CODE FOR DETERMINING WATER PERCOLATION.

In the fragmentation analysis code, we define the neighbors of atoms as those within a certain radius. Those outside the radius are excluded. In analyzing water distribution, a single fragment is a group of water molecules that are all 'connecting' neighbors. Below, the red particles are all within the cutoff radius of another particle in the fragment, and so they are grouped. The blue particle is too far away and is a second fragment. At the point of percolation, there will be a significant decrease in the number of fragments. This is noticeable on a profile and quantitative evidence of percolation.

Glass transition temperature: The glass transition temperature is another way our results may be checked against experiment. To calculate glass transition we heat the polymer model system ~100 to ~500K using a slow ramp (over a few ns), taking snapshots of the structure will at various temperatures, and compute the thermodynamic properties for each snapshot. A plot of entropy versus temperature from these results shows a marked discontinuity in the first derivative (a "kink") at the glass transition.

COARSE-GRAIN MODEL SYSTEMS

With Dreiding it is practical to apply MD simulations to the atomic-level dynamics of systems ~10^{6-9} times larger than for QM. But this may be too small to fully understand the dynamics/mechanics of water in a latex film. To enable even larger scale simulations using our finer scale results (from 10's ns to microseconds), we have been working on extending our existing technique for parameterizing a coarse-grain force field[6] for latex simulations.

Coarse-grain and constrained MD methods enable increased length- and time-scales. We demonstrated a simple approach using a FENE potential and colloidal beads to simulate the latex synthesis process during water evaporation, during the first stage of this project (see slides 9-10 in the May report, DOW-report-1.pdf). The idea here is that coarse grain (CG) models carry enough information about the atomistic behavior of interest while at the same time efficiently scale in both time (>1ms) and length (>10's nm). We are currently determining what are the atomistic behaviors/properties that we need to port into the coarse-grain in order to produce the coarse-grain description.

There are two unique characteristics to our approach:

1. How we systematically determine coarse-grain force fields from our finer scale Dreiding force field, and
2. How we solve the constrained MD equations of motion for systems described as coupled rigid bodies.

For 1) we define pseudo-atoms to represent clusters of atoms in a bead or rigid-body definition. The number of atoms per pseudo-atom will determine if its mass has, or not, tensorial properties. For systems in a solvent, we will define explicit H-bond beads. Statistics of the potential of mean force (between sets of atoms representing each bead) will be computed from various fully atomistic MD simulations. Preliminary calculations have been reported on the dihedral angle statistics for the hydrophilic system (see pp 22-26 from Progress-9-21-2011.pdf). These distributions are then fitted to standard potentials described in equations in order to obtain the interaction parameters for every bead. The resulting force-field uniquely describes the interaction of each bead with every other bead in system, whose total energy is given by,

$$E_{Total} = E_{Bonds} + E_{Angles} + E_{Torsions} + E_{nonBond} + E_{hBond} \tag{1}$$

where E_{Bonds}, E_{Angles} and $E_{Torsions}$ take the same form as those from Dreiding while the $E_{nonBond}$ corresponds to a Morse type potential,

$$E_{nonBond} = D_0 \left[e^{-\alpha\left(-1+ r_{ij}/r_0\right)} - 2e^{-0.5\alpha\left(-1+r_{ij}/r_0\right)} \right], \tag{2}$$

and the E_{hBond},

$$E_{hbond} = D_0 \left[\left(\frac{r_0}{r}\right)^{12} - 2\left(\frac{r_0}{r}\right)^{6} \right] \cos^{2p}\theta \tag{3}$$

where θ corresponds to the angle between a hydrogen and the corresponding donor-acceptor pair.

The distance between the bead centers of mass will be statistically collected through histograms during the MD runs to determine the equilibrium 2-body bond lengths, 3 body angles and 4 body dihedrals. An equivalent approach is taken to determine the non-bond parameters. The average energy per center of mass separation is computed and fitted to the Morse potential in Equation (2) using a least squares approach.

For 2) we efficiently solve the rigid multibody equations of motion using internal coordinates that explicitly contain motion constraints as in [96].

We have yet to port our coarse-grain and constrained MD methods into LAMMPS[74] as part of this effort.

The way we expect to partition the latex polymers is skematically represented in Figure 4. There is a carbon backbone running the length of the polymer that is of particular interest for this analysis. Pseudo-atom beads will be constructed based on the properties gathered from the atomistic analysis.

