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Research Article

Modulating Functionality of Starch-Based Patchy Particles by Manipulating Architecture and Environmental Factors

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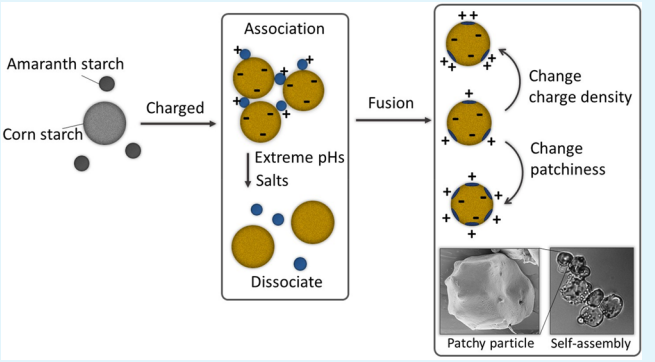
ABSTRACT: Starch as a food-grade thickener has been commonly used in food products to modulate textural properties. Improving viscosity-enhancing ability, so as to be able to use less starch for the same texture, has been considered as an approach to reduce the dietary consumption of carbohydrates. We have positively charged amaranth starch (~1 μm) and negatively charged corn starch (>10 μm) and physically fused the particles together to create a starch with a heterogeneous pattern. This starch has a negatively charged main body, due to the larger corn particles, and positively charged patches from the amaranth starch. These patchy particles self-assembled through electrostatic interactions into a shear-reversible thickener. The impact of patchiness and charge density on material functionality was investigated. The degree of patchiness was controlled by manipulating the ratio between the two starches, and results showed that viscosity was reduced when the patchiness was higher. With the same patchy area, a higher charge density did not contribute to higher water-holding capacity. The more charged particles were able to enhance the viscosity, however, due to the stronger interparticle electrostatic interaction. The effects of environmental factors including pH level and ionic strength were also investigated, and the results showed that at extreme pH levels, or in the presence of Na^+ or Ca^{2+}, the charges on the starch particles were screened, and this inhibited interaction and reduced viscosity. The present work demonstrates that the texture of starch slurries can be fine-tuned by manipulating the degree of patchiness and the charge density of patchy particles. It also evaluates the application potential in food products with different pH levels and ionic strengths.



KEYWORDS: *patchy particles, starch, rheology, self-assembly, patchiness, charge density, ionic strength*

1. INTRODUCTION

Starch is the most common carbohydrate present in foods; it not only functions as a calorie source but also is frequently used as a label-friendly additive to provide texture.[1] Dietary guidelines, however, emphasize that nutrient-dense diets containing more proteins and micronutrients per unit calorie are favorable and that the consumption of starch should be limited.[2] As starch contributes substantially to the flavor, texture, and pleasurable organoleptic properties of food, eliminating it from the diet entirely is not only unfeasible but also undesirable. To that end, there has been an increasing interest in improving the functionality of starch so that the benefits remain but the amount of starch in food can be reduced.

The thickening ability of starch relies on the gelatinization process where a hydrothermal treatment dissociates the intermolecular hydrogen bonds between hydroxyl groups in the semicrystalline region which creates space to retain and hold water.[3] When water is held inside starch particles, their granular size increases. As a result, they have a higher effective volume and are more resistant to water flow, thus exhibiting higher viscosity. Meanwhile, amylose molecules are leached from these gelatinized starch granules and, if a sufficient amount is present, form a settled gel.[3] Shearing can break the soft swollen granules of a conventionally cooked starch slurry and disrupt the gel structure, causing nonrecoverable matrix degradation and changes in food texture.[4] Therefore, exploring new shear-reversible approaches beyond swelling-based thickeners is currently of great interest to the food industry.

Patchy particles are microstructures designed such that they have a nonhomogeneous pattern on the surface,[5] with the patches having different properties to the rest of the particle body, thus giving them self-assembly behaviors.[6] The self-

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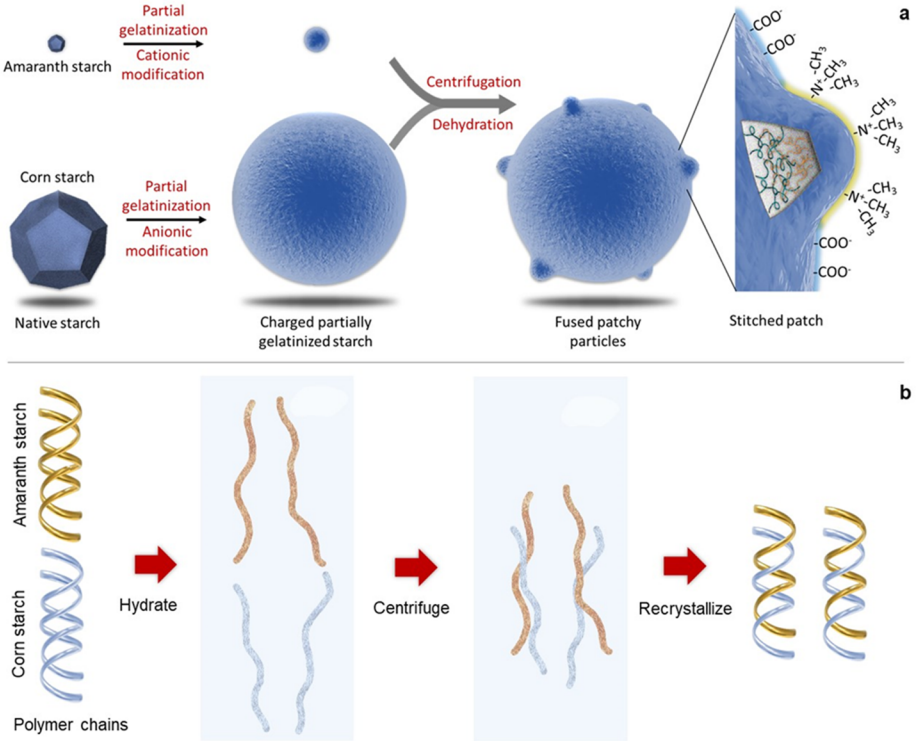

Figure 1. Steps (a) and schematic illustration (b) of the fusion-based method for producing starch-based patchy particles. Reproduced with permission from ref 16.

assembly of patchy particles is driven by lower free energy, such as electrostatic and hydrophobic interactions. Patchy particles, because of their self-assembling properties,[7] can serve as shear-reversible platforms. Numerous creative methods have been reported to fabricate this state-of-art material, such as masking lithography,[8] antisolvent deswelling,[9] emulsion templating,[10] phase separation,[11] vapor deposition,[12] DNA coating,[13] capillary cojetting,[14] and colloidal fusion,[15] which involved a variety of materials including polystyrene, latex, and poly(methyl methacrylate). However, there is a gap in knowledge about the fabrication of self-assembling particles using natural or food-grade materials, such as starch, to produce patchy particles.

