Polyelectrolyte Complex Coacervate Assembly with Cellulose Nanofibers

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**ABSTRACT:** Polyelectrolytes are used in paper manufacturing to increase flocculation and water drainage and improve mechanical properties. In this study, we examine the interaction between charged cellulosic nanomaterials and polyelectrolyte complex coacervates of weak polyelectrolytes, polyacrylic acid salt, and polyallylamine hydrochloride. We observe that by changing the order of addition of the polyelectrolytes to cellulose nanofibers (CNFs), we can tune the interactions between the materials, which in turn changes the degree of association of the coacervates to the CNFs and the rate at which they aggregate. Importantly for the papermaking process, when adding the polyelectrolytes sequentially to the CNFs, we found faster aggregation to the fibers and lower water retention values compared to those when preformed coacervates or CNFs by themselves were used. Coarse-grain molecular dynamic simulations further support the fundamental mechanism of aggregation by taking into consideration the interaction between cellulose and the complexes at the molecular level. The simulations corroborate the experimental observations by showing the importance of strong electrostatic interactions in aggregate formation.

**INTRODUCTION**

The US pulp and paper industry is the third largest manufacturing user of energy, using 400 trillion Btu of energy for paper drying in 2010 to produce 83 million tons of paper and paperboard. The dryer section uses about 20% of the total energy for the papermaking process and so provides an excellent opportunity for increasing energy efficiency. Among many approaches to decreasing energy usage is increasing the percent solids in the paper web going into the dryer section, and the industry has specifically set a goal to increase solids from 45–55 to 65% by 2030. Because of the strong tendency of water to bind to cellulose, wet chemistry approaches that lead to flocculation, aggregation, or coating of the cellulose (which decreases water binding) can increase the percent solids in the web. Positively charged polyelectrolytes (polycations) have been used historically to neutralize the negatively charged cellulose fibers and act as fluidcants and strength additives in the papermaking industry. The appropriate selection of polyelectrolytes can increase flocculation and improve drainage of excess water, allowing the drying process to be more energy efficient, but challenges remain in designing these systems to maximize solid content while also considering manufacturability.

Historically, cationic polyelectrolytes have been added to the furnish as flocculating agents, dry strength and wet strength agents, retention aids, and paper web strength promoters. Polycations used in papermaking include cationic starches, polyvinyl amines, polyacrylamide, polyethyleneimine, and more. The use of polycations allows negatively charged fibers to flocculate when their surface charge is adequately neutralized. Depending on the molecular weight and charge density, polycations adsorb electrostatically onto the surface of negatively charged cellulose fibers in different conformations. The adsorption of the polycations plays a role in the papermaking process in two main ways: they improve water drainage from the individual fiber surface by penetrating into the open pores and preventing water absorption and they increase interactions between fibers in the network, preventing loss of fillers during drainage. Despite negative charge repulsion, anionic polyelectrolytes have also been reported to show some degree of adsorption to cellulosic material, particularly in the presence of a salt, which screens the negative charges. However, anionic polyelectrolytes also tend to create larger flocs of fibers compared to cationic ones.

Instead of single polyelectrolytes, mixtures of oppositely charged polyelectrolytes have also been added to cellulosic or negatively charged particles to improve network formation and
increase water drainage. A swollen network allows the water molecules to drain well during pressing in the papermaking process, as it has been shown that microscale densification provides a major barrier to water flow during pressing.16 When oppositely charged polymers are mixed, they form polyelectrolyte complexes (PECs), which form solid precipitates or liquid-phase separated coacervates.18–23 Illustrations and microscopy images of these solid-like and liquid-like PECs are shown in Figure 1A,B, respectively. The liquid–liquid phase separation of the coacervate phase has the potential to further separate water from cellulose and improve drainage and drying times compared to cationic polyelectrolytes alone, given their low interfacial tension with water24 and high degree of swelling.

Common polyelectrolytes used in these complexes for papermaking include permanently charged quaternary amines,2,10,25 carboxy methyl cellulose,25,26 and polyamide amine epichlorohydrin,26 with weak (pH sensitive) polyelectrolytes used less frequently.5,27 Much of the work done on PECs in papermaking has been focused on the interaction between negatively charged fibers or particles and preformed PECs, where the polyelectrolytes are mixed separately and the resulting complexes are added to the particles.2,10,25,26,28–31 Preformed PECs were shown to be retained at fiber interfaces,2,26,30 increase mechanical properties of bulk paper systems,9,25,26 and flocculate charged clay particles at high settling velocities.28 Despite these improved properties, preformed PECs have been shown to plug up channels in the fiber network, which would allow water to pass through during paper formation.21 In addition, more recent studies have shown that instead of adding preformed complexes, forming complexes in the presence of charged particles (cellulose and others) can further increase adsorption of the polyelectrolytes and retention of the complexes on the fibers.2,14,26,30

