

# ADVANCES IN POLYMER SCIENCE

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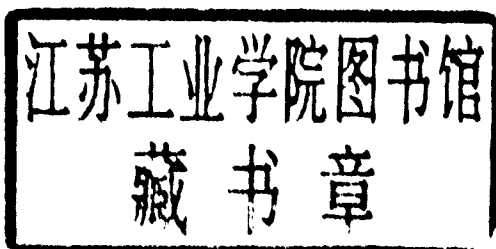
## Polymer Physics and Engineering



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With contributions by  
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# Generation, Characterization, and Modeling of Polymer Micro- and Nano-Particles

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Polymer micro- and nano-particles are important in many technological applications, including polymer blends or alloys, biomaterials for drug delivery systems, electro-optic and luminescent devices, and polymer powder impregnation of inorganic fibers in composites. They are also critical in polymer-supported heterogeneous catalysis. This article reviews recent progress in experimental and simulation methods for generating, characterizing, and modeling polymer micro- and nano-particles in a number of polymer and polymer blend systems. A description of the use of gas atomization (of melts) and microdroplet (solution) approaches to generation and characterization of spherical polymer powders and microparticles represents their unique applications, giving the non-specialist reader a comprehensive overview. Using novel instrumentation developed for probing single fluorescent molecules in submicrometer droplets, it is demonstrated that polymer particles of nearly arbitrary size and composition can be made with uniform size dispersion. This interesting finding is ascribed to new dynamic behavior, which emerges when polymers are confined in a small droplet of solution the size of a molecule or molecular aggregates. Solvent evaporation takes place on a time scale short enough to frustrate phase separation, producing dry pure polymer or polymer blend microparticles that have tunable properties and that are homogeneous within molecular dimensions. In addition, it shows how a number of optical methodologies such as Fraunhofer diffraction can be used to probe polymer particles immobilized on two-dimensional substrates or levitated in space using a three-dimensional quadrupole (Paul) trap. Unlike conventional methods such as electron-beam microscopy, the optical diffraction methods provide a unique look inside a polymer particle in a measurement time scale of a few milliseconds, making it attractive to in-line production applications. In particular, it shows that it is possible to use computational neural networks, extensive classical trajectory calculations (i.e., classical molecular dynamics methods) in conjunction with experiments to gain deeper insights into the structure and properties of the polymer microparticles. Overall, it is possible to use the new understanding of phase separation to produce a number of useful, scientifically interesting homogeneous polymer blends from bulk-immiscible components in solution. Additionally, this new knowledge provides useful guidelines for future experimental studies and theory development of polymer and polymer blend micro- and nano-particles, which are not widely studied.

**Keywords.** Polymers, Micro- and nano-particles, Particle characterization, Microdroplet, Gas atomization, Molecular dynamics and neural network modeling, Optical diffraction-based probes

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1

**Introduction**

Polymer particles of different shapes and sizes are critical in numerous applications, including polymer blends or alloys [1], polymer powder spray coating [2], and polymer powder impregnation of inorganic fibers in composites [2] and in polymer-supported heterogeneous catalysis [3–6]. Recently, significant commercial and scientific attention has been focused on multi-component polymer systems as a means for producing new materials on the micrometer and nanometer scale. Composite polymer particles or polymer alloys with specifically tailored properties could find many novel uses in such fields as electro-optic and luminescent devices [7–8], thermoplastics and conducting materials [9], hybrid inorganic-organic polymer alloys, and polymer-supported heterogeneous catalysis.

The feasibility of using gas atomization processing to prepare micrometer-sized spherical particles directly from molten polyolefins was recently demonstrated [10–12]. Gas atomization processing of polyolefins shows promise for efficiently producing large amounts of polymer powders with particle sizes ranging from 25–200 micrometer. However, it is felt that generating monodisperse polymer particles and polymer blend microparticles from bulk-immiscible components may lead to new polymer alloys on the nanometer and micrometer scale with specifically tailored material, electrical, and optical properties. The microparticle generator will offer a new tool for studying multi-component polymer blend systems in femtoliter and attoliter volumes, where high surface area-to-volume ratios play a significant role in phase separation dynamics.

