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Review

Synthesis of polymer–inorganic filler nanocomposites in supercritical CO$_2$

Yuvaraj Haldorai [a,b,*], Jae-Jin Shim [a], Kwon Taek Lim [c]

[a] School of Chemical Engineering, Yeungnam University, Gyeongsan, Gyeongbuk 712-749, Republic of Korea
[b] Department of Materials Science and Engineering, University of Texas at Dallas, Texas, USA
[c] Division of Image Science and Engineering, Pukyong National University, Pusan 608-739, Republic of Korea

A R T I C L E   I N F O

A B S T R A C T

Organic–inorganic nanocomposites have become a prominent area of current research and development in the field of nanotechnology. Nanocomposites are materials composed of a polymeric host in which particles of nanoscale dimensions such as metal oxides, carbon materials, semiconductor metallic nanocrystals, and clays are incorporated. Nanocomposites are currently being used in a number of fields and new applications are continuously being developed including thin-film capacitors, electrolytes for batteries, biomaterials and a variety of devices in solar and fuel cells. The synthesis of polymeric composites usually involves solution chemistry, and because of this, the use of a large amount of organic solvents may raise serious concerns regarding air and water pollution. Therefore, effective and green synthetic methods have gained a strong interest in the synthesis of polymeric composites. During the past two decades, supercritical carbon dioxide (scCO$_2$) has attracted a great deal of attention as an alternative to the conventional processing. This review article provides an overview on the synthesis of polymer–inorganic filler nanocomposites in scCO$_2$.

Contents

1. Introduction

Nanotechnology is the study of the science and technology of nanostructured materials at the dimensions from roughly 1 to 100 nm. Due to their small dimensions, the physical properties of nano-structured materials differ fundamentally from those of the corresponding bulk materials. In the last two decades, the synthesis of organic–inorganic nanocomposites has been intensely studied due to their extraordinary properties and wide-spread potential applications [1–4]. Nanocomposite materials play a major role in the development of advanced nanomaterials as they exhibit unique properties that cannot be found in traditional composites [1,2]. Research in functional nanocomposites is supported by the growing interest of chemists, physicists, biologists and material scientists who are looking to fully exploit this opportunity for creating smart

materials that benefit from the best of the three realms: inorganic, organic and biology. Organic–inorganic nanocomposites are generally organic polymer composites with inorganic nanoscale building blocks. They combine the advantages of the inorganic material (e.g., rigidity, thermal stability) and the organic polymer (e.g., flexibility, dielectric, ductility and processability). Moreover, they also contain special properties of nanofillers leading to materials with improved properties. A defining feature of polymer nanocomposites is that the small size of the fillers leads to a dramatic increase in interfacial area as compared with traditional composites [5–13]. This interfacial area creates a significant volume fraction of interfacial polymer with properties different from the bulk polymer even at low loadings. Nanocomposites do not only represent new materials for academics, but their improved or unusual features allow applications in many areas such as optics, ionics, electronics, energy, environment, biology and medicine. Applications include smart membranes and separation devices, functional smart coatings, photovoltaic, fuel cells, photocatalysts, sensors, smart microelectronics, nanophotonics, innovative cosmetics, therapeutic vectors and combine targeting, imaging, controlled drug release, automobiles and packing industries, etc.

There are three general methods used to prepare organic–inorganic nanocomposites:

The organic component can be introduced as (i) a precursor, which can either be a monomer or an oligomer, (ii) a preformed linear polymer (in molten, solution, or emulsion states), or (iii) a polymer network, physically (e.g., semi-crystalline linear polymer) or chemically (e.g., thermosets, elastomers) cross-linked. The mineral part can be introduced as (i) a precursor or (ii) preformed nanoparticles. Organic or inorganic polymerization generally becomes necessary if at least one of the starting moieties is a precursor. This leads to the following three general methods for the preparation of organic–inorganic nanocomposites according to the starting materials and processing techniques: blending or mixing, sol–gel processes, and in situ polymerization. Blending is simply mixing of the inorganic fillers into the polymers; a sol–gel process can be done in-situ in the presence of a preformed organic polymer or done simultaneously during the polymerization of the monomer(s); the method of in situ polymerization first involves the dispersion of inorganic fillers in the monomer(s) followed by polymerization. In addition, considerable efforts have been devoted to the design and controlled fabrication of hybrid nanocomposite particles with tailored morphologies in recent years. The preparation, characterization, properties, and applications of nanocomposites have become a quickly expanding field of research. Even though several books and review articles [14–29] that were partly devoted to the polymer/inorganic filler nanocomposites, this subject has never been reviewed.

Several advanced polymeric nanocomposites have been synthesized with a wide variety of fillers such as metals, semiconductors, carbon nanotubes, and magnetic nanoparticles. Many attractive properties of polymers such as non-corrosiveness, light weight, mechanical strength, and dielectric property can be utilized to make multifunctional materials. However, processing of polymers generally employs a large quantity of organic solvents that are noxious and harmful to the environment. Thus, processing with supercritical fluids have attracted a great interest as an alternative to the conventional processing. There has been a continuing growth of interest in replacing conventional organic solvents by environmentally friendly $scCO_2$ in the chemical processes.

The aim of this review is to summarize the recent developments in this field based mainly on the literature during the last two decades. However, it is impossible to completely describe this field due to the vast number of published papers on polymer–inorganic filler nanocomposites in $scCO_2$. Therefore, this review will give a general overview of the techniques and
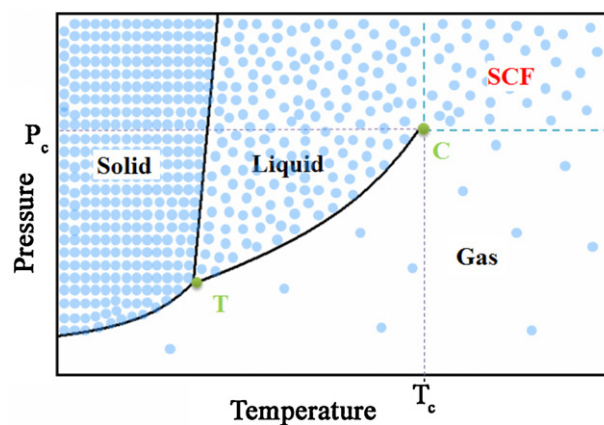

Fig. 1. Carbon dioxide temperature–pressure phase diagram.

strategies used for the preparation of polymer-surface-modified inorganic filler nanocomposites in $scCO_2$. Selected examples that represent different routes and systems will be reported. More detailed descriptions on specific themes will be referred from related references.

2. Supercritical CO₂

Large amounts of organic solvents are used worldwide every year as reaction media, dispersants, processing, and cleaning agents. Reducing the emissions of hazardous volatile organic compounds has been vigorously pursued. To this account, an environmentally benign solvent for chemical synthesis and processing to reduce the emission of hazardous compounds has gained a keen interest.

A supercritical fluid is any substance at a temperature and pressure above its thermodynamic critical point. It has unique properties such as a liquid-like density (which allows for solvation of many compounds) and a gas-like diffusivity (which has important implications for reaction kinetics). Moreover, these properties are "tunable" by varying the pressure and/or temperature [30]. Supercritical fluids are being examined as a substitute for organic solvents in several industrial and laboratory processes. The choice of which supercritical fluid is used for chemical and industrial processes must be determined by a compromise of practical factors. Supercritical processes are associated with costs arising from the need for high pressure reactors and therefore solvents with low critical constants will reduce this cost and associate with ease of handling, solvent reactivity and safety factors. Most of the organic solvents suitable for supercritical applications are flammable, often dangerously so. They also tend to have potentially harmful effects on people's health and the environment. Although water shares some of these advantages of non-toxicity and availability, the high critical parameters (critical temperature (T_c) = 374.4 °C, critical pressure (P_c) = 22.12 MPa) and corrosion problems with metal reactors impede its wider application.

Carbon dioxide (CO_2) is the most commonly used supercritical fluid due to its moderate critical constants (T_c = 31.0 °C, P_c = 7.38 MPa) [31] and its non-flammable and innocuousness nature. The temperature–pressure phase diagram CO_2 is shown in Fig. 1. Not only is CO_2 naturally occurring and abundant, it is also generated in large quantities as a byproduct in ammonia, hydrogen, and ethanol plants and in electrical power generation stations that burn fossil fuels. CO_2 is a gas that can be easily removed at ambient temperatures and pressures and leaves no solvent residues in the processed material [32]. The ease of its removal contrasts with the high energy-costs of drying for the removal of conventional solvents. The easily tunable density and solvent strength allow facile

control of reactions and processes. Many of the processes for which $scCO_2$ is used are aided by its negligible surface tension, allowing hydrophobic behavior normally associated with liquid to substrate interactions, and other phenomena such as drying-induced substrate damage, to be avoided. This has allowed $scCO_2$ to be utilized as an ideal solvent for the cleaning and processing of delicate electronic components and microdevices [33]. In recent years, $scCO_2$ has also been used in extraction, dry cleaning, nano and microparticle formation, and chemical reactions including polymerizations as a reaction medium [34–43].

3. Surface-modification of inorganic fillers

Compared to the conventional micron-sized particles, nanoparticles have a much higher surface-to-volume ratio. Due to the large surface area per particle [44] volume and the extremely small size, it is difficult to overcome the aggregation by the inherent thermodynamic drive of nanoparticles. Even well-dispersed nanoparticles naturally aggregate to form clusters whose size extends to length scales exceeding 1 μm [13]. As a result, the major challenge for synthesizing polymer nanocomposites is learning how to disperse nanoparticles into a polymer matrix and avoid aggregation of the nanoparticles. Excellent dispersion and interfacial load transfer are usually required to achieve optimum properties of the synthesized polymer nanocomposites. Due to the enormous interfacial area in nanocomposites, the surface energy is an important contributor for the stabilization energy. In order to minimize interface energies between particles and polymer matrix, several surface-functionalization and stabilizing techniques have been developed. There are two basic requirements for a surface-modifier to be used for the stabilization of particles in polymer matrices. Anchor groups are needed for adsorption or covalent binding of the modifier on the particle surface, while other parts interact with the polymer and therefore decrease the interface energy.

3.1. Modification by covalent bond formation

Great attention has been devoted to the surface-modification of inorganic fillers by chemical interaction since it can lead to a much stronger interaction between modifiers and inorganic fillers. Chemical methods involve modification either with modifier agents or grafting polymers. Silane coupling agents are the most popular type of modifier agents. They generally have hydrolysable and organofunctional ends. Organofunctional silanes are often in the form of $RSiX_3$ [45], where X represents a halide, alkoxide, acrylate, amino or alkyl group; and R an organofunctionality. They can act as a bridge between organic and inorganic layers. X is hydrolysable to react with filler surface hydroxyl groups to form a covalently bound siloxy derivative. Many of organosilanes have three hydrolysable substituents on each silicon center which would enable the formation of a cross-linked siloxane network of the condensation of adjacent adsorbed silantriols with each other as well as the O–H groups. The functional groups R in the silanes generally possess one or more non-hydrolysable alkyl or aryl groups which are used to provide compatibility with organic polymers. They may also contain substituent groups that can provide reactive centers for graft formation between a polymer and the filler surface. The reactive substituent groups can be tailored for specific applications and include vinyl, acrylate and methacrylate, chloro, amino, epoxy and mercapto groups.