Our research group, in a search for food-grade texturizers, has recently extended patchy particle construction to starch. To our best knowledge, this is the first report where patchy particles were made by using natural food-grade ingredients that is both facile and scalable.[16] Our approach took advantage of starch granules that naturally have different sizes depending on the botanical sources,[17] and then we physically grafted smaller amaranth starch particles (~1 μm) onto larger maize starch granules (>10 μm) (Figure 1a). In the grafting process, both starches were first partially gelatinized in aqueous alcohol so that the granules swell,[1,18,19] then as the gelatinized polymer chains gained a higher degree of freedom, the subsequent centrifugation process forced the soft swollen granules together, causing them to penetrate each other. Once dehydrated, the biopolymer chains of the starch are tangled together and recrystallize during storage.[20] This results in effectively stitching particles together to form a single fused particle (Figure 1b). The patches were robust and remained on the particles when redispersed in water.[16] Prior to fusing, the two starches were modified to give the corn starch an anionic charge[21] and the amaranth starch a cationic charge;[22] therefore, the patchy particle that was produced had a core with a negative charge and patches on the surface that carry a positive charge. The fused particles then associate via electrostatic interactions, and the particle matrix shows a 3-fold higher water-holding capacity as well as 1000 times higher viscosity than the unmodified starch. In addition, the slurry texture was found to be stable against heating and shearing, which showed potential for use as a thickener in the food industry. The bottom-up method is facile and versatile, allowing for modifications to be performed before and after synthesis and providing convenient control of the degree of particle patchiness by simply controlling the ratio between the two starches in the fusing process.

In addition to our successful preparation of starch-based patchy particles, we needed a more holistic understanding of the modulation of their functionality. We hypothesized that the degree of patchiness and the charge density of a single patch are key variables that influence their self-assembly properties, thus affecting the overall texturizing properties. The study presented here manipulates the degree of patchiness and the charge density of these novel starch-based patchy particles and investigates the impact on starch functionality. Additionally, as real food products are complicated in composition with a wide range of pHs and salt concentrations, we also studied the effect of environmental factors on the slurry texture. The exploration of a shear-reversible platform with an increased ability to provide a range of viscosities has the potential to reduce the starch content from foods, allowing consumers to reduce their caloric intake from energy-dense carbohydrates.

2. MATERIALS AND METHODS

Materials. Corn starch (50% amylose) was sourced from a local vendor. Amaranth flour was purchased from a supermarket (NY, USA). Absolute ethanol (>99% purity) was requested from bioPLUS

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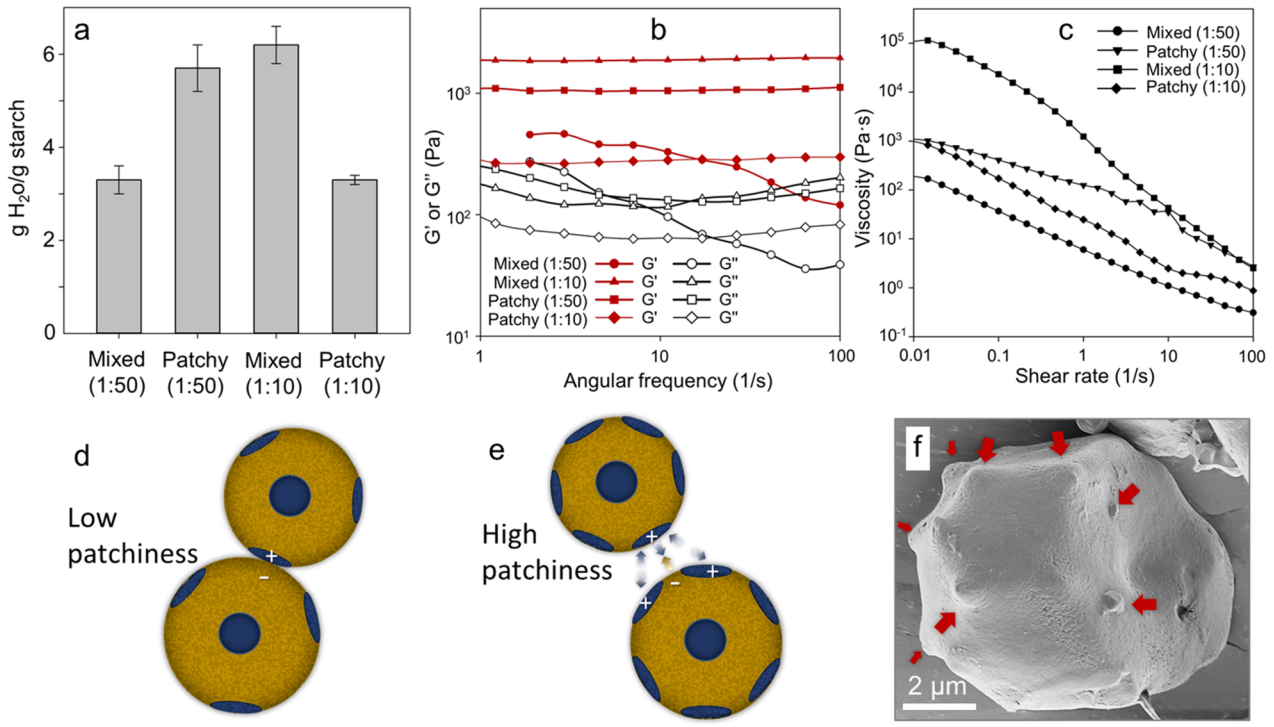

Figure 2. (a) Water-holding capacity, (b) rheological moduli, and (c) viscosity of starch slurries with different starch ratios (amaranth:corn = 1:10 or 1:50); schematic diagrams illustrating the (d) attraction of fused particles with low patchiness (2%) or (e) the repulsion of the of fused particles with high patchiness (10%) (e). (f) SEM images of fused patchy starch with 10% patchiness.

