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Visualization of Film-Forming Polymer Particles with Liquid Cell Technique in Transmission Electron Microscope†

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Lili Liu *[a], Yi Liu [b], Wenjun Wu [a], Christopher. M. Miller [a] and Elizabeth C. Dickey [b,c]

One of the long-standing challenges in studying structure-property relationships in latex films is to directly characterize the size and morphology of corresponding polymer particles, especially the particles with low film formation temperatures. Here we present an in-situ transmission electron microscopy (TEM) study that allows characterization of film-forming latex particles in solution. Liquid cell TEM provides the opportunity to image latexes with a range of particle sizes and glass transition temperatures. Together with staining technique, it can also be used as a tool to characterize the internal structure of particles in solution.

Latex polymer particles with low minimum film formation temperature (MFFT) and/or glass transition temperature ("soft latexes") are useful in many applications such as low volatile organic compound (VOC) coatings, adhesives, elastomeric sealants, etc. Those skilled in the art of emulsion polymerization will often intentionally vary the location of key polymeric components to create unique compositional profiles or shapes (morphologies) thus engineering specific performance attributes into the latex particles. In order to properly design high performance materials for these applications a detailed understanding of the particle size and morphology of the latex particles is critical.

One of the biggest historical challenges of characterizing the morphologies of "soft" latexes by transmission electron microscopy is maintaining the polymer particles' shape during measurement. This is due to the fact that these techniques typically rely on drying the latex particles under ambient conditions followed by examination under vacuum conditions with no aqueous medium present. As a consequence, the conditions for preparing the particles for characterization alter the size and morphology of the particles to be examined.

In order to overcome this obstacle, a number of techniques have been used for determining the particle size and morphology of soft latex particles. Cryo-transmission electron microscopy (cryo-TEM) together with cryo-microtoming[1-3] or vitrification[4] technique is by far the most widely used method for direct characterization of soft latex particles. However, the preparation of cryo-TEM samples is very time-consuming because the whole process needs to be kept under low temperature. As an alternative to TEM, indirect measurements are also applied to characterize the morphology of submicron soft particles. These techniques include atomic force microscopy (AFM)[5], solid-state nuclear magnetic resonance (NMR) spectroscopy[6], and differential scanning calorimetry (DSC)[7]. Recently, Proetto and co-workers have reported in their work to characterize dynamics of soft nanomaterials labeled with Pt(II) using in-situ liquid cell technique[8]. The Pt(II) labelled polymer nanoparticles provides good contrast in TEM. Their work demonstrated a viable approach for imaging the motion of organic and polymeric soft nanomaterials in liquid water. However, polymer particles are not always labelled for general applications.

In the present work, we developed a simple and direct characterization technique by utilizing a novel liquid cell sample holder (Poseidon made by Protochips, Inc.) to image the latex particles in aqueous dispersion. With the combination of staining technique, the internal structure of latex particles can also be clearly revealed. This technique has the same capabilities as the conventional TEM without the cryo-requirements for characterizing soft latexes.

Latex samples were prepared using semi-batch emulsion polymerization. Major polymer components were butyl acrylate (BA), methyl methacrylate (MMA), and methacrylic acid (MAA). Commonly available surfactants and initiators were used during the polymerizations. Deionized (DI) water was used as the continuous phase in all polymerization processes. All latex samples in this study have a MFFT lower than 25ºC. In most examples, the copolymer composition of the latex particles was kept constant throughout the polymerization. The composition or particle size was varied using standard emulsion polymerization techniques. In one latex example, a fluoropolymer was introduced to the composition. Because of the difference in the electron density, fluoropolymer can be differentiated from backbone acrylate polymers without sample staining. In another two examples, structured particles (SP1 and SP2) were prepared in multi-stage processes. Specifically, SP1 has 50% one phase with a calculated theoretical[9] T_g of -5ºC and 50% another phase with a T_g of 20ºC. SP2 has 75% one phase with a

theoretical T_g of -5ºC and 25% another phase with a T_g of 20ºC. Both latexes have MAA composition on the outer phase.