Although these earlier research studies focus on engineering design, the fundamental understanding of PEC-CNFS coacervate formation as a function of the mixing order and intermolecular interaction strengths and the effect of electrostatics at the monomer level is poor. In this study, we examine the formation of CNF and PEC coacervates from weak polyallylamine hydrochloride (PAH) and polyacrylic acid sodium salt (PAA) using a combination of experiments and large-scale molecular dynamic (MD) simulations. These components represent a model paper furnish system that includes the cellulosic material, water, and polyelectrolytes. We focus on the fundamental aspects of PEC coacervate formation and assembly and agglomeration of PECs with CNFs as the sequences of mixing of PAH, PAA, and PEC coacervates with negatively charged CNFs are altered. PAH and PAA are weak polyelectrolytes and at pH ~6.5, both polyelectrolytes are highly charged.33 We examine approximately the same molecular weight PAH and PAA salts having the same charge density.33 We evaluate how the order of addition of the polycation, polyanion, or preformed complexes affects their interaction with CNFs experimentally through microscopy and surface charge analysis. MD simulations are carried out to corroborate our experimental findings and enhance our understanding of the self-assembly arising from electrostatic interactions between charged polymers and CNFs in the presence of other molecular interactions and behaviors, as captured in the simulation setup. Finally, we show the application of these materials to the paper industry through examination of the effect of PECs on the water retention values (WRVs).

# RESULTS AND DISCUSSION

Formation of PECs with PAA and PAH. To understand the interaction between PEGs and CNFs, we first identified the precipitate and coacervate regimes with the PAH and PAA in the presence of NaCl. The formation and appearance of these regimes at various concentrations and molecular weights of PAA with NaCl and other salts have been previously reported.19,21,33,34 We verified this and tested higher concentrations to select conditions for coacervate formation with CNFs at polymer concentrations important for the remaining studies in this work. Through a combination of microscopy and turbidity analysis, we determined that the transition from the precipitate to coacervate occurs at salt concentrations of 0.1, 0.2–0.4, 0.4–0.5, and 0.7–0.8 M NaCl for 1, 5, 50, and 110 mM total polyelectrolyte concentrations, respectively. Experimental procedures are available in the Supporting Information Section 1.6. Results and more detailed discussion of these are in the Supporting Information Section 2. We have thus selected a salt concentration of 1 M to move forward with for the remaining studies, as coacervate formation is established under these conditions, even for higher concentrations of polyelectrolytes.

Formation of Coacervates with CNFs. Once the salt concentrations at which coacervates are formed were established, 0.05 wt % CNFs were introduced into the system. Using microscopy to observe the interactions, we examined how the order of addition of PAH and PAA affected their coacervation and association with CNFs. This was done at 5 mM total polyelectrolyte concentration with the same mixing procedure as the coacervates but varying the order of addition of the components. In the first scenario, PAH (+) is added to the fibers and salt solution first and then, PAA (−) was added last. The second scenario is the opposite, where PAA (−) is added to the fibers and salt solution first, and PAH (+) added last. Finally, in the third scenario, preformed coacervates were formed with PAH, PAA, and salt. These were then added to fibers. The coacervates form and are left to move and coalesce over time without additional agitation.

The micrographs in Figure 2 show the differences between the three scenarios when the last component is added to the well plate for 5 mM total polyelectrolyte concentration. Time-lapse videos up to approximately 130 min are supplied as files Video 1>: CNF 1 M NaCl 5 mM PAH 1st PAA 2nd.avi, Video 2>: CNF 1 M NaCl 5 mM PAA 1st PAH 2nd.avi, and Video 3:
CNF 1 M NaCl 5 mM preformed PAH PAA in the Supporting Information. In the first scenario (Figure 2A,D,G,J,M,P), when PAA is added last [PAH (+) is already present], the coacervates form in solution and move from the solution to the fibers. The formation of the coacervates occurs almost immediately upon addition of the last component, and the association of the coacervates to the fibers starts to occur around 4 to 5 min and continues over approximately the next 20–30 min. As the coacervates become localized near the fibers, they become less mobile than those in the bulk and are primarily attached to the CNF particles and not exchanging with the coacervates dispersed in the solution (see Video 1: CNF 1 M NaCl PAH 1st PAA 2nd.avi in the Supporting Information). The fibers are mostly covered at the 40 min mark (Figure 2D) and almost completely covered at 70 min (Figure 2G), when a dense aggregation of coacervates can be observed. In scenario two (Figure 2B,E,H,K,N,Q), where PAH was added last [PAA (−) already present], many coacervates form in the bulk solution and eventually move to the fibers as well, but it takes somewhat longer than in the first case. At the 40 min mark (Figure 2E), less of the fibers are covered with coacervates and they are primarily seen in the bulk. At this 40 min timepoint, there appears to be some difference in the rate of aggregation of the coacervates to the fibers, but by 70 min, both the polycation (PAH+) and polyanion (PAA−) systems show similar amounts of association to the fibers and form a tighter network than they had at earlier timepoints (Figure 2G,H). The small difference in the aggregation speed may not be significant for performance in an industrial application and short-time-scale behavior (as studied with the electrophoretic mobility and fluorescence microscopy work in the next sections) and contrasts with preformed coacervates may be more significant. At 100 min (Figure 2J,K), the aggregation of coacervates to the fibers looks similar to that at 70 min. After 24 h (Figure 2M,N), the fibers in both cases are covered with coacervates that are tightly bound and after approximately 3 days (Figure 2P,Q), the coacervates have started to coalesce into larger coacervates with the fibers still attached.