(NY, USA). Chloroacetic acid, epoxypropyltrimethylammonium chloride (ETMAC), sodium chloride, sodium hydroxide, and calcium chloride were ordered from Sigma-Aldrich (St. Louis, MO).

Isolation of Amaranth Starch. Amaranth starch was extracted from amaranth flour by using a method our group developed previously.[16,23] Briefly, the starch was liberated from proteins and insoluble fibers by using an alkaline solution and freeze-dried for further use.

Preparation of Partially Gelatinized Starch. By use of alcohol as the antisolvent of starch, both corn starch and amaranth starch were partially gelatinized in aqueous ethanol according to the previously published method.[1,16]

Preparation of Anionic Corn Starch. The partially gelatinized corn starch was modified to carry a negative charge based on the reported procedure for carboxymethylation by chloroacetic acid.[16,21]

Preparation of Cationic Amaranth Starch. The partially gelatinized amaranth starch was positively charged by using a modification method previously reported.[16,22] The modification used ETMAC to partially substitute the hydroxyl groups on starch molecules with trimethylammonium groups. The reaction was conducted for 3 or 24 h, depending on desired outcome, to obtain amaranth starch with different charge density.

Preparation of Patchy Starch via Particle Fusion. The partially gelatinized amaranth starch and corn starch were hydrated with excess water (starch:water = 1:5) and were mixed together (with the weight ratio of amaranth starch:corn starch = 1:10 or 1:50) to control patchiness. The mixture was incubated at 40 °C for 20 min and then centrifuged 12000*g* for 15 min. When the granules are swollen with water, they are less stiff, and the conformational freedom of polymer chains increased due to less hydrogen bonding.[16,24] The soft hydrated granules penetrate the neighboring particles when compacted via centrifugation, and the polymer chains tangle together (Figure 1). After centrifuging, the supernatant was removed, and the starch was dehydrated at 25 °C for 4 days and then stored in the refrigerator at 4 °C.

ζ-Potential. The ζ-potential of starches was measured with a NanoZS90 ζ-sizer (Malvern Instruments Ltd., UK) with a He/Ne laser (λ = 633 nm) at 25 °C. Starch was homogenized in water (0.1%); the ζ-potential was calculated from electrophoretic mobility based on the Smouluchowski model and was reported as an average value from triplicates.

Scanning Electron Microscopy (SEM). All samples were coated with Au−Pd by using a sputter coater (Denton Desk V, NJ, USA). The coated samples were examined with an SEM (Zeiss Gemini 500, Jena, Germany). Objects were scanned with 1 keV and imaged by a high-efficiency secondary electron detector with a 20.0 μm aperture.

Water-Holding Capacity. A 10 wt % slurry was prepared by mixing dry starch in DI water or the solutions with different pH levels and ionic strength. The slurries were vortexed for 1 min. The self-assembly sedimentation was allowed to occur overnight, after which the volume of the slurry was recorded.[1] The difference between the supernatant volume and the original volume of water (5 mL) added provided the amount of water retained by the slurry. Experiments were performed in triplicate.

Quantification of Flocculation. A 2 wt % starch slurry of the patchy particles was used to visualize the self-assembly.[16] The slurry was vortexed and further homogenized at 5000 rpm for 1 min; 20 μL of each sample was pipetted onto a microscope slide and covered with a glass slip. Using a Leica model DMIL LED inverted phase contrast microscope at 100×, we took 10 images which contained >10000 particles in total. The particle size was further analyzed by ImageJ software (v1.51, National Institutes of Health, USA) based on pixel calculation. The mean size (μm^2) for each sample was recorded, and the relative degree of flocculation (DF) was calculated by using native starch as control: DF = mean size of sample/mean size of native starch.

Examination of the Assembling Process. A 1% slurry was prepared by mixing in patchy particles in DI water with a high-shear homogenizer at 5000 rpm for 1 min (T25 digital Ultra-Turrax, IKA Works, NC, USA). An aliquot of the homogenized slurry (20 μL) was transferred to a glass slide, and the image was observed with a Leica model DMIL LED inverted phase contrast microscope at 200×. Immediately, 2000 photos were collected at a 40 Hz frame rate and a

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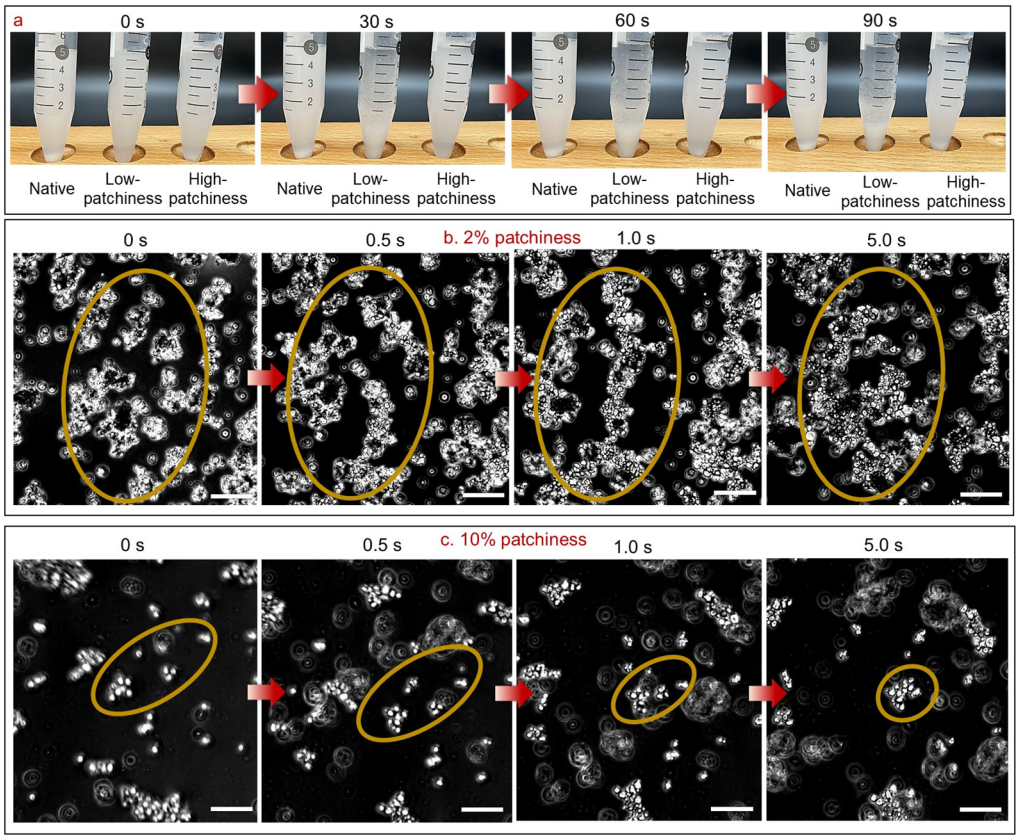

