Electronic Supplementary Information for

Nanoparticle assembly modulated by polymer chain conformation in composite materials

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Materials & Experimental Methods

Chemicals: Zinc oxide dispersion (<100 nm, Aldrich), Zinc oxide nanopowder (<50 nm, >97%, Aldrich), Titanium(IV) oxide nanopowder (~21 nm, Aldrich), Hydroxyethyl starch (>1,000,000 g/mol, Aldrich), Hydroxyethyl cellulose (90,000 g/mol, Aldrich), Hydroxyethyl cellulose (1,300,000 g/mol, Aldrich), Tween20 (1288 g/mol, Aldrich), Na polyphosphate (≥68%, Aldrich), Ammonium hydroxide (28-30%, Fischer), Cyclohexane (100%, Aldrich) Tetraethyl orthosilicate (≥99%, Aldrich) L-arginine (≥98%, Aldrich), Hydrochloric acid (>99%, Aldrich).

Silica Nanoparticle Synthesis: To synthesize the nanoparticles a 6mM (0.182g) L-arginine solution was added to a 400mL Erlenmeyer flask equipped with a stir bar. A volume of cyclohexane was then added as an organic layer. The two-phase mixture was allowed to warm up to 60C for 30 min. under slow stirring (160 RPM). Once the reactants have warmed up, 11.2mL tetraethyl orthosilicate (TEOS) was slowly added to the organic phase. The solution was allowed to mix for 20 hr. with a stirring rate fixed at 160 RPM. This enabled the top organic layer to be left almost undisturbed while the water phase was well mixed. After the reaction has finished, the top cyclohexane layer was siphoned off, and the remaining aqueous solution was quenched with hydrochloric acid. The particles were then washed with water via centrifuge (15,000 RPM/ 30 min. intervals X3).

Coating Formulation: In a glass vial, modified starch/cellulose (1.2 g) was diluted to 4 wt %. The mixture was stirred at 550 RPM for 2 min, modified with ammonia hydrodroxide (to pH 9), and stirred once more for 5 min. The solution was then heated under microwave irradiation. Following, a separate mixture of nanoparticles (TiO_2 or ZnO) (0.24 g), Na polyphosphate (0.006 g), and deionized water (0.95 mL) was stirred and sonicated for 5 min. The solution was diluted with deionized water (3 mL), stirred 5 additional min, and then homogenized for 5 min. A ZnO or SiO_2 nanoparticle dispersion can replace the previous, with Tween 20 (0.075 g) as the dispersant and an additional 20 min of sonication in place of the homogenization step. The binder solution and nanoparticle dispersions were combined at 550 RPM for 10 min. In the case of the nanopowder dispersion, the mixture was homogenized for 5 min, whereas with the commercial dispersion, the mixture was sonicated for 20 min. After thorough homogeneity has been achieved, the formulation was drawn down on corona-treated polyethylene plastic with a stainless steel drawdown bar of 75 μm wet thickness.

Material Characterization

SEM Imaging: A Verios XHR SEM (FEI) was used for electron microscopy characterization. The microscope was operated at 5-10 kV with the ET detector. Bright field and secondary electron images were simultaneously recorded. The samples were prepared by sputtering a thin layer of gold on the film surface to eliminate charging of the nonconductive surface.

Supplementary Videos

Videos S1-S3: Representative structural evolution of polymer-nanoparticle mixtures solvated with 50% water in equilibrium runs at K = 2, 20, and 50, respectively. The small blue beads represent water beads. The different sizes for different types of beads are just for visual clarity.

Videos S4-S6: Time evolution of the polymer-nanoparticle solutions under evaporation at K = 2, 20, and 50, respectively.

Videos S7-S8: Equilibration of the systems of stiff polymer chains (K = 50) with side chains in the presence of 50% water for the side chain concentrations of 10% and 40%, respectively.

Videos S9-S10: Corresponding structural evolution during evaporation for the K = 50 polymer systems with side chain concentrations of 10% and 40%, respectively.