

Strategies in Polymeric Nanoparticles and Hybrid Polymer Nanoparticles

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Abstract

Polymer nanoparticles have gained significant research interest in increasing number of fields. Various techniques have been used for the synthesis of polymeric nanoparticles including polymerization of monomers as well as dispersion or processing of the synthesized polymers. While performing nanoparticle synthesis, the resulting particle size, distribution, cost, and end use must be considered beforehand. In addition to polymeric nanoparticles, certain hybrid polymeric nanoparticles have been prepared. The hybrid polymeric nanoparticles include the combination of polymer nanoparticles with other organic or inorganic particles such as carbon nanotube, graphene, graphene oxide, carbon black, silica, zinc, nickel, and several metal oxide nanoparticles. This review actually covers the basics and strategies used for the design of polymer nanoparticles and hybrid polymeric nanoparticles. In future, several crucial parameters must be identified and improved to design these nanoparticles to attain desired properties for high performance applications.

Keywords

Polymer, Nanoparticles, Hybrid, Polymerization, Application

Introduction

Although, the arena of polymer nanoparticles is new, it is quickly growing and playing an essential role in wide spectrum of applications ranging from electronics, devices, and biomedical to environmental technology [1, 2]. The term polymeric nanoparticle is collectively used for any type of polymer nanoparticle, nanospheres, nanoellipsoids, or other similar nanostructures. The advantageous properties and applications of polymeric nanoparticles can be obtained and optimized using various preparation techniques. Polymeric nanoparticles can be prepared using as prepared polymers or through polymerization of the desired monomers. Techniques such as evaporation, precipitation, osmosis, salting out, emulsion, and interfacial polymerization have been used for the preparation of polymeric nanoparticles [3-5]. The monomer polymerizations through emulsion, micro-emulsion, and mini-emulsion are also popular. Thus, these nanoparticles can be prepared using polymers and copolymers along with different solvents and stabilizers. There have been continuous search efforts for synthesizing polymeric nanoparticles with optimum properties using suitable stabilizing agent and solvent system. Key properties of polymer nanoparticles depend on particle size and the particle size distribution. Hybrid nanoparticles have been prepared using polymer nanoparticles and inorganic nanoparticles [6-10]. Efficient hybrid nanoparticle interfacial adhesion and uniform dispersion may lead to transparent films, coatings, and membranes. However, the fundamental knowledge about the

processes in the preparation of hybrid polymer nanoparticles is still limited. The control of size, distribution, and morphology of hybrid nanoparticles are not also fully understood. This review article examines unique chemical and physical aspects of polymer-based nanoparticles. It covers different preparation techniques for polymeric nanoparticles and insists parameter control such as particle size, particle size distribution, surface area, etc. Future direction and opportunities for the development of new polymeric and hybrid nanoparticles have also been portrayed. Exploration of structure-property relationship of polymeric nanoparticles is challenges to open new frontier of these materials.

Polymeric Nanoparticles

Nanoparticles can be defined as solid or colloidal particles having size in the range 10 - 100 nm [11]. Polymer nanoparticles are usually nanospheres, nanocapsules, or oval nanoparticles [12]. The organic molecules or inorganic nanoparticles can be adsorbed on nanoparticle surface or encapsulated in the particles to form a core-shell structure [13]. The size and shape of nanoparticles are of course essential to attain improved material properties for various applications such as optics, catalysis, electronics, etc. The nanoparticle size, size distribution, surface area, and homogeneity are still challenging. Polymer nanoparticles have been used as building blocks to create mesoscale assemblies. The enhanced inter-particle interactions and perfect geometric shape are essential to develop self-assembled ordered mesoscale structure. The polymer nanoparticle assemblies have been used instead of inorganic nanoparticles. Different types of polymers have been used to form polymeric nanoparticles. Variation in polymer architecture and surface functionalization may affect the inter-particle interactions and final nanoparticle properties.

Processing of Polymeric Nanoparticles

Polymeric nanoparticles have been prepared using range of facile techniques [14]. Figure 1 shows the schematic for the preparation of polymer nanoparticles from monomers. Polymer can be directly converted to polymeric nanoparticles using different techniques such as evaporation, precipitation, salting out, dialysis, supercritical fluid technology, etc. On the other hand, monomers can be *in situ* polymerized through emulsion, interfacial, and dispersion methods. The polymerization of monomers through micro-emulsion, mini-emulsion, and free emulsion have found success. Figure 2 shows osmosis method for the preparation of polymeric nanoparticles. As the name osmosis indicates, it uses a semipermeable membrane as physical barrier to the polymer solution [15]. The membrane allows passive transport of solvent molecules to control the mixing of polymer solution with non-solvent.