Figure 3. (a) Sedimentation of nonpatchy native corn starch and patchy starch with different patchiness in 1 wt % slurries. (b) Assembling process of starch with 2% patchiness. (c) Assembling process of starch with 10% patchiness. The scale bars are 100 μm.

200 MHz pixel readout rate with low noise by using a camera control-system to capture the assembling process (Andor Solis, UK).[16]

Rheological Measurements. To measure viscoelasticity of slurries, a dynamic oscillation test was conducted on slurries containing 25 wt % starch.[16] The amplitude sweep was performed at 1 Hz from 0.1 to 100% strain to identify the linear viscoelastic region (LVR). The 0.3% strain was employed, and the frequency sweep was performed from 0.5 to 100 Hz. A 25 mm parallel plate was used with the gap set at 0.5 mm. The storage modulus (G') and loss modulus (G'') were measured (Anton Paar MCR301). The rotational study was also performed from 0.01 to 100 1/s shear rate, and the viscosity was plotted against the shear rate.

Statistical Analysis. Analyses were performed in triplicate, and the results were presented as means ± standard deviations, which were tested by one-way analysis of variance (ANOVA) followed by Tukey's multiple comparison using JMP Pro (version 14, SAS Institute, USA) to identify significant difference ($p < 0.05$).

3. RESULTS AND DISCUSSION

The effects of the number of patches (patchiness) and the number of charges (charge density) were investigated. To study the effect of patchiness (Section 3.1), we used starch with the same ζ-potential and varied the ratio between amaranth starch and corn starch (1:50 or 1:10) when we prepared the patchy starch particles. Slurries of mixed charged starch that were not physically fused were used to elucidate the impact of physically fusing the starches versus the simple association of oppositely charged starches. To study the effect of charge density (Section 3.2), we used the same ratio of starch (amaranth:corn = 1:10) and used starches with different ζ-potentials (9.9 or 19.4 mV) to prepare mixed charged starch or patchy starch.

3.1. Effect of Patchy Area or Mixed Ratio. The ratio between amaranth starch to corn starch was tested at 1:50 in our previous work and showed a 1000 times higher viscosity compared to the control.[16] With the amaranth and corn starch approximated as 1 and 10 μm spheres, the number ratio between the small and large spheres is predicted to be 20:1. However, as amaranth starch shows strong aggregation with itself due to a hydrophobic protein on the surface, the number ratio was lower than we expected according to our SEM images. Therefore, we increased the weight ratio to 1:10 to investigate how the functionality change responds upon higher patchiness.

The water-holding capacity, storage modulus, loss modulus, and viscosity of mixed charged starch (mixed group) versus physically fused starch (patchy group) with different numbers of patches are presented in Figure 2. We used the same ratio of amaranth to corn starch for both types of samples, either 1:50 or 1:10, amaranth to corn starch.

When less amaranth starch was used (ratio = 1:50), the water-holding capacity of the slurry of the patchy group was superior to the mixed group. We attributed this to the greater freedom of motion that the unfused amaranth starch has in the slurry, and therefore the mixed slurry was less effective in trapping the water molecules. However, when the ratio increased to 1:10, the water-holding capacity of the patchy group decreased from 5.7 to 3.1 g, and the water-holding capacity for the mixed slurry group was superior to the patchy group (Figure 2a).

The viscoelasticity obtained from the oscillation test showed that the storage modulus was higher than the loss modulus for all groups, which means that the slurry exhibited solidlike

