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1 Sodium Alginate-Grafted Submicrometer Particles
2 Display Enhanced Reversible
3 Aggregation/Disaggregation Properties

4 *Faezeh Sabri, Kevin Berthomier, Antoine Marion, Louis Fradette, Jason R. Tavares*
5 *and Nick Virgilio**

6 ^a Center for Applied Research on Polymers and Composites (CREPEC), Department of
7 Chemical Engineering, Polytechnique Montréal, Montréal, Québec, H3C 3A7, Canada

8
9 * Corresponding author:

10 Phone: 1-514-340-4711 #4524

11 Fax: 1-514-340-4159

12 Email address: nick.virgilio@polymtl.ca

13 Postal address: Department of Chemical Engineering, Polytechnique Montréal, C.P. 6079

14 Succursale Centre-Ville, Montréal, Québec, H3C 3A7

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18 **ABSTRACT.** In this article, we demonstrate that submicrometer particles with surface-grafted
19 sodium alginate (SA) display enhanced and reversible aggregation/disaggregation properties in
20 aqueous solution. 300 nm silica particles were first functionalized with an aminosilane coupling
21 agent, followed by the grafting of pH-sensitive SA, as confirmed by zeta potential, XPS and FTIR
22 analyses. The SA-modified particles show enhanced aggregation properties at acidic pH compared
23 to unmodified silica, with a 10 times increase in average aggregate diameter. The process is
24 reversible, as the aggregates can be broken and dispersed again when the pH is increased back to
25 7.0. As a result, the sedimentation rate of SA-modified particles at pH 3.0 is both significantly
26 faster and complete compared to the unmodified particles. This enhanced aggregation is most
27 likely due to the formation of intermolecular hydrogen bonds between neighboring SA-modified
28 particles. This work illustrates how surface-grafted macromolecules of natural origins can be used
29 to tune interparticle interactions, in order to improve separation processes.

30 **KEYWORDS:** submicrometer particle, surface modification, sodium alginate, pH sensitive,
31 aggregation.

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34 **1. Introduction**

35 The controlled aggregation and dispersion of colloids is a key step in separation processes
36 involving complex fluids comprised of immiscible liquids and/or micro/nanoparticles (*e.g.*
37 Pickering emulsions), in fields such as petrochemistry (Doshi, Repo, Heiskanen, Sirvio, &
38 Sillanpaa, 2017; Hosseini et al., 2016; Mohammadi, Rashidi, Mousavi-Dehghani, & Ghazanfari,
39 2016) and waste water treatment (Bakhteeva et al., 2016; Chai et al., 2015; Leudjo Taka, Pillay,
40 & Yangkou Mbianda, 2017). When particle separation is required, it is often desirable to form
41 aggregates and flocs as large as possible, in order to ease the separation process and decrease costs.
42 Furthermore, if those particles were originally added to the process, for example as supports for
43 much smaller catalytic nanoparticles (Ballauff & Lu, 2007), reversible aggregation/disaggregation
44 behavior would be a desirable feature for recycling purpose.

45 The Derjaguin–Landau–Verwey–Overbeek (DLVO) theory is a classical framework to
46 understand and analyze the stability of colloidal suspensions (Chin, Yiacoumi, & Tsouris, 2001;
47 Ohki & Ohshima, 1999). It models particle-particle interactions as a combination of repulsive
48 double-layer overlap forces and attractive dispersion (van der Waals) forces (Verwey, 1947). In
49 the energy landscape, the contribution of the electrostatic repulsion superimposes to the Van der
50 Waals attraction and generates an energy barrier that can reduce or inhibit particle aggregation in
51 a suspension (Rodgers, Velicky, & Dryfe, 2015). Other forces that can also enhance or inhibit
52 aggregation include the hydrophobic effect, hydrogen bonding, steric interactions, and depletion
53 forces (Durand-Gasselin, Sanson, & Lequeux, 2011). As a result, the typical ways to control the
54 aggregation level of micro/nanoparticles in a suspension are via pH and/or ionic strength (salt
55 addition) adjustments (Yan et al., 2013), which control the electrical double layer properties.
56 Grafting water-soluble polymer/polyelectrolyte chains on particle surface, which promote

57 stabilization via steric interactions (Hemraz, Lu, Sunasee, & Boluk, 2014), and/or adding
58 polyelectrolytes (Borkovec & Papastavrou, 2008) or water-soluble macromolecules (Bakumov &
59 Kroke, 2008) are two other approaches.

60 Recently, nanoparticles responding reversibly to external stimuli, such as changes in pH (Chen et
61 al., 2017; Jia et al., 2016; Stular, Jerman, Naglic, Simoncic, & Tomsic, 2017; Xu et al., 2015) or
62 temperature (Abreu et al., 2016; Qiao, Niu, Wang, & Cao, 2010), have generated an interest for
63 chemical engineering processes, drug delivery and biomedical applications. For example, thermo-
64 and pH-sensitive particles have been employed to stabilize (Kawaguchi, 2007; Morelli, Holdich,
65 & Dragosavac, 2016) and destabilize Pickering emulsions (Binks, Murakami, Armes, & Fujii,
66 2005) – allowing separation of the liquid constituents. They were also used as carriers for \approx 1-10
67 nm catalytic nanoparticles, easing their separation and recovery process (Ballauff & Lu, 2007).
68 However, separating particles from a liquid phase remains an energy intensive process. As a result,
69 the formation of flocs or aggregates facilitates separation and, if reversible, allows re-dispersion
70 for multiple reuse.

71 We hypothesize that grafting sodium alginate (SA) polymer chains onto the surface of
72 submicrometer particles can increase interparticle interactions and enhance their aggregation
73 properties reversibly, since SA undergoes reversible gelling at low pH due to the protonation of
74 its carboxylate groups and the formation of intermolecular hydrogen bonding. The main objective
75 of this work is to design, synthesize and evaluate the stabilization and aggregation properties of
76 model submicrometer silica particles modified with SA, and to compare the results to unmodified
77 particles in order to confirm if the aggregation/disaggregation process is enhanced.