For trialkoxysilanes, the initiation of the silanization reaction [46–54] occurs through hydrolysis of the alkoxy groups promoted by water molecules either added to the reaction medium or present as a moisture adsorbed on the inorganic filler surface (reaction (1) in Scheme 1). The trivalent silanol head group can participate in
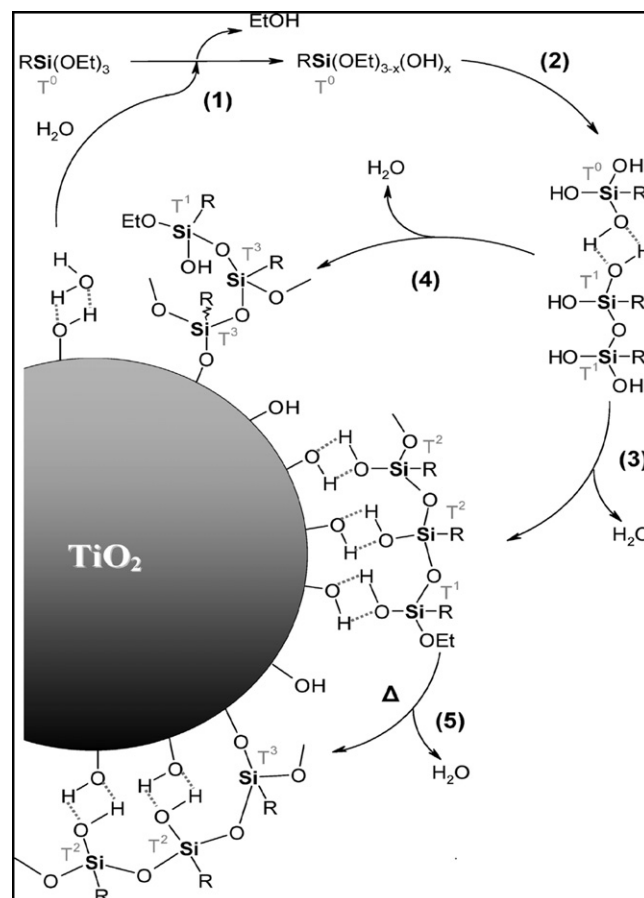
Scheme 1. Schematic representation of the different steps (1–5) of the silanization reaction occurring on the surface of TiO_2 nanoparticles.
Reprinted with permission from [54]. Copyright 2009 American Chemical Society.

multidirectional and interchangeable intra- and interlayer modes of coupling, which can be either covalent (siloxane bonds) or due to physical interaction (hydrogen bonds). The silanol group forms covalent bonding with the either other silanol molecule (reaction (2)) or with the hydroxyl groups present on the surface of the inorganic filler (reaction (3)). Additionally, the formation of siloxane bonds due to the condensation of silanol molecules may also lead to the production of highly branched polycondensed structures (reaction (4)). Finally, a polysiloxane layer on the surface of the particles is formed (reaction (5)), where hydrogen bridges with the surface are the predominant mode of binding [51,55–57]. The robust chemical nature of the obtained silane coatings may offer extensive ways for engineering the surface chemistry at nanoscale [58–62] in the processes of chemical modification, such as immobilization of organic molecules, metal cations and proteins or polymer grafting on silanized nanoparticles [63–66].

The thickness of silane coating is largely determined by the silane concentration in the used solution [50]. Monolayer deposition is usually preferred (reaction (5)) for most applications. However, polycondensed multilayer coating (reaction (4)) and particle agglomeration are difficult to avoid in the utilization of conventional methods based on the use of liquid solvents (e.g., methanol, ethanol, toluene, tetrahydrofuran) [46,56,67–71]. Silanizations performed in solution need a precise control of the amount of water added to the liquid solvent to initiate the reaction in order to prevent polycondensation and multilayer formation. The anhydrous vapor phase deposition is a potential method used for monolayer formation [72]. Nevertheless, this deposition technique

usually requires long-lasting reaction times (4–24 h), high temperatures (330–400 K), and limited to the deposition of volatile silane compounds (e.g., molecules with high vapor pressure and thermal stability). Further, in these vapor processes, only the methoxysilanes can be used without the presence of catalysts [56].

In the search for an alternative sustainable process to overcome the problems encountered in the silane monolayer deposition, the use of scCO$_2$ [73] has been proposed [46,47,53,72–74]. The low viscosity, the absence of surface tension and the inert behavior of scCO$_2$ make it adequate to manipulate complex surfaces, very small pieces of matter and nanostructured materials. Synthesis of inorganic nanoparticles in the scCO$_2$ reaction medium is even reported in the literature [75–81]. These properties of scCO$_2$ allow the complete wetting of substrates with intricate geometries, including the interparticle surface of mesoporous agglomerates and the inner surface of microporous materials [82–84]. Further, in the anhydrous supercritical silanization process, water comes from moisture adsorbed on the powder surface. Thus, the hydrolysis step takes place preferentially near the surface of the inorganic nanoparticles [47].

Recently, García-González et al. optimized a generic method of silanization using scCO$_2$ [54,85–88] for the surface-modification of inorganic fillers in order to obtain new hybrid materials. For the first time the surface-modified TiO$_2$ nanoparticles using octyltriethoxysilane as a silane coupling agent. In the first step, the solubility of silane coupling agent and the reaction kinetics of silanization under scCO$_2$ were studied. This study was performed to control the degree and the quality of the silane coating [54,85]. The next step was screening the properties of silanized TiO$_2$ nanoparticles obtained at different operating conditions through a chemometric analysis [86,87]. Finally, the process was implemented for other substrates (maghemite) and different mono and trialkoxysilanes in order to assess the versatility of the supercritical silanization method [88]. Some typical silane coupling agents used for the surface-modification of inorganic fillers are listed in Table 1.

An improved approach would be modifying the surface of inorganic fillers and the covalent attachment of stabilizing polymer ligands by either the "grafting from" or "grafting to" methods. The "grafting from" technique involves growing the polymer chains from the inorganic backbone, while the "grafting to" technique involves the attachment of preformed polymer chains to the backbone, minimizing agglomeration while strengthening the interaction between the inorganic filler and polymer matrix.

In the "grafting to" method, the surface is first functionalized with an organic component, labeled "O" in Scheme 2. Following this, polymer chains synthesized by conventional polymerization methods are grafted to the surface using one end group of the chain such as "P". Using this approach, the number of polymer chains that one can graft to the surface is generally small because the free volume occupied by each grafted chain acts as a barrier to the attachment of subsequent chains. This means that the "grafting to" approach is increasingly difficult as more chains are added to the surface, limiting the degree of control over the molecular weights and polydispersity.

On the other hand, the "grafting from" approach that uses initiators anchored to the surface, labeled "I", allows chain growth from the surface of a substrate with the chains propagating outward into the solution (Scheme 3). Low molar mass monomer molecules can easily diffuse to the surface, allowing chain growth to occur. As in solution or bulk polymerizations, the initiator is able to polymerize any of the broad arrays of vinyl monomers. Using the "grafting from" approach, the surface density can be controlled by varying the amount of initiator immobilized on the surface of inorganic fillers. For these reasons, the "grafting from" approach has emerged in the literature as the most promising route to synthesize polymer grafted inorganic filler nanostructures in a controlled manner.

Besides the above-described chemical methods, grafting of polymers to nanoparticles can also be realized by irradiation. Zhang and co-workers [89–94] have published a series of studies on irradiation-grafted nanosilica-filled nanocomposites. They found that modification of nanoparticles through graft polymerization was very effective in constructing nanocomposites because of (i) an increase in hydrophobicity of the nanoparticles that is beneficial to the filler/matrix miscibility, (ii) an improved interfacial interaction yielded by the molecular entanglement between the grafting polymer on the nanoparticles and the matrix polymer, and (iii) tailorable structure–properties relationship of the nanocomposites provided by changing the species of the grafting monomers and the grafting conditions since different grafting polymers might bring about different interfacial characteristics.

3.2. Modification involving physical interaction

Surface-modification based on physical interaction is typically implemented by using of surfactants or macromolecules adsorbed onto the surface of filler particles. The principle of surfactant treatment is the preferential adsorption of a polar group of a surfactant to the surface of filler by electrostatic interaction. Amphiphilic molecules, such as stearic acid, oleic acid, oleic amine or long chain alcohols, can adsorb on the particle surface by ionic attractions, hydrogen or coordinative bonding. A surfactant can reduce the interaction between the inorganic filler particles within agglomerates by reducing the physical attraction leading to easy incorporation into a polymer matrix. For example, silica was treated with cetyl trimethyl ammonium bromide (CTAB) to improve the chemical interaction between SiO$_2$ and polymer [95]; SiO$_2$ nanoparticles were modified with stearic acid to improve their dispersion and the adhesion between the filler and polymer matrix [96,97]; nanosized SiO$_2$ was modified with oleic acid, which was bonded to the SiO$_2$ surface with a single hydrogen bond [98–102]. In contrast to small molecular modifiers resulting in only the thin adsorbed layers, some polymers are capable of forming thick, solvable and adsorbed layers on the filler surface. Depending on their structures, the adsorbed polymers may act as dispersants, dispersion stabilizers, or as processing aids. Adsorption of polymer can also promote the surface hydrophobicity of filler particles. Reculusa et al. [103–105] modified the SiO$_2$ surface by adsorption of an oxyethylene-based macromonomer. This macromonomer is mainly hydrophilic due to the presence of ethylene oxide groups, which are able to form hydrogen bonds with silanol groups present on the filler surface. At one of its ends, this molecule also contains a methacrylate group, capable of copolymerizing with styrene (St). Lu and coauthors [106] chose a natural bio-macromolecule, chitosan, as an adsorbent to alter the surface properties of SiO$_2$. Ashmead et al. modified the TiO$_2$ surface using polydimethylsiloxanes or derivatives containing polar hydroxyl or amino substituent. The adsorbed silicones reduced moisture adsorption and aided in preventing agglomeration of TiO$_2$. The adsorption of the silicone on the TiO$_2$ occurs largely by hydrogen bond formation [107].

4. Synthesis of polymer–inorganic filler nanocomposites in scCO$_2$

Generally, there are three preparative methods to synthesize polymer/inorganic filler nanocomposites (Scheme 4). The first is direct mixing or blending of the polymer and the inorganic fillers either as discrete phases (known as melt mixing) or in solution (solution mixing). The second is sol–gel process which starts with a molecular precursor at ambient temperature and then forms metal oxide framework by hydrolysis and condensation. The third is in situ polymerization of monomers in the presence of fillers.