All samples were diluted to 0.5% solids content. Uranyl acetate solution was applied when staining was required. 3% uranyl acetate solution was diluted using DI water into a series of concentrations before usage. Diluted uranyl acetate and the same amount of diluted latexes were then pre-mixed on a piece of parafilm or petri dish for staining purposes.

The liquid cell technique is a new testing system (Poseidon system, Protochips, Inc[10-13]) that allows liquid samples to be studied in TEM without a traditionally required sample preparation. On the Poseidon testing platform, a well-sealed specimen cell is designed to accommodate liquid samples via a pair of so-called "E-Chips". Each E-Chip contains a small window with the dimension of either 500 x 20 µm, or 400 x 50 µm, and with an amorphous SiN membrane 50 nm in thickness. The space between the two window membranes varies from 150 nm, 500 nm, to 5 µm, which allows soft matter with different sizes to be investigated. The liquid samples can be either dropped directly onto the bottom E-Chip and sealed by a top E-Chip, or driven into the well-sealed cell through tubing and pumps.

In the present study, E-chips with 500 x 20 µm in dimension and 500 nm spacer were used. Before being used, the E-chips were glow-discharged in an environment of 25% O_2 mixed with Ar in a plasma cleaning system (Gatan, Inc.) for 10 minutes to improve wettability of the surface prior to assembling. One drop (appx. 1 µl) of the liquid sample was dispensed onto the bottom E-chip, which has a 500 nm spacer. A second E-chip was placed over the bottom E-Chip to seal the liquid cell. Two E-Chips were further sealed by two O-rings and held mechanically in place by a metal plate and brass screws. Then the Poseidon specimen holder was pumped to 10^{-6} Torr using a plasma cleaner (Fischione Instruments, Model 1020) before being inserted into the column of the TEM to check the integrity of the seal. A JEOL 2010F field emission TEM operated at 200 kV was used for the liquid cell experiments.

Latex particles usually are amorphous with the constitution of light elements, such as carbon, nitrogen, oxygen, etc. In TEM, they show very low or even no contrast and they are beam sensitive. It is even more challenging to conduct liquid cell TEM experiments on wet latexes, because the electron beam interacts with both latex particles and water molecules (water is the dispersion medium for latex particles). When the liquid cell is exposed to the electron beam, it is hard to observe anything through the cell window initially, due to the scattering of electrons by water molecules, as shown in Fig. 1a (observing window is not transparent). Another experimental difficulty is that when the latex sample has been observed under the high-voltage electron beam for a long time, most water in the sample will escape locally to its surroundings. It may be possible that some of the evaporated water molecules are absorbed by the 50 nm SiN window with the aid of electron beam. With no standing water in the liquid cell, soft latex particles will then coalesce and form transparent films (no individual particles can be observed in Fig. 1b. Supporting information: Movie_Fig1b shows the process of particles deforming and coalescing under electron beam). In addition, since the particles are in motion, they can be located at different heights in the liquid cell, causing a variation in the focal plane. These interactions result in images with low resolution (Fig. 1c-1d).

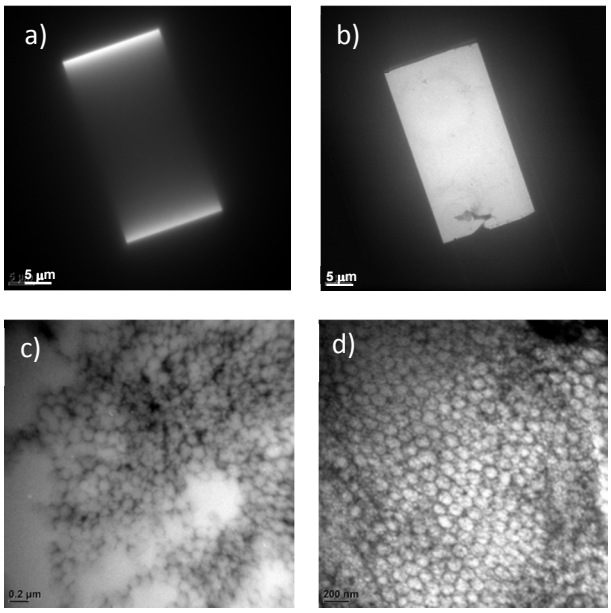
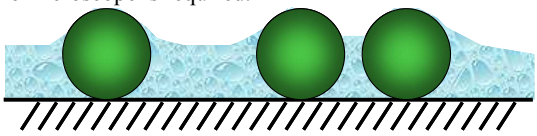