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80 2. Experimental Section

81 2.1 Materials

82 Sub- μm silica particles (SP) were supplied by Nippon Shokubai Trading Co., Ltd (average
83 diameter $d = 290 \pm 13.2$ nm by SEM, see Supporting Information **Figure S1**; specific surface area
84 $S = 42 \pm 2$ $\text{m}^2\cdot\text{g}^{-1}$, measured by BET with an ASAP 2020 instrument from Micromeritics Instrument
85 Corporation). Sodium alginate (SA) from brown algae was supplied by Sigma-Aldrich (CAS.
86 9005-38-3, low viscosity, molecular weight ≈ 60 kDa, $\text{pK}_a = 3.5$) (Harnsilawat, Pongsawatmanit,
87 & McClements, 2006). The M/G ratio ($= 1.83$) was measured at 80 $^\circ\text{C}$ with a 10 $\text{mg}\cdot\text{ml}^{-1}$ solution
88 in D_2O for the ^1H NMR using a Bruker Avance 500 instrument (11.7 T) at a frequency of 500
89 MHz (Rahelivao, Andriamanantoanina, Heyraud & Rinaudo, 2013). 128 scans using 32 000 data
90 points were acquired with a relaxation time (D1) of 5 s, a 4 kHz spectral window and a 30°
91 impulsion. (3-Aminopropyl) trimethoxysilane (APTMS, 97%), *N*-(3-Dimethylaminopropyl)-*N'*-
92 ethylcarbodiimide hydrochloride (EDC, $> 98\%$), *N*-Hydroxysuccinimide (NHS, 98%) and urea ($>$
93 98%) were all purchased from Sigma-Aldrich and used without further purification. Ethanol
94 (99.8%) was obtained from Thermo Fisher Scientific. HCl 1N and NaOH 12N solutions were of
95 analytical grade and prepared without further purification with Milli-Q water (DI water, 18.2 Ω ,
96 Synergy 185 system by Fisher Scientific).

97 2.2 Particle Surface Modification

98 2.2.1 Silane Coating Grafting

99 In order to graft SA on silica sub- μm particles, a silane coupling agent was first covalently grafted
100 on its surface. In a typical batch, 10 g of SP particles were added in a hydrophobized Erlenmeyer
101 flask containing 100 ml of a 95% v/v ethanol solution and DI water, while stirring at 600 - 700 rpm
102 with a magnetic stirrer (Arkles, 2006). The pH was then adjusted to 4.5 - 5.5 using HCl 1N.

103 APTMS was then added dropwise while stirring at room temperature, following three targeted
104 surface concentrations: 0.01 (SP-A), 0.1 (SP-B) and 1 (SP-C) APTMS molecule·nm⁻² (based on
105 particle specific surface) (Pickering, Khimi, & Ilanko, 2015). For example, to treat 10 g of particles
106 with a desired surface APTMS density of 1 molecule·nm⁻² (SP-C), 0.131 ml of APTMS was added
107 to the reaction medium. The reaction was then carried for 12 h. The particles were collected by
108 centrifugation (Sorvall RC 6+, Thermo Fisher Scientific) at 8000 rpm for 15 min, and cleaned by
109 washing twice with ethanol in order to rinse off any remaining unreacted silane. The particles were
110 finally dried in a vacuum oven at 70 °C for 2 hrs.

111 2.2.2 Sodium Alginate Grafting

112 A fraction of the APTMS modified SPs were further modified by grafting SA using two different
113 solution concentrations (**Table 1**): 0.1% (1) and 1% (2) w/v. As an example, following this
114 terminology, SP-C-2 particles were modified with a silane coating targeting an APTMS surface
115 density of 1 APTMS molecule·nm⁻², followed by grafting of SA with a 1% w/v solution. In a
116 typical experiment for the preparation of SP-((B-2) or (C-2)) particles, 0.2 g of SA was first
117 dissolved in 20 ml of DI water (1% w/v). 0.29 g of EDC and 0.17 g of NHS (EDC/NHS molar
118 ratio = 1) were then added to the solution (EDC/-COOH molar ratio = 0.5, relative to the -COOH
119 groups of alginate) (Giani, Fedi, & Barbucci, 2012). Then, 2 g of APTMS modified SPs were
120 added to the mixture and the pH was adjusted to 4.5 with HCl 1N. The reaction proceeded for 15
121 hrs at room temperature and the mixture was subsequently centrifuged at 8000 rpm to collect the
122 modified particles, which were washed with DI water 3 times. Finally, the particles were dried in
123 a vacuum oven at 70 °C for 10 hrs. The synthesis conditions of the surface-modified SPs are
124 summarized in **Table 1**.

125 **Table 1.** Synthesis conditions of surface modified particles with APTMS and SA

Particle ID	Targeted APTMS density (molecule·nm ⁻²)	APTMS (ml) ^a	EDC ^b (g)	NHS ^b (g)	SA solution concentration/volume ^b ((%w/v)/ml)
SP-A	0.01	1.31×10 ⁻³	-	-	-
SP-B	0.1	1.31 ×10 ⁻²	-	-	-
SP-C	1	1.31×10 ⁻¹	-	-	-
SP-A-1	0.01	1.31×10 ⁻³	0.29×10 ⁻²	0.17×10 ⁻²	0.1/20
SP-B-2	0.1	1.31×10 ⁻²	0.29×10 ⁻¹	0.17×10 ⁻¹	0.1/20
SP-C-2	1	1.31×10 ⁻¹	0.29	0.17	1/20

126 ^aFor the modification of 10 g of silica particles (SP) with (3-Aminopropyl)trimethoxysilane
127 (APTMS); ^bFor 2 g of APTMS-grafted SP with *N*-(3-Dimethylaminopropyl)-*N'*-
128 ethylcarbodiimide hydrochloride (EDC) and *N*-Hydroxysuccinimide (NHS).