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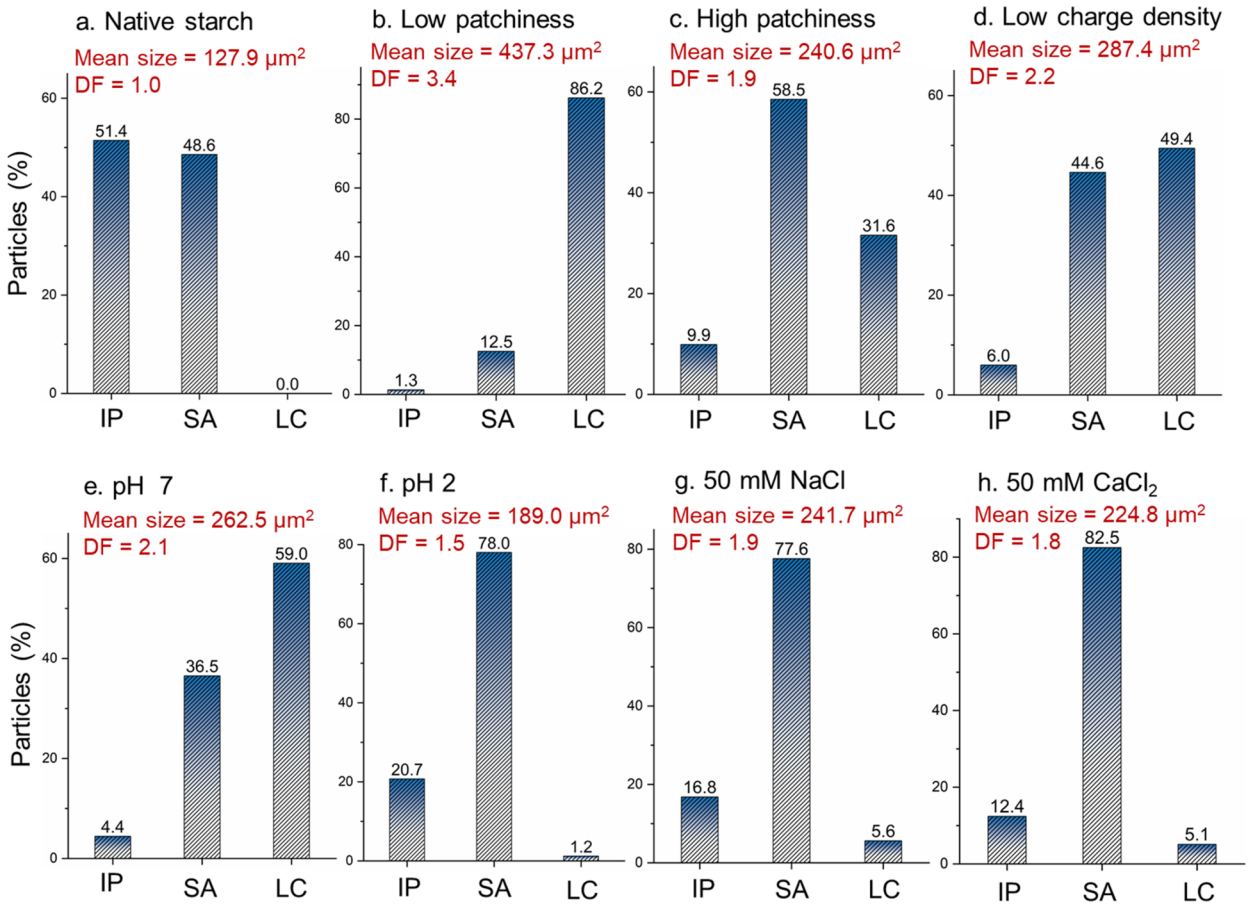

Figure 4. (a) Distribution of particles (%) in individual particles (IP), small aggregates (SA), and large clumps (LC): native starch, (b) patchy starch with 2% patchiness, (c) patchy starch with 10% patchiness, (d) patchy starch with 10% patchiness and low charge density (9.9 mV). The effect of environmental factors was tested by mixed charged starch at (e) pH 7, (f) pH 2, (g) 50 mM NaCl, (f) and (h) 50 mM $CaCl_2$.

properties (Figure 2b). When less amaranth starch was used (ratio = 1:50 or 2% patchiness), the patchy group exhibited higher moduli than the mixed group. When the percentage of patches on the patchy particles increased to 10%, however, both G' and G'' decreased sharply. The same trend was also observed in viscosity (Figure 2c). The viscoelasticity of the patchy group was negatively impacted when the percentage of patches increased. With a higher degree of patchiness, the surface becomes densely populated with more positively charged patches. As a result, with fewer regions of negative charge to attract neighboring particles, and therefore more repulsion between particles exists, we lose the self-assembly functionality (Figure 2d,e). We observed that the patchy group with low patchiness (2%) showed rapid assembly after the slurry was homogenized and were able to form sediments within 1 min. By contrast, sedimentation was noticeably slower when patchiness increased to 10% (Figure 3a). According to Stokes' law, the velocity of sedimentation, $v = gd^2\Delta\rho/18\eta$, is governed by the size of aggregates (d) given the same gravitational acceleration (g), density contrast ($\Delta\rho$), and viscosity of continuous phase (η). The time-lapse images demonstrate that patchy starch favors clumping together extensively when the degree of patchiness is low and forms smaller aggregates when the degree of patchiness is higher (Figure 3b,c). This was confirmed by examining the processed images of the patchy starch suspensions which showed that the degree of flocculation decreased from 3.4 to 1.9 when the patchiness increased from 2% to 10% (Figure S2b,c). For the low-patchiness group, 86.2% of the particles clumped extensively and only 12.5% particles were in small aggregates, but when the patchiness increased to 10%, only 31.6% of the particles were found in large clumps. The remaining particles were mostly dissociated as small aggregates (58.5%) (Figure 4b,c).

The SEM shown in Figure 2f illustrates the density of the fused patches when a 1:10 amaranth to corn starch ratio is used; the patches appear as raised bumps on the surface. As the number of patches on the surface of a starch granule increases, the surface overall takes on a more positive charge; this results in greater repulsions. That is, as the number of negatively charged regions on the surface decreases, the possibility of a cationic patch encountering another cationic patch increases; thus, self-assembly is inhibited. By contrast, in the mixed groups, because the particles were free to glide instead of being locked on the surface, they could still thermodynamically associate via electrostatic interactions.

Although the patchy starch with high patchiness did not interact significantly, we found that blending them with nonpatchy anionic starch revealed the functionality. Comparing the water-holding capacity of blends of nonpatchy anionic starch and the highly patchy starch (10%), we found that the blends exhibit higher water-holding capacity, and the optimum ratio for highest water-holding capacity was found to be 1:1 (Figure S1a). This trend was also observed in the rheological results (Figure S1b). We attributed this phenomenon to the fact that although the highly patched starch's dense positive