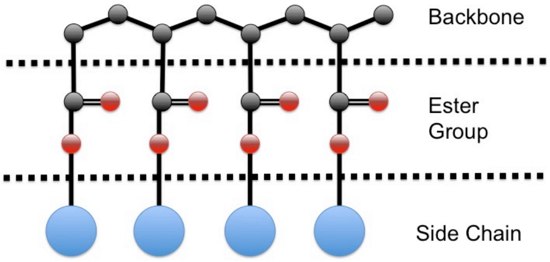

FIGURE 4 GENERAL COARSE GRAIN REPRESENTATION OF THE POLYMERS IN LATEX

When the parameterization is complete there will be a bead for the backbone atoms, one for the polar ester group, and one or more beads for each type of monomer side chain. This should allow us to increase the integration timestep by more than an order of magnitude (i.e. 30-40fs, if not more).

SUMMARY OF RESULTS (OCTOBER 1ST, 2011)

Initially, four random 100-mer copolymer chains were constructed for the hydrophobic case using the composition specified in the May 2011 report (total atoms per system ~10,000). Using the amorphous building procedure described above, a periodic three-dimensional system was prepared. These had a resulting density of ~0.67g/cc. Five 100-mer random copolymer chains were constructed using the hydrophilic composition. With all five chains, total system size is ~10,000 atoms. Rapid estimation of mechanical response at 0K on these structures showed high stiffness (Figure 5 shows E and B for the hydrophobic case). This indicates the need for chains with a higher degree of polymerization (i.e. more torsional degrees of freedom) and increased amorphization. Isothermal characterization of mechanical properties will be performed and compared to the experimental values from DOW (if and when available).

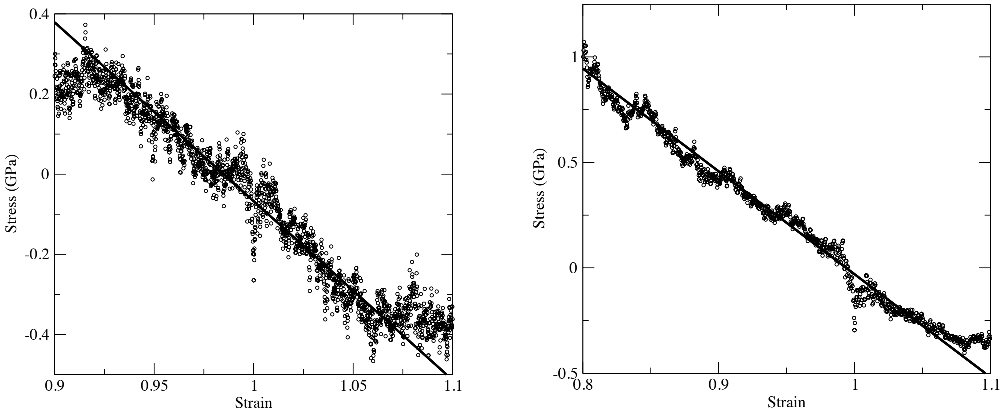

FIGURE 5 YOUNG'S AND BULK MODULUS STATIC CALCULATION ON THE DRY HYDROPHOBIC CASE SHOW A STIFF POLYMER BULK (E=4.46GPA FITTING WITH STRAIN 0.95~1.0 AND B=4.88GPA FITTING WITH STRAIN 0.90~1.05, RESPECTIVELY). FOR EXPERIMENTAL COMPARISON WE WILL USE THE DYNAMIC STRAINING FOR UNIAXIAL, ISOTROPIC AND SHEAR STRAIN.

Solvated models of the hydrophilic and hydrophobic compositions have been prepared at different water concentrations, starting from 40wt% all the way down to vacuum. The procedure involved adding water molecules in random positions (excluding solute volume) until a concentration of 40wt% was reached, and equilibrating the system as described. Water molecules were then randomly removed to generate lower water contents at certain wt% intervals (see September report). Each of these structures was equilibrated with the same procedure. Each structure was equilibrated for 1ns in the NPT ensemble.

A preliminary estimation of the glass transition temperature (T_g) of the hydrophobic system resulted in a Tg between 220-250K (or -50 to -23C). The system was equilibrated using NPT at 10 temperature points ranging from 100K to 500K. Five “snapshots” of the structure were taken once the energy converged, and 2PT calculations performed on each snapshot. This approach was somewhat faster to perform than the method described previously, which involves a slow, continuous temperature ramp. However, we expect the slow ramp will provide increased accuracy. We are currently finishing the Tg calculations for the hydrophilic system in order to perform quantitative comparisons.