129 2.3 Particle Surface Characterization

130 2.3.1 Zeta Potential Measurements

131 Particle zeta potential (ζ) was measured with a Zetasizer Nano ZSP instrument (Malvern
132 Instruments Ltd., Worcestershire, UK). Samples were dispersed in DI water at pH 7.0 (adjusted
133 by adding NaOH 12N), and the measurements were performed at 25 °C. ζ after modification with
134 APTMS and SA, at different pHs (3.0, 7.0 and 10.0), were measured on at least three different
135 samples by microelectrophoresis at a particle concentration of 0.001 g·ml⁻¹. Disposable zeta
136 potential folded capillary cells (DTS1070) were used and all samples tested were freshly prepared.
137 The instrument determined the electrophoretic mobility, and the Smoluchowski model was then
138 applied by the software for the calculation of ζ (Lattuada & Hatton, 2007).

139 2.3.2 High-resolution X-ray Photoelectron Spectroscopy (XPS) Analysis

140 Elemental analyses of unmodified and modified silica particles with APTMS were realized with a
141 VG ESCALAB 3 MKII X-ray photoelectron spectroscope (XPS) equipped with a non-
142 monochromatic Mg K α radiation source operated at 300 W (15 kV, 20 mA). XPS analyses were
143 conducted to detect electrons with a takeoff angle normal to the surface of the sample, yielding a
144 probed depth around 10 nm. The pass energy was 100 eV for survey scans and 20 eV for high-
145 resolution scans, at 1.00 and 0.05 eV increments, respectively. The pressure during analysis was
146 kept under 5×10^{-9} Torr (6.67×10^{-11} Pa). Particles were stored under vacuum overnight prior to
147 analysis. The results were analyzed using the Avantage XPS software package. The elemental
148 distribution of the samples was determined on the basis of peak area comparison (C1s, O1s, etc.),
149 normalized to their corresponding sensitivity factors, after the removal of the scattered electron
150 background. In the case of higher resolution spectra, binding energies were referenced to the C1s
151 peak at 285.0 eV to adjust for possible charging effects, and the Shirley method was applied for
152 background noise subtraction. According to the data trend for each distribution of binding energy,
153 the baseline was manually placed. Each curve is represented by its maximum binding energy (BE)
154 in the Supporting information (**Figure S2**). The species' elemental distributions are obtained via
155 Gaussian/Lorentzian curve fitting on the original curve. The number of sub-curves and their
156 corresponding species were obtained with full width at half maximum (fwhm) = 1.6, 1.8, 2.2, and
157 2.4 eV for C, O, Si, and N, respectively.

158 **2.3.3 Fourier Transform Infrared (FTIR) Spectroscopy Analysis**

159 A Perkin Elmer Spectrum 65 FTIR spectrometer operating in attenuated total reflectance mode
160 (Zn/Se crystal) in the range of 650-4000 cm^{-1} was used to characterize unmodified SiO₂ sub- μm
161 particles, as well as modified particles with APTMS and SA. For each sample, 32 scans were

162 recorded at a resolution of 4 cm^{-1} . The spectra of SP, SP-C and SP-C-2 are presented as Supporting
163 Information (**Figure S3**).

164 **2.4 Characterization of Aggregation and Disaggregation Properties**

165 **2.4.1 Visual Inspection of Sedimentation Kinetics**

166 0.2 g of each particle type was dispersed in 10 ml of DI water using an ultrasonic homogenizer
167 equipped with a microtip (Cole-Parmer, instrument model CP505, 500 watts) at an amplitude of
168 20 % for 1 min (approximately $60\text{ J}\cdot\text{ml}^{-1}$). The pH was then adjusted to 3.0 with HCl 1N when
169 required. Particle sedimentation was monitored by taking photographs (Nikon DX equipped with
170 an AF-S DX NIKKOR 18-55mm f/3.5-5.6G VRII objective) every 3 min after dispersion, for a
171 total duration of 60 min. For all particle types, three samples were tested.

172 **2.4.2 Optical Microscopy Observations**

173 Unmodified and surface modified particles were observed by dark field optical microscopy
174 (Olympus BX51 by Cytoviva, Objectives = 10x and 50x Plan Fluorite, and 60x UPL Fluorite Oil,
175 and 100x UPL Fluorite Oil camera Q imaging, Retigna 2000R fast 1394, cooled color 12 bit). For
176 each type of particle, 0.02 g of particles was dispersed in 2.0 ml of DI water at pH 7.0 using the
177 ultrasonic homogenizer at a 20% amplitude for 1 min ($\approx 300\text{ J}\cdot\text{ml}^{-1}$); the pH was subsequently
178 adjusted to 3.0 with HCl 1N when required. Solutions were subsequently diluted by adding 3
179 droplets into 5 ml of water at the corresponding pH while stirring with a magnetic stirrer for 30 s
180 at 600 rpm. Finally, three drops of freshly prepared samples were placed on microscope glass
181 slides and observed at different locations and magnifications. The images were analyzed using the
182 ImageJ software, to calculate the average size (Ferret diameter) of the observed aggregates
183 (between 200 and 4000 aggregates were analyzed for each condition).

184 **2.4.3 Measurement of Sedimentation Rate by UV-Vis Spectroscopy**

185 UV-Vis transmittance measurements as a function of time were performed to determine the
186 sedimentation rate of unmodified and surface modified particles, using a UV-Vis spectrometer
187 (Model DH-2000 from Ocean Optics, 10 ms integration time). For each particle type, one
188 concentration was analyzed ($0.01 \text{ g}\cdot\text{ml}^{-1}$) at 2 different pHs (3.0 and 7.0), by dispersing the required
189 amount of particles in 2 ml of DI water (pH 7.0) using an ultrasonic homogenizer, as described
190 previously; the pH was subsequently adjusted to 3.0 with HCl 1N when required. Then, 1 ml of
191 each sample was transferred into a disposable polystyrene cuvette with a 1 cm path length for
192 transmittance measurements at 656 nm every 3 min for a total duration of 60 min. The height of
193 the beam path was located at 1.3 cm from the bottom of the cuvette. For each particle type, the
194 transmittance measurements were repeated 3 times. The spectral measurements were normalized
195 with the DI water transmittance values at pH 3.0 and 7.0 respectively.