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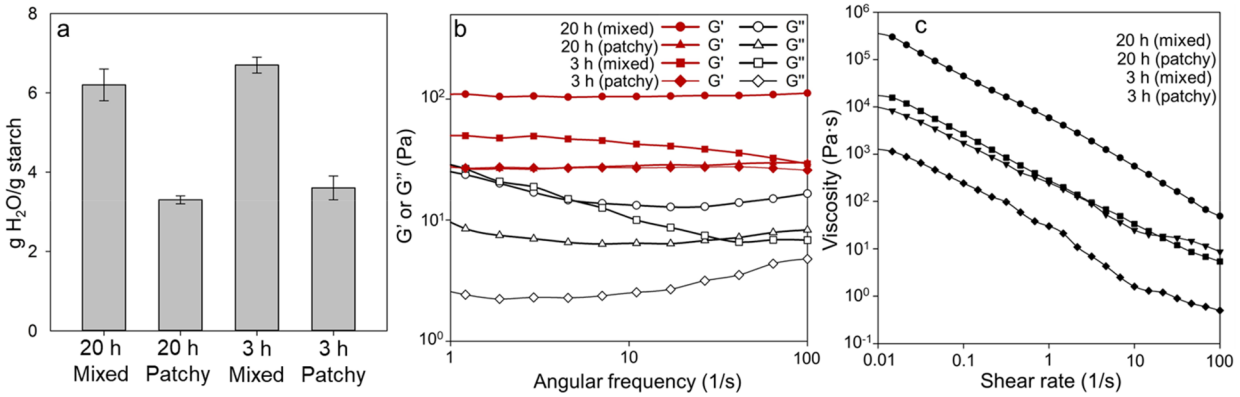

Figure 5. (a) Water-holding capacity, (b) rheological moduli, (c) and viscosity of charged patchy starch or charged mixed starch prepared from cationic starch treated for different durations (3 and 20 h) producing starch with high (9.9 mV) and low (19.6 mV) ζ-potentials.

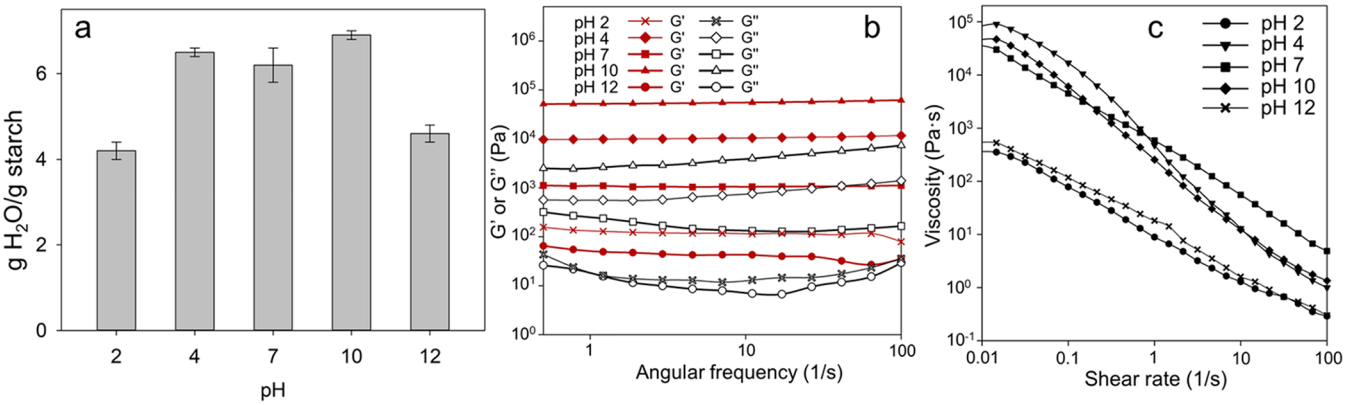

Figure 6. Water-holding capacity (a), rheological moduli (b), and viscosity (c) of mixture of charged starch at different pHs.

patches inhibited assembly between themselves, blending with anionic nonpatchy starch introduced more reactive sites and thus changed the functionality of the slurry (Figure S1c).

3.2. Effect of Charge Density. To produce different charge densities, the cationic treatment was reduced from 20 to 3 h, and the resultant amaranth starch showed lower ζ-potential (Table S1). With the same amaranth starch to corn starch ratio (1:10), patchy starch and mixed starch with different charge density on individual patches were prepared. The charge density did not affect water-holding capacity for either the mixed group or the patchy group (Figure 5a). The reason for this could be because the water-holding capacity was measured in the steady state, so the degree of flocculation was close to the same when the number of interactive sites was identical (Figure 4c,d). However, the rheological measurements indicated that groups with stronger charge showed higher viscosity as well as higher rheological moduli (Figure 5b,c). The disparity could be attributed to the stronger electrostatic attraction inhibiting the separation of particles during shearing or oscillation, which trapped water better, causing the slurry to be more viscous.

These results were in contrast to previous reports where the viscoelasticity of particle suspension was reduced by higher charge density of cellulose nanocrystals.[25,26] When particles carry the same charge, the higher charge results in a stronger interparticle repulsion and a shorter effective diameter; therefore, they exhibit lower viscosity. Conversely, when particles, like our patchy particles, carry opposite charges, the higher charge density of opposite charges would strengthen particle association.

3.3. Effect of pH Level. Because the mixed charged starch group (amaranth starch:corn starch = 1:10) showed the most improved viscosity, we chose this group as a simple model to study the effect of environmental factors. The water-holding capacity, rheological moduli, and viscosity of mixed charged starch at different pH levels ranging from 2 to 12 were investigated.

The water-holding capacity of the slurry did not change significantly from pH 4 to pH 10 (Figure 6a). However, when the pH was reduced to 2 or increased to 12, the ability of the slurry to store water was inhibited significantly. The reduced water-holding capacity, as expected, affected the viscoelastic properties; if water cannot be trapped in the matrix, then there is less resistance to flow exhibited by the sample (Figure 6b,c). This could be attributed to the fact that at the extremes of the pH range the charges on the starches could be neutralized. Under highly basic conditions, the cationic starch is neutralized, and at extremely acidic conditions, the anionic starch can be protonated (Table S1). The microscopic images showed that the flocculation was inhibited at pH 2. At neutral pH 59.0% of the starch particles formed large clumps (Figure 4e), whereas at pH 2 this percentage dropped to 1.2% (Figures 4f). Similar findings were reported on cellulose nanofibril suspensions, which showed that the gel was not stable at acidic pH levels as the carboxyl groups were neutralized by protons and water was eluted from the entangled matrix.[27]

