Polymer Particle Technology

White Paper

Xerox Research Centre of Canada
Introduction to Polymer Particle Technology

Polymer particle technology is the fabrication of primary Nano to Micron size range resin particles, and its scope for a range of industries that include chemical, petrochemical, agricultural, food, pharmaceuticals, mineral processing, and advanced materials. These particles can be directly obtained from monomers, via addition type (or chain growth) polymerization methods such as emulsion, suspension, and dispersion process, or indirectly from step-growth polymers (Polyester, polyamides...), through waterborne processes (dissipation), phase inversion, solvent homogenization, coacervation/precipitation or spray-drying. Pulverization (grinding) methods from bulk polymers can also yield micron size polymer particles. Polymer particles in organic liquid media, or aqueous (latex) form are obtained with particles size in the range of nanometers to microns, and in some processes, with narrow geometric size distributions.

DIRECT POLYMERIZATION METHODS

Polymer particles are easily obtained directly from unsaturated monomers by free-radical polymerization most commonly in aqueous media (Emulsion/ Suspension). The mechanism involves the initiation of radicals, stabilized by surfactants in the media and subsequent addition of monomers to propagate the polymer.

The process can be done in batch, semi-batch or by continuous polymerization. Homogenization of the monomers in water can also be employed (Micro-suspension/ Mini-emulsion). Also, termination can be avoided by utilizing stable-free radicals (Living). Particles generated by this method typically range from 10 nm to over 200 nm, however, larger sizes in the micron range can be obtained, especially in Dispersion polymerization, wherein the reaction mixture starts out as a homogeneous solution in an organic solvent and the resulting polymer precipitates as spherical particles, stabilized by a steric barrier of dissolved polymer. The final polymer particle size is determined by the inherent polymer aggregation behavior under a given set of conditions. Other direct polymerization such as cationic in aqueous media, have been successfully made utilizing specialized catalyst that can tolerate water, with resulting polyolefin particles generated in the nm to 200 nm range. The compositions of these polymer particles, are typically limited to olefin or unsaturated monomer building blocks such as styrene, (meth) acrylic, (meth) acrylonitrile, butadiene, ethylene and propylene. Molecular weight of the polymer particle, as well as the size and distribution, can be controlled by the initiator, monomer surfactant concentration and polymerization conditions.
Indirect Waterborne Methods

**Dissipation**
Particles can be generated in aqueous media from polymers that are inherently comprised of hydrophilic components such as alkali (Na⁺, Li⁺, K⁺) sulfonated moieties, and a hydrophobic backbone. These polymers, readily disperse in water to generate particles (hence waterborne), and are also referred to as “Dissipatable Polymers”. These polymers, are typically condensation type, such as polyesters, polyamide, polyimides, polyester amides, polyurethanes. Typically, the resin is heated in water to above the glass transition temperature (Tg) of the polymer, to generate self-stabilized particles without the necessity of surfactants.

The particle size, is in the nm to 250 nm range, and controlled by the concentration of sulfonated species, and to a lesser extent, its molecular weight and overall composition. Larger particle sizes in the micron range can also be achieved by growing the submicron particles through coalescence with the controlled addition of di or multi-valent cations (Mg²⁺, Zn²⁺, Ca³⁺) above the resin Tg, as well as increasing the ionic strength of the colloid by the addition of water soluble species with heat.

**Phase Inversion Emulsification**
Hydrophobic polymers (oil-like) when heated in molten phase, or dissolved in organic solvents can be converted to polymer particles by the addition of water until a saturation thermodynamic inversion proceeds wherein the water droplets in oil inverts to an oil droplets in water. The oil droplets comprised of the polymer is then cooled to below its glass transition and the solvent (optionally) is removed by distillation.

The hydrophobic polymers are typically comprised of acidic moieties, such as carboxylic acids, which are neutralized with ammonia or amines. Surfactants can be added to stabilize the final emulsions. The particle size, is in the nm to micron range, and can vary from unimodal to multimodal distribution. The compositions of these polymer particles, are typically limited to condensation type polymers comprised of acidic moieties at chain ends such as polyester resin with acid values ranging from 8 to 20 mg of KOH/ g.

**Homogenization**
Hydrophobic Polymeric resins dissolved in low boiling point (< 90°C) organic solvents immiscible with water, can be homogenized (high energy mixing) in the presence of surfactants in water to result in stabilized oil droplets in water. The solvent is then distilled (flashed) from the oil droplets to result in polymer particles in water. The particle size, is in the nm to micron range, and typically with broad distribution. The compositions of these polymer can be quite broad, and are only limited to hydrophobic polymers soluble in low boiling point organic solvents. Alternatively, hydrophobic monomers, either unsaturated (chain type) or condensation type (organic diols) can also be homogenized in water in the presence of surfactants to result in oil droplets, which can then be polymerized by free-radical polymerization, or by interfacial polymerization (condensation) with water soluble diacids or diamine. Additionally, use of both monomers and polymers can lead to core-shell structures. The particle size, is typically in the micron range with broad distribution.
In principle, any polymer can be pulverized to smaller particle size range, but must have some brittleness characteristics, and the final size range depends on these mechanical properties.

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COACERVATION

Coacervation, involves the separation of a liquid phase of coating material from a polymeric solution and wrapping of that phase as a uniform layer around suspended core particles. Coacervation may be brought about when the surface energies of the core material and coating material are adjusted by varying a parameter of the system such as temperature, pH, or composition, for example. The coating material is then solidified by means of heat, cross-linking, or solvent removal techniques. The particle size, is typically in the micron range with broad distribution.

PULVERIZATION (GRINDING)

Pulverization (grinding) methods of bulk polymers can also yield micron size polymer particles. These methods involve several steps, comprised of fits milling to millimeter size particles followed by high energy fluidization in chambers wherein the particles collide and breakdown to smaller particles. These polymer particles can also be classified such as fractionating the size ranges suspended in air (cyclone chamber). The particle size, is typically in the micron range with broad distribution. The particle morphology, is irregular, but can be spheronized by applying heat to the suspended particles.

ABOUT THE XEROX RESEARCH CENTRE OF CANADA

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