196 **2.4.4 Aggregation/Disaggregation Reversibility Evaluation**

197 Each sample was prepared by dispersing 0.01 g of particles (SP, SP-A or SP-A-1) in 1 ml of DI
198 water at pH 7.0. UV-Vis transmittance at 656 nm was then measured as a function of time for 60
199 min, using 1 ml disposable polystyrene cuvettes. Subsequently, the sample was transferred back
200 into a vial and the pH was adjusted to pH 3.0 with HCl 1N. The sample was again transferred into
201 a disposable cuvette for transmittance measurements at 656 nm for 60 min. Once the experiment
202 was completed, the sample was transferred back again into a vial and the pH was again brought
203 back to 7.0 with NaOH 12.0N. The particles were next re-dispersed by ultrasonication (20%
204 amplitude for 20 sec). This whole cycle process was repeated 4 times. The spectral measurements
205 were normalized with DI water transmittance values at pH 3.0 and 7.0 respectively.

206

207

208 2.4.5 Effect of urea on sodium alginate solubility as a function of pH

209 Two vials, each containing 10 ml of 0.05% (w/v) SA in DI water solution at pH 7.0, were
210 prepared. Then, urea was added into one of the vial ($1.0 \text{ mol}\cdot\text{l}^{-1}$), and the pH of both vials was
211 adjusted to 3.0 with HCl 1N. Pictures were taken before and after pH adjustment.

212 3. Results

213 3.1 Surface Modification Analyzed by Zeta Potential, XPS and FTIR

214 The particles zeta potential ζ was measured as a function of pH for bare silica particles (SP),
215 modified particles with APTMS (SP-A to C), and with SA (SP-(A-1), (B-2), and (C-2)) (Table 2).

216
217 **Table 2.** ζ of silica particles: untreated (SP), APTMS treated (SP-A to C), and APTMS+SA treated
218 particles (SP-(A-1), (B-2) and (C-2)), as a function of pH (3.0, 7.0 and 10.0).

Particle ID	ζ (mV)		
	pH = 3.0	pH = 7.0	pH = 10.0
SP	5.7 ± 0.8	-56.4 ± 1.4	-57.0 ± 1.4
SP-A	11.0 ± 1.2	-58.4 ± 1.1	-57.0 ± 1.3
SP-B	49.4 ± 4.7	24.7 ± 0.7	-24.2 ± 0.7
SP-C	52.1 ± 1.4	13.3 ± 0.3	8.4 ± 0.4
SP-A-1	6.5 ± 1.0	-50.9 ± 1.1	-49.4 ± 0.6
SP-B-2	3.4 ± 0.8	-45.6 ± 0.6	-45.1 ± 1.6
SP-C-2	-0.8 ± 0.3	-43.2 ± 1.0	-43.8 ± 1.4

219
220 SP particles display a slightly positive ζ at pH 3.0 that decreases to negative values at pHs 7.0 and
221 10.0. This behavior is expected due to the deprotonation of hydroxyl groups on the SP surface as
222 the pH increases (Knoblich & Gerber, 2001). SP particles modified with APTMS (SP-A SP-B,

223 SP-C) generally display higher positive values at pH 3.0. Increasing the initial concentration of
224 APTMS in solution results in an increasing positive ζ , from +11.0 mV to +52.1 mV. At pH 3.0,
225 SP-A particles present a similar behavior as compared to unmodified SP particles due to low
226 APTMS surface density. For SP-B and SP-C, ζ increases significantly (49.4 and 52.1 mV) due to
227 the expected higher APTMS surface density, confirming grafting of APTMS. Grafting of APTMS
228 was also confirmed by XPS, the spectra revealing two different components related to N-H bonds
229 (revealed from the N1s peak using high resolution XPS), and one component related to C-N bonds.
230 The component at a BE \cong 399.8 eV corresponds to $-\text{NH}_2$ and the component at BE \cong 401.5 eV
231 corresponds to $-\text{NH}_3^+$ groups (see Supporting Information, **Figure S2**). Grafting of APTMS was
232 independently confirmed by FTIR with the appearance of a band at 1450 cm^{-1} , associated with N-
233 H bond asymmetrical deformation vibration (**Figure S3**).

234 When the pH increases to 7.0 and 10.0, ζ of SP-A, SP-B and SP-C all shift towards lower positive
235 (almost neutral) or negative values. This is explained by (1) the significant deprotonation of surface
236 bound hydroxyl groups, yielding negatively charged $-\text{O}^-$ (Knoblich & Gerber, 2001), and (2) the
237 gradual deprotonation of APTMS $-\text{NH}_3^+$ groups.

238 At pH 3.0, SA modified particles (SP-A-1, SP-B-2 and SP-C-2) display nearly neutral ζ values
239 (slightly positive or negative). This behavior is due to the protonation of the SA carboxylic acid
240 groups ($\text{pK}_a = 3.5$) (Harnsilawat et al., 2006) – confirming grafting of SA with APTMS. At pH
241 7.0 and 10.0, SP-A-1, SP-B-2 and SP-C-2 particles display almost identical and nearly constant ζ
242 values. At pH 7.0, ζ drops to negative values ranging from -43.2 mV to -50.9 mV, while at pH
243 10.0 it reaches nearly -50 mV. This is expected since at pH 7.0 and 10.0, above the pK_a of SA, the
244 $-\text{COOH}$ groups on the surface are deprotonated and become negatively charged, like a number of
245 other polysaccharides (*e.g.* xanthan gum) (Wang, Natale, Virgilio, & Heuzey, 2016). Grafting of

246 SA was also confirmed by FTIR (see **Figure S3**). Observed bands at 1649 and 1460 cm^{-1} were
247 attributed to asymmetric and symmetric stretching vibrations of carboxylate $-\text{COO}-$. Finally, the
248 disappearance of the N-H band at 1450 cm^{-1} is attributed to the grafting of SA and the formation
249 of N-C=O bonds.

250 Zeta potential measurements, XPS and FTIR analyses confirm graftings of the silane coupling
251 agent and sodium alginate. The next section will look at the aggregation state of the particles as a
252 function of pH and surface chemistry.