Full characterization of the resulting structures has been performed via RDFs and reported in the report slides available online.

For the hydrophobic system see the September report, slide #13. The free energy of the hydrophobic system is dominated by enthalpy. Relative to the dry polymer, the free energy of solvated structures is highly unfavorable (large and positive). However, the relative free energy decreases upon adding more water to any solvated structure. In other words, the free energy takes a large “jump” from 0 to 1% water then decreases almost monotonically thereafter. There is a very slight local minimum in the free energy at approximately 2wt%. This could represent a metastable state, suggesting the following interpretation: Starting from a completely dry polymer, it is thermodynamically very unfavorable to take up water. However, with water already present, even in very small quantities (as is very likely the case after the drying of the latex film), it is thermodynamically favorable to continue taking up more water (except for a small local minimum at 2 weight percent). A graphical representation of the van der Waals surface of the water molecules for each water content is shown in the 9-21-2011 report, slides 3-5.

For the hydrophilic system relative to the dry bulk polymer, we observed that it is energetically favorable for the system to take on water until 5wt% where an energy barrier is visible. Another minimum is present near 15wt%. Despite this polymer composition’s designation as “hydrophilic” because it lacks the extremely hydrophobic dodecyl chains of lauryl methacrylate, the polymer is expected to have an unfavorable interaction with water.

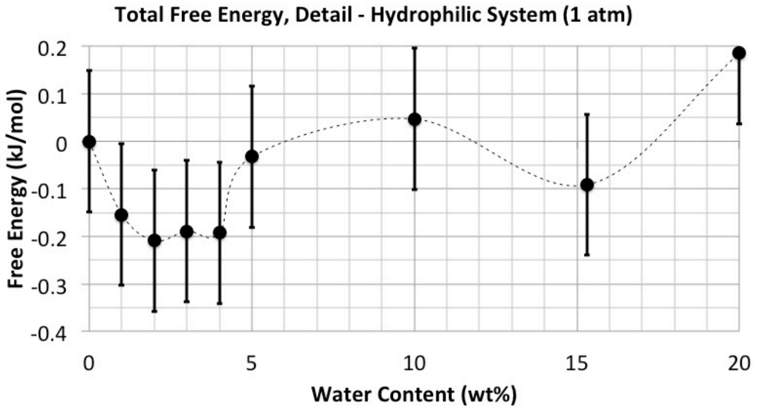

FIGURE 6 FREE ENERGY LANDSCAPE FOR HYDROPHILIC SYSTEM AS A FUNCTION OF WATER CONTENT

The 2PT method has been able to locate distinct free-energy minima. While this is true in general for the free energy profile, the hydrophilic system is plagued with local minima that undermine it’s resistance to water incursion. In particular, the minimum near the percolation point (likely ~15 wt%) indicates that the state of percolation is metastable, which is extremely undesirable for a material to be used as a water barrier.

To compare with the reported energies of the hydrophobic composition; the hydrophobic system exhibits a strong barrier to accepting water in the system, but the polymer is so hydrophobic as to induce the phase separation. This gathers waters together, encourages the uptake of additional water and the formation of the very water channels we wish to avoid.

From these two systems we can determine that the use of a strongly hydrophobic material as a water barrier is an unlikely approach. Future polymer compositions should strive to exhibit a more artful resistance to water, in terms of limiting water transport across the polymer-air interface and in resisting percolation of water in the hydrated material. One could think of a composition that initially accepts water into the system at low concentrations, exhibits a deep energy minimum and therefore a strong barrier to percolation at higher water contents. Incorporating hydrophilic behavior into a polymer intended to resist water incursion seems counter intuitive, but this strategic approach could provide a superior material.

The structures for which thermodynamic properties of both the hydrophobic and hydrophilic systems were calculated at densities too low compared to the estimated true density of 1.0-1.1. These structures have now been improved, to a density which we believe is approximately ~10% lower than experimentally reported values (as we had originally expected). This was achieved by increasing the equilibration times in the CED cycles, which enable an improved packing of the dry polymer. For improved level of entanglement (i.e. mechanical response) we will use longer 200-mer chains. The current densities are 0.90g/cc for the hydrophilic case and 0.87g/cc for the hydrophobic case (see Figure 7).