Table 1
Typical silane coupling agents used for the surface-modification of inorganic fillers.

| Abbreviation	Name	Chemical structure
MPS or MPTMS	3-(Trimethoxysilyl)propyl methacrylate (or) 3-methacryloxypropyl trimethoxysilane	$CH_2=C(CH_3)COO(CH_2)_3Si(OCH_3)_3$
APMDMOS	(3-Acryloxypropyl) methyldimethoxysilane	$CH_2=CHCOO(CH_2)_3(CH_3)Si(OCH_3)_2$
APTES	3-Aminopropyltriethoxysilane	$H_2N(CH_2)_3Si(OC_2H_5)_3$
APTMS	3-Aminopropyltrimethoxysilane	$H_2N(CH_2)_3Si(OCH_3)_3$
APTMS (APTMOS)	(3-acryloxypropyl) trimethoxysilane	$CH_2=CHCOO(CH_2)_3Si(OCH_3)_3$
APTMS	Aminophenyltrimethoxysilane	$H_2NPhSi(OCH_3)_3$
TESPT	Bis(triethoxysilylpropyl) tetrasulfane	$(C_2H_5O)_3Si(CH_2)_3S_4(CH_2)_3Si(OC_2H_5)_3$
DDS	Dimethyldichlorosilane	$(CH_3)_2SiCl_2$
GPTMOS	3-Glycidoxypropyl trimethoxysilane	$CH_2(O)CCH_2O(CH_2)_3Si(OCH_3)_3$
ICPTES	3-Isocyanatopropyl triethoxysilane	$OCN(CH_2)_3Si(OC_2H_5)_3$
MMS	Methacryloxymethyltriethoxy silane	$CH_2=C(CH_3)COOCH_2Si(OC_2H_5)_3$
APMDES	Aminopropyl methyl diethoxysilane	$H_2N(CH_2)_3(CH_3)Si(OC_2H_5)_2$
MPTES	3-Methacryloxypropyl triethoxysilane	$CH_2=C(CH_3)COO(CH_2)_3Si(OC_2H_5)_3$
MPTS	Mercaptopropyltriethoxysilane	$SH(CH_2)_3Si(OC_2H_5)_3$
MTES	Methyltriethoxysilane	$CH_3Si(OC_2H_5)_3$
PTMS	Phenyltrimethoxysilane	$PhSi(OCH_3)_3$
VTES	Vinyltriethoxysilane	$CH_2=CHSi(OC_2H_5)_3$
VTS	Vinyltrimethoxysilane	$CH_2=CHSi(OCH_3)_3$
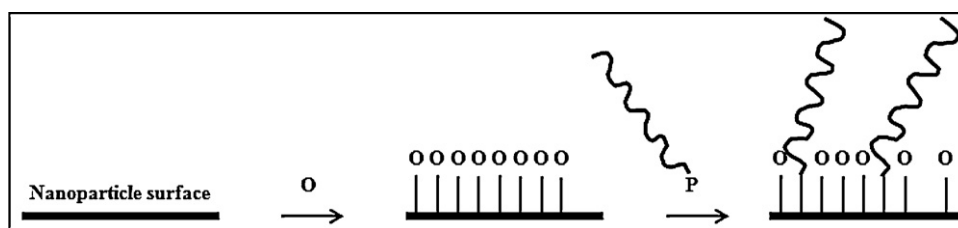
Scheme 2. Mechanism of "grafting to" approach.
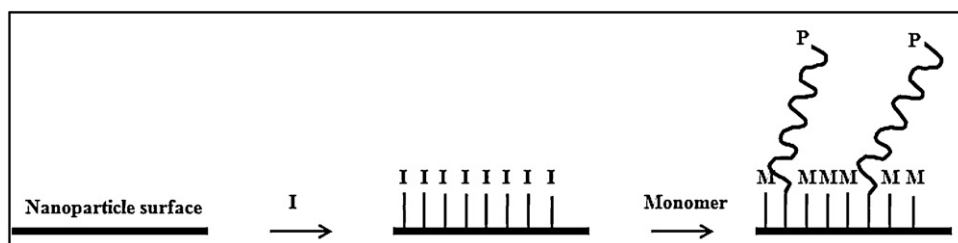
Scheme 3. Mechanism of "grafting from" approach.
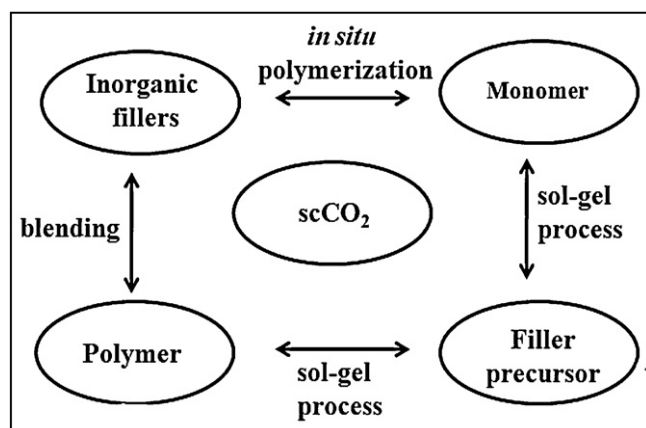
Scheme 4. The three general approaches for preparation of polymer/inorganic filler nanocomposites in scCO₂.

4.1. Blending or direct mixing

The traditional and simplest method of preparing polymer–inorganic filler composites is direct mixing of the fillers into the polymer. The mixing can generally be done by melt blending and solution blending. The main difficulty in the mixing process is always the effective dispersion of the fillers in the polymer matrix because they often tend to agglomerate. In this chapter, we are mainly concentrating on melt blending of polymer/layered silicate (PLS) nanocomposites. Melt blending is the most commonly used method because of its efficiency, operability, and environmental containment.

There are four principle methods for producing PLS nanocomposites [108–111]: (1) template synthesis (sol–gel technology), by which the clay minerals are synthesized within the polymer matrix, using an aqueous solution containing the polymer. (2) Intercalation of polymer or prepolymer from the solution, a technique that the layered silicate is exfoliated into individual layers using a solvent where the polymer is soluble. The polymer is then added in the solution and intercalates into the clay layers. (3) In situ intercalative polymerization, which is the first method used to produce nylon-6/clay nanocomposite [112]. In this method, the layered silicate is swollen by a liquid monomer or monomer solution and the polymerization reaction takes place between the intercalated layers. (4) Melt intercalation, in which the layered silicate is directly blended with the polymer matrix while in its molten state. If the clay layer surface is compatible with the chosen polymer matrix

then polymer chains can diffuse into the interlayer spaces and form either an intercalated or exfoliated nanocomposites. Among these four basic techniques, template synthesis is not suitable for most PLS nanocomposites due to two serious disadvantages: the high temperature needed to synthesize the clay mineral destroys the polymer itself, and a tendency for the growing silicate layers to easily aggregate. Methods 2 and 3 usually require large quantities of suitable monomer/solvent or polymer solvent pairs, which lead to a series of economic and environmental issues. Melt intercalation offers a number of appealing advantages such as no requirement of a solvent, ease of processing with conventional compounding devices such as extruders, relatively low cost and being environmentally sound. Thus, melt intercalation has become the mainstream for preparing PLS nanocomposites in recent years.

The degree of delamination of silicate platelets and their dispersion in polymer matrix are dependent on the details of the melt intercalation process. Among a variety of shear devices, twin screw extruders were found to be most effective because they provide sufficient amount of shear and intense mixing [113]. There are two different patterns for intermeshing twin screw extruders. In the counter-rotating pattern, the screws rotate counter to each other, so that the materials are built up in the junction of the two screws. The disadvantage of this system is that high shear only occurs when the materials pass between the screws; however, total shear is lower than that of co-rotating systems. In the case of co-rotating patterns, the screw rotates in the same direction, which ensures that most of the materials will be subjected to the same shear force when they pass between the screws and the barrel. Moreover, co-rotating systems provide a higher contact time with the extruder barrel, which improves the efficiency of heating. In other words, the co-rotating twin screw extruder is more favorable for producing PLS nanocomposites. It is also believed that chemical compatibility between the clay and polymer matrix is the most crucial factor in melt intercalation. Only moderate shear intensity is enough to achieve exfoliation structures for well compatible polymer/clay system, while both shear and chemical compatibilization are necessary for thermoplastic elastomer based nanocomposites. Obviously, full exfoliation of clay within non-polar polymers like thermoplastic elastomer and polypropylene (PP) remains a great challenge due to the poor miscibility between the polymer and organoclay. In recent years, some novel strategies have been developed to improve the intercalation or exfoliation, of which adding a small amount of compatibilizers was the most popular. Other methods, such as the use of ultrasound irradiation [114], have been reported to improve the exfoliation of the clay only for specific matrices. Recently, another novel processing method with the aid of supercritical fluids has gained attention from the plastic industry [115–121].

Generally speaking, the use of scCO$_2$ to reduce the melt viscosity and to delaminate silicate layers is an appealing approach for melt intercalation. The presence of scCO$_2$ in the polymer phase will increase the inter-chain distance and free volume, and reduce the inter-chain interactions. Thus, scCO$_2$ leads to significant changes in properties of polymers such as lowering interfacial tension and reduction of viscosity of the polymer melt [122]. It was found in the presence of CO$_2$ that the melt viscosity of polystyrene (PS) melt decreased, even with the addition of clay [123]. Ma et al. achieved a relatively uniform dispersion of sepiolite in PP using scCO$_2$ even without the aid of maleated PP as a compatibilizer [122], which is contrary to an earlier stated theory that a compatibilizer must be involved in melt intercalation for a non-polar polymer. Since scCO$_2$ is known as a good solvent and carrier agent for maleic anhydride [124], the interaction between scCO$_2$ and maleic anhydride affects the natural function of compatibilizer.

Recently, there have been three approaches reported in the literature on the preparation of PP/montmorilloinite (MMT)
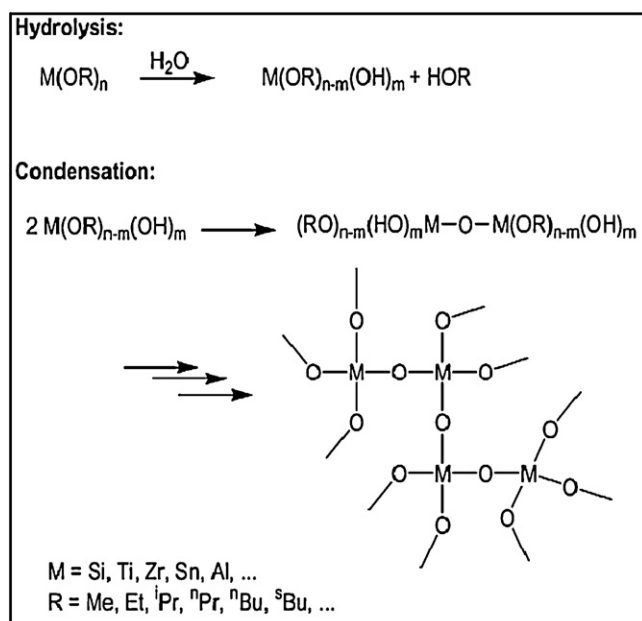
nanocomposites by melt intercalation with the aid of scCO$_2$. The first is direct injection of scCO$_2$ into a molten nanocomposite [117,125]; the second is pretreating the organoclay in the presence of scCO$_2$ before adding to the melt [118]; the third is injection of clay along with CO$_2$ into the polymer melt [117,126] and compared the effectiveness of clay dispersion between the conventional twin screw extrusion and a novel single extrusion with the aid of scCO$_2$. The authors confirmed that a twin screw extruder which provides sufficient shear and intense mixing is more effective for clay dispersion, and the improvement of exfoliation with the aid of scCO$_2$ was observed. They also suggested that pretreating the clay with scCO$_2$ prior to the extrusion may better improve clay dispersion and exfoliation. In a different work, Litchfield et al. [115] reported that injecting the organoclay within a supercritical suspension into a single screw extruder resulted in better dispersion. Horsch et al. [127] proposed a mechanism of how to delaminate silicate layers using scCO$_2$. First, CO$_2$ or its mixture with polymers diffuses between the organoclay interlayers under supercritical conditions. This step should take sufficient time to allow polymer chains and CO$_2$ to fully intercalate. A fast depressurization follows during which the CO$_2$ dramatically expands and pushes the interlayers apart. Finally, the polymer chains remain in the interlayers after CO$_2$ is removed to prevent reformation of the layered structure.