Recently, a new experimental method for producing polymer particles with arbitrary size and composition was reported [13]. The method is based on using droplet-on-demand generation to create a small drop consisting of a polymer mixture in some solvent. As the solvent evaporates, a very precise polymer particle is produced. These particles in the nano- and micrometer size range will provide many unique properties due to size reduction to the point where critical length scales of physical phenomena become comparable to or larger than the size of the structure. Applications of such particles take advantage of high surface area and confinement effects, leading to interesting nano-structures with different properties that cannot be produced using conventional methods. Clearly, such changes offer an extraordinary potential for developing new materials in the form of bulk, composites, and blends that can be used for coatings, opto-electronic components, magnetic media, ceramics and special metals, mi-



cro-or nano-manufacturing, and bioengineering. The key to beneficially exploiting these interesting materials and technology is a detailed understanding of the connection of microparticle technology to atomic and molecular origins of the process. It is felt that microparticle technology may lead to rational approaches and complementary theories of the unresolved problem of phase-separation in polymer blends, as discussed in Sect. 4.

While great success has been achieved in understanding the kinetics of phase-separation in polymeric systems [14–21], finding the conditions that frustrate phase separation in polymer blends remains an elusive goal. To develop materials for new applications, progress in approaches that exploit phase-separation mechanisms as well as approaches that frustrate it are needed. Bates and co-workers reported an approach for generating such unusual structures. Their approach relies on exploiting microphase separation driven by chemical incompatibilities between different blocks that make up block copolymer molecules [22]. Similar approaches on the role of metastable states in polymer phase transitions can be found in a book by Hamley [23] and in the classic, elegant review by Cheng and Keller [21]. Comparatively, however, the microdroplet and gas atomization approaches to generating and characterizing polymers, polymer composites, and alloys on the micron and submicron scale have not been investigated to the same extent despite their theoretical and practical importance.

The present article is intended to discuss state-of-the art experimental approaches to generation, characterization, and theoretical analysis of polymer microparticles. Chemical synthetic routes (such as dispersion and macromonomer techniques) to generating polymer microparticles have been recently reviewed [24–25]. Therefore, we intend here to mention a few examples of chemical synthetic routes to polymer microparticle generation and describe only the very recent important developments in polymer microparticle science and technology. Generation, characterization of polymer powders and microparticles by use of gas atomization and microdroplet approaches will be described in some detail to give the non-specialist reader a comprehensive overview and to represent their unique applications. Using instrumentation developed for probing single fluorescent molecules in submicrometer droplets, it will be demonstrated that polymer particles of nearly arbitrary size and composition can be made with a size dispersion of typically approximately 1%. Extensive classical trajectory calculations (using classical molecular dynamics methods) will be used to gain deeper insights into the structure and properties of the polymer microparticles.

Some comprehensive textbooks covering earlier engineering aspects of polymer powder technology are available [1–2].

## 2

### **Survey of Polymer Powder and Microparticle Generation Techniques**

Fukui et al. [26–27] and Kung et al. [28] reported molecular dynamics simulation of nanometer scale polyethylene (PE) particles generated with  $\leq 12,000$  atoms to gain insight into some thermodynamic properties of ultra-fine polymer

powders. They found that simulation of the molar volume and total energy as a function of temperature resulted in values for melting point, glass transition, and heat capacity that were dependent on the size of the polymer particles. The simulation predicted a reduction of the melting point on comparison to the bulk system. Further, they found that the ratio of surface atoms for the polymer particles was extremely large and surface-free energy was dramatically dependent on the size of the particles. Using a piezoelectric driven droplet generator, Kung et al. [28] produced ultra-fine polymer particles for both water-soluble and water-insoluble polymers. Spherical particles of PEG, PVA, and PVC ranging in size from 300 nm to 10  $\mu\text{m}$  with approximately 1% monodispersity were generated by varying the solution concentration and orifice size [28–29].