Fig. 1 TEM images of experimental difficulties encountered when performing in-situ experiments: a) liquid cell filled with dilute latex samples; b) dried liquid cell when water from the latex sample has been evaporated by electron beam; c) moving particles under the electron beam; d) stacking particles under the electron beam.

To overcome the experimental difficulties shown in Fig. 1, limiting the irradiation exposure and observation time is critical. We believe the best condition to observe the latex particles in solution is to have sufficient water to keep the wet environment of the latex particles, but not enough for the latex particles to fast move in the liquid cell (see Scheme 1 for the illustration). In addition to the physical environment of latex particles, careful and fast observation with the microscope is required.



Scheme 1 Water need to be just enough to fix particles in place while preventing particles coalesce.

Fig. 2 presents images of latex particles in solution with such optimized conditions at higher magnifications. Fig. 2a and Fig. 2b show latex particles with different polymer components but similar particle sizes of around 120 nm. Fig. 2d shows a physical blend of two latex particles that have different electron densities. Specifically, as pointed in Fig. 2d, lighter particles (shown in grey) are BA/MMA latexes, while darker particles (shown in black) are BA/MMA latexes with fluoropolymers (FP) incorporated into the polymer backbone. The characterization of FP/acrylic blended system sets up a good control reference to studies in FP/acrylic composite or hybrid particles. In addition, nanosized latex particles can also be clearly imaged via liquid cell TEM. Fig. 2c demonstrates that latex particles in the range of 10~ 20 nm can also be clearly observed.

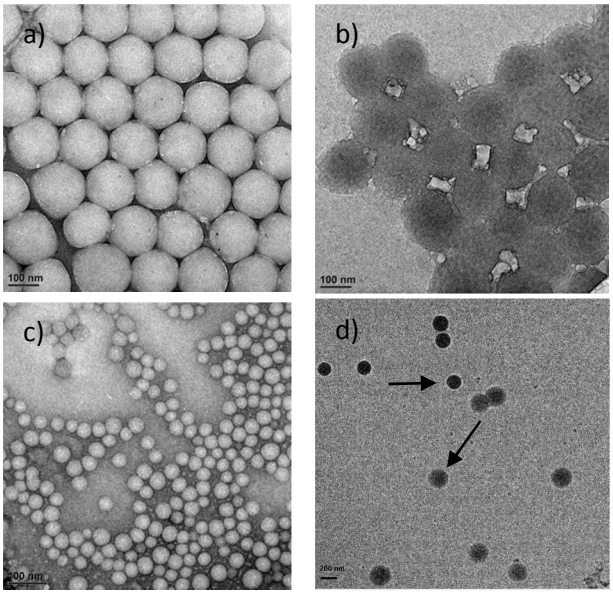


Fig. 2 TEM images of a) latex with a MFFT of 16.9ºC; b) latex with a MFFT of 16.4ºC; c) latex with a MFFT of 19.8ºC; and d) a physical blend of two latexes with different electron densities. Arrows indicate latex particles with different electron densities. Darker particles have a MFFT of 16.4ºC and lighter particles have a MFFT of 21.4ºC.