In the preformed coacervate scenario (Figure 2C,F,I,L,O,R), the coacervates are already well-dispersed in the bulk solution.

**Figure 2.** Microscope images of CNFs and coacervates after 10, 40, 70, and 100 min, ~24 h, and 3 days after adding the last component on the microscope while varying the order of addition of 5 mM total polyelectrolytes to CNF solutions. In (A,D,G,J,M,P) PAH (+) was added first and then, PAA (−), in (B,E,H,K,N,Q) PAA (−) was added first, then PAH (+), and in (C,F,I,L,O,R) preformed coacervates were added to the CNFs. The rows are the time points.

**Figure 3.** Schematic representation of the association of the coacervates with fibers over time with varying the mixing order for 5 mM total polyelectrolytes.
They also move to the fibers, similar to the other cases, but the association has only begun at the 40 min mark, with many coacervates still in the bulk even up to 70 min, and significant coverage only occurs at 100 min and beyond (Figure 2F, I, L). It is not until after 24 h that there is a large amount of coacervates on the fibers (Figure 2O) and they do not form the same close aggregation as in the first two scenarios, which is still evident 3 days later (Figure 2R). As discussed in the Introduction, preformed coacervates have been used to improve paper strength properties in paper formulation. However, these results suggest that their interaction is weaker than in the case where positively charged polyelectrolytes are added first, at least at short time frames. Over time, however, the preformed coacervates continue to move to the fibers and adhere along the surface.

As illustrated in the schematic in Figure 3, when adding the polyelectrolytes to the CNF and salt solution, coacervates form and become immobilized on the fibers. The coacervates seen in the bulk solution move to the fibers and become relatively scarce over time. The differences between the three scenarios of mixing order is the relative time it takes for the coacervates to be immobilized and the association with the fibers with the coacervates, with the most significant difference being between the preformed coacervates and the sequential addition.

**CNF and Polyanion Interactions with Fluorescently Labelled Polycation.** To better visualize the interaction between coacervates and CNFs while changing the order of addition of the polyelectrolytes, fluorescently labelled PAH was used to prepare the coacervates. Figure 4 shows 0.05 wt % CNFs, 1 M NaCl, and 5 mM total polyelectrolytes with the three different orders of addition scenarios. Unlike the images shown in Figure 2, where the last component was added directly to the well plate, the samples in Figure 4 were vortexed immediately after the addition of the last polyelectrolyte in the centrifuge tube. They were then placed on glass slides and covered with a coverslip. Figure 4A, C, E show differential interference contrast (DIC) images with fluorescence overlay (where the CNFs can be seen), and Figure 4B, D, F show just the fluorescent images.

These results further confirm that even with complete mixing, there is a difference in the attachment of the coacervates to the fibers with the order of addition. When the PAH-FITC is added first (Figure 4A, B), the coacervates largely cover the fibers in large droplets with few free coacervates in the free space in the solution. The PAH-FITC coats the fibers, and the free PAH-FITC and PAA form large coacervates that have coalesced together. Although coacervates are also attached with the PAA-first case (Figure 4C, D), these are small and disperse and many are still in the bulk solution. Here, the added PAH-FITC will complex with PAA preferentially, but some of the PAH-FITC is electrostatically attracted to the negatively charged fibers and coats them as well. In the preformed coacervate case, the fibers are difficult to distinguish in the fluorescent image (Figure 4F) because PAH-FITC has not significantly adsorbed to their surface. The PAH-FITC that would electrostatically be attracted to the fibers is already complexed with the PAA. Consequently, significantly fewer coacervates are seen to be attached to the fibers and the majority of them remain in solution instead.

Our results are consistent with Zhao and Zacharia who showed that the mixing order of PAH and PAA had greater encapsulation of negatively charged bovine serum albumin when PAH was first added to it, then followed by PAA to make coacervates. Additionally, previous studies with PECs and negatively charged surfaces showed that the adsorption of preformed PECs to negatively charged surfaces increases with increasing salt concentration (0–100 mM NaCl) for both strong and weak polyelectrolyte systems. Our results showed that even with higher salt concentrations (1 M NaCl), attachment of the PEC coacervates to the negatively charged CNFs is less in the preformed case as compared to that when the coacervates are formed in the presence of the fibers.