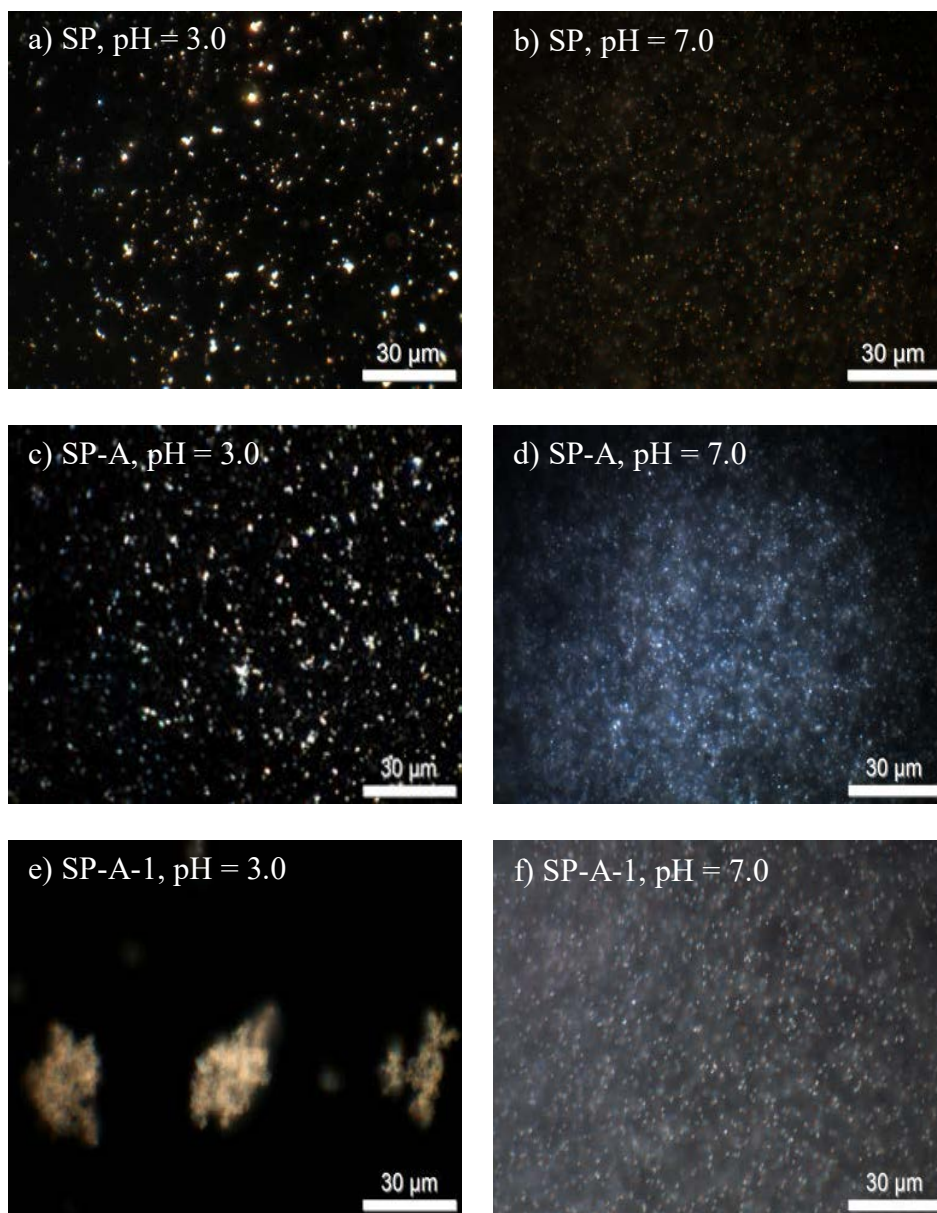
253 **3.2 Particle aggregation behavior**

254 **Figure 1** displays the aggregation behavior of SP, SP-A, and SP-A-1 particles at pH 3.0 and
255 7.0, respectively. At pH 3.0, unmodified SP particles tend to form small aggregates due to their
256 slightly positive charge (**Figure 1a**), while at pH 7.0 they are almost individually dispersed
257 (**Figure 1b**). These observations agree with the ζ measurements reported in **Table 1**: at pH 3.0,
258 the small positive value results in an unstable dispersion, while at pH 7.0, the significant negative
259 value leads to a stable dispersion.

260

261

262



263 **Figure 1.** Dark field optical microscopy micrographs showing the aggregation state, as a function
 264 of pH (3.0 or 7.0), of SP (a, b), SP-A (c, d), and SP-A-1 (e, f) particles.

265 Grafting APTMS at the surface of SP changes their electrostatic surface potential (**Table 2**) and
 266 their state of aggregation (**Figure 1c and d**). **Table 3** reports arithmetic mean diameter \pm mean
 267 absolute deviation, as a function of particle type – the size distributions are reported in **Figure S4**.
 268 For SP-A, at pH 3.0 (**Figure 1c**), the aggregates' average diameter ($D = 1.5 \pm 0.9 \mu\text{m}$, **Table 3**) is

269 comparable to unmodified SP particles ($D = 1.7 \pm 1.0 \mu\text{m}$), SP-B and SP-C particles ($D = 0.9 \pm$
 270 $0.4 \mu\text{m}$ and $D = 0.8 \pm 0.5 \mu\text{m}$, respectively). At pH 7.0, the presence of APTMS at the surface
 271 increases the average aggregate size (**Figure 1d**), as compared to unmodified SP at pH 7.0, due to
 272 the low zeta potential value.

273 D approximately increases by an order of magnitude, at pH 3.0, when SA is subsequently grafted
 274 onto the particles' surface (**Figure 1e, Table 3**), as compared to unmodified particles (**Figure 1a**,
 275 see also **Figure S5**) – the effect is quite striking. At pH 7.0 however (**Figure 1f**), SA grafted
 276 particles form much smaller aggregates ($D = 1.3 \pm 0.3 \mu\text{m}$) due to the deprotonation of SA
 277 carboxylate groups.

278

279 **Table 3.** Average aggregate diameter D as a function of particle type, at pH 3.0 (N = number of
 280 analyzed aggregates).

