Electronic Supplementary Material (ESI) for Polymer Chemistry.

Synthesis of clay-armored poly(vinylidene chloride-*co*-methyl acrylate) latexes by Pickering emulsion polymerization and their film-forming properties

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SUPPORTING INFORMATION

1) Calculation of the targeted solids content, the monomer conversion, the concentration and the density of the composite latex particles

The targeted solids content without clay is defined by:

$$\tau_{theo}(\%) = \frac{\sum W_{monomer}}{W_{total}} \times 100 \qquad \text{(S1)}$$

Where $\sum W_{monomers}$ is the weight of monomers (g) and W_{total} is the weight of all the components (g).

The monomer conversion was determined by gravimetric analysis on samples collected from the reaction mixture. The latex was dried in an oven to a constant weight. The dry extract and the conversion were calculated according to the following equations:

$$Dry\ extract\ (\%) = \frac{W_{dry}}{W_{latex}} \times 100 \quad \text{(S2)}$$

$$Conversion\ (\%) = \frac{Dry\ extract - \tau_{nonvolatile}}{\tau_{theo}} \times 100 \quad \text{(S3)}$$

Where W_{dry} is the weight of the dry extract (g), W_{latex} is the weight of the latex (g), $\tau_{nonvolatile}$ is the solids content of the nonvolatile compounds (%) and τ_{theo} (%) is the targeted solids content at 100% conversion.

The concentration of the composite latex particles $C_{polymer(composite)}$ (g L^{-1}) was calculated according to Equation S4:

$$C_{polymer(composite)} = \frac{m_{clay} + (m_{MA} + m_{VDC}) \times X}{m_{water}} \times 1000 \quad \text{(S4)}$$

where m_{clay}, m_{MA}, m_{VDC} and m_{water} (g) are the weight of the clay, MA, VDC and water, respectively, and X is the monomer conversion expressed in %.

The density of the composite latex particles: $\rho_{polymer(composite)}$ (g cm^{-3}) was calculated according to Equation S5:

$$\frac{1}{\rho_{polymer(composite)}} = \frac{wt\%_{clay}}{\rho_{clay}} + \frac{wt\%_{P(VDC-co-MA)}}{\rho_{(VDC-co-MA)}} \quad \text{(S5)}$$

where ρ_{clay} (2.57 g cm^{-3}) and $\rho_{P(VDC\text{-}co\text{-}MA)}$ (1.65 g cm^{-3}) are respectively the densities of the clay and P(VDC-*co*-MA), and $wt\%_{clay}$ and $wt\%_{P(VDC\text{-}co\text{-}MA)}$ their corresponding weight percentages determined from the monomer conversion and the initial clay content.

2) ***Calculation of the latex surface coverage by the Laponite clay platelets***

The following nomenclature was used below (equations S6 to S10):

d_L	Diameter of a Laponite disc	25 x10^{-7} cm
D_h	Diameter of a particle (measured by DLS)	cm
h	Height of the platelet	1 x10^{-7} cm
m_L	Mass of Laponite	g
m_p	Mass of the polymer taking in account the monomer conversion	g
N_L	Number of Laponite platelets	-
N_p	Number of polymer particles (without Laponite)	-
ρ_L	Laponite density[i]	2.57 g cm^{-3}
ρ_P	Polymer density[ii]	1.65 g cm^{-3}
S_L	Area occupied by one Laponite disc	cm^3
S_p	Surface area of one polymer particle	cm^3

The percentage of surface coverage of the latex particles by the clay platelets was discussed by Bon[iii] and defined as:

$$Cov\ (\%) = \frac{N_L \times S_L}{N_p \times S_p} \qquad \text{(S6)}$$

It was assumed that the discs lie flat on the surface; so the area occupied by the Laponite discs can be considered as a 2D square, which leads to the following equations:

$$S_L = {d_L}^2 \qquad \text{(S7)}$$

$$S_p = \pi \times {D_h}^2 \qquad \text{(S8)}$$

$$N_L = \frac{m_L \times 4}{\rho_L \times \pi \times {d_L}^2 \times h} \qquad \text{(S9)}$$

$$N_p = \frac{m_p \times 6}{\rho_p \times \pi \times {D_h}^3} \qquad \text{(S10)}$$

Introducing equations (S7), (S8), (S9) and (S10) in equation (S6), the percentage of coverage can be calculated as follows:

$$Cov\ (\%) = \frac{m_L \times 4 \times \rho_p \times D_h}{\rho_L \times \pi \times h \times 6 \times m_p} \qquad \text{(S11)}$$

3) Synthesis of (PVDC-co-MA) latexes in the presence of surfactant

In a typical experiment (run 24), APS (0.31 g), $Na_4P_2O_7$ (0.31 g) and Disponil® LDBS 25 (1.2 g of a 258 g L^{-1} commercial solution) were dissolved in 70 g of water. The dispersion was then introduced into a 250 mL jacketed glass reactor vessel (Parr Instrument Company) equipped with a stainless steel anchor and internal pressure and temperature sensors. The reaction medium was purged with nitrogen for 20 minutes with a stirring rate fixed at 300 rpm. After deoxygenation of monomers by bubbling with nitrogen for 20 minutes, 6.4 mL (6.1 g) of MA and 45.3 mL (55 g) of VDC were introduced via the injection valve into the reactor (time zero). The autoclave was pressurized at 1 bar with nitrogen and connected to a pre-heated water bath. The reaction mixture was stirred with an anchor at 300 rpm and heated at 70 °C (pressure raised to 4 bars). After 1 hour, the stirring rate was decreased to 100 rpm. The reaction was stopped when the pressure came back to 1 bar. The autoclave was then depressurized and residual monomers were then stripped with nitrogen under gentle stirring during 1 hour.