Polymer-assisted synthesis of ultra-fine metal or semiconductor particles in solution, to arrange the particles in a matrix in well-controlled fashion, for possible electro-optical applications was recently reported by Scholz et al. [30]. This method allows synthesis of gold nanoparticles by reducing gold chloride. Gold was found to be present in the form of complexes, to the polyelectrolytes, or in form of nanoparticles or larger aggregates, depending on the relative concentrations of the reagents and polymer molecular weight. Using a relaxative auto-dispersion (RAD) process, consisting of preparing an amorphous polymer, vapor depositing the metal onto the polymer, and heat treating Deki et al. [31] obtained ultra-fine metal particles (5–10 nm) embedded in a nylon 11 matrix. An amorphous nylon 11 was prepared by quenching rapidly from the melt by a splat method and high-speed twin roller method. The resulting composites showed colors characteristic of the constituent colloidal metals. The RAD process was used by Masui et al. [32] to prepare ultra-fine particles of cerium oxide dispersed in polymer thin films. Selected-area electron-diffraction patterns of the particles were completely indexed as those of cerium (IV) oxide with cubic fluorite structure, and the lattice constant calculated from the radii of the Debye-Scherrer rings was 5.41 Å. Noguchi et al. [33] developed a similar RAD process for the uniform dispersion of ultra-fine metal particles in a uniform, isolated condition in nylon 11 films. The composite films could be used as electrical, magnetic, optical, and chemical materials.

Hifumi et al. [34] applied ultra-fine platinum particles protected by poly(Me acrylate-*co*-*N*-vinyl-2-pyrrolidone) to immunological detection of methamphetamine (MA). The polymer-protected ultra-fine particles chemically bound anti-methamphetamine monoclonal antibody to their surfaces. The antibody-fixed particles behaved like an antibody in the immunoreaction, making it possible to detect the MA to a concentration of ca. 10 ng/mL. Uda et al. described a similar application of polymer-protected ultra-fine platinum particles to the immunological detection of human serum albumin [35]. Tamai et al. [36] showed that ultra-fine metal particles could be immobilized on fine copolymer particles that were produced by reducing copolymer particles-metal ion complexes. Transmission electron microscopy and X-ray diffraction were used to confirm that ultra-fine noble metal particles with a diameter below 10 nm were formed and uniformly immobilized on the surface of copolymer particles.

Chen et al. [37] studied a series of complexes of styrene-4-vinylpyridine copolymers or poly(4-vinylpyridine) and transition metal chlorides. The transition metal-polymer complexes were used to prepare ultra-fine metallic particles dispersed in a polymer matrix by chemical reduction. Upon reduction, the metal ions were transformed into the corresponding nanometer scale metal particles with the protective polymers preventing the metal particles from oxidation and excessive aggregation. Ohtaki et al. reported the effects of polymer support on the substrate selectivity of covalently immobilized ultra-fine rhodium particles as a catalyst for olefin hydrogenation [38].

Synthesis of cobalt nanoparticles in a polystyrene/triphenylphosphine polymer matrix was reported by Leslie-Pelecky et al. [39] who showed that magnetic properties of the as-synthesized nanocomposites ranged from super-paramagnetic to ferromagnetic with coercivities on the order of 130 Oe. They found that annealing in vacuum produced coercivities of up to 600 Oe and remanence ratios of up to 0.4.

A method for cationic polymerization of bulk liquid monomers that incorporates ultra-fine metal particles into polymer matrices has been reported by El-Shall and Slack [40]. In this technique, pulsed-laser vaporization was used to initiate polymerization in the gas phase and cationic oligomers were injected into the monomer liquid phase, forming metal clusters that rapidly condensed to form ultra-fine metal particles which provided catalytic centers for the propagation of the polymer chains. Using two kinds of ultra-fine CdS particle-dispersed acrylonitrile-styrene polymer films, Hayashi et al. [41] showed that narrowing particle size distribution enhanced the values of third-order nonlinear optical susceptibility due to the decreasing overlap between the higher energy levels and the lowest energy level in the UV-visible adsorption spectra.

Spherical ultra-fine polymer particles (10–35 nm) were prepared by chemical polymerization of aniline in an inverse water-in-oil microemulsion [42]. This microemulsion method provided a denser, more uniform and compact film of higher condensation than that produced in an aqueous medium [16].

Titania and silica glass thin films containing Au and Pt ultra-fine particles can be prepared under ambient temperature and pressure using a sol-gel process described elsewhere [43]. The sol-gel processing conditions can be adjusted to give Au particles with the smallest mean diameter of 2.8 nm, leading to films showing plasma absorption at 530–620 nm and absorption coefficients up to  $1.0 \times 10^3 \text{ cm}^{-1}$ . Tsubokawa and Kogure [44] reported on surface grafting of polymers onto inorganic ultra-fine particles. They prepared polymer-grafted ultra-fine titania, silica, and ferrite particles by reacting functional polymers containing terminal hydroxyl or amino groups, such as poly(propylene glycol) and diamine-terminated di-Me siloxane with acid anhydride groups on these ultra-fine inorganic particles [44]. The percentage of grafting increased with the increasing acid anhydride group content of the surface. The polymer-grafted ultra-fine particles gave a stable colloidal dispersion in organic solvents [44].