Particle type	Aggregate average diameter D (μm)	Average number of particles per aggregate ^a
SP	1.7 ± 1.0 (N = 659)	182
SP-A	1.5 ± 0.9 (N = 917)	128
SP-B	0.9 ± 0.4 (N = 3634)	28
SP-C	0.8 ± 0.5 (N = 1979)	22
SP-A-1	17 ± 10 (N = 231)	18.2×10^4
SP-B-2	12 ± 7 (N = 1124)	5.8×10^4
SP-C-2	12 ± 8 (N = 915)	6.4×10^4

281 ^aaverage number of particles per aggregate was obtained from $(D_{\text{aggregate}}/D_{\text{particle}})^3$

282

283 3.3 Sedimentation Kinetics

284 **Figure 2** displays the sedimentation behavior of SP, SP-A and SP-A-1 particles dispersed in water
285 at pHs 3.0 and 7.0, respectively. At pH 3.0, SP particles display a clear sedimentation onset after
286 3 min – the process is fast for the first 9 min, and then slows down since most of the particles have
287 then sedimented. In contrast, no sedimentation is observed at pH 7.0 even after 60 min (**Figure 2a**
288 **and b**). This difference is consistent with the measured ζ values. SP-A particles do not display any
289 significant sedimentation over the whole duration of the experiment, for both pHs tested (**Figure**
290 **2 c and d**). At pH 3.0, the positively charged protonated amino groups' repulsive forces lead to a
291 stable dispersed state, while at pH 7.0 the remaining negatively charged deprotonated hydroxyl
292 groups stabilize the dispersion. However, as the surface density of APTMS increases (SP-B and
293 SP-C), sedimentation occurs at pH 7.0 (results not shown).

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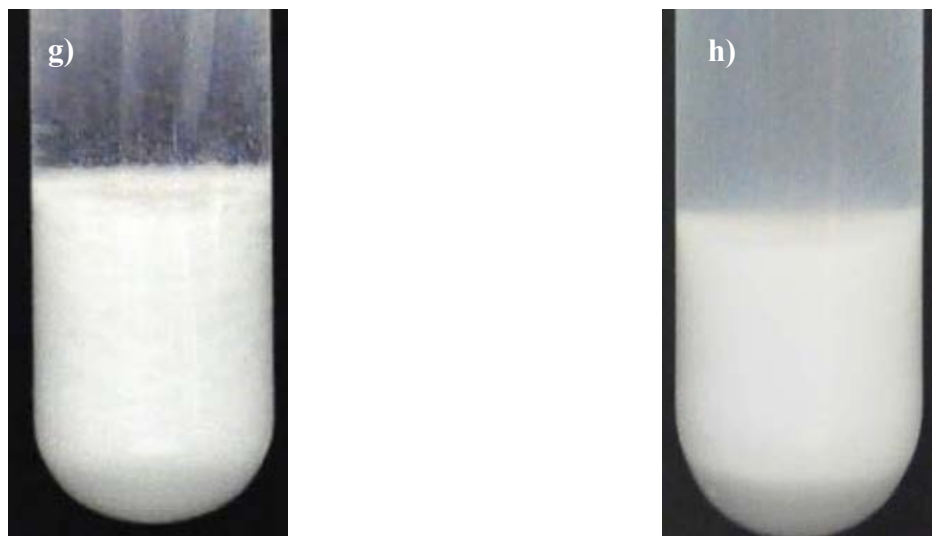
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302 **Figure 2.** Pictures of the sedimentation process (height of test tube = 15.3 cm) for SP (a, b), SP-A
303 (c, d), and SP-A-1 (e, f) particles over 60 min at pHs 3.0 and 7.0 respectively; g, h) close-ups of
304 SP-A-1 and SP sedimented particles, showing a clear difference in particle texture. Additional
305 results for SP-B-2 and SP-C-2 particles are displayed in Figure S6.

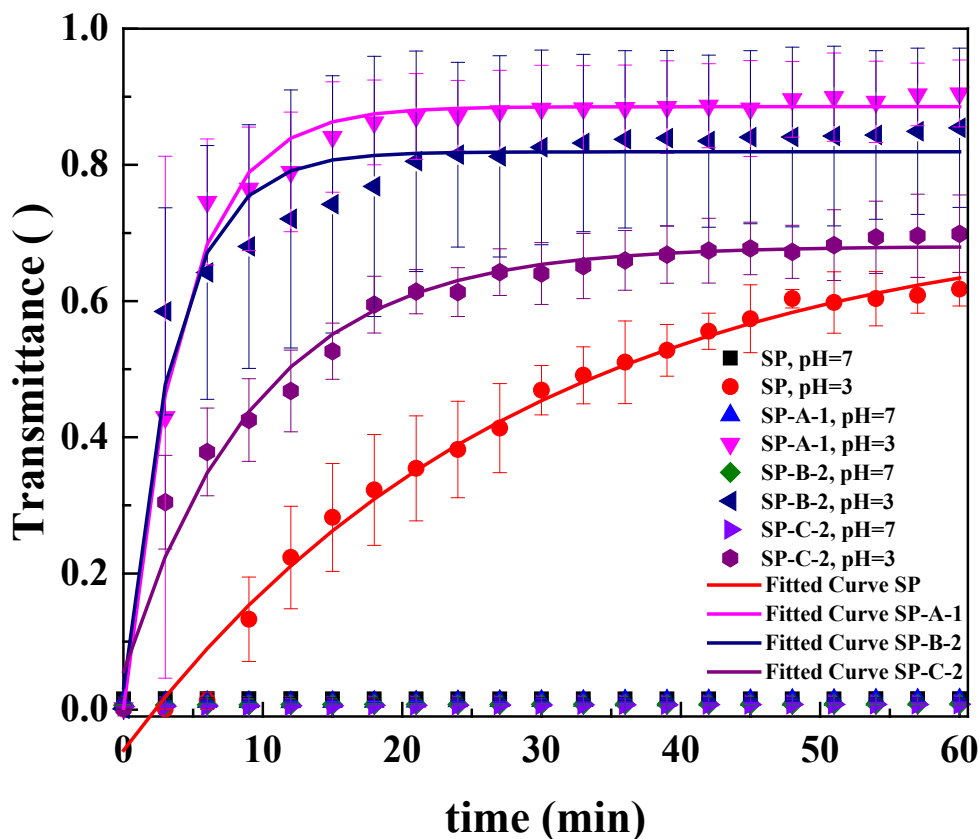
306 For SP-A-1 particles, shown in **Figure 2e-f**, sedimentation starts right away at pH 3.0 and after
307 3 minutes, it is already fairly advanced. After 6 min, the process significantly slows down, whereas
308 at pH 7.0, SP-A-1 particles stay well dispersed for the whole duration of the experiment, as shown
309 in **Figure 2f**. Note that a similar behavior was observed for SP-B-2 and SP-C-2 particles (results
310 not shown). Another distinct feature is the “grainy” texture of the sedimented SP-A-1 particles
311 (**Figure 2g**), as compared to unmodified SP particles (**Figure 2h**) – indicating the presence of large
312 aggregates at pH 3.0, which is not the case for SP particles.

