SUPPORTING INFORMATION

Tailored microstructure and mechanical properties of nanocomposite films made from polyacrylic/LDH hybrid latexes synthesized by RAFT-mediated emulsion polymerization

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Experimental Part (from [1])

$Mg_3Al(OH)_8(CO_3)_{0.5}{\cdot}2H_2O$ (abbreviated Mg_3Al-CO_3) LDH synthesis : A mixture of Mg and Al nitrate salts (Mg/Al = 3, total [M] = 0.10 M) was prepared in water (1 L) and rapidly added to a NaOH solution (0.25 M, 800 mL) under vigorous magnetic stirring. The pH value was adjusted to 10.0 using NaOH (0.25 M, ca. 20 mL), and the suspension was stirred for a further 30 min. The resulting slurry was washed twice with water (with centrifugation between each washing), redispersed in water (100 mL) after the final wash, and hydrothermally treated in an autoclave at 150 °C for 4 h. The resulting nanoparticles were stored as a colloidal suspension at 4 °C. The intensity average particle diameter ($Z_{av.}$) determined by dynamic light scattering (DLS) using the NanoZS instrument from Malvern was 81 nm (PDI = 0.25) in good agreement with the TEM analysis (see Fig S1). The formation of pure LDH phase was confirmed by powder X-ray diffraction (XRD) analysis (Fig S1).

Latex preparation : Using P(AA-BA)$_{35}$-R as a representative example, a stock solution of macroRAFT agent (43.1 mg mL^{-1}, 11.6 mM) was prepared by adding NaOH solution (1.0 mol L^{-1}) to an aqueous solution of the macroRAFT agent until a pH value of 8.0 and the desired concentration was reached. LDH suspension (6.64 mL, 36.1 g L^{-1}, pH = 8.0) was added in one portion to stirred macroRAFT agent solution (3.34 mL, 5.94 x 10^{-5} mol, 1 eq.) and the mixture was subjected to ultrasound for 10 min. A solution of ACPA (8.33 mg, 5.94 x 10^{-5} mol, 0.5 eq.) dissolved in water and adjusted to pH value 8.0 was added, followed by water (3.38 mL) to give [macroRAFT] = 12.0 g L^{-1} (3.22 mM), [LDH] = 20.0 g L^{-1}, and a total volume of 12.0 mL. An aliquot (2.0 mL) was removed and dried to give the initial solids content by gravimetry. The remaining solution was transferred to a 25 mL round-bottom flask fitted with a magnetic stir bar, was sealed with a rubber septum, and was degassed by nitrogen bubbling for 15 min. In parallel, the monomer mixture (MA/BA 80/20 mass/mass, c.a. 1 mL) was degassed. The round bottom flask was accurately weighed, and then placed in an oil bath at 70°C. The monomer solution was taken up in a 1 mL nitrogen-purged syringe fitted with a long needle, the needle was inserted through the septum in the macroRAFT/LDH solution, the syringe was placed in a Perfusor® compact syringe pump, and injected at a rate of 0.3 g h^{-1}. Monomer injection was ceased after 2 h, and the reaction was continued for 2 h. After cooling, a portion of the final solution was dried and weighed to determine the conversion gravimetrically, and DLS and cryoTEM were performed on appropriately diluted aliquots. For SEC analysis, a portion of dried sample (c.a. 20 mg) was stirred overnight in THF (5 mL) containing conc. HCl (ca. 2 eq. relative to COOH groups), sonicated for 10 min, filtered using a 0.45 μm PTFE filter, then the filtrate was directly methylated according to a previously published procedure.[2]

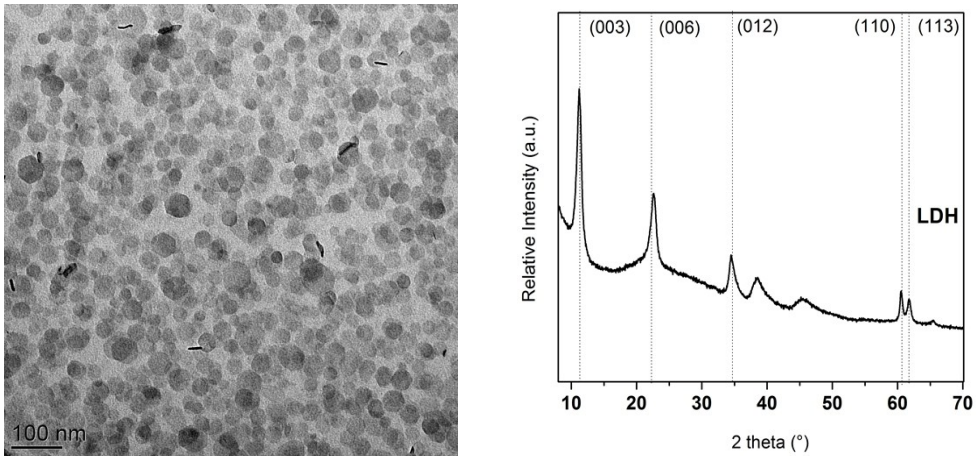

Figure S1: TEM image (left) and PXRD pattern (right) of Mg_3Al-CO_3 nanoparticles.