Figure 3 shows the expansion of supercritical solution in liquid solvent [16]. The nano-sized particles were attained through the suppression of particle growth in expansion jet. The nanoparticles were collected in solvent, and can be dried through solvent evaporation. Figure 4 shows the emulsion polymerization method utilizing solvent, monomer, stabilizer,

and surfactant/initiator. The difference between the emulsion polymerization and mini-emulsion polymerization is basically the use of low molecular weight compound as stabilizer. Mini-emulsion polymerization needs high-shear to attain steady state. The emulsion method may produce colloidal polymer particles of high molar mass. Micro-emulsion polymerization is also an effective approach for nano-sized polymeric nanoparticles. The particle size and average number of chains per particle are smaller in this polymerization [17]. Table 1 shows the differences among various emulsions techniques [18-20]. In typical emulsion polymerization, usually water soluble initiator is added to thermodynamically stable emulsion. The emulsion possess swollen micelles. These particles with monomer and initiator are completely covered with the surfactant molecules. The polymer chains are formed in the micelles. The emulsions are finally broken due to increase in the particle size of micelles.

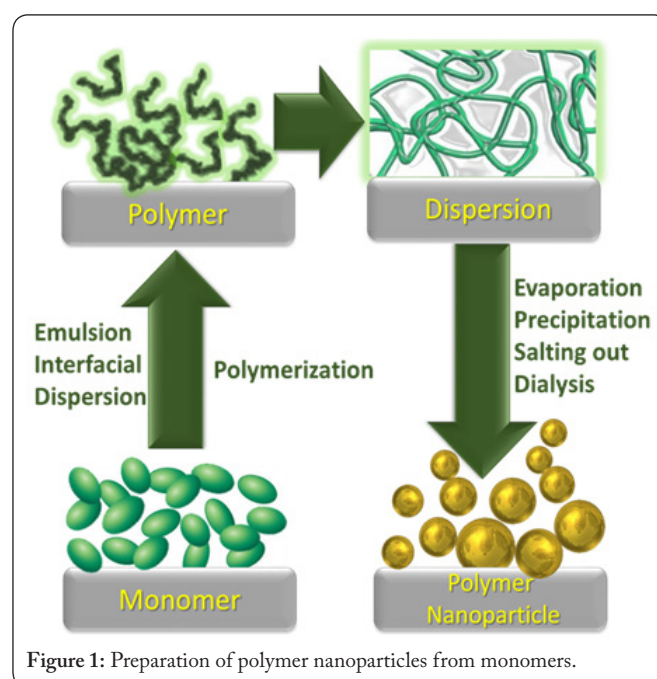


Figure 1: Preparation of polymer nanoparticles from monomers.

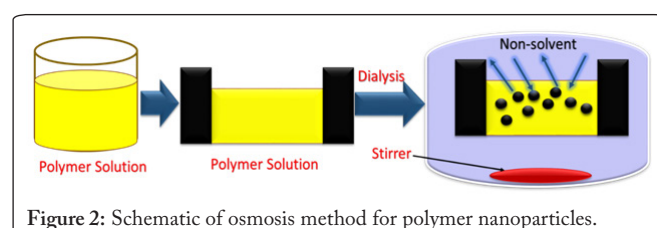


Figure 2: Schematic of osmosis method for polymer nanoparticles.

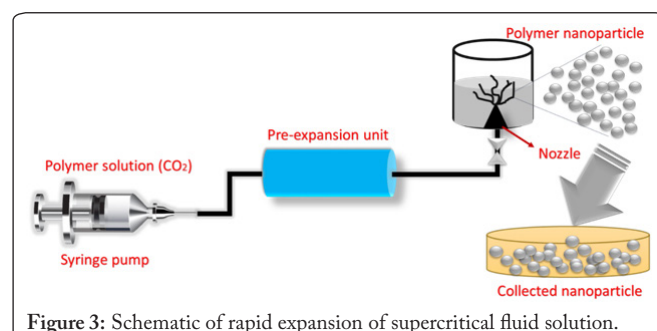


Figure 3: Schematic of rapid expansion of supercritical fluid solution.

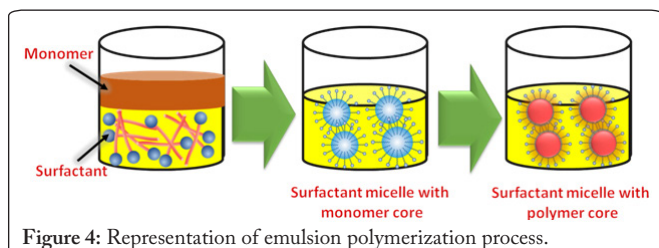


Figure 4: Representation of emulsion polymerization process.

Table 1: Comparison of emulsion polymerization systems.