313 **3.4 Kinetic test by UV-Visible spectroscopy**

314 **Figure 3** displays the normalized UV-Vis transmittance results T of the solutions during 60 min,
315 right after processing, at both pHs 3.0 and 7.0. The results at pH 3.0 were fitted with power laws
316 ($T = A+B \exp(-t/C)$). SP particles sediment moderately fast at pH 3.0 (as indicated by the initial

317 transmittance slope ($-B/C$) = 0.03, $R^2 = 0.98$), while no net sedimentation is detected at pH 7.0 (T
318 = 0). These results are consistent with the behavior expected based on zeta potential results (**Table**
319 **1**) and visual observations (**Figure 2**). After ≈ 35 min, T has increased up to 50 % for SP particles,
320 and to 60 % after 60 min, with sedimentation still in progress. In contrast, sedimentation is
321 occurring significantly faster at pH 3.0 for SA modified particles (initial slope ($-B/C$) = 0.22 ($R^2 =$
322 0.98), 0.22 ($R^2 = 0.95$) and 0.07 ($R^2 = 0.98$) for SP-A-1, SP-B-2 and SP-C-2 particles respectively).
323 For SP-A-1, T increases up to 50 % after only ≈ 5 min, and reaches a plateau value of nearly 90 %
324 after 30 min. Similar results are obtained for SP-B-2 particles, while SP-C-2 particles show a
325 slower sedimentation process compared to SP-A-1 and SP-B-2, but still faster compared to SP.
326 Finally, note that all solutions at pH 7.0 displayed no significant UV-Vis T increase.

327



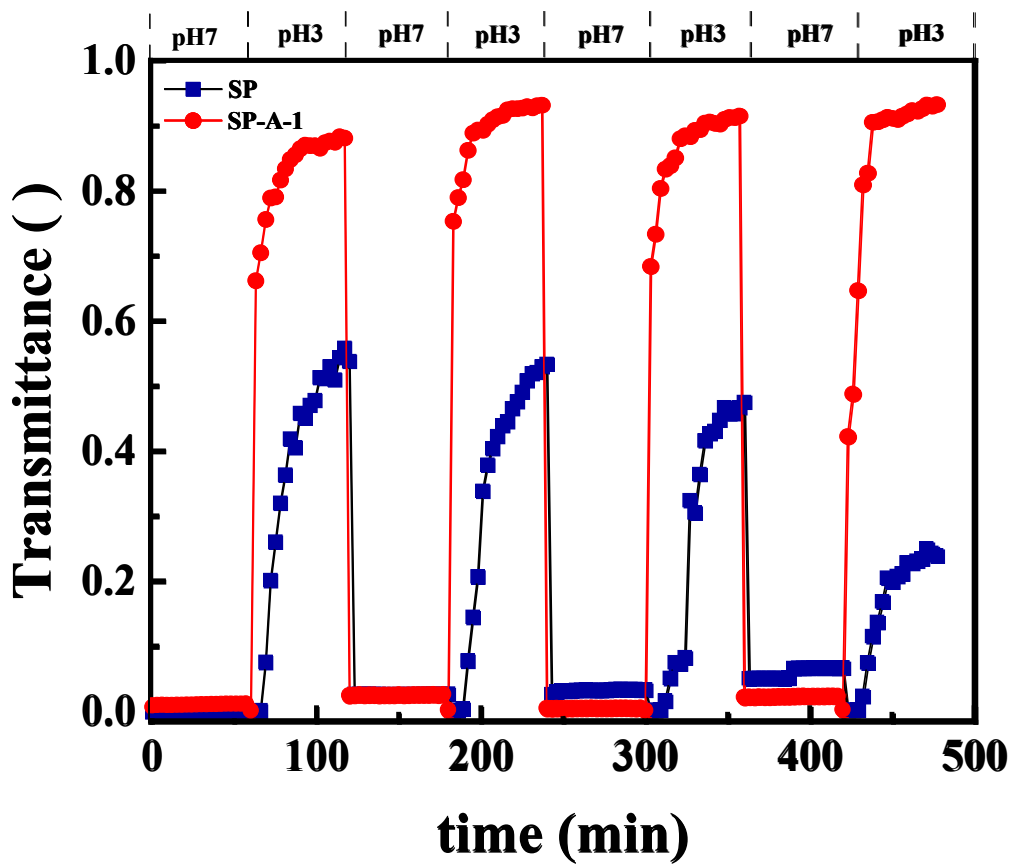
328
 329 **Figure 3.** Normalized transmittance T as a function of time for SP, SP-A-1, SP-B-2 and SP-C-2
 330 particles at pH 3.0 and 7.0, and fitted curves for SP, SP-A-1, SP-B-2 and SP-C-2 particles at pH
 331 3.0 over 60 min.