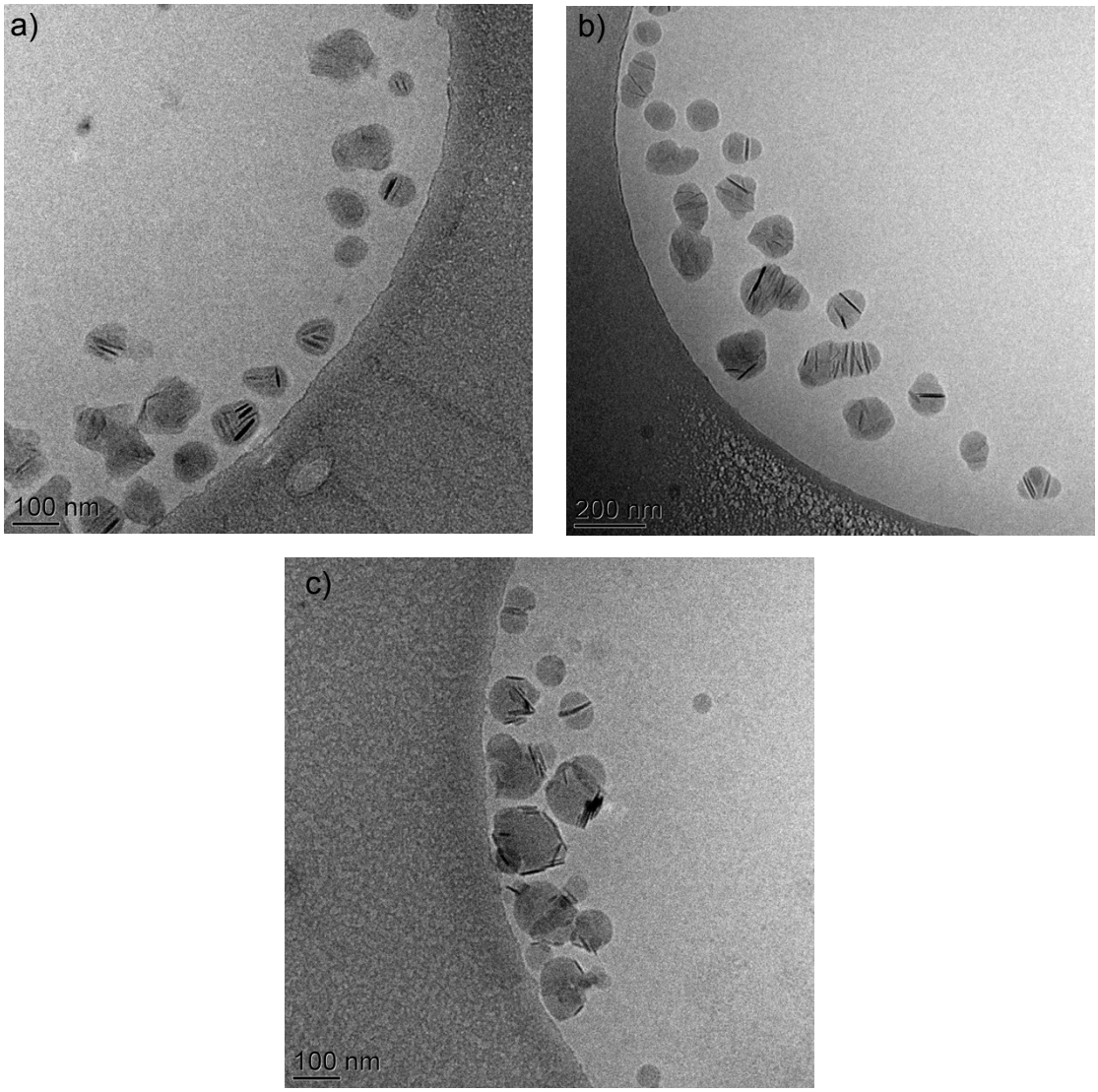

Figure S2: Cryo-TEM images of the latexes obtained using a) P(AA-BA)$_{15}$-R to give encapsulated, b) P(AA-BA)$_{35}$-R to give dumbbell, and c) P(AA-BA)$_{35}$ to give armoured particles.