	Particle size	Droplet size	Polydispersity
Emulsion	<300 nm	1-10 μm	Low
Mini-emulsion	10-30 nm	<200 nm	Very low
Micro-emulsion	<100 nm	~10 nm	Very low

Hybrid Polymeric Nanoparticles

Hybrid polymeric nanoparticles may have ability to combine the processability of polymers with mechanical, thermal, and optical properties of inorganic nanoparticles. The combination of properties may be useful for wide range of commercial, engineering, and device applications. In this regard, ordered array of silica spheres and polymer nanoparticles have been designed. The polymer nanoparticles incorporated gold nanospheres have also been designed. Thus, the core-shell particles and composite particles have been reported [21-23]. The polymeric nanoparticle have also been combined with the nanocarbons such as multi-walled carbon nanotube [24-31]. Graphene and graphene oxide nanoparticles have also been combined with the polymeric nanoparticles to form hybrid nanoparticles [32, 33]. Fullerene and nanodiamond are also excellent contenders to form combinations with the polymers to form hybrid nanoparticles [34-38]. The interactions between the polymeric nanoparticles and other organic or inorganic nanoparticles must be strengthened to avoid aggregation. The physical adsorption of polymers nanoparticle on inorganic/organic nanoparticles may lead to better dispersion and affect the rheology and viscosity of the polymer used. However, physical polymer nanoparticle-other nanoparticle interactions can be easily dissolved compared with the covalently attached nanoparticles. There have been increasing scientific interest in hybrid nanoparticles owing to high electrical conductivity, thermal conductivity, strength, stiffness, optical, and other physical properties.

Technical Significance and Outlook

From the point of view of materials chemistry, fundamental and advances of polymeric nanoparticle materials are essential to understand. Manipulation of individual nanoparticles and hybrid nanoparticles can be exploited for self-assembly procedures. Linear homopolymers have been most preferably used to develop polymeric nanoparticles. The liquid crystalline polymers and block copolymers also show high aspect ratio to promote supramolecular organizations. Hybrid polymeric nanoparticles may contribute to the development of future optical and electronic devices, engineered products for

automotive and aerospace, and biomedical applications [39-41]. The hybrid polymeric nanoparticles may also be useful for coatings [42-46], textiles [47], electromagnetic interference shielding [48, 49], and sensors [50, 51]. *In situ* generated nanoparticles and nanostructure in cross-linkable resin have yielded novel systems with improved properties. Mascia et al. [52, 53] studied the generation of siloxane domains in epoxy network to form epoxy-silica hybrids. Amine-silane functional bisphenol-A resin was reinforced with siloxane precursor using tetraethoxysilane and glycidoxypropyltrimethoxysilane coupling agent. The *in situ* developed hybrids have shown enhanced mechanical properties such as modulus, strength, and ductility, at low temperature curing. The epoxy-silica hybrids can be employed for uptake of water from environment. In another attempt, molybdate anions were introduced in epoxy-silica hybrid domains using *in situ* method [54]. Incorporation of molybdate anions in epoxy-silica network has enhanced the corrosion protection capability of the coatings. Mallakpour and Behranvand [55] designed nanoparticles using biodegradable polymers. Owing to small size and large surface area, polymeric nanoparticles have been employed in application areas such as drug delivery systems, biosensors, nanoreactors, and catalysts. Polymeric nanoparticles in delivery systems must be biocompatible and biodegradable with the living systems in terms of non-toxicity and non-antigenicity. Polymeric nanoparticle-based materials with unique physical and chemical characteristics are also demanding for employment in bio-imaging and diagnostics. The main advantage of polymeric and hybrid nanoparticles is as composite additives. These nanofillers may have several advantageous properties relative to the traditional additives at low loading requirements. In this regard, efficient nanoparticle dispersion and nanoparticle-nanoparticle interfacial adhesion may allow exciting possibilities for developing films, coatings, and membranes. There are several chemical and physical aspects associated with the polymer-based nanoparticles. Future directions and opportunities for the development of new hybrid materials must be focused. Understanding the structure-property relationship of polymer-based nanoparticle materials is challenging to discover new frontiers in these hybrids.

Summary

The field of polymer nanoparticles is relatively new and needs lot of attention on fundamentals as well as advance applications of these materials. The review offers not only primary information regarding the polymeric and hybrid nanoparticles, but also presents the fabrication strategies and future prospects of these intriguing polymer nanoparticles. Polymer nanoparticle is a state-of-the-art technology which demands appropriate monomer or polymer dispersion, initiator, surfactant, precipitant, and other optimum process conditions for the preparation of small size, high surface area, and smooth surface nanoparticles. The controlled parameters may definitely lead to the desired property enhancement of these nanoparticles. To further enhance the potential of polymer nanoparticles, various organic and inorganic

nanoparticles have been processed with these nanoparticles. The hybrid polymeric nanoparticles can be used for range of potential applications where polymers alone are ineffective. Future research on the development of polymeric and hybrid polymeric nanoparticle should be focused on precise control over particle size and morphology for potential relevance. Advances may lead to the commercial utilization of polymeric nanoparticles for high performance applications.

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