Despite the previously mentioned advantages of melt intercalation, polymer degradation may be a considerable issue that should not be overlooked. Since a certain high temperature is normally needed during melt intercalation, not only the polymer matrix and compatibilizer may degrade but also the organic surfactant, which can lead to a significant reduction in the mechanical properties of the final products.

4.2. Sol–gel process

The sol–gel process is a wet-chemical technique widely used in the fields of materials science and ceramic engineering. Such methods are used primarily for the fabrication of materials (typically metal oxides) starting from a colloidal solution (sol) that acts as the precursor for an integrated network (or gel) of either discrete particles or network polymers. Typical precursors are metal alkoxides and metal salts (such as chlorides, nitrates and acetates), which undergo various forms of hydrolysis and polycondensation reactions (Scheme 5). The sol–gel processing includes two approaches: hydrolysis of the metal alkoxides and then polycondensation of the hydrolyzed intermediates. This process provides a method for the preparation of inorganic metal oxides under mild conditions starting from organic metal alkoxides. The sol–gel processing of fillers inside the polymer dissolved in a non-aqueous or aqueous solution is the ideal procedure for the formation of interpenetrating networks between inorganic and organic moieties at the milder temperature in improving good compatibility and building strong interfacial interaction between two phases [15]. This process has been used successfully to prepare nanocomposites with silica, alumina, calcium oxide and titania in a range of polymer matrices.

Several strategies for the sol–gel process are applied for the formation of hybrid materials. One method involves the polymerization of organic functional groups from a preformed sol–gel network; vinyl [128] or epoxy groups [129] and free-radical or cationic polymerization processes are common. Hsiue et al. [130] synthesized a series of organic–inorganic hybrid materials by copolymerizing St and alkoxysilane-methacrylate via the sol–gel process. The alkoxysilane-containing copolymer precursors were synthesized by free-radical copolymerization of St with an alkoxysilane-containing monomer, methacrylic acid 3-(trimethoxysilyl) propyl ester (MAMSE), at several feeds. The copolymer precursors were then hydrolyzed and condensed to

Hydrolysis:

$$M(OR)_n \xrightarrow{H_2O} M(OR)_{n-m}(OH)_m + HOR$$

Condensation:

$$2\,M(OR)_{n-m}(OH)_m \longrightarrow (RO)_{n-m}(HO)_m M-O-M(OR)_{n-m}(OH)_m$$

M = Si, Ti, Zr, Sn, Al, ...
R = Me, Et, ^{i}Pr, ^{n}Pr, ^{n}Bu, ^{s}Bu, ...

Scheme 5. Sol–gel process.
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generate PS–SiO$_2$ hybrid sol–gel materials. The hybrid copolymers possess excellent optical transparency and a nanoscale microphase separation. Alternatively, the sol–gel hydrolysis and condensation of a precursor such as tetraethyloxysilane (TEOS), tetrabutyl titanate, aluminum isopropoxide are carried out starting from a preformed functional organic polymer such as poly(vinyl acetate) (PVAc) [131], poly(methyl methacrylate) (PMMA) [132], polyetherimide (PEI) [133], poly(vinyl alcohol) (PVA) [134], polyamides (PA) [135], polyimide (PI) [136] and several other polymers [137,138]. For example, a recent report on the non-aqueous sol–gel process by polycondensation of phenyltriethoxysilane mixing with PI in a polyamic acid solution resulted in excellent dispersion of nanoscale SiO$_2$ in PI. Comparatively, mechanical mixing of SiO$_2$ to the PI melts led to serious aggregation.

A combination of the above two methods has been used to synthesize polydimethylsiloxane (PDMS)/SiO$_2$ nanocomposites. The unfilled PDMS network was first formed with the stoichiometric amount of TEOS as an end-linking agent. Next, the network was swollen with additional TEOS which was suspended in excess water containing the catalyst such as an acid or base and the sol–gel reaction was catalyzed [139]. Finally, the two distinct polymerization processes can be carried out simultaneously, although coupling or compatibilization of the two main components and the subsequent formation of a true hybrid can be an elusive task in this case. For example, PS/SiO$_2$ nanocomposites were prepared by the simultaneous polymerization of St and TEOS, which resulted in a continuous interpenetrating network of SiO$_2$ and PS [140]. Therefore, sol–gel process is an effective method for the preparation of nanocomposites and has been reviewed elsewhere [141,142]. The sol–gel method is attractive for industrial production because of the low temperature process and a relatively simple scale-up procedure [143]. However, the process involves using large amounts of organic solvents and/or surfactants to promote the miscibility of metal alkoxide and water [128]. Hence, an organic solvent and surfactant free process are very attractive for potential scale-up purposes.

ScCO$_2$ has attracted a great deal of interest as a polymerization and processing medium, primarily driven by the need to replace conventional solvents with more environmentally benign and economically viable systems. It is alternative substituents for the organic solvents for a variety of reactions [144–147]. The first direct sol–gel process in scCO$_2$ was reported in 1997 by Loy et al. [148] who prepared SiO$_2$ monoliths by polycondensation of tetramethyl orthosilicate (TMOS) reacting with formic acid. In a different work, Sui et al. [149] prepared silica aerogel particles in scCO$_2$ by reacting silicon alkoxides with acetic acid and formic acid and subsequent depressurization using a rapid expansion of supercritical solvent (RESS) process. Because of its poor solubility in scCO$_2$ (0.1 wt%), water is not suitable for the sol–gel process without the aid of surfactants. However, carboxylic acids (e.g., formic acid and acetic acid) are miscible with scCO$_2$ and hence are attractive candidates for the polycondensation agents. This direct sol–gel technique in scCO$_2$ simplifies the aerogel formation process by combining the polycondensation and supercritical drying into one step, promising a new avenue for synthesizing SiO$_2$/polymer nanocomposite materials.

The same group examined a novel one-pot synthesis of PVAc–SiO$_2$ nanocomposites in scCO$_2$ [150]. The process showed the feasibility of performing simultaneous polymerization reactions (e.g., initiation, propagation), sol–gel reactions and linkage of the resulting nanoparticles to the polymer matrix. Although this one-pot process can work with essentially any vinyl monomer and silane linker that are soluble in scCO$_2$, vinyl acetate (VAc) was chosen as the monomer of interest due to its relatively high solubility in scCO$_2$ [151,152] and the wide-spread industrial and biomedical applications of PVAc. Vinyltrimethoxysilane (VTMO) was applied as the second monomer for coupling to the sol–gel-derived nanoparticles. This methodology provides the advantage of combining the reaction, aging, and drying into a one-pot process. They also synthesized polyethylene (PE) and SiO$_2$ nanocomposites via a green route by in situ polycondensation of TEOS with acetic acid within the matrix of PE in scCO$_2$. Yu et al. [153] reported a simple approach for the synthesis of cellulose/TiO$_2$ hybrids by combining scCO$_2$-assisted adsorption and impregnation into cellulose fibers with a TiO$_2$ sol which was prepared through a non-hydrolytic sol–gel route. This method avoids the use of solvents for cellulose regeneration and high temperatures. It was found that the penetrating and swelling effect of scCO$_2$ influenced the interactions between the molecular chains of cellulose. The effect of scCO$_2$ to access and impregnate TiO$_2$ particles into the crystalline structure of cellulose fibers by formation and stabilization of hydrogen bonds with abundant hydroxyl groups of cellulose, resulting in a change of its thermal stability in pyrolysis.

More recently, Wang et al. [154] synthesized SiO$_2$-poly(N-isopropyl acrylamide) (PNIPA) nanocomposite through a one-pot approach in scCO$_2$. All raw materials, N-isopropylacrylamide, vinyltriethoxysilane (VTEO), TEOS, AIBN, cross-linker N,N′-methylenebisacrylamide and hydrolysis agent acetic acid were introduced into one autoclave. The parallel reactions of the free-radical polymerization of vinyl monomers and the hydrolysis/condensation of siloxanes occurred simultaneously in the reaction mixture with scCO$_2$ as the solvent. VTEO was applied as the second monomer for coupling to the sol–gel-derived SiO$_2$ nanoparticles. In the absence of cross-linker, some liquid residue was obtained rather than powder composite particles. The cross-linking structure reduces the solubility of PNIPA chains in scCO$_2$ and the polymers with a higher cross-linking degree precipitated out of the CO$_2$ faster. Increase of the cross-linker generates more active nuclei in the reaction system and reduces the particle diameters, resulting in powder particles with a higher conversion of the vinyl monomers. The TEM characterization of polymer nanocomposite showed that well-dispersed particles with diameter less than 100 nm were formed and the linkage of SiO$_2$ onto the PNIPA elevated the low critical solution
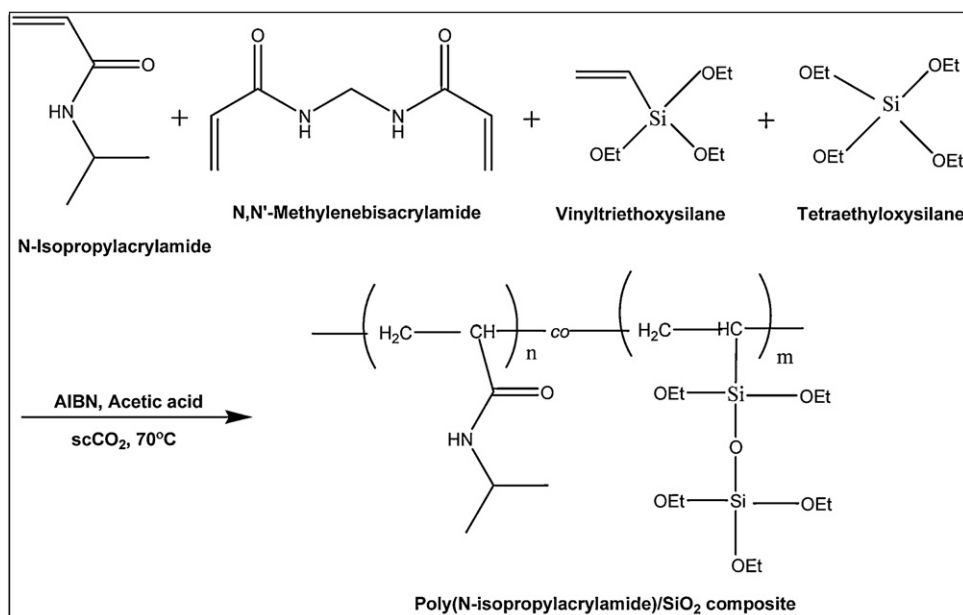
Scheme 6. Synthesis of SiO_2-PNIPA in $scCO_2$.
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temperature (LCST) of the sensitive polymer. The simplified reaction mechanism for the synthesis of SiO_2-PNIPA is shown in Scheme 6.