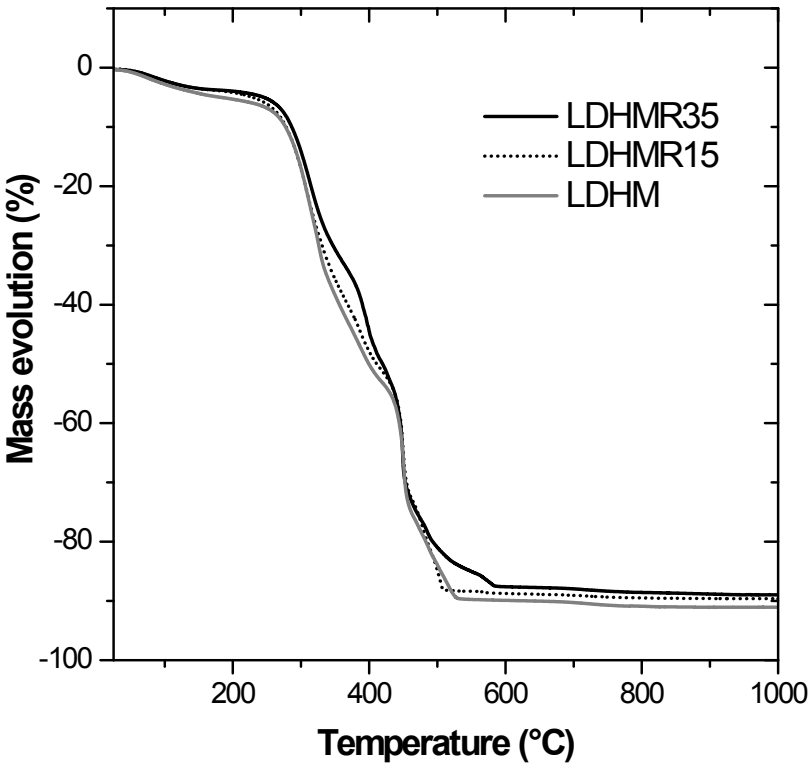

Figure S3: TGA curves of the different LDH nanocomposite films studied.

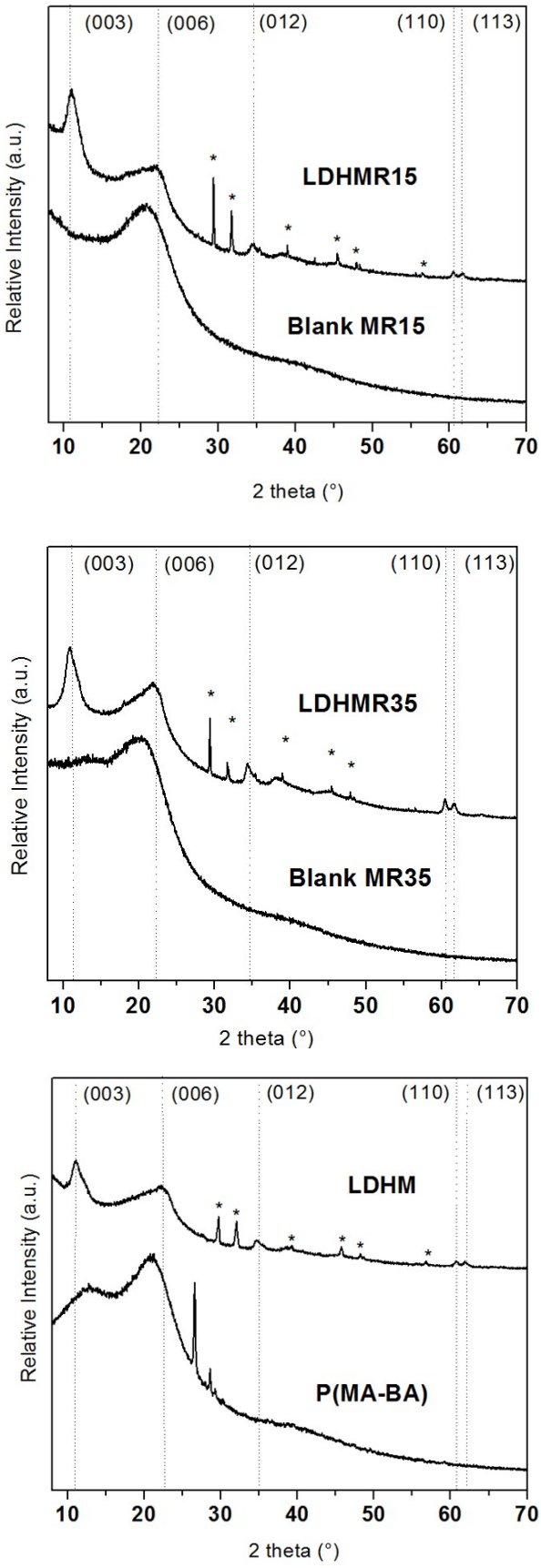

Figure S4: PXRD patterns of the different LDH nanocomposite films studied and of the corresponding blank matrices

References

(1) Pearson, S.; Pavlovic, M.; Augé, T.; Torregrossa, V.; Szilagyi, I.; D'Agosto, F.; Lansalot, M.; Bourgeat-Lami, E.; Prévot, V. Controlling the Morphology of Film-Forming, Nanocomposite Latexes by RAFT Emulsion Polymerization. *Macromolecules* **2018**, *Under subm*.

(2) Couvreur, L.; Lefay, C.; Belleney, J.; Charleux, B.; Guerret, O.; Magnet, S. First Nitroxide-Mediated Controlled Free-Radical Polymerization of Acrylic Acid. *Macromolecules* **2003**, *36* (22), 8260–8267.