

ABSTRACT

Thermodynamic incompatibility between the polymer and water is a major challenge in the design of production and application of modern, environmentally and user-friendlier water-based materials. Presented PhD thesis deals with three research and commercial issues in the preparation of aqueous polymer binders for the purposes of coatings industry.

Polyurethane aqueous dispersions (PUD) represent an important alternative to the very well established solvent-based polyurethane binders as they drastically reduce the health and environmental risks. Despite numerous researches, achieving a comparable quality of the final product is often problematic. Chemical and physical parameters of the PUD were studied after the synthesis. Prepolymer mixing process with a limited-chain extension step was used in order to examine polymer and dispersion behavior with respect to ageing time. Measurements of free isocyanate group amount were performed by Fourier Transform Infrared Spectroscopy (FT-IR). Pseudo-first-order kinetics of NCO disappearance was proposed and the value of corresponding constant was determined. Additionally, particle size, particle size distribution, pH, conductivity and molecular weight were monitored and compared.

2-Hydroxyethyl methacrylate (HEMA)-rich latex was synthesized via a semibatch monomer-starved emulsion polymerization process. Six emulsion polymerizations, containing 0 – 40 mol% HEMA in monomer composition were synthesized and compared. Calculations of mass balances were made in order to predict final particle size and particle size development during the course of polymerization. Average particle sizes obtained by Dynamic Light Scattering (DLS), were compared to Ultrasound Acoustic Attenuation Spectroscopy (UAAS), Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM). The influence of HEMA content on polymerization and on the onset of secondary nucleation was evaluated using each technique. The DLS, TEM, and UAAS secondary nucleation data were compared to physical latex blends with similar composition. Additionally, conductivities and Surface tensions were monitored. TEM, AFM and UAAS were found to be more appropriate method(s), than widely used DLS, for particle size and particle size distribution characterization. Increasing HEMA content to 20 mol% resulted in formation of significant amount of secondary particles via proposed homogeneous nucleation of HEMA-rich oligomers.

In third part, influences of semibatch, '*shot-addition*' and '*power feed*' feeding strategies on micro- and macroscopic carboxylated latex properties were investigated. As a source of carboxyl groups Acrylic (AA) and Methacrylic acid (MAA) were used. Proposed differences in the distribution of carboxyl groups between feeding strategies were verified through rheology, potentiometric/conductometric titrations, Transmission Electron Microscopy and FT-IR. Upon

neutralization, particle swelling was observed using Dynamic Light Scattering. Both AA and MAA based latexes showed significant increase in hydrodynamic diameter when pH raise lead to dissociation state of carboxyl groups. However, only MAA-based latexes exhibit very pronounced increase in viscosity and storage modulus and were therefore characterized as gels. As expected, effect of feeding strategies was found to be more pronounced at the MAA functionalized latexes. By using mentioned three procedures, significant differences in the rheological behavior of the neutralized dispersions were achieved. Acquired knowledge from this study was used in the design of commercial acrylic binder with which we won 3rd place at the 9th Slovenian Innovation Forum.