4.3. In situ polymerization

4.3.1. Polymer/metal nanocomposites

Polymer/metal nanocomposites are receiving considerable interest in recent years due to their potential applications. The embedding of nanoscopic metals or metal oxides into dielectric matrices represents a solution to manipulation and stabilization problems. For functional nanostructured materials starting from a metal precursor, polymers are of particular interest as an embedding phase since they may have a variety of characteristics: they can be an electrical and thermal insulator or conductor. Also, they may have a hydrophobic or hydrophilic nature, can be mechanically hard (plastic), or soft (rubbery), and so on. Finally, polymer embedding is the easiest and most convenient way for nanostructured metal stabilization, handling and application [155]. This has fuelled investigation into the preparation of polymer/metal nanocomposites. These composites most commonly take the form of thin polymer films or powders, as this is normally the simplest structure to prepare and also good for exploiting the desired properties. Preparation techniques can be classified as in situ and ex situ methods [155]. In the in situ method, the monomer is polymerized, with precursors introduced before or after the polymerization. The precursors in the polymer matrix are then reduced, chemically, thermally, or by UV irradiation, to form nanoparticles. In the ex situ process, the metal nanoparticles are synthesized first, and their surface is organically passivized. The derivatized nanoparticles are then dispersed into a polymer solution or liquid monomer which is then polymerized.

Supercritical fluids have been used to deposit thin metal films onto a wide range of surfaces and to incorporate metallic particles into different inorganic and organic substrates for microelectronic, optical and catalytic applications [156]. This technique has allowed both highly dispersed and uniformly distributed metal nanoparticles, as well as agglomerated clusters of nanoparticles of wider size distribution, to be generated in host materials. These various solid substrates have included silicon wafer, metal foil, inorganic

nanotubes, bulk polymers and polymer membranes, organic and inorganic porous materials. The nanoparticle impregnation process involves dissolving an appropriate metallic precursor in $scCO_2$ and then exposing the substrate to the solution. The $scCO_2$ facilitates the infusion of the precursor into the host material. After the incorporation of the precursor with the substrate, the metallic precursor is reduced to its metal form by a wide variety of methods resulting in films or particles. The reduction methods employed are chemical reduction in the $scCO_2$ with a reducing agent such as hydrogen and alcohols, thermal reduction in the $scCO_2$, and thermal decomposition in an inert atmosphere or chemical conversion with hydrogen or air [156] (Fig. 2).

The use of $scCO_2$ for this impregnation process is advantageous in comparison to conventional solvents for many reasons. For many of the substrates used, a conventional solvent would be unsuitable. For high surface area substrates such as highly porous inorganics for catalysis or microstructured materials for electronics, the use of conventional solvents is not appropriate. The surface tension and viscosity of common solvents, along with poor wetting of the pores, causes very slow and often incomplete impregnation of precursor solutions into porous supports. The low surface tension of $scCO_2$ not only permits better penetration and wetting of pores than liquid solvent, but also avoids pore collapse which can occur on certain structures such as organic and silica aerogels with liquid solvents. This damage is caused during the drying step as liquid solvents are removed from the substrate. Strong localized forces occur in the pores due to their small diameter in relation to the meniscus of the retreating liquid. This causes cracking of the material. Even without this factor, extended heating of the substrate to remove liquid solvents can be costly and time consuming. In comparison, $scCO_2$ can be much more easily introduced and removed from such systems. For polymer impregnation, $scCO_2$ allows modification that would be otherwise difficult with conventional solvents. $ScCO_2$ can be easily infused into polymers without the need to dissolve the polymer and re-blend, and displays a high permeation rate in virtually all polymers. The exposure of polymers to $scCO_2$ results in various extents of swelling and enhanced mobility of the polymer chains, which makes it possible to incorporate metallic precursors. Moreover, the solvent strength can be adjusted via changes in temperature and pressure [156,157].
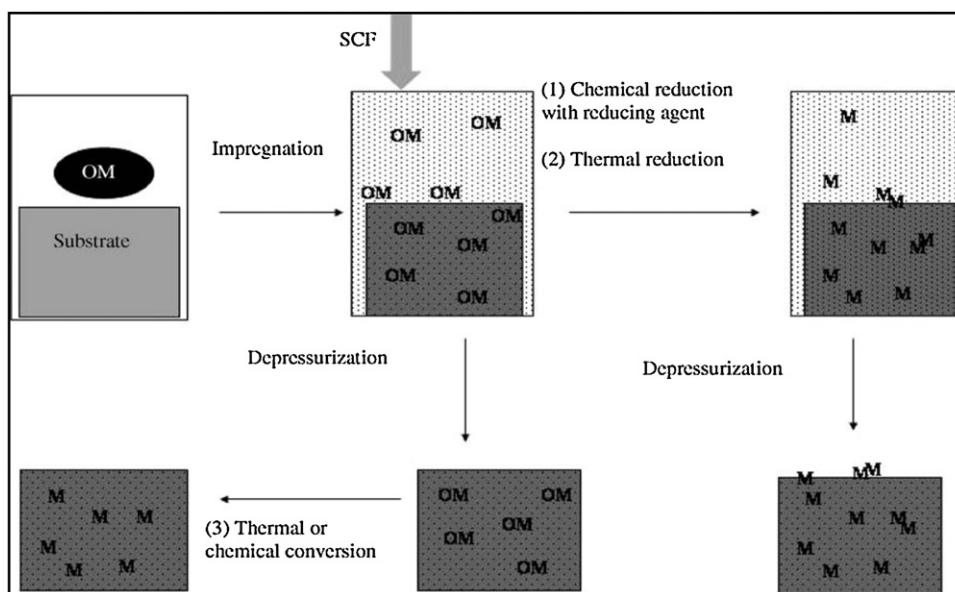
Fig. 2. Supercritical fluid mediated impregnation or deposition of nanoparticles into a substrate. OM represents a soluble organometallic precursor. Reprinted from [156] with permission from Elsevier.
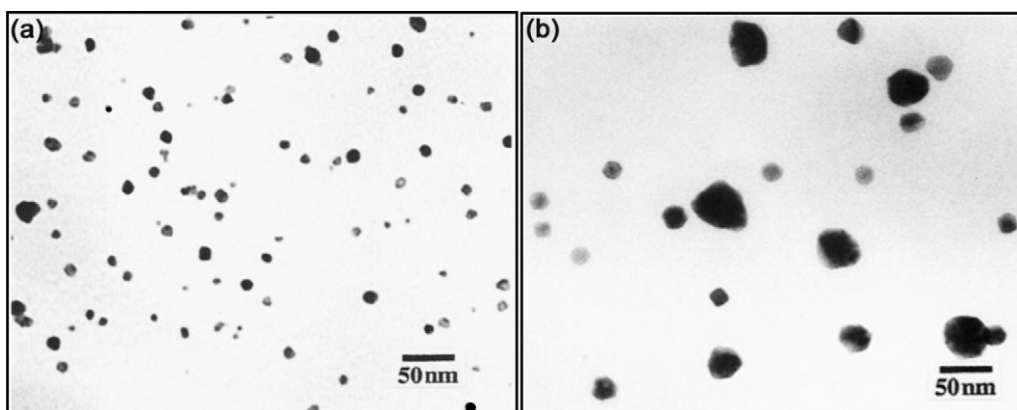

Fig. 3. TEM images of poly(4-methyl-1-pentene)/platinum nanocomposites synthesized by (a) hydrogen reduction of precursor after depressurization of scCO$_2$ and (b) hydrogen reduction of precursor in the presence of scCO$_2$.
Reprinted with permission from [157].

The groundbreaking work in this field was undertaken by Watkins and McCarthy in 1995, and was the first use of scCO$_2$ for the impregnation of metal nanoparticles into a polymer substrate [157]. In this case, the polymers impregnated were poly(4-methyl-1-pentene) (PMP) and poly(tetrafluoroethylene) (PTFE). The organometallic precursor used was dimethyl(cyclooctadiene)platinum (II) (CODPtMe$_2$), which was chosen because it was a readily available chemical vapor deposition (CVD) precursor, high platinum content (58.5 wt%) and heptane solubility, which is a good indicator of solubility in the scCO$_2$. Fig. 3 shows the transmission electron micrographs (TEM) of metal nanoparticles impregnated PMP composites. The comparison of Fig. 3a and b is useful for understanding the implications of the two alternative reduction routes shown in Fig. 2, i.e. reduction after or before depressurization. When the precursor was reduced after depressurization of the scCO$_2$ (Fig. 3a), the product appeared to be homogeneous throughout with nanoparticles of size ∼15 nm were evenly distributed, apart from occasional larger clusters. When the precursor was reduced by hydrogen before venting the scCO$_2$, a sharp concentration gradient was seen close to the

surface. The nanoparticles in the bulk of the PMP were mostly up to ∼50 nm, but close to the surface which had a silver sheen, a greatly increased concentration of nanoparticles was present with a diameter of ∼50–100 nm (Fig. 3b). This difference was caused by the effect of reducing the metal while scCO$_2$ was still present in the polymer. The polymer was still scCO$_2$ swollen and the precursor molecules were still able to diffuse freely during the reduction step. This allowed the nanoparticles in the bulk to grow larger in diameter, and also caused a greater deposition of metal into the surface layer. This is because the precursor was still able to infuse from the solvent phase into the polymer and the metal nanoparticles growing in the solvent phase seemed to be unstable and deposited into the polymer surface. Therefore, when the control of nanoparticle size and uniformity is desired, post-depressurization reduction is a preferred process.

This method was expanded by Watkins's group to deposit different metal nanoparticles or films, including platinum, palladium, gold, rhodium, cobalt, nickel and copper in scCO$_2$ by the reduction of desired precursors with hydrogen or alcohols [158–163]. Other groups then took this new technique forward, adapting it to other

substrates and metals. Ye et al. prepared highly dispersed nanoparticles of palladium, rhodium and ruthenium through reduction of adsorbed metal-β-diketone precursors by hydrogen in scCO$_2$ [164–166]. The nanoparticles were deposited onto functionalized multi-walled carbon nanotubes or SiO$_2$ nanotubes for catalytic applications.