The internal structure of a structured latex is as important as the particle morphology (shape). In most cases, due to the amorphous status and the constitution of light elements, latex particles show very low contrast under TEM. In order to enhance the contrast of latex internal structure, a staining technique is required. As an effective negative staining agent, uranyl acetate solution also provides some benefit in positive staining due to direct interaction of the uranyl cation with available negatively charged carboxyl groups[14]. It is very useful for latex characterization, because methacrylic acid, as one of the most commonly used functional monomers, can be stained to gain better contrast. Fig. 3 shows the latex sample (SP1) stained with uranyl acetate solution at different concentrations. The internal structure of the particles cannot be observed without staining (Fig. 3a), while too much (3% solution) negative stain also obscures the internal structure (Fig. 3b). Only with a diluted 0.15% uranyl acetate solution can the core-shell structure be clearly observed (Fig. 3c). The particle size is around 180 nm and the shell thickness is around 20 nm, which is consistent with the latex composition. The dependence of TEM contrast on the uranyl acetate concentration can be explained by the competition between uranyl cation physical deposition and chemical interaction with carboxylic acid group in the latex particles. Since the diffusion of uranyl cations into the particles takes time, the physical deposition of heavy cations on the membrane of the liquid cell window is probably faster than the chemical interactions within particles. Therefore, when the concentration of uranyl cations is high (3% in the study), instead of reacting with carboxyl groups, the cations are more likely to settle down on the substrate and deposit quickly.

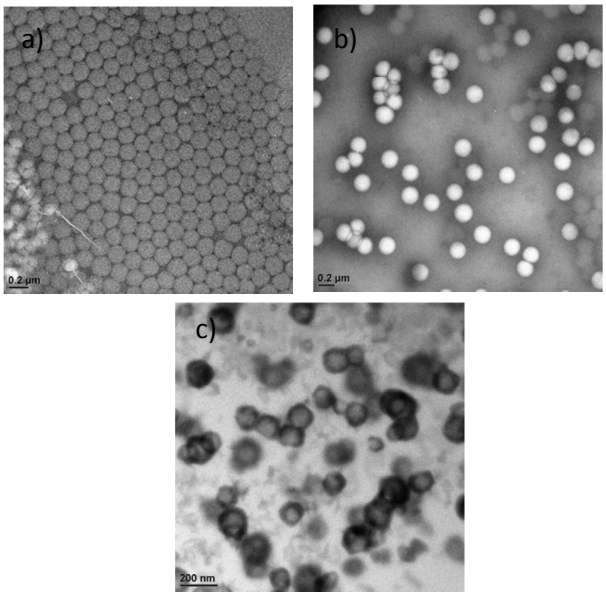


Fig.3 TEM images of latex sample SP1 (with MFFT=16.9ºC) stained with different concentrations of uranyl acetate solution: a) no staining; b) 3% solution; c) 0.15% solution.

This core-shell structure of sample SP1 has been confirmed via AFM (see Fig. 4) using a diluted SP1 dispersion embedded in a homogeneous film-forming latex matrix. Both SP1 and the matrix latex have been dialyzed for four days to remove the excess of surfactants that may contribute to the phase difference in the system. The core-shell structure is clearly shown in the AFM phase diagram (see Fig. 4b). The honeycomb structure shown in the background is contributed by the incomplete coalescence during the film-formation process, at which point particles still retain their boundaries. The boundaries gradually disappear after further drying under ambient temperature for one week. Fig. 5 shows the direct comparison of the cross-sections from the same specimen immediately and one week after film formation. It is obvious that the honeycomb structure almost disappear from the background after one week of continuous drying and the core-shell structure of the doped latexes can still be clearly observed. It should be noted that the different shell thicknesses depicted from the AFM images are due to the different fracture paths from the specimen after being quenched in liquid nitrogen.

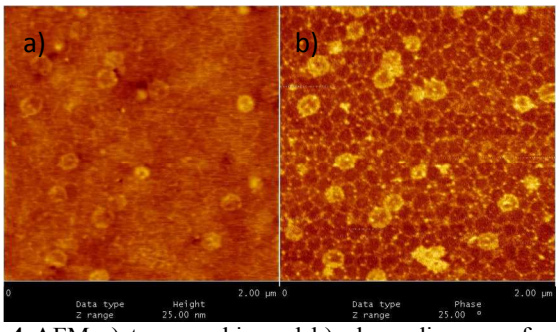


Fig. 4 AFM a) topographic and b) phase diagram of a cross-section of latex sample SP1 (with MFFT=16.9ºC) embedded in a single-phase film-forming latex matrix.

