

SYNTHESIS OF HYBRID NANOPARTICLES FOR ADVANCED COATINGS APPLICATIONS

Olga Kammona¹, Katerina Kotti¹, Costas Kiparissides¹, Jean-Pierre Celis² and Jan Franssaer²

¹ Department of Chemical Engineering, Aristotle University of Thessaloniki and Chemical Process Engineering Research Institute, P.O. Box 472, 54124 Thessaloniki, Greece

² Department of Metallurgy and Materials Engineering, Katholieke Universiteit Leuven, Kasteelpark Arenberg 44, B-3001 Leuven, Belgium

Introduction

The major limitation for the use of steel is its low corrosion resistance which requires the use of protective layers like zinc coatings and solvent-borne paints. Efforts have been made to improve the corrosion resistance of zinc coatings by the codeposition of particles [1]. These composite zinc coatings can be prepared by electrolytic codeposition of uniform polymeric, inorganic or hybrid nanoparticles (NPs). The NPs employed in the codeposition process should have a fairly narrow particle size distribution within a specific size range depending on the thickness of the coating and they should be compatible with the electroplating bath.

Monodisperse polymeric NPs with functionalized surfaces can be prepared by emulsifier-free emulsion polymerization of a basic monomer (e.g., styrene, MMA) incorporating small amounts of a hydrophilic ionic or nonionic comonomer [2]. Polymer/silica composite NPs can be prepared by the same method [3], employing in some cases auxiliary monomers (e.g., 4-vinylpyridine, 1-vinylimidazole) [3,4] to promote the silica NPs-polymer interaction.

In the present study, uniform anionic and cationic poly(methyl methacrylate) (PMMA) and polystyrene (PS) NPs with various functional groups (e.g., amide, hydroxyl, pyridine) on their surfaces and raspberry-like poly(styrene / 1-vinylimidazole) / silica P(St/1-VID)/Si hybrid NPs were prepared by (emulsifier-free) emulsion polymerization for advanced coatings applications.

Experimental

(Emulsifier-free) emulsion polymerization experiments were carried out in laboratory scale, water-jacketed, glass reactors of 0.1, 0.5 and 1 L equipped with a six-blade impeller, an overhead condenser and a nitrogen purge line. The polymerization reactions were carried out to high conversions. The most successful experiments were scaled-up in a 5L stainless-steel fully-automated pilot-scale reactor system. The effect of the type of initiator and comonomer, type and concentration of surfactant and reactor scale on the particle size and stability was examined for the polymeric NPs, whereas the effect of the initial monomers molar ratio and pH on the particle size, morphology and silica content was examined for the P(St/1-VID)/Si hybrid NPs.

The surface morphology of the NPs was assessed by scanning electron microscopy (SEM) and transmission

electron microscopy (TEM) and their size distribution was measured by dynamic light scattering. The zeta potential (ζ) of the silica sol (Ludox AM) and the hybrid NPs at different pH values was calculated from aqueous electrophoresis measurements. Thermogravimetric analysis (TGA) was employed for the measurement of the silica content.

The electrolytic codeposition experiments were carried out on a rotating disc electrode (RDE). The NPs were electrodeposited from an acid zinc plating bath in the presence of surfactants (e.g., cetyl trimethyl ammonium hydrogen sulfate, CTAHS).

Results and Discussion

Monodisperse anionic and cationic polymeric particles with diameters in the range of 60 - 1400 nm were prepared by emulsion polymerization in the presence or absence of surfactants. It was shown that the increase in surfactant concentration (e.g., aerosol OT) (Fig. 1) or the presence of a functional comonomer (e.g., 2-hydroxyethyl methacrylate, 2-HEMA) in the case of emulsifier-free emulsion polymerization leads to a decrease in particle size. Replicates of some representative experiments, which were run both in lab and pilot-scale reactors, indicated excellent reproducibility of the polymerization process (Fig. 1). Uniform, polymer-containing zinc coatings were produced by electrolytic codeposition of the polymeric NPs from an acid zinc plating bath in the presence of the cationic surfactant CTAHS and high deposition rates were observed (Fig. 2). It was shown that the amount of codeposited PMMA NPs with zinc in the presence of CTAHS is independent of the rotation rate.

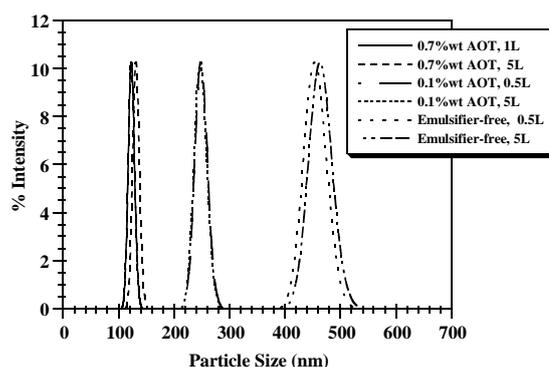


Fig. 1 Effect of AOT concentration and reactor scale on the size distribution of PMMA NPs.