**CNF and Polyelectrolyte Complex Mixture Surface Charge Analysis.** The observations of the interactions of CNFs with the complex coacervates can be explained by the surface charge of the CNFs as measured using electrophoretic mobility. As seen in Figure 5A, CNFs with 1 mM NaCl are negatively charged at pH values between 4 and 10. This includes a negative charge at a pH value of 6.5, which is what we used for the polyelectrolyte solutions for the coacervation experiments (electrophoretic mobility here is between −0.86 and −1.4 μcm/Vs). Because these electrophoretic mobility values correspond to zeta-potential values of approximately −10 to −20 mV, these can be considered slightly negatively...
charged. Although the CNF surface charge is primarily reported as the zeta-potential in the literature using the Henry equation with Smoluchowski or Hückel approximations,\textsuperscript{37–39} electrophoretic mobility is a more accurate measure of the surface charge character because it requires fewer assumptions.\textsuperscript{37} CNFs have high aspect ratios and can aggregate so assumptions from Smoluchowski equations, which treat the particles as spherical, may not be appropriate.\textsuperscript{37,40}

Because these CNFs are negatively charged, it can be expected that the oppositely charged polyelectrolyte will adsorb to the surface of the particles and neutralize the surface charge, while the negatively charged polyelectrolyte will repel and the particle surface charge will not change. It has been reported that low molecular weight and highly positively charged polyelectrolytes readily adsorb onto the surface of cellulose fibers in flat configurations within seconds to minutes.\textsuperscript{13} The adsorption was confirmed by adding increasing concentrations of either PAH (+) or PAA (−) to a 0.05 wt % CNFs and 1 mM NaCl dispersion at pH 6.5 and measuring the electrophoretic mobility at each concentration. Figure 5B shows that the electrophoretic mobility increases linearly with PAH concentration on a semilog scale. The surface charge switches from negative to positive at a PAH concentration of 0.05 mM and is positive at higher PAH concentrations, which correspond to the minimum polyelectrolyte concentrations used in this study. This also confirms that for the 5 mM total polyelectrolyte concentration scenario, adding PAH first results in excess polycations at the surface. As expected, increasing the concentration of PAA did not appreciably change the surface charge of the CNFs. At all concentrations of added PAA tested, the electrophoretic mobility stayed between −0.85 and −1.5 μmcm/Vs and did not significantly change when compared to CNFs with 1 mM NaCl at pH values near 6.5, which have electrophoretic mobility values between −0.86 and −1.4 μmcm/Vs.

Finally, the electrophoretic mobility was measured over time for each of the three order of addition scenarios at pH 6.5 (Figure 6). Interestingly, for the case where PAH (+) was added first, upon addition of the PAA (−), the electrophoretic mobility appreciably shifted from a positive mobility to a negative one. This change of sign was not seen when PAA (−) was present first and PAH (+) was added. Similarly, the electrophoretic mobility did not significantly change in the case where fibers were added to preformed complexes. This, when taken in context with the 2-system mixtures in Figure 5, indicates that the PAH adsorbs onto the fibers when mixed, unlike the PAA and preformed coacervates. This may increase the local PAH concentration near the fibers or provide a position for new coacervates to form after the initial rapid bulk formation, leading to faster kinetics for aggregation of coacervates onto the fibers. In these short timescales, the difference in the behavior of PAA-first and PAH-first is more clear and significant than that at larger timescales. These results further support the importance that the order of addition plays in the overall system.

**MD Simulations.** To augment our understanding of coacervate formation at the molecular level, we performed CG MD simulations for three different systems; for System-I, we demonstrated the PEC coacervate formation of just the polyelectrolytes, polycations (PAH), and polyanions (PAA), at

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**Figure 5.** Electrophoretic mobility of 0.05 wt % CNFs and 1 mM NaCl: (A) at various pH values and (B) with increasing concentrations of PAH (+) or PAA (−) at pH 6.5. Each point is an average of three samples and error bars represent the standard deviation.

**Figure 6.** Electrophoretic mobility over time of 0.05 wt % CNFs with 1 mM NaCl with PAH (+) first, then PAA (−) added (red squares), PAA (−) first and then PAH (+) added (blue triangles), preformed coacervates first, then CNFs added (orange diamonds). Each data point is an average of three samples and error bars represent the standard deviation.
9% salt concentration. The simulations are performed in a canonical ensemble (NVT). As can be seen from the coacervate formation in Figure 7A, the choice of our concentration of polycations and polyanions is higher than the critical aggregation concentration (CAC) regime and hence, this concentration can be used for the rest of the simulations (for simulation detail, please see the Supporting Information Section 4). We built the initial system by putting coarse-grained CNFs and polycation and polyanion molecules randomly in a box of size $100 \times 100 \times 100 \sigma^3$, where $\sigma$ is the monomer bead diameter (Figure S4). As discussed in the Methods section, the other two systems (in the presence of CNFs) are affected by the order of polyanion and polycation addition. We refer to these two systems as (Set 1) polycation-first (PAH-first) and (Set 2) polyanion-first (PAA-first). Snapshots of these two sets of simulations are shown in Figure 7B,C.