Neinhaus et al. [45] used simple model systems such as ultra-fine  $\text{Fe}(\text{OH})_3$  particles (approximately 30 Å in diameter) with pronounced dynamical features

to get deeper insight into the complicated dynamics of large molecular networks such as the cation exchanger Dowex 50 W solvated with 60 wt. % aqueous sucrose. For such systems, they observed broad diffusional lines of varying widths in the Mossbauer spectra recorded at 80–350 K, proving the bounded nature of the diffusion [45].

The preceding section shows that relatively little information on polymer microparticles is available in the scientific journal literature, which is surprising considering their potential technological importance. Comparatively, much work on novel production methods and technological applications of this special class of materials has been disclosed in the patent literature by our gifted industrial colleagues. To appreciate the useful application in the design of polymer microparticles, we intend in the next section to outline briefly and describe only the recent important developments in the field.

## 2.1

### Survey of Patent Literature

Table 1 shows a listing of patents on production methods and applications of polymer micro and nanoparticles. Recently, Otaigbe et al [46] described a method for making polymer microparticles, such as spherical powder and whiskers (a whisker is defined here as a polymer microfiber with  $<100\text{ }\mu\text{m}$  in length and a diameter of  $<10\text{ }\mu\text{m}$ ). The method involves melting a polymer under conditions that avoid thermal degradation of the polymer, atomizing the melt in a special gas atomization nozzle assembly in a manner to form atomized droplets, and cooling the droplets to form polymer microparticles. The gas atomization parameters can be controlled to produce polymer microparticles with desired particle shape, size and distribution. The dynamics of the gas atomization processing method and the properties of the product polymer microparticles are described in Sect. 3. Handyside and Morgan [47] used rotary, two-fluid, or ultrasonic wave melt atomization processes to prepare thermosetting polymer powder compositions suitable for powder coating processes. The thermosetting resin may consist of polyester or epoxy polymer containing a curing agent and one or more coloring agents. The melt-atomized powder is characterized by improved particle size distribution and by a generally rounded particle shape [47].

Noid et al. [48] used a new device called a microdroplets-on-demand generator (MODG) to produce polymer micro- and nano-particles from solution. The proof of concept was demonstrated using poly(ethylene glycol) microparticles generated with the MODG and captured in a microparticle levitation device. The potential application of the MODG in materials science and technology is described later.

Aoki et al. [49] developed a method for making aqueous dispersions of ultra-fine cross-linked diallyl phthalate polymer particles with average diameter 10–300 nm by polymerizing aqueous solutions containing up to 15% diallyl phthalates in the presence of 7–30% (on diallyl phthalate) water-soluble polymerization initiators without the presence of surfactants. The dispersions are useful as

**Table 1.** Examples of patents on production methods and applications of polymer micro and nanoparticles

Method	Microparticle	Application	Ref.
Gas atomization	Polyolefins and blends, and Epoxies and PET	Polymer microparticles	46, 47
Microdroplet	PEG, PS, EVA, blends	Polymer micro and nanoparticles	48
Dispersion polymerization	Diallyl phthalate polymer	Rubber and plastic modifiers	49
Free radical polymerization	PMMA	Good purity powders for medical uses	50
Melt blending	Polyolefins	Adsorbents and antiblocking agents	51
Mixing and ionization	Metal salt and PET	Electrically conducting polymers	52
Ultrasonic grinding	PTFE	Molding compounds	53
Macromonomer	Poly ( <i>N</i> -vinylacetamide- <i>g</i> -styrene)	Antistatic and abrasion-resistant thin films	54
Dispersion	Fe and poly acrylates	Printing ink jet inks and products	55
	PMMA		56
	Resins and pigments		57, 58
Microphase separation	Poly(2-vinyl pyridine)	Heterogeneous catalysts	59
Grinding	Ca(OH) <sub>2</sub> /Polyolefins	Molding compounds for batteries	60
Dispersion polymerization	Fe and organic polymer	Magnetic permeable composites	61
Dispersion	SiO <sub>2</sub> and PVC	Far-IR radiation emitting films	62
Collision crushing	PE-PP blend	Thin film formers	63
Solution spreading	PS coated on chrome	Composite thin films	64
Dispersion	Au, Pt/organic polymer	Colorant for transparent films	65
Evaporation and precipitation	Pigments and polyolefins	electrostatic photog. image developing agents	66
Dispersion polymerization	Fe and organic polymer	Superparamagnetic composites	67
Graft copolymerization	Vinyl polymers	Acid-rain and soil resistant topcoats	68
Spreading and curing	Polyisocyanates/acrylates	Water-resistant coating	70