Over the last few years, the substantial investigations in this field have been undertaken by Howdle's group. The method used by this group was generally similar to the commonly used method, except instead of reducing the metallic precursor at ambient pressure following scCO$_2$ impregnation, chemical reduction with pure hydrogen at an elevated pressure was used to synthesize silver nanoparticles in porous poly(styrene-co-divinylbenzene) (PS-co-PDVB) beads and silica aerogels, and palladium nanoparticles in silica aerogel [167,168]. The palladium nanoparticles in silica aerogel supports were shown to demonstrate good catalytic activity for hydrogenation of cyclohexene in a continuous flow reactor. Similar impregnations allowed the clean synthesis of silver nanoparticles in polymer substrates for biomedical applications, and some success was demonstrated in initial applications testing [169]. Recently, the group was able to extend the versatility of this technique to the synthesis of gold nanoparticles supported on silica, PA, PP and PTFE [170]. Two precursors; dimethylacetylacetonato gold (III), and its fluorinated analogue dimethylhexafluoroacetylacetonato gold (III), were compared for their effectiveness in the production of gold nanoparticles, which have catalytic applications. Interestingly, the non-fluorinated organometallic precursor was found to produce more effective nanocomposite material. This may be attributed to the fact that the fluorinated ligands preferentially aid the partition of the precursor into the mobile scCO$_2$ phase, thus resulting in poor deposition/processing. The majority of the fluorinated complex likely remains dissolved in the scCO$_2$, therefore venting into atmosphere upon release. In addition, the fluorinated analogue is not completely stable under the processing conditions used thus partially decomposing/precipitating on to the surface of the autoclave.

Some of the most advanced polymer results are evidenced by the researches of Boggess et al. and Yoda et al. Boggess et al. performed the synthesis of highly reflective silver–PI films by impregnation of (1,5-cyclooctadiene-1,1,1,5,5,5-hexafluoroacetylacetonato)silver (I) into PI [171]. Similarly, Yoda et al. synthesized Pt and Pd nanoparticles dispersed PI films as a precursor for the preparation of metal-doped carbon molecular sieve membranes for hydrogen separation [172]. The impregnated precursors were Pt (II) acetylacetonate and Pd (II) acetylacetonate. Recently, they also [173] described a novel method for the in situ formation of Cu or Ag nanoparticle–polymer composites in which organometallic precursor species 1,5-cyclooctadiene (1,1,1,5,5,5-hexafluoroacetylacetonato)silver (I) [Ag (I) (hfac) (1,5-COD)] and 1,5-cyclooctadiene-copper (I) hexafluoroacetylacetonate [Cu (I) (hfac) (1,5-COD)] are dissolved into a monomer phase prior to a wet-chemistry free-radical suspension polymerization or bulk polymerization. The precursor molecules can be naturally trapped inside the polymer matrix once it is formed during the reaction with a uniform spatial distribution, and subsequently converted into metallic nanoparticles through hydrogen-assisted reduction in a separate process. The reduction reaction takes place in scCO$_2$ for the convenience of H$_2$ delivery and ligand removal by the same solvent following polymer plasticization, resulting in a clean nanocomposite material. This is advantageous in comparison to the thermal decomposition and photo reduction techniques. The experimental technique reported in this work is not much more complicated than the routine free-radical suspension/bulk polymerization. These initial investigations into the use of scCO$_2$, although interesting and successful, only represent the beginning of what will be a considerably larger body of research that must be undertaken to bring this

exciting field into a full understanding. The early work, however, has supplied an excellent foundation for the establishment of core knowledge and the instigation of current and future study.

More recently, an ex situ dispersion of silver (Ag) nanoparticles within the monomer (St) and subsequent emulsion polymerization using water-in-scCO$_2$ medium was carried out by Kamrupi et al. [174]. Ag nanoparticles were synthesized by chemical reduction of silver nitrate using sodium borohydrate as a reducing agent and PDMS as a stabilizer in the water-in-scCO$_2$. The stable dispersion of Ag nanoparticles was added slowly during the polymerization of St in the water-in-scCO$_2$ maintaining the temperature at 70 °C and pressure at 20.68 MPa. This work represents an easy method to synthesize the Ag/PS nanocomposite particles by ex situ addition of Ag nanoparticles during the polymerization. They also prepared copper/PS nanocomposite particles by the same method [175].

4.3.2. Polymer/clay nanocomposites

Polymer/clay nanocomposites in which a small percentage of layered silicates are embedded in a polymer matrix are of interest because they exhibit improved material properties compared to the neat polymer. Among various approaches used to prepare nanocomposites, in situ polymerization has proved to be the most successful one, which was pioneered by the researchers from Toyota Motor Company who synthesized the first exfoliated nylon-6/clay hybrid for automotive applications [112]. Since then, several useful vinyl polymer/clay nanocomposites have been prepared via in situ polymerization. However, a drawback of in-situ polymerization is that it typically involves large quantities of aqueous/organic solvents which are both environmentally unfriendly and economically prohibitive for industrial-scale applications. On the other hand, scCO$_2$ has attracted an extensive interest as a polymerization medium [30].

Zerda et al. [176] used the in situ polymerization route to prepare highly filled PMMA/clay nanocomposites in scCO$_2$. In their work, CO$_2$ was primarily used to lower the viscosity resulting from high loadings (up to 40%) of clay; the clay was modified by conventional hydrocarbon surfactants and resulted in intercalated PMMA/clay nanocomposites. Dong et al. [177] employed a similar in situ polymerization technique to prepare intercalated PS/clay nanocomposites with a more conventional loading (1–10%) of clay in scCO$_2$. They also modified the clay with a hydrocarbon surfactant and found that a longer 'soaking time' during the impregnating process can lead to more exfoliated nanocomposites. Yan et al. [178] also synthesized PS/MMT nanocomposites in scCO$_2$ where organically modified MMT can be produced through an ion-exchange reaction between native hydrophilic MMT and an intercalating agent (alkyl ammonium). Li et al. [179] described a modified synthetic route to produce polymer/clay nanocomposites where St monomer and initiator were directly intercalated into organomonmorillonite (OMMT) with the aid of scCO$_2$ followed by depressurization and free-radical polymerization. Nevertheless, in all the above studies, no information on the yields or morphologies of the polymers has been mentioned, nor was it clear why in situ polymerization with clay can produce nanocomposites in higher yields while polymerizations in the absence of stabilizer typically result in a non-descriptive, low-yield oligomers in scCO$_2$. Furthermore, by using the hydrocarbon surfactant-modified clay in the above studies, only intercalated nanocomposites were obtained regardless of the concentration of clay.

Alternatively, Zhao and Samulski [180] reported a route to produce partially exfoliated PMMA/clay nanocomposites via in situ polymerization in scCO$_2$, in which they found that the fluorinated surfactant-modified clay can itself serve as a stabilizer and help produce PMMA in high yields (85%) in scCO$_2$. Although the clay is not soluble in CO$_2$, the stabilization mechanism is similar to that in a conventional dispersion polymerization. This technique was

referred as a pseudo-dispersion polymerization. The use of a different system was reported with a commercially available surfactant aminopropyl-terminated PDMS (AP-PDMS) modified clay as the stabilizer for the pseudo-dispersion polymerization of MMA and St in scCO$_2$ [181]. This PDMS-based surfactant is known to be CO$_2$-philic and its longer siloxane chain is expected to provide better steric stabilization compared to the previously used shorter fluorinated chain. Furthermore, they extended the system to PS, which does not have a hydrogen bonding site as PMMA does.

Recently, Urbanczyk et al. [182] used masterbatch technique to prepare polymer/clay nanocomposites. The masterbatch technique is nothing but the preparation of polymer/clay nanocomposites by combining the in situ intercalative polymerization and the melt intercalation process. They successfully prepared poly(ε-caprolactone) (PCL)/clay masterbatches by in situ intercalative polymerization in scCO$_2$ using stannous octate as a catalyst [182]. This unique medium allows reaching of a very high clay loading in the masterbatch. Also, the product obtained after depressurization is an easily recoverable fine powder. Another advantage of using scCO$_2$ is its capacity to extract the residual monomer during depressurization, leading directly to a ready-to-use dry powder. These clear advantages show the superiority of this process compared to the classical synthesis in bulk. In fact, all of these advantages allow this process to be upgraded to an industrial scale, which was not feasible with the classical process. The obtained organically modified clay/polymer masterbatches were then redispersed in a commercial chlorinated PE, known to be miscible with PCL, in order to compare the quality of clay delamination with the direct melt blending of classical organoclay. The same group [183] used scCO$_2$ as a polymerization medium for the polymerization of D,L-lactide in the presence of organo-modified clays. Depending on the functional group borne by the organo-modifier, an intercalated or exfoliated nanocomposite was obtained when a low clay level (3 wt%) was reached. With the increase in the amount of clay, a decrease in the polymerization kinetics was observed, which may be due to a significant sterical hindrance of the clay. Clay levels as high as 35 and 50 wt% have been reached in these nanocomposites, which can then be used as masterbatches. The PLA/clay masterbatches have been dispersed into a commercial PLA matrix by melt mixing to reach a final clay content of 3 wt%. These well delaminated nanocomposites show significant improvement in both stiffness and toughness compared to the unfilled matrix.

More recently, Hossain et al. [184] reported the synthesis of PMMA/clay nanocomposites via free-radical polymerization of MMA in the presence of alkyl ammonium substituted polysilsesquioxane surfactant-modified clay and AIBN initiator in ethanol and scCO$_2$. The reactions were also conducted by adding small amount of water to observe the intercalation and exfoliation behavior of the clay and the properties of the nanocomposites. Since the surfactant is three dimensional, it has been found that the organophilization of the surfactant enhances hydrophobicity, stability of clay separation and dimension stability of the nanocomposites. Furthermore, a small amount of water molecules greatly changed the surface free energy of the clay leading to weaker forces between the layers, which might have facilitated the intercalation of monomer inside the clay gallery. Polymerization media also greatly affected the dispersion of organically modified clay resulting in different distributions of the clay that seemed to play an important role in the morphologies of nanocomposites. TEM images of PMMA/clay nanocomposites are shown in Fig. 4. In ethanol solvent, the agglomerated clay tactoids were observed in the PMMA matrix, while clay stabilized spherical nanocomposite beads were observed in the ethanol/water. On the other hand, highly intercalated nanocomposites with larger expanded intergallery spaces were produced in scCO$_2$ and partially exfoliated nanocomposites were formed in scCO$_2$/water. The TEM results

suggest that in scCO$_2$/water, the clay is dispersed more homogeneously in polymer matrix due to the high diffusivity of scCO$_2$ as well as dispersibility attributed to the lower surface energy of clay with 1% of water.

4.3.3. Polymer/metal oxide nanocomposites

In recent years, much attention has been paid to the in situ synthesis of nanocomposites, particularly core–shell type particles due to their potential applications [26]. The preparation strategy is carried out via polymerization of monomers in the presence of inorganic fillers. Prior to the dispersion, the inorganic fillers must be modified with organic materials to improve their compatibility and dispersion. In particular, emulsion polymerization is a traditional method to produce mono dispersed metal oxide/polymer core–shell composites. Dispersion polymerization has also been reported to be a viable method used to prepare core–shell nanocomposites [26].