The snapshots in Figure 7B,C show the two different orders of coacervate formation. Full system snapshots with the counterions and salt are shown in Figure S6. In the polycation-first case (Figure 7B), the polycations are strongly attracted to the CNFs because of electrostatic interactions between opposite charges, forming complexes with the CNFs. Although a majority of the polycation charges attach to the negatively charged CNFs, a good amount of the residual polycation charges remain free because of the excluded volume interactions arising from the chain conformation. Successive addition of polyanions helps form larger coacervates with the residual positive charges on the polycations on the CNF surface. Hence, the polycation-first case shows a large number of smaller PEC coacervates that are attached to the CNF surface as observed in the experiments in Figures 2 and 4. In the polyanion-first case (Figure 7C), the polyanions feel strong repulsive interactions with the negatively charged CNFs, and hence, the polyanions do not attach to the CNFs. Consequently, as the polycations are added next, the majority of the polycations form PECs with the polyanions that are already present in solution. Additionally, because of their affinity toward negatively charged CNFs, some of the polycations attach to the CNFs, which draws a few polyanions to the CNF surface. Hence, the polycation-first case mostly forms large PEC coacervates with very few polycations attached to the CNFs. The same is observed in the experiments, as shown in Figures 2 and 4 and in the schematics of Figure 3. For reference, a clean picture of the polycation–polyanion agglomerated structures without counterions and CNFs is shown in Figure S7.

We must emphasize here the importance of counterions in these highly charged polyelectrolyte systems. Although we have discussed in detail the polyelectrolyte CNF coacervates, we have excluded the discussion on counterions, as the counterions are mostly released in the solution. In polyelectrolytes in the solvent, the counterions are either released or condense on the polyelectrolytes. Condensation occurs when counterions attach to a single type (either positive or negative) of highly charged polyanion in a dilute solution with no moieties present and when the charge density between the neighboring charges along the polyanion is reduced below a
critical value (Manning condensation). This results in the screening of the polyelectrolytes from closing the pores in the CNFs. For systems with oppositely charged polyelectrolytes, the conformational entropy of the polymer chain together with strong Coulombic interactions between oppositely charged polyelectrolytes favors the polyelectrolyte agglomeration instead of screening by counterions.41,42 Hence, we do not observe counterion condensation, as our system consists of two types of polyelectrolytes and negatively charged CNFs that overtake the comparatively weaker counterion/polyelectrolyte interactions.

The radial distribution function (RDF), g(r), near the CNF surface in Figure 7D shows a sharp peak for fibers with polycation charges for both of the cases (black and red lines). This indicates strong electrostatic affinity of polyelectrolytes to the CNFs. The first peak in the polycation-first case (black line) is a little higher than that in the polyanion-first case (red line), suggesting higher agglomeration in the PAH-first case. In the experiments, the PAH-first (polycation) case shows rapid coacervate formation with CNFs, while the PAA-first (polyanion) case shows slow attachment of coacervates to the CNFs. Similarly, the g(r) from the MD simulation shows enhanced polycation and CNF agglomeration because of strong electrostatic interactions between oppositely charged polyelectrolytes and CNFs. This can be related to the faster coacervate formation in the PAH-first case in experiments. It should be noted that the simulations show a strong polycation-fiber peak for both the polycation-first and polyanion-first cases. This is due to strong electrostatic interactions between oppositely charged (polyelectrolytes and CNFs) molecules. At long times, the polyanion/polycation coacervates become localized to the fibers irrespective of the order of sequential addition of the polymers. This is consistent with the experimental findings that the two sequentially added systems have similar long-time aggregation, as discussed earlier. It should be noted that this does not represent small and large polyelectrolyte–polyanion coacervate sizes that are attached to the CNFs as observed in the previous section. The PAA-fiber (blue and green lines) for both the cases shows no attachment. This can be attributed to the repulsion between the polyelectrolytes and negatively charged CNFs.

In Figure 7E, we show the g(r) between the polyanion and polycation charges near the CNF surface. The g(r) shows two peaks, indicating two layers of charges near the CNF surface. The large peak heights of this g(r) show strongly agglomerated polycation–polyanion coacervates. The g(r) along with the snapshots shows aggregation mechanisms that depend on the order of addition of the polyelectrolytes. We have not examined the alignment of the polyelectrolytes on the CNF surface because these simulations are performed in solution and our focus is to see how the order of polyelectrolyte addition affects the coacervate formation. This phenomenon may also play a role in how CNFs interact with PECs during processing and in the dried state and could be an interesting area of future study.

In Figure 7F, we show the mean square displacement (MSD) of the different charged species coming from polyelectrolytes, polyanions, and CNFs for both the systems. The MSD for CNFs shows faster motion than the polyelectrolytes for both the cases. In the diffusive regime, long-time MSD shows higher diffusivity for the fibers, representing a greater number of mobile CNFs that are weakly attached to the polyanions. For the polycation-first case (magenta line), the MSD is slightly lower as most of the CNF monomers are part of the coacervate that restricts their motion. For both of the systems, the diffusivity of the polyelectrolytes and polycations is slower as they are a part of the agglomerate, as observed in Figure 7E. It should be noted that we have not calculated diffusion coefficients as that will require much longer simulation time and hence can be computationally expensive. Instead, we preferred to explain the diffusive motion by analyzing the long-time MSD.