**Table 1.** continuing

Dispersion polymerization	Polystyrene	Coatings, adhesives, and medical uses	71
Emulsion polymerization	Vinyl polymers	Alkali and freeze-thaw cycle resistant films	69
Emulsion polymerization	Polyacrylates	Functional coatings and water-resistant adhesives	72–74
Emulsion polymerization	Polyacrylates, etc.	Polymer latexes	75–78
Dispersion	SiO <sub>2</sub> and polyacrylics	Artificial stones	79
Chalcogenation reaction	Polyvinylpyrrolidone and metal compounds	Optical filters and nonlinear optical materials	80
Dispersion	Cuprous halide-dispersed PMMA	Optical filters and nonlinear optical materials	81

modifiers for rubbers and plastics. Organic monomers such as MMA or oligomers, optionally containing polymerization initiators, can be sublimed into reactors in vacuo in inert atmospheres and irradiated with UV light to give ultra-fine PMMA particles (3000 to 5000 Å particle sizes) with good purity [50]. A method for manufacturing spherical and uniform-size polyolefin ultra-fine particles is reported by Yamazaki and Takebe [51]. In this method, the ultra-fine particles (approximately 1.5 µm particle size), useful for supports of absorbents, anti-blocking agents, etc., are prepared by blending polyolefins in liquid organic compounds, melting the blends, cooling to form spherical polyolefin particles, and removing the organic compounds by extraction. In another method [52], electrically conductive polymer ultra-fine particles (0.5 to 10 µm particle size) are prepared by mixing an organic solvent solution of a metal salt with another organic solvent solution of a thermoplastic polymer, cooling or pouring this mixed solution into water or a poor solvent of the thermoplastic polymer to separate the metal salt-containing thermoplastic polymer particles, and conducting the precipitation of metal from the metal salt by the difference of ionization or by the addition of a reducing agent. Powdered poly(tetrafluoroethylene) (PTFE) with a specific surface area of 2 to 4 m<sup>2</sup>/g and a low pressure molding coefficient of 20–150 is ultrasonically ground to give powdered PTFE that has a specific surface area of 4 to 9 m<sup>2</sup>/g and a low pressure molding coefficient of <20 [53]. The PTFE powders are useful for moldings having high density (e.g., 2.1872) and good surface smoothness.

Polymeric ultra-fine particle-adsorbed structures with antistatic, low-friction, and abrasion-resistant properties were prepared by Akaishi, et al. [54]. The structures comprise various substrates laminated with charged polymeric thin films on which charged polymer ultra-fine particles, prepared by a macromon-

omer method are adsorbed. The structures are manufactured by immersing charged polymeric thin film-laminated substrates into a solution containing dispersed charged polymeric ultra-fine particles prepared by the macromonomer method to adsorb the particles on the thin films. As an example of this invention by Akaishi et al. [54], a quartz oscillator microbalance as a substrate was alternately immersed 10 times into solutions of polyallylamine hydrochloride and Na styrenesulfonate homopolymer to form multi-layer films having the homopolymer layer as the outermost layer. This was immersed in a solution containing dispersed *N*-vinylacetamide-grafted styrene polymer ultra-fine particles in the presence of NaCl to give a polymeric particle-adsorbed structure in which the adsorption of particles depended on the concentration of NaCl. For a review of the macromonomer method for preparing polymer particles, the reader is referred to the classic, elegant review by Ito and co-workers [24–25].