Dispersion polymerization [185–187] may be defined as a type of precipitation polymerization; the polymerization reaction is performed in the presence of a suitable polymeric stabilizer that is soluble in the reaction medium. The selected continuous medium is a solvent for the monomer to be polymerized and a non-solvent for the resultant polymer. A steric stabilizer is used to produce a colloidally stable dispersion, without which the polymerization would generate macroscopic polymer particles of uncontrolled size. The dispersion polymerization process takes place in a homogeneous medium of monomers, free-radical initiator, and polymeric stabilizer dissolved in a suitable solvent. At an elevated temperature, the initiator decomposes and generates free radicals, which initiate chain growth by the addition of monomers. The growing chain remains in solution until a critical chain length is reached; then the polymer precipitates in a process known as nucleation. These unstable nanoparticles aggregate into larger particles, stabilizing themselves against further aggregation by adsorbing the stabilizer from the medium. These particles grow by capturing small nuclei and oligomeric radicals from the continuous phase, and polymerizing the absorbed monomer inside the particles. This continues until all of the oligomeric radicals and nuclei generated in the reaction medium are consumed.

DeSimone et al. reported the first dispersion polymerization of MMA in scCO$_2$ [188]. Because the product, PMMA is insoluble in scCO$_2$, they used a CO$_2$-soluble fluorinated homopolymer, poly(dihydroperfluorooctylacrylate) (PFOA) as the stabilizer. Consequently, the successful dispersion polymerization led to a significant improvement in the yield, molecular weight and morphology of the resultant polymer. Moreover, CO$_2$ offers high mass transport rates and allows in situ removal of unreacted monomers and other impurities upon depressurization. Since scCO$_2$ has a strong solvent power for dissolving many organic compounds and swelling of most organic polymers [189], it has been successfully utilized in the synthesis of polymer/polymer composites [190,191]. Although few studies have been reported based on the polymer/polymer composites, reports on the synthesis of metal oxide/polymer core–shell composites in scCO$_2$ are scarce in the literature. Recently, Wang et al. [192] prepared PS–C$_{60}$ composite microparticles using PDMS-methacrylate as a stabilizer through a one-step seed dispersion polymerization method in which scCO$_2$ was used simultaneously as an anti-solvent and a polymerization medium. C$_{60}$ was initially dissolved in St monomer with initiator and stabilizer, and was then injected into scCO$_2$. Since scCO$_2$ acted as an anti-solvent, C$_{60}$ was precipitated and dispersed in scCO$_2$. The resulting particles then acted as the seeds for the dispersion polymerization of St in scCO$_2$, leading to the formation of the PS–C$_{60}$ composite microparticles.

Substantial investigations in this field have been undertaken by Lim and coauthors. They successfully produced spherical
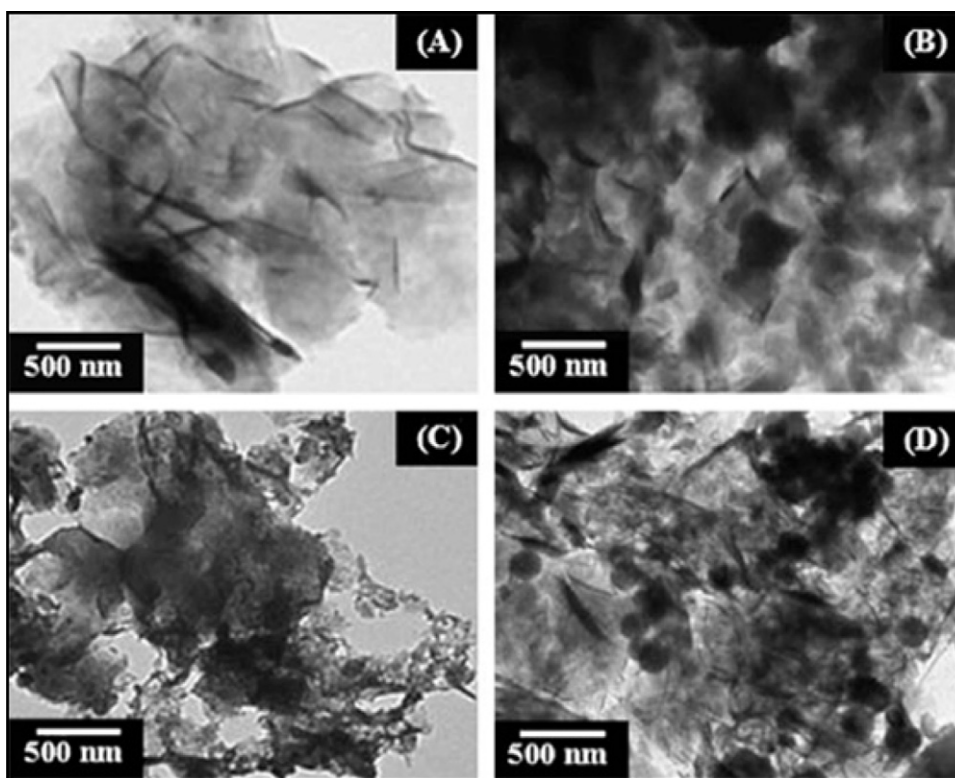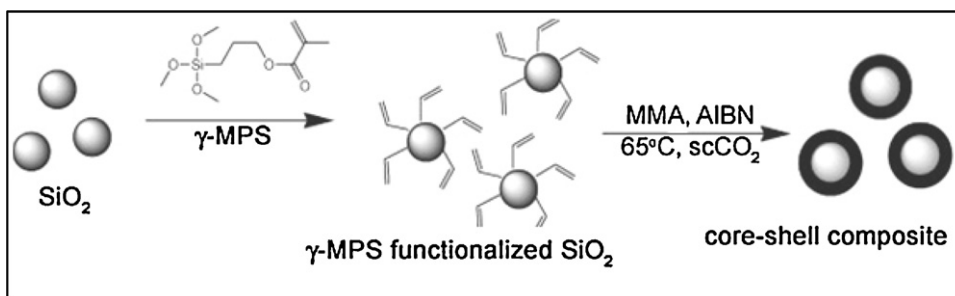
Fig. 4. TEM images of PMMA/MMT nanocomposites synthesized in (a) ethanol, (b) ethanol/H_2O, (c) $scCO_2$ and (d) $scCO_2$/H_2O. Reprinted from [184] with permission from Elsevier.

Scheme 7. Schematic representation of the process for the synthesis of SiO_2/PMMA composite particles. Reprinted with permission from [193]. Copyright Wiley-VCH Verlag GmbH & Co. KGaA.

SiO_2/PMMA nanocomposite particles via dispersion polymerization in $scCO_2$ [193]. Nanosized silica particles pretreated with 3-(trimethoxysilyl) propyl methacrylate (MPS) were used as seeds in the polymerization. The MPS-functionalized SiO_2 were first dispersed in the reaction medium, followed by the polymerization with MMA. The reaction conditions were 20% MMA (v/v to CO_2), 5% MPS-functionalized SiO_2 (w/w to MMA), 2% AIBN (w/w to MMA) and different amounts of stabilizer (5, 10 and 15% w/w to MMA) at 65 °C with the initial pressure of 34.5 MPa for 12 h. The schematic representation for the preparation of nanocomposite is shown in Scheme 7. Polymeric stabilizer, poly(dimethylsiloxane)-b-poly(methacrylic acid) (PDMS-b-PMA) copolymer provided sufficient stabilization to the composite latex particles in $scCO_2$ to prevent a flocculation during the polymerization. The size of composite particles was adjusted with varying the stabilizer concentration. The morphology of as-synthesized nanocomposites is shown in Fig. 5. They also synthesized PS/SiO_2 composite microparticles in $scCO_2$ using 15% St (w/w to CO_2), 1% AIBN (w/w to monomer), and different amounts of stabilizer (5 and 10% w/w to St) at 65 °C with the initial pressure of 34.5 MPa for 40 h [194].

The surface-modification of SiO_2 particles with MPS provided both the good dispersion of the particles in the polymerization mixture of St and CO_2 and the anchoring of PS on the SiO_2. The random copolymer, poly(1,1-dihydroheptafluorobutylmethacrylate-co-diisopropylaminoethyl methacrylate) [poly(FBMA-co-DPAEMA)] served as an effective stabilizer for the polymerization of St in $scCO_2$ without agglomeration of composite latexes. Fig. 6 shows the TEM images of PS/SiO_2 composite with 5 and 10% SiO_2. All the composites showed spherical micron-sized particles, where dark silica nanoparticles of 130 nm were embedded inside light PS shells. The primary particles were considered to be incorporated in the composite latex as individual or slightly agglomerated form via either absorption or copolymerization with St, which was stabilized by the copolymeric stabilizer. The multi-core microsphere might originate from the association during the polymerization of several latex particles, each of them containing one SiO_2 bead or a small aggregate. Each composite particle contained several SiO_2 particles, the number of which depends on the size of SiO_2 particles and on the SiO_2 content. More SiO_2 particles were incorporated in the composite with 10% SiO_2 (Fig. 6b) than 5% SiO_2 (Fig. 6a). It
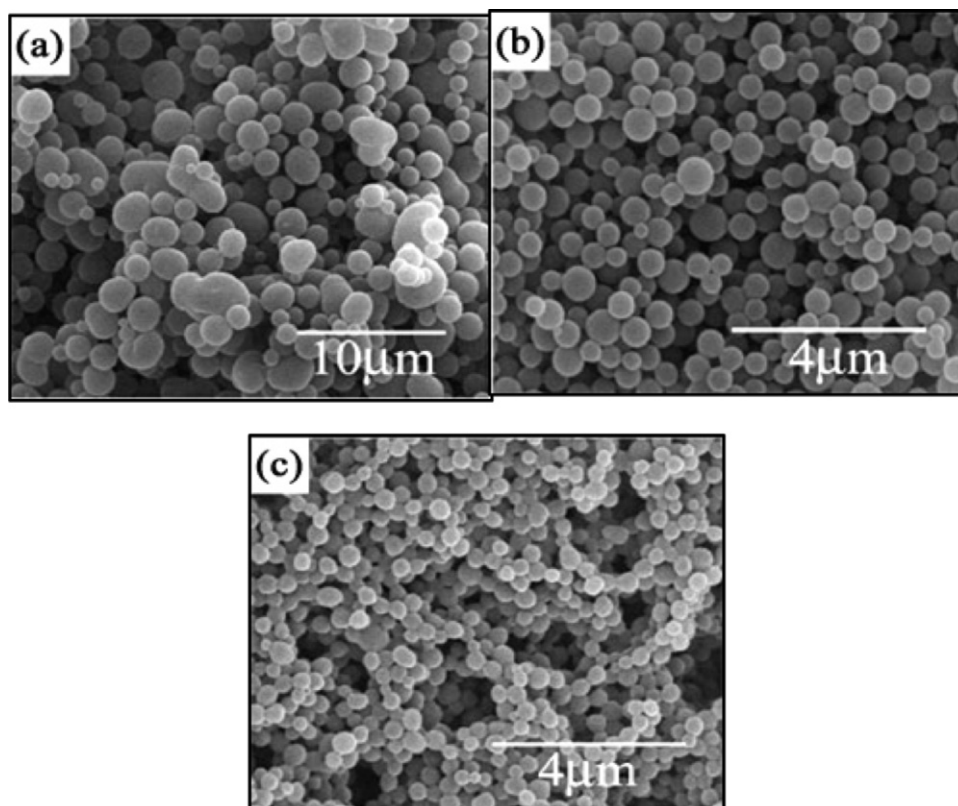
Fig. 5. SEM images of silica/PMMA composite particles synthesized using different amounts of stabilizer (a) 5%, (b) 10% and (c) 15%. Reprinted with permission from [193].
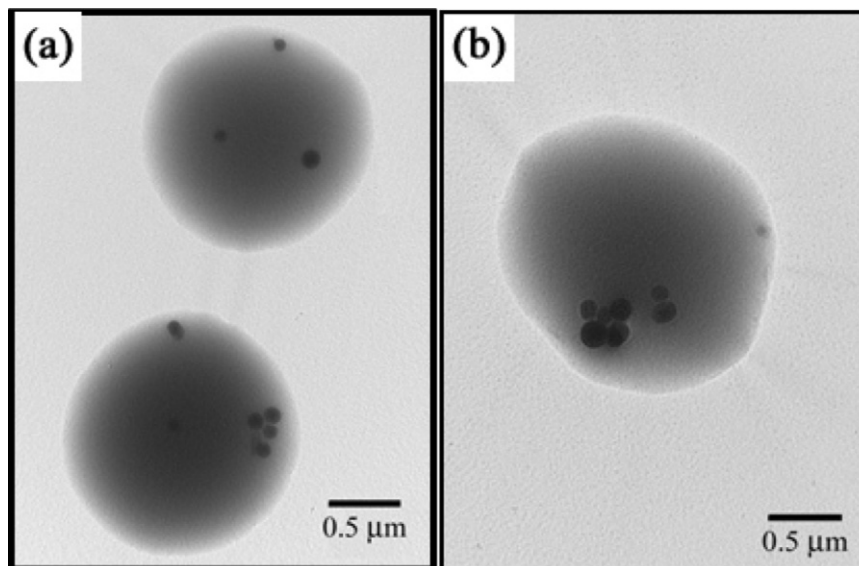