Measurement of the WRV is a standard technique used in paper manufacturing and research to evaluate the water retained by pulps through their pores and the swelling of the cell wall16,43–45 Given the high surface area and fibrillation of CNFs, they are expected to retain water and have high measured WRVs.16,46,47 The PECs in this work are designed to decrease water retention in cellulose fiber materials in the papermaking process, so in addition to the fundamental studies on the PEC phase behavior and surface interactions, we also measured the WRV of PECs mixed with CNFs.

**Water Retention Values of CNFs with Polyelectrolytes.** The WRVs we obtained for the CNFs by themselves (269 ± 11.2%) are consistent with the values that have been reported in the literature for other CNF sources with functional group modifications or additional refining.47–49 and some larger pulps.30,45,50,51 As seen in Figure 8, for all three PEC-CNF mixtures (PAH-first, red; PAA-first, blue; and preformed, yellow), the WRVs are lower than those of CNFs by themselves (green). The preformed coacervates had the highest WRV (212 ± 1.30%) of the three PEC cases. This was not significantly different than the WRV of the control sample, CNFs with 1 M NaCl (216.7 ± 14.7%), or significantly different from the WRV of the CNFs with 50 mM PAH and 1 M salt control (225.1 ± 17.8%). Consequently, the interaction between preformed coacervates and CNFs at 1 M NaCl is minimal and does not impact the water retention of the fibers in this scenario. This is consistent with the microscopic results that showed coacervates formed primarily in the bulk and are not closely associated with the CNFs. This will prevent the polyelectrolytes from closing the pores in the CNF fibers and cell walls and allow the fibers to retain their water.5,14,45 The sequentially added PEC-CNF mixtures (red and blue in Figure

showed significantly lower WRVs than the CNFs, PAH-only control, and preformed coacervates. It is notable that they show lower WRVs than the PAH-only and preformed coacervates, as this indicates that moving to sequential addition with oppositely charged polyelectrolytes has the potential to significantly improve dewatering of cellulose in papermaking.

Between the PAH-first (140 ± 10.5%) and PAA-first cases (149 ± 12.1%), the average of the PAH-first case is slightly lower. The averages of the two scenarios were compared by performing a t-test with the null hypothesis that PAA-first has a higher WRV. With a one-tail distribution, the PAA-first case is higher with 94% confidence. This insignificant difference is consistent with the optical microscopy results, where the two cases behave similarly at longer timescales and indicate that although the surface charge behavior at short timescales and the morphology with rapid vortex mixing show a difference between the polycation- and polyanion-first cases, at longer timescales and in more relevant bulk systems, there is little difference. However, optical microscopy, fluorescence microscopy, surface charge analysis, simulations, and WRV tests show that preformed coacervates consistently show a significantly different behavior than sequential addition.

CONCLUSIONS

In this study, we investigated coacervate formation between the PAA and PAH PECs and slightly negatively charged cellulose nanofibers. Through optical microscopy, fluorescence microscopy, surface charge analysis, and simulations, we showed that adding PAA and PAH sequentially or as preformed coacervates to the CNFs affects the association of the PECs to the fibers, both the extent/strength of the association and the time it takes for the coacervates to fully associate with the fibers. Specifically, when preformed coacervates were used, there was a loose association to the fibers and it took up to 3 days for full agglomeration. In contrast, when the polyelectrolytes were added sequentially to the slightly negatively charged CNFs, there was significantly more association of the coacervates to the fibers and they were mostly fully associated by the 40 min timepoint. This behavior is driven by the electrostatic interactions between the polymers and the surface of the CNFs, as shown using electrophoretic mobility measurements and MD simulations. We demonstrated the significance of this to the paper industry by measuring the WRVs for CNFs mixed with PECs and showed that the WRV was not significantly different for preformed coacervates compared to the control sample and was lowest for the case where the polycation was added first. This is consistent with the experimental examination of coacervate association with the CNFs, as the WRVs are expected to be lower when the polyelectrolytes are able to fill the pores in the cellulose fibers and cell walls. These in-depth studies on the interactions between polyanions, polycations, and CNFs will have a significant impact on the formulation design for improving drainage in paper manufacturing and helping to reach the goal of 65% solids going into the dryer section by 2030. More broadly, this work improves the understanding of how the order of addition, not just the polyelectrolyte charge and structure, plays a significant role in polyelectrolyte complexation and interactions with particles.

METHODS

To represent a paper furnish system while allowing for fundamental experimentation and approximately representative simulations, we carefully selected a model system containing CNFs. CNFs are extensively mechanically refined fibers with nanometer scale dimensions (lengths of 100–200 nm and widths of ~20–500 nm) and therefore large aspect ratios.38 Some of our materials’ dimensions are greater than 100 nm, and thus, the term microfibrillated cellulose is sometimes used to describe them. Such materials are most commonly referred to as cellulose nanofibers. Our material source uses that terminology, so we will use CNFs throughout this work. The surface charge and chemistry of cellulosic materials are determined by their processing, including pretreatment and mechanical shearing.38 Residual lignin, hemicellulose, and extractive components from the cellulose source can also have an influence on the surface charge and properties of the material, so there is no one consistent model system.39,40 Additionally, although the fiber charge depends partly on the amount of acid functional groups, it is affected by the pH, ionic strength, and swelling of the fibers.61,62,64 The high aspect ratio and surface area of CNFs allow for greater water retention than other pulps, making them among the highest users of energy for drying and providing a good basis for evaluation of the water retention and phase behavior with PECs.37-39 CNFs have also been previously studied using molecular simulations,65-67 although their interactions with polyelectrolytes and complexation behavior have not been examined, so there is a need to understand the full system, which includes CNF and polyelectrolytes, for further improving the material design principles.