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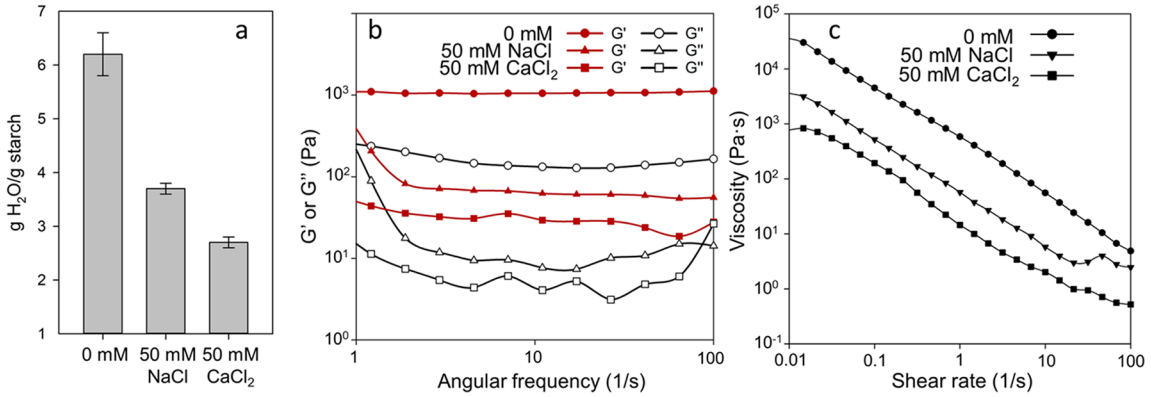

Figure 7. (a) Effect of 50 mM NaCl and $CaCl_2$ on water-holding capacity, (b) rheological moduli, and (c) viscosity of mixed charged starch.

The results suggest the electrostatic interaction is stable in most foods (pH > 4.5) but could be a challenge for applications in acidic foods such as fruit juices (pH 2−3). To mitigate this sensitivity, increasing charge density can be used to cancel out the effect of additional protons and change functionality.[26] Another way could be to switch to a different charged functional group (e.g., sulfonate group) with lower pK_a and to leave the food pH levels in the safe zone. The results also demonstrated that the system is stable at weak alkaline conditions. Although basic pH levels are not common in foods, the application of charged starch could be extended to other fields such as paints.

3.4. Effect of Salts. Foods are complex systems; therefore, the effects of salts on water-holding capacity, rheological moduli, and viscosity of charged starches were studied. In DI water, the mixed charged starch was able to hold more than 6 g of water per unit starch (Figure 7a). However, when the salt concentration was increased by 50 mM, flocculation was inhibited drastically. From the processed images of particle association, the groups with salts showed less than 10% starch particles in large clumps (Figure 4g,h), and the dissociated particles were not effective for storing water. This phenomenon could be attributed to counterions blocking the starch particle charges and thus inhibiting flocculation. A similar trend was also observed where the viscoelasticity was reduced in the presence of salts, weakening the texture and trapping less water (Figure 7b,c). This suggested that in food products salt content poses a challenge to the practical application of this technology.

The regression model summarizing the water-holding capacity and the degree of flocculation suggests that the water-holding capacity of slurries is positively related to the degree of flocculation (Figure 8). When water-holding capacity is measured, the starch granules tend to sediment due to gravity. Interactions between adjacent particles, however, can inhibit gravitational sedimentation as the charged-induced attraction can support the starch and thus balance the gravity which alters the packing behavior. This means that the particles cannot be packed densely and therefore produce voids in which to store water. Trapping water in such a matrix can inhibit the movement of water molecules, and therefore the viscosity of the slurries is higher. The viscosity is positively related to water-holding capacity because the assembled particles act as obstacles to slow down movement of water molecules. The correlation between water-holding capacity and viscosity is not always positive. For instance, with the same patchiness, the water-holding capacity is the same because the

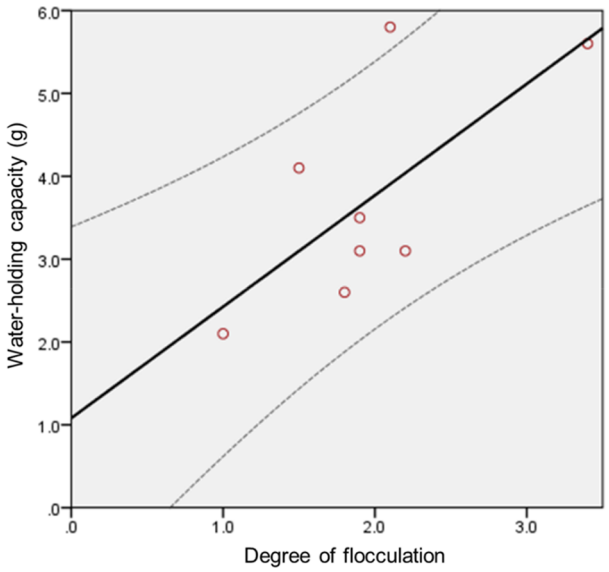

Figure 8. Regression model of the effect of particle flocculation on water-holding capacity. The dashed lines indicate the 85% confidence intervals.

number of reactive sites is identical, but the viscosity is enhanced by the charge density carried on the individual patch and can have more or less attraction. Therefore, although similar patchiness results in similar water-holding capacity, the particles with the stronger charge are more resistant to dissociation and therefore exhibit higher viscoelasticity. In other words, viscosity is more dependent on charge than on patchiness, while water-holding capacity is more dependent upon total patchiness.

3.5. Effect of Starch Content. To assess the impact of starch content on viscosity, slurries of mixed native starches (10%) at different total starch contents (5−35%) were made. The viscosity of the slurries do not change significantly with an increase in shear rate (Figure 9a), which suggests that the systems were predominantly composed of Newtonian fluids. The slurry viscosity of the mixed charged starch (10%) showed shear-thinning behavior (Figure 9b); that is, the slurry was less viscous when the electrostatic interaction between particles was dissociated by shearing. The viscosity of the mixed charged starch (Figure 9b) was significantly higher than that of native starch (Figure 9a). The viscosity at a specific shear rate (10 s^{-1}) was selected, and the viscosity was replotted against starch content (Figure 9c). A sharp increase was observed when the