332 3.5 Aggregation/disaggregation Reversibility

333 **Figure 4** illustrates the reversible nature of the aggregation process for SP and SP-A-1 particles
 334 over 4 pH-swing cycles using UV-Vis spectroscopy, starting at pH 7.0, for 60 min. After that time,
 335 the pH is decreased to 3.0 for 60 min, and the cycle is repeated 3 other times. Both SP-A-1 and
 336 SP particles are able to aggregate and disaggregate reversibly over the course of the 4 tested cycles.
 337 At pH 3.0, SP-A-1 particles sediment rapidly within minutes and form aggregates, with UV

338 transmittance reaching a maximum near 90% each time the pH is brought down to 3.0. When the
339 pH is increased to 7.0 and the solution is sonicated, the dispersion remains stable ($T \approx 0\%$).

340 SP particles also display a reversible aggregation behavior, but the maximum transmittance after
341 60 min never goes over 60% - in fact, it decreases as the process is repeated. Furthermore, slight
342 aggregation is also observed at pH 7.0 as the process is repeated. It should be noted however that
343 if the pH is just increased without any sonication, the disaggregation process is very slow.



344
345 **Figure 4.** Reversibility test for SP (■) and SP-A-1 particles (●) over 4 cycles, during which the
346 pH jumps back and forth from 7.0 to 3.0.

347

348 4. Discussion

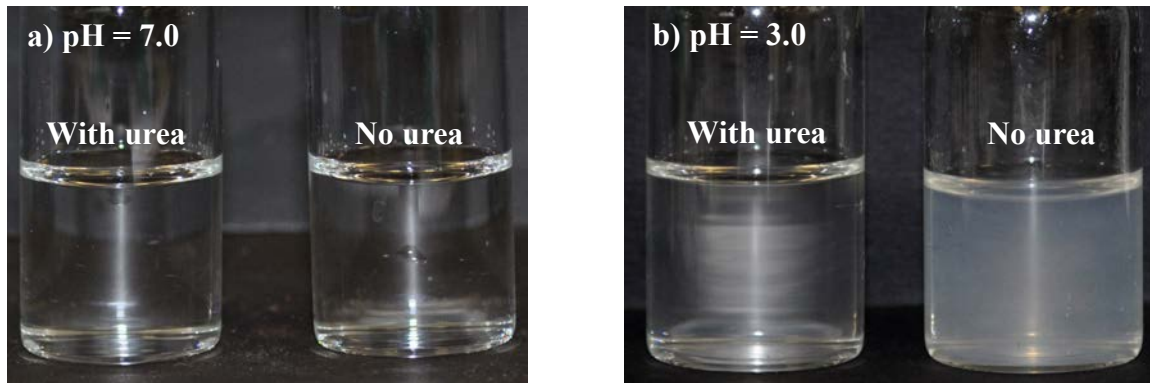
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350 The ζ measurements, along with the XPS and FTIR results, confirm that the SP particles have
351 been modified sequentially with covalently grafted APTMS and SA. The average diameter of
352 individual silica particles is $d \approx 300$ nm - in contrast, the average diameter D of particle aggregates
353 at pH 3.0, for SA modified particles, is about 10 times superior as compared to aggregates of
354 unmodified particles. Since the volume of an aggregate $\sim D^3$, there is approximately 10^3 more
355 particles in an aggregate of SA modified particles as compared to an aggregate comprising
356 unmodified particles, as reported in the third column of **Table 3** – a significant difference.

357 We propose that the main mechanism leading ultimately to the reversible, enhanced aggregation
358 properties of SA modified particles, compared to unmodified particles, originates from hydrogen
359 bonding between neighboring particles grafted with SA. At pH 7.0, SA carboxylic acid groups are
360 deprotonated and maintain the particles in suspension. However, once the pH is brought down to
361 3.0, the carboxylate groups are protonated and ζ is in-between 0-10 mV, which leads to an unstable
362 suspension and particle agglomeration. This gives rise to SA intermolecular interactions via
363 hydrogen bonding, enhancing aggregate formation. Recently, Chen et al. (K. Chen et al., 2017)
364 used SA-modified nanoparticles to prepare pH-sensitive Pickering emulsions. Their work
365 demonstrated that SA significantly alters the emulsions' rheological behavior due to pH-dependent
366 interparticle interactions.

367 **Figure 5a and b** illustrate the effect of urea on alginate association in solution at pHs 7.0 and
368 3.0, respectively. Urea is a well-known hydrogen bond disruptor, which should then limit or inhibit
369 hydrogen bonding and aggregate formation. At pH 7.0, urea has no visible effect on solution

370 turbidity. However, when the pH is brought down to 3.0, alginate phase separate (and can
371 ultimately form a gel when the SA concentration is high enough), a phenomena that is not observed
372 when urea is added to the solution.



373 **Figure 5.** Pictures of 0.5 % solution of pure SA in DI water at pH 7.0 (a) and at pH 3.0 (b), with
374 and without urea (16 M). Solution with urea at pH 3.0 remains clear, while without urea it becomes
375 turbid.

376 Furthermore, investigating the effect of SA molecular weight and architecture
377 (guluronic/mannuronic ratio), and other gelling polysaccharides, is currently in progress.

378 **5. Conclusion**

379 This article demonstrates that submicrometer silica particles functionalized with a pH sensitive
380 polysaccharide, sodium alginate, display enhanced aggregation properties at low pH, and
381 reversible aggregation/disaggregation properties in aqueous solutions. The aggregation properties
382 are due to interparticle hydrogen bonding between neighboring sodium alginate modified particle.
383 The particles surface modification was characterized by zeta potential measurements, XPS and
384 FTIR analyses, and UV-Vis was used to characterize the sedimentation kinetics. The results

385 illustrate how stimuli sensitive surface modified particles can be used as a potential approach to
386 facilitate the aggregation of particles, and to ease separation processes.

387

388 **Supporting Information.** Silica particles SEM micrographs, XPS and FTIR spectra of
389 unmodified and modified particles; particle aggregates size distribution; optical microscopy and
390 sedimentation test results.

391

392 AUTHOR INFORMATION

393 **Corresponding Author**

394 *(N.V.) Telephone: 514-340-4711 #4524. FAX: 514-340-4152. E-mail: nick.virgilio@polymtl.ca

395 **Author Contributions**

396 The manuscript was written through contributions of all authors. All authors have given approval
397 to the final version of the manuscript.

398

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408

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