MATERIALS

PAA sodium salt (degree of polymerization, N = 160, molecular weight = 15,000 g/mol) in a 35 wt % aqueous solution was purchased from Sigma-Aldrich. PAH was purchased as a powder from Sigma-Aldrich (N = 186, molecular weight = 17,500 g/mol). They were used without further purification. Detailed methods for the production of polyelectrolyte stock solutions may be found in the Supporting Information Section 1.1.

CNFs were received in 3 wt % aqueous slurry (with 90% fines grade) from the University of Maine Process Development Center and kept refrigerated. All CNFs were from the same lot (Lot#U935) to minimize variability between sources. Because variability is a significant challenge in the use of natural products,37,67 we have included further discussion and characterization of these CNFs in the Supporting Information Section 1.2.

Mixture Preparation. Precipitate or coacervate phases were achieved by mixing the stock solutions of the polyions or polyanions with appropriate amounts of 5 M NaCl solutions and water, which were also adjusted to pH ~6.5 using HCl or NaOH. Detailed mixing methods, including methods for static and timed studies, and a discussion of the selected concentrations are included in the Supporting Information Section 1.3. The final mixtures were at 1, 5, 50, and 110 mM total polyelectrolyte concentrations, equimolar polyions and polyanions by degree of polymerization (N).

Briefly, the time studies were performed by vortexing the first four components together and then adding the last component without further mixing. The samples for these
studies were all made with 5 mM total polyelectrolyte concentrations.

**Optical Microscopy.** Approximately, 50–100 μL of samples were imaged in optically clear Corning ultralow attachment surface 96 well microplates using a Leica DMi8 inverted microscope.

**Fluorescent Labelling and Microscopy.** PAH was fluorescently labelled with a fluorescein isothiocyanate isomer (FITC) purchased from Sigma-Aldrich (CHEM IMPEx INT'L INC M_w: 389.39 g/mol). Experimental details of fluorescent labelling are described in the Supporting Information Section 1.4. Samples made for microscopy were prepared in a similar manner to the timed studies for the microscopy studies. The CNFs, water, salt, and samples were prepared in a similar manner to the timed studies for the microscopy studies.

**Electrophoretic Mobility Measurements.** Electrophoretic mobility values were measured using a Zetasizer Nano Z unit of PAH-FITC. Fluorescence imaging was conducted on a Zeiss AxioObserver Z1 Fluorescent Microscope.

**Fluorescence Imaging.** Immediately after preparation, 500 μL of the sample was pipetted into Milli-Q Ultrafree-MC centrifugal filter tubes with a 0.22 μm pore size Durapore hydrophilic PVDF membrane. The samples were then centrifuged at 12,000g for 30 min. These conditions are more stringent compared to typical standards44 and comparable to methods in the literature on other CNF systems47,49. These are sufficient to reach the asymptote of WRVs for the time and force used.47 Immediately after centrifugation, the samples were removed and weighed and then put in an oven at 25 °C. The oven was set and ramped to 110 °C; then, the samples were dried for additional 30 min at this temperature, before turning the oven back down to 25 °C. The heating and cooling rates were ~5 and ~1 °C/min, respectively. The weights were measured after the samples reached room temperature again.

**WRV Measurements.** Samples of 0.5 wt % CNFs, 1 M NaCl, and 50 mM total polyelectrolyte concentration were prepared and the mixture preparation methods used are described in the Supporting Information Section 1.5. Immediately after preparation, 500 μL of the sample was pipetted into Milli-Q Ultrafree-MC centrifugal filter tubes with a 0.22 μm pore size Durapore hydrophilic PVDF membrane. The samples were then centrifuged at 12,000g for 30 min. These conditions are more stringent compared to typical standards44 and comparable to methods in the literature on other CNF systems47,49. These are sufficient to reach the asymptote of WRVs for the time and force used.47 Immediately after centrifugation, the samples were removed and weighed and then put in an oven at 25 °C. The oven was set and ramped to 110 °C; then, the samples were dried for additional 30 min at this temperature, before turning the oven back down to 25 °C. The heating and cooling rates were ~5 and ~1 °C/min, respectively. The weights were measured after the samples reached room temperature again.