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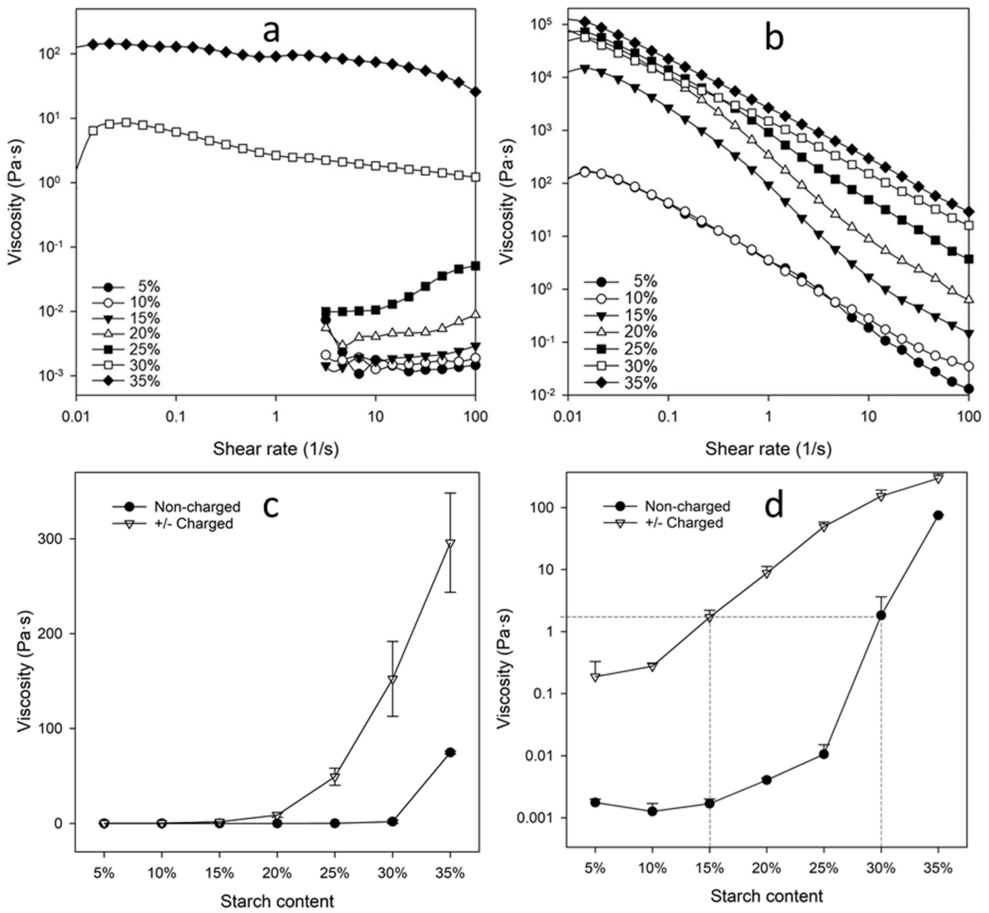

Figure 9. (a) Effect of starch content of slurry (5%−35%) at different shear rates on viscosity of native starch and (b) the mixture of charged starch. (c) Viscosity of slurry with different starch contents at the shear rate of 10^{-1} is plotted in a linear scale and (d) log scale. The mixed ratio between amaranth starch and corn starch was 1:10.

starch content of native starch was higher than 30%, but using the charged particles, we were able to reduce the critical content to 20%. The log-scale plot in Figure 9d discriminates between the two groups at low starch content and suggested that even with 5% starch, the charged group provided a 2 orders of magnitude higher viscosity compared with the native group. This suggests that the thickening ability provided by the interaction between particles in the mixed charge starch could be leveraged to reduce the amount of carbohydrates used in foods. For example, to achieve a similar viscosity of 1.7 Pa·s, only 15% mixed charged starch was needed, which was half of the starch content of the native group (Figure 9d). This drop in the amount of mixed charged starch needed for the same thickening ability demonstrates that electrostatic assembly can be used as a promising approach to retain food texture while reducing carbohydrate content.

As many food products require thermal processing or to be served hot, future work needs to investigate the effect of temperature on the assembly and functionality to evaluate the potential of such patchy particles to be practically used. The electrostatic force between two charged particles is described as Debye−Hückel approximation,[28] $F = Q_1Q_2(1 + \kappa R)e^{-\kappa R}/4\pi\varepsilon_0 k_m R^2$. As the dielectric constant (k_m) decreases at higher temperature, the electrostatic force is expected to be strengthened.[29] However, a higher temperature brings higher kinetic energy meaning water molecules move faster; thus, the viscosity of the aqueous phase is expected to be lower. These two effects may cancel each other and alter the overall behavior. In addition, the nature of starch makes this question more complicated. With higher temperature, individual starch particles swell to a larger size and thus provide a higher volume fraction, and consequently the viscosity increases. When the starch is completely gelatinized, the starch polymers could untangle and the patchy particles may irreversibly dissociate, which is a challenge for food applications as many food products involve thermal processing such as soups. Future work may cross-link the fused starch to stitch particles covalently and improve the thermal stability.

4. CONCLUSIONS

The present work used colloidal fusion and prepared starch-based patchy particles with anionic corn starch as core and cationic amaranth starch as patches on the surface. Such a heterogeneous design on the surface was able to be associated and could be used as a solution thickener. The slurry was characterized by using water-holding capacity and rheological properties, and our results showed that the texture could be fine-tuned by manipulating microstructures such as patchiness and charge density. The patchiness was controlled by changing the ratio between the two starches, and the results showed that high patchiness resulted in a lower water-holding capacity. Additionally, with the same patchiness, a higher charge density did not contribute to a higher water-holding capacity, but the rheological properties were appreciably different. We believe

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this is due to the stronger attraction between particles that helped the slurry resist shearing. Understanding the impact of environmental influences that would be present in food applications is key to using this technology in food applications. We found that extreme pH, either acidic or basic, and ionic strength were found to reduce the interaction by neutralizing charge, thus impairing slurry properties. Future work exploring hydrophobic interactions by attaching hydrophobic patches on hydrophilic starch surfaces might overcome the challenges of counterions in the food matrix.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.2c09091.

> ζ-potentials of native and modified starches; the water-holding capacity and rheological moduli of the blended starch of nonpatchy anionic:patchy starch; suspension of corn starch and patchy starch; time-lapsed images of the assembly process (PDF)

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Notes

The authors declare no competing financial interest.

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