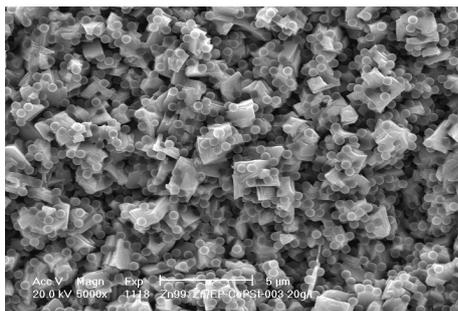


Fig. 2 SEM photomicrograph of a composite zinc coating.

The codeposition of PMMA NPs with Zn in the presence of CTAHS was found to increase dramatically as the current density increases up to 50 A/dm² (Fig. 3) indicating that the codeposition of polymeric NPs with zinc is viable for industrial coil coating lines where current densities of 50 to 200 A/dm² are used.

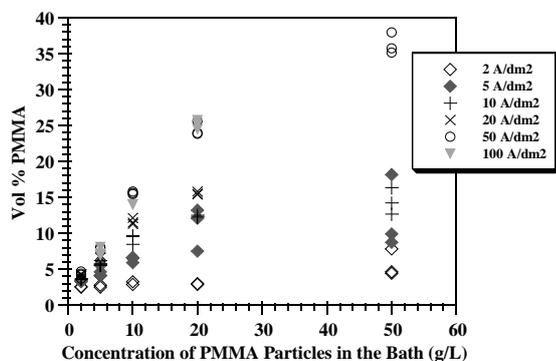


Fig. 3 Effect of current density on the codeposition of PMMA NPs with zinc.

Spherical P(St/1-VID)/Si NPs with diameters up to 200nm and a raspberry-like morphology were prepared (Fig. 4). The silica content in the P(St/1-VID)/Si NPs was found to increase up to 38.3 % wt with the increase of 1-VID in the monomer feed and the decrease of pH. However, it was shown that there is an optimum pH value (pH~8) at which the silica content is maximized.

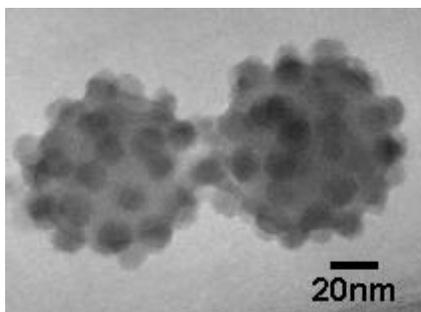


Fig. 4 TEM photomicrograph of P(St/1-VID)/Si NPs.

Fig. 5 shows the variation of zeta potential with pH for the silica sol and P(St/1-VID) NPs of various St/1-VID

molar ratios. As can be seen, Ludox AM has a negative zeta potential over the whole pH range examined. On the other hand, the P(St/1-VID) NPs exhibit classic S-shaped curves with isoelectric points at approximately pH~4 and positive zeta potential values up to 30mV at low pH.

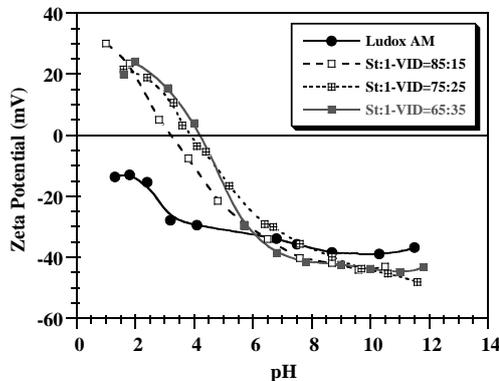


Fig. 5 Variation of zeta-potential with pH for silica sol and P(St/1-VID)/Si NPs.

Conclusion

The present study revealed that uniform anionic and cationic polymeric NPs with functional groups on their surfaces can be prepared in a reproducible manner by (emulsifier-free) emulsion polymerization and that their production can be successfully scaled-up from lab- to pilot-scale reactors. The NPs were found to codeposit from an acid zinc plating bath on an RDE in the presence of the cationic surfactant CTAHS resulting in the production of uniform composite zinc coatings aiming to be used as topcoatings on steel and as undercoats for painted steel. In addition, it was shown that perfectly spherical polystyrene/silica hybrid NPs with raspberry-like morphology, uniform size and increased silica content can be successfully prepared via emulsifier-free emulsion polymerization.

References

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