Printing inks and products made from them employ polymer and inorganic ultra-fine particles. In one method, Yamada [55] mixed UV-curable resins with ultra-fine Fe-based strong magnetic powders to give ink that could be printed on flexible films, fabrics, or paper to form electromagnetic shields. Polyester acrylate, epoxy acrylate, or urethane acrylate resins were used as the UV-curable binder and the ultra-fine magnetic powder was mixed at 80–100 vol % (based on the binder resins) [55]. In a second method, Suwabe et al. [56] prepared aqueous ink-jet inks, with good anticlogging ability and smudge prevention, by mixing aqueous dispersion of non-film-forming ultra-fine inorganic or synthetic polymer particles (e.g., PMMA particles) with pigments and film-forming resin fine particles. In a third method, Sawada et al. [57] and Uraki et al. [58] prepared ink-jet aqueous dispersion inks containing dispersed colored resin particles with an average diameter of 50–300 nm that were prepared by kneading organic pigments with water-soluble inorganic salts and water-soluble solvents in water and mixing with aqueous dispersions containing fine resin particles. The inks were easily filtered through a 0.45- $\mu\text{m}$  membrane to form ink showing good discharge ability and transparency.

Composite structures consisting of metallic nanoparticles coated with organic polymers or organic polymer blend nanoparticles have been reported [59–67]. Funaki et al. [59] prepared a metal-organic polymer composite (especially porous) structure composed of a microphase-separated structure from a block copolymer in which a metalphilic polymer chain and a metalphobic polymer chain are bonded together at each end, and ultra-fine metal particles (<10 nm) were contained in the metalphilic polymer phase of the microphase-separated structure. Preferred polymers are a poly(2-vinylpyridine) and 2-vinylpyridine-isoprene block copolymer. The composite structures just mentioned are useful as functional material (e.g., catalyst) in heterogeneous catalysis. Ehrat and Watriner [60] prepared thermoplastic polyolefin or olefin copolymer powders with average particle size of 80 to 120  $\mu\text{m}$ , by grinding in an impact mill together with fillers, such as Al, Mg and/or Ca hydroxides, carbonates or oxides. The composite mixtures are useful as highly filled molding compositions for battery electrodes or as powder coatings. Tamura [61] developed anisotropic magnetic-per-

meable composites. The composite contains ultra-fine particles of ferromagnetic Fe oxide that are smaller than single domain sizes dispersed in a solid organic polymer as oriented in domain direction of the particles and substantially separated from each other. The composites are prepared by dispersing the particles in a monomer and polymerizing the monomer in a magnetic field. Far-infrared radiation-emitting bodies from polymer microparticles and inorganic compounds have been reported [62]. The bodies are prepared from polymer particles with ultra-fine inorganic particles (e.g.,  $\text{Al}_2\text{O}_3$  or  $\text{SiO}_2$ ) bonded to their surfaces. The bodies are useful for accelerating fermentation, preserving fresh food, and promoting plant growth. A typical method for producing the radiation-emitting bodies involves mixing an aqueous dispersion of PVC particles (2  $\mu\text{m}$ ) with  $\text{AlCl}_3$  and  $\text{NH}_4\text{OH}$  to give PVC particles with adhering alumina hydrate particles (0.01  $\mu\text{m}$ ). The product can be extruded to give a film that is capable of far-IR radiation emission. The preparation of composite ultra-fine organic polymer mixture particles has been reported by Kagawa [63]. The composite particles were prepared by dissolving two different organic polymers in a solvent with a boiling point higher than the melting point of the polymers, and collision crushing with pressure to give particles with diameter  $<0.05 \mu\text{m}$ . The composite particles have good film-forming property (e.g., formed 5–10  $\mu\text{m}$  film on Al foil that can be readily peeled off from the foil). Ultra-fine polystyrene particles and their composites with other materials can be prepared by adding dropwise polystyrene (weight-average molecular weight 3,840,000) solution (approximately 0.0002% in  $\text{C}_6\text{H}_6$ ) to the surface of  $\text{H}_2\text{O}$  and the solvent evaporated to give a thin layer of ultra-fine particles which could be collected by moving barriers. The particles are cumulated on a chrome plate at a surface pressure of 1 to 50  $\text{dyne/cm}^2$  to give composite materials having area occupied with the particles ranging from 11 to 90%.