Table S1: Experimental conditions and characteristics of the final latexes obtained by emulsion copolymerizations of VDC/MA in the presence of Disponil® LDBS 25[a]

Run	VDC/MA (wt/wt)	Conv.[b]	τ_{exp}[c] (%)	D_h (nm) (PdI) [d]	pH
24	85/15	100	46	137 (0.02)	3.5
25	87/13	100	46	130 (0.02)	2.5
26	90/10	100	46	129 (0.04)	2.4

[a] All polymerizations were performed during 60 minutes at 70 °C and 300 rpm with water: 70 g, total monomer weight: 61.1 g, APS: 0.31 g, $Na_4P_2O_7$: 0.31 g and Disponil® LDBS 25: 1.2 g. [b] Overall monomer weight conversion determined by gravimetric analysis. [c] Overall solids content. [d] Average diameter and PdI determined by DLS.

4) Cryo-TEM images showing the presence of free clay platelets for runs 20 and 23 (Table 4 and 5, respectively)

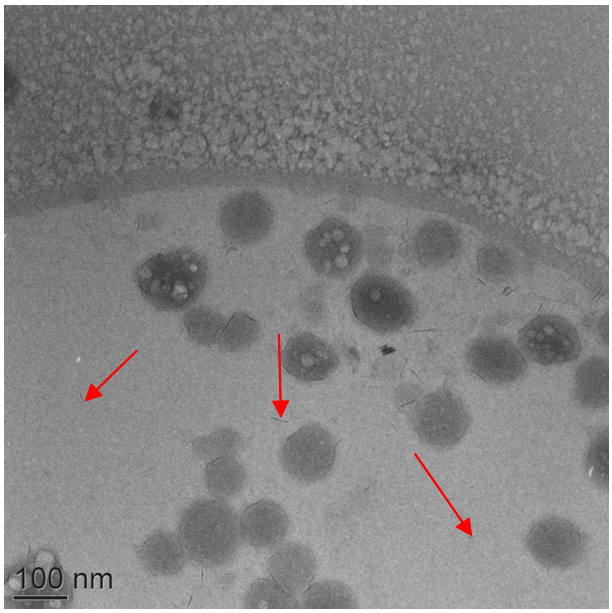

Figure S1: Cryo-TEM image of P(VDC-*co*-MA) particles stabilized by 15 wt% of Laponite® S482 (VDC/MA = 87/13 wt/wt and τ_{exp} = 30 wt%, run 20 in Table 4). The arrows point to Laponite®. The white spots on the right-hand side image correspond to a fast damage of the particles by the beam during the cryo-TEM analysis.

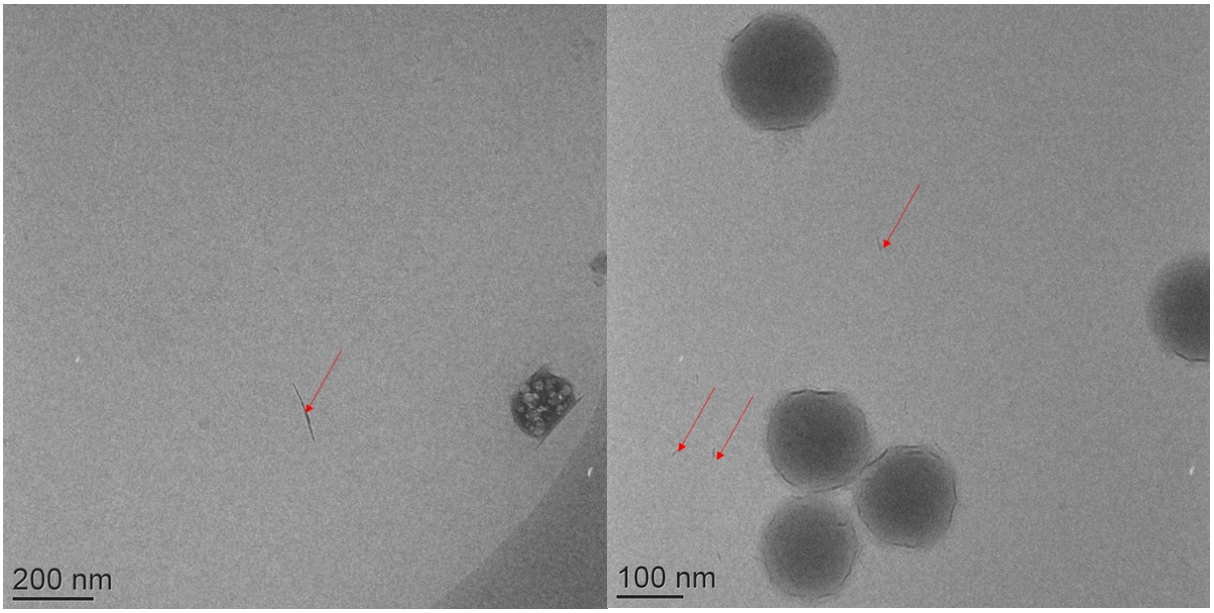

Figure S2: Cryo-TEM images of P(VDC-*co*-MA) particles stabilized by 2.5 wt% of MMT Na^+ and 5 wt% of Laponite® S482 (VDC/MA = 87/13 wt/wt and τ_{exp} = 30 wt%, run 23 in Table 5). The arrows point to Laponite® and MMT platelets. The white spots on the right-hand side image correspond to a fast damage of the particles by the beam during the cryo-TEM analysis.

[i] Laponite Data Sheet (Rockwood Industries)
[ii] Brandrup, J.; Immergut, E. H.; Grulke, E. A. Polymer Handbook. 4th ed. New York:John Wiley & Sons, 1999
[iii] Bon, S. A. F.; Colver, P. J. *Langmuir* 2007, 23, 8316-8322.