Fig. 6. TEM images of PS/SiO$_2$ composites with different amounts of stabilizer (a) 5% and (b) 10%. Reprinted from [194] with permission from Springer.

was explained that the association might occur in the course of the polymerization due to the close mean distance between the surfaces of two adjacent SiO$_2$ beads in the reaction medium and a lack of stabilizer, especially with the smaller SiO$_2$ particles. It is known that the PS chains grow in the continuous phase and reach a particular molecular weight at which they are no longer soluble. At this point, either the polymer chains precipitate on the SiO$_2$ surface by partially copolymerizing with the methacryloyl groups

on the surface, or they associate with other growing polymer chains in the continuous phase and form small polymer aggregates. Associations between composite particles could happen until the concentration of stabilizer at the surface of the polymer is high enough to ensure a good stabilization of the composite particles which then contain several SiO$_2$ particles. ScCO$_2$ offers high monomer diffusivity for the growth of the tethered chains. It also brings the plasticization effect that increases the chain
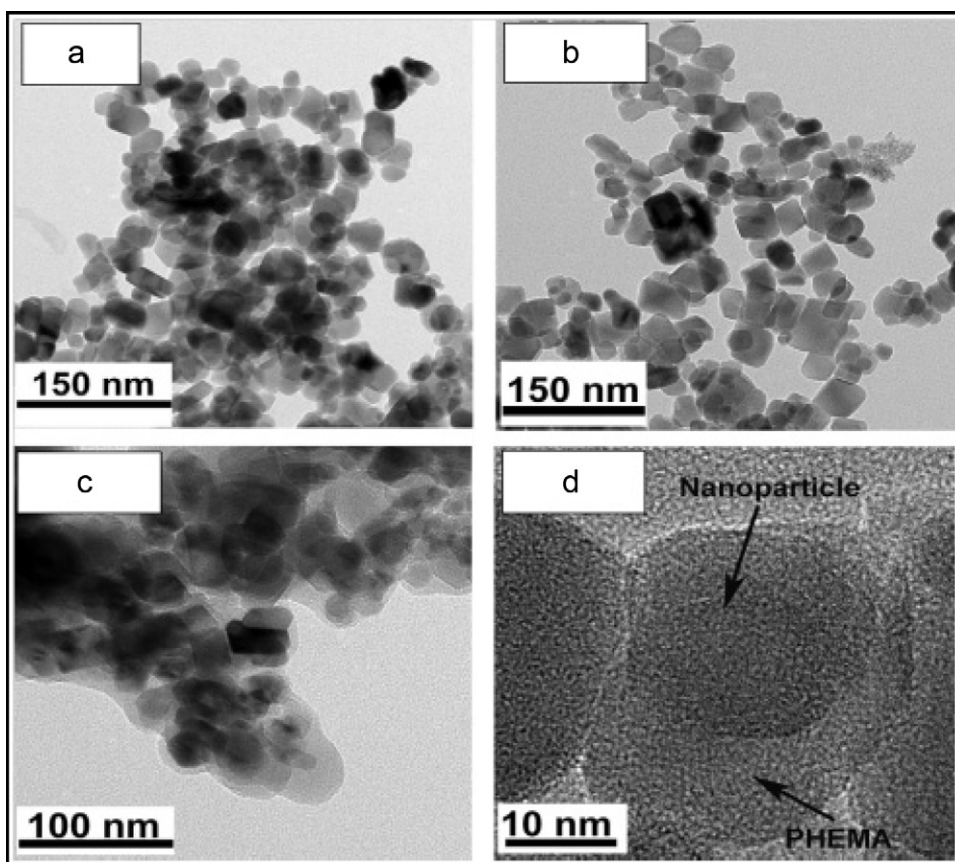
Fig. 7. TEM pictures of (a) pristine Fe_3O_4, (b) MPTMS-modified Fe_3O_4, (c) nanocomposite with 40 wt% Fe_3O_4 and (d) close inspection of composite. Reprinted from [197] with permission from Elsevier.

mobility and enhances the incorporation of SiO_2 particles into the polymer matrix.

The same group expanded their work to synthesize PMMA/TiO_2 [195] and PDVB/SiO_2 [196] composites in scCO$_2$. TiO_2 nanoparticles were first surface-grafted by the coupling agent methacryloxypropyltrimethoxysilane (MPTMS), possessing a methacrylate end group which copolymerized with MMA. Relatively stable composite latexes were formed in scCO$_2$ at 7.5% w/w TiO_2 with respect to MMA in the presence of PDMS-b-PMA stabilizer, which resulted in dry white uniform spherical particles [195]. With increasing the ratio of TiO_2 concentration to 15 and 20% (w/w MMA), agglomerated particles were obtained due to the insufficient stabilization of latexes in CO_2. In the case of PDVB/SiO_2 composites [196], the as-synthesized SiO_2 particles (130 nm) were surface-modified using MPS and used as seeds in the dispersion polymerization of DVB in scCO$_2$. The composite particles were successfully synthesized with the effective stabilization provided by poly(FBMA-co-DPAEMA). Uniform and spherical composite particles with an average diameter of 1.60 μm were produced at a 6% stabilizer concentration and 5% SiO_2 loading ratio, whereas agglomerated particles with irregular shapes resulted from a 3% stabilizer concentration due to the reduced stabilization effect. At the higher loading of 10% SiO_2, the particle size increased to 2.01 μm, but the morphology became less uniform with slight aggregation.

Other researches also contributed some important results in this field. Matsuyama and Mishima [66] synthesized PMMA–TiO_2 and PS–TiO_2 composites by pseudo-dispersion polymerization in scCO$_2$ in the presence of MPS-modified TiO_2 nanoparticles. The MPS-modified TiO_2 nanoparticles serve as a stabilizer, and their anchoring segments adhere to the MMA monomer through

physical adsorption and chemical grafting. The hydrogen bonding between the carbonyl group of MMA and the hydroxyl group on the TiO_2 surface leads to the formation of PMMA–TiO_2 composite particles in scCO$_2$ without the use of fluorinated and siloxane-based stabilizers. On the other hand, the polymerization of PS yields a bulk solid. This reason is St does not have hydrogen bonding site, as MMA does. So, there is no interaction between St and the hydroxyl
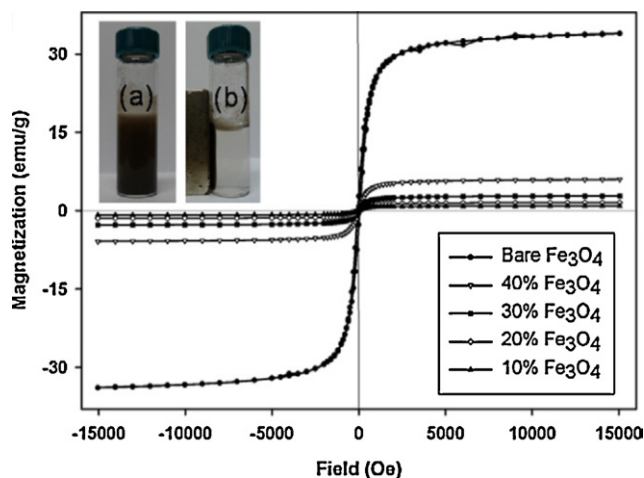

Fig. 8. Magnetization curves of pristine Fe_3O_4 and nanocomposites with different Fe_3O_4 content at 300 K.
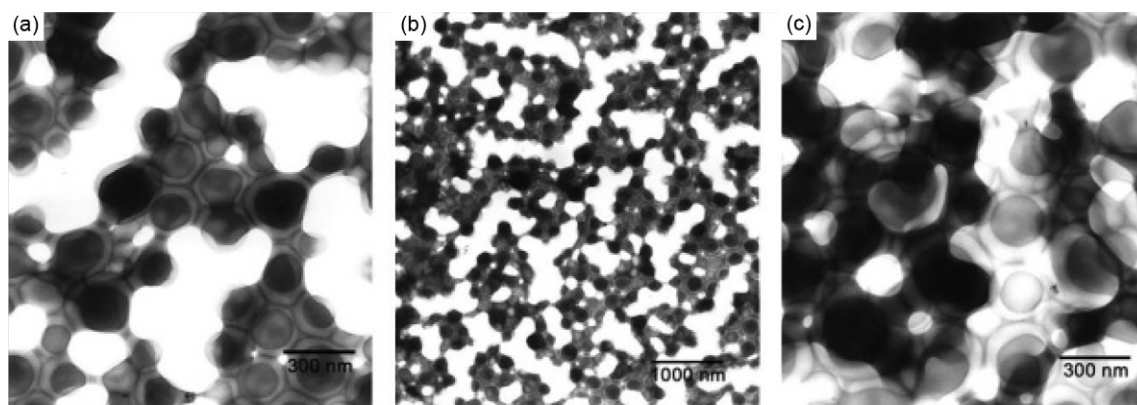