Hayashi et al. [65] and Suda et al. [66] developed low-temperature, glass-coloring agents containing ultra-fine noble metal particle – polymer composite and ultra-fine colored polymer particles, respectively. The former coloring agents contain a composite of ultra-fine Au, Pt, Pd, Rh, or Ag particles dispersed in a polymer without coagulation, an organo-metallic compound for fixing the ultra-fine particles in glass, a printing binder, glass powder, and an organic solvent [65]. The low-coloring temperature decreases strain in the colored glass and improves its cutting property. The ultra-fine colored polymer particles developed by Suda et al. [66] are useful for electrostatic photographic image developing agents or cosmetics. The particles are prepared by mixing the pigments with COOH (or ester)-containing polyolefins and non-aqueous solvents and precipitating. Stirring the pigment-coated carbon black, Zn naphthenate, and saponified EVA polymer in organic solvents, evaporating, and precipitating, resulted in particles with a median diameter of 1.564  $\mu\text{m}$ .

Super-paramagnetic composites have been developed by Tamura [22]. The super-paramagnetic composite material consists of ultra-fine particles of ferromagnetic Fe oxide smaller than sizes of single domain structures dispersed as substantially separated in an organic polymer, and prepared by dispersing the



particles in a monomer and polymerizing the monomer. An aqueous dispersion of the ultra-fine particles is prepared by a chemical reaction, hydrophobic coating of the particles by adding a surfactant to the dispersion, separating the particles, and adding the mixture to the monomer. The resulting composite has an extremely low residual magnetization and coercive force [67].

Ultra-fine polymer particles can be prepared from vinyl polymers [68, 69], polyisocyanates and acrylates [70], polystyrene [71], and polyacrylates [72–74] by graft copolymerization [68], spreading and curing [70], dispersion polymerization [71], and by emulsion polymerization [69–74]. The resulting particles are useful for water-resistant coatings and films [68, 70, 72], adhesives [71, 73, 74], and for freeze-thaw cycle resistant films [69]. Ultra-fine particle polymer latex is obtained by emulsion polymerization using a redox-type polymerization initiator in the presence of a compound serving as polymerization inhibitor solution in the monomer [75]. Coagulation of rubber-modified polymer latexes has been reported by Kitayama et al. [76]. In [76], a 30% acrylonitrile-butadiene-Me methacrylate-styrene graft copolymer (melting temperature 90 °C) latex was coagulated with an aqueous solution of  $\text{CaCl}_2$  (11 mmol/L) at a concentration of 12 mmol/L and 95 °C, separated, water washed, de-watered, and dried to form a powdered polymer without any particles  $\leq 200$  mesh. Ultra-fine, particulate polymer latex based on unsaturated monomers with an average size  $< 100$  nm, a cross-linked structure, and glass transition temperature lower than that calculated by weight fraction method can be used to give a film excellent transparency, smoothness, tack, water resistance, and mechanical strength [77]. The polymer particle properties are dependent on the surfactant used. The latex is useful as a component in paints, adhesives, binder, additive for hydraulic inorganic material, fiber processing, reinforcement for optical glass fiber, electroconductive film, paper making, and photosensitive compositions [77]. Stable, aqueous colorants, useful in cosmetics, writing inks, and textiles, are prepared by encapsulating ultra-fine, primary particles with polymers which are not substantially altered in the process [78].

Artificial stone compositions for high-gloss products resistant to chemicals, water, and weathering can be prepared by mixing: 1) hydraulic inorganic material, 2)  $\text{SiO}_2$ -based fly ash with an average particle size 1–20  $\mu\text{m}$ , 3) water-dispersible ultra-fine granular acrylic polymer with an average particle size 50–2000 nm, and 4) pigment [79]. The ultra-fine granular acrylic polymer was prepared by emulsion polymerization.

Ultra-fine particles can be dispersed in organic polymers to form composites that exhibit good transparency and stability, making the composites useful for selective wavelength-shielding optical filters and nonlinear optical materials [80, 81]. Yao and Hayashi [80] prepared ultra-fine particle-dispersing polymer compositions from the reaction (which forms ultra-fine particles) of metal compounds and chalcogenation agents in an organic solution of polymer bearing pyrrolidone groups and stabilizer, followed by removal of the solvent. A typical preparation of the ultra-fine particle-dispersing polymer compositions consists of injecting 0.5 ml  $\text{H}_2\text{S}$  (g) into a tube containing 3.08 mg  $\text{Cd}(\text{NO}_3)_2 \cdot 2.4\text{H}_2\text{O}$  and 0.01 g polyvi-