**MD Simulations.** Coarse-grained (CG) MD simulations are performed using the LAMMPS MD package.64 We used bead-spring polymer model, where the monomer beads of the polymer are connected by finite extensible nonlinear elastic (FENE) bonds. In LAMMPS, short-range repulsive LJ interactions between the beads are embedded in FENE potential that ensures no overlapping between two monomer beads. The experiments are designed to examine how the order of addition of the polyanions (PAA), polycations (PAH), or preformed complexes affects their interaction with CNFs. To complement these and give a qualitative picture of the fundamental physics of the system, we performed three sets of simulations: (1) polycation and polyanion complexation, (2) CNFs, polycation, and polyanion coacervate formation with polycation (PAH) added first and (3) CNFs, polycation, and polyanion coacervate formation with polyanion (PAA) added first. It should be noted that we have not performed the preformed coacervates added to CNF simulations because of limited computational time. The coarse graining is done at the monomer level following the bead-spring polymer model,65 as shown in Figure S4a,b. Modeling microscale fibers such as CNFs, carbon fibers, and so on with a stiff rod, that is, beads connected by stiff bonds, is very common in Kremer-Grest bead-spring models and has been in the field for a long time.66–69 In MD simulations, chain lengths can influence the self-assembly process. Similarly, salt concentration can also influence the self-assembly processes. Experience from our prior simulations on PECs helped us to properly estimate the CNF and chain concentrations that would lead to coacervate formation.51,62,70 Hence, we choose 0.75% CNF concentration, 1.2% PAA and PAH coarse-grained monomer concentration, and 9% salt concentration (both positive and negative ions). The percentage of negative charges on the CNF backbone is 25%. The PAA and PAH backbones have 80% charges each and are modeled as polyanions and polycations, respectively.
The same number of positive and negative counterions is randomly added to neutralize the CNFs and PAA and PAH charges. Salt ions are incorporated as single bead positive and negative charges.

The simulations are performed under the implicit solvent conditions, that is, no explicit water is used. It is a common practice in the bead-spring polymer simulation to use the “implicit solvent” method to avoid large computational costs associated with “explicit” water molecule simulation. Modeling of water as an “implicit solvent” is a common but simplistic approach in CG simulations of polyelectrolytes; however, we must emphasize that water plays a crucial role in polyelectrolyte self-assembly. In this CG Langevin dynamics, the solvent interactions with polyelectrolytes are governed by the damping coefficient of the Langevin equation and dielectric constant of the medium that can capture the effect of solvent fairly well. Therefore, the “implicit solvent” technique can provide us with enough insight into the self-assembly and coacervate formation in this polyelectrolyte—CNF system.

It should be noted that these concentrations are much higher than the experimental concentrations, which was done because there is a minimum limit of the overall number of monomers in MD simulations which is needed to form coacervates. Moreover, the simulating system is much smaller than the experimental system. Hence, to follow the exact experimental system, the simulating system’s total number of monomers would become significantly low, so much so that any substantial and physically meaningful effect can hardly be observed. The chain length of PAA and PAH is 60 monomer units, which is below the entanglement length of polymers in the coarse-grained simulation. Salts and counterions are added as discussed in the Supporting Information. As the focus of this work is to understand the coacervate formation driven by strong Coulombic interactions, we have chosen the chain length to be less than the entanglement length. The energy parameter, $\varepsilon$, for the LJ interaction was kept at 1.0 for the interactions between different monomer beads, except for the charged beads. For the charged beads, a strong interaction parameter was used, that is, $\varepsilon = 2.0$.

In the first set of simulations, we performed polyanion—polycation complexation to understand coacervate formation. Thereafter, two sets of simulations were performed. For Set I, the polyanion (PAA) interacts first with the CG CNF monomers and then, PAH is introduced in the system. For Set II, the polycation (PAH) interacts with the CG CNF monomers first and then, polyanions (PAA) are introduced in the system. The construction of the MD model is such that both the polycations and polyanions are simultaneously present in the initial system. The experimental conditions are mimicked by allowing interactions between CNF monomers and polyanions and polycations to begin at different simulation timesteps, while the experiments are performed by physically adding PAA and PAH in two different orders. Therefore, the order of addition behavior is achieved by effectively introducing zero interaction of all types between CNFs and polycations or polyanions in Set I and Set II, respectively. Although this approach allows the other type of polyelectrolyte to be present in the system, the other polyelectrolytes do not contribute to any interaction except occupying their respective spaces. In simulations, addition of large macromolecules, in this case the polycations and polyanions, separately becomes difficult and computationally intractable, and hence, we choose to use the method described here. For further simulation details, please see the Supporting Information Section 4.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00977.

Detailed methods and material descriptions of polyelectrolyte stock solutions preparation, PEC mixing and preparation, fluorescent labelling, water retention value sample preparation, turbidity testing procedure and results, CNF conductivity titration, time lapse videos, and MD simulation details (PDF)

- Video 1: CNF 1 M NaCl 5 mM PAH 1st PAA 2nd (MOV)
- Video 2: CNF 1 M NaCl 5 mM PAA 1st PAH 2nd (MOV)
- Video 3: CNF 1 M NaCl 5 mM preformed PAH PAA (MOV)
- Video 4: coacervates 2 M NaCl 110 mM PAH PAA (MOV)
- Video 5: precipitates 0 M NaCl 110 mM PAH PAA (MOV)

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