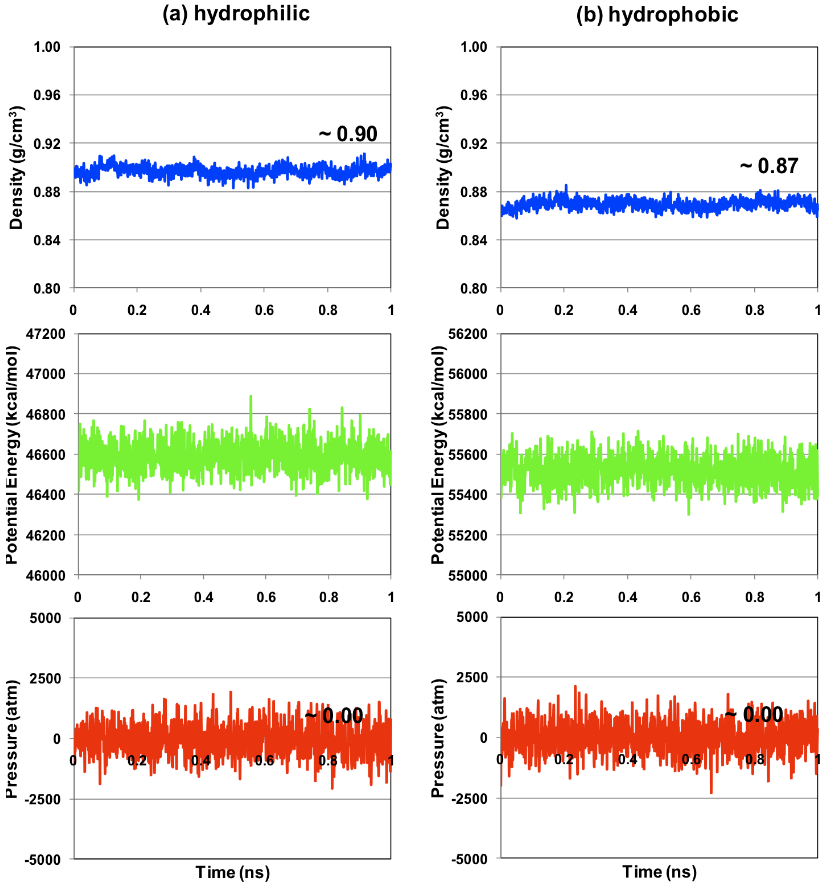

FIGURE 7 HYDROPHILIC AND HYDROPHOBIC MODEL DENSITIES AFTER 1NS NPT EQUILIBRATION (100-MER SYSTEMS).

Additionally, we are investigating the possibility that the pendant groups are complicating the structure equilibration and leading to the wrong density. To check this, we have built systems consisting only of the backbone. The pendant groups will be reinserted after the backbone has been equilibrated by the procedure described above. Finally, significant software development is underway to replace the outdated version of our amorphous builder, which yields correct structures for systems up to 10,000 atoms but with small side-chains.

WORK IN PROGRESS AND UPCOMING EFFORT

New structures are being built and equilibrated to the expected densities, using the modified structure preparation approaches described earlier (i.e. longer chains and longer equilibration times, and building amorphous backbone first and placing side chains later). The entire set of properties is being recalculated for these systems, i.e. bulk, thermodynamic, water distribution, and glass transition temperature.

A slight modification is being tested for the solvated systems. A grand canonical Monte Carlo approach will be used to 'solvate' incrementally from drier systems. The GCMC approach explicitly accounts for density fluctuations at fixed volume and temperature, so we expect this would favor a better packing of our latex models.

We are also looking at different models to capture the water polymer interface, which we believe is critical in proposing improvements to the latex structure/composition/production. For this we are analyzing systems with large water pockets in the bulk solvated polymer structures. Properties of interest at the interface include diffusion of water under varying conditions, free-energy landscape of water shells around the polymer, and chemical differences on the composition of water exposed species in the polymers.

We will continue to use the 2PT method to further investigate the swelling properties of these polymer systems as a function of water content, in particular to understand how swelling causes changes in structural properties that affect water adsorption/impermeability. We have demonstrated that entropy is key for determining equilibrium water content and structural changes due to water swelling.

Once we have fully validated our latex structure characterization techniques (static and dynamic, including water), we will focus on steering the chemical structure and composition design effort for subsequent experimental testing.

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