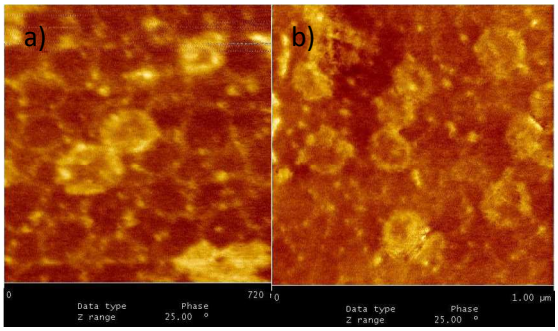


Fig. 5 AFM phase diagram of a cross-section of latex sample SP1 (with MFFT=16.9ºC) embedded in a single-phase film-forming latex matrix a) immediately after film forming b) one-week after film forming.

Another latex sample with different phase composition (SP2) has also been studied to explore a proper range of concentrations needed for an efficient negative staining. 0.15% uranyl acetate stain is confirmed to be enough to reveal the core-shell structure (Fig. 6a). In the meantime, we also found that the effective stain concentration can be as low as 0.06% (Fig. 6b).

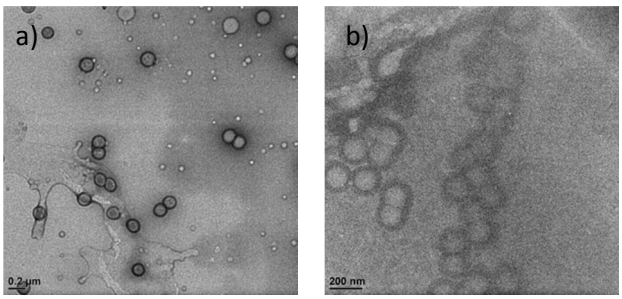


Fig. 6 TEM images of latex sample SP2 (with MFFT=8.5ºC) stained with different diluted uranyl acetate solutions: a) 0.15%; b) 0.06%.

It is worth mentioning that Cryo-TEM characterization was attempted on SP1 and SP2 samples as well; however, the sample preparation did not yield useful specimens as polymer particles in the solution mixtures were easily blotted away during standard plunge-freezing procedures. At the same time, conventional TEM with negative staining technique was also performed by embedding the diluted samples in a heavy-metal (uranyl cation) solution. The particles could be trapped during the staining process, which might prevent them from forming a film upon air drying[15]. However, the observed particle boundaries were not clearly defined, which obscured visualization of the fine structural details inherent in the particles [14,16].

In summary, our work demonstrates the utility of in-situ characterization of film-forming latex particles in solution using a liquid-cell TEM technique. Together with staining technique, liquid cell TEM can also be used to characterize the internal structure of particles in solution. Such in-situ techniques are important when it is necessary to study the morphology of the film-forming latex particles in solution and can complement more conventional cryo-TEM techniques.

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[a] Arkema Coating Resins, Cary, NC 27511.
[b] Analytical Instrumentation Facility, North Carolina State University, Raleigh, NC 27695.
[c] Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC 27695.

† Electronic supplementary information (ESI) available. Movie_Fig1b shows the process of particles deforming and coalescing under electron beam.

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ABSTRACT: One of the long-standing challenges in studying structure-property relationships in latex films is to directly characterize the size and morphology of corresponding polymer particles, especially the particles with low film formation temperatures. Here we present an in-situ transmission electron microscopy (TEM) study that allows characterization of film-forming latex particles in solution. Liquid cell TEM provides the opportunity to image latexes with a range of particle sizes and glass transition temperatures. Together with staining technique, it can also be used as a tool to characterize the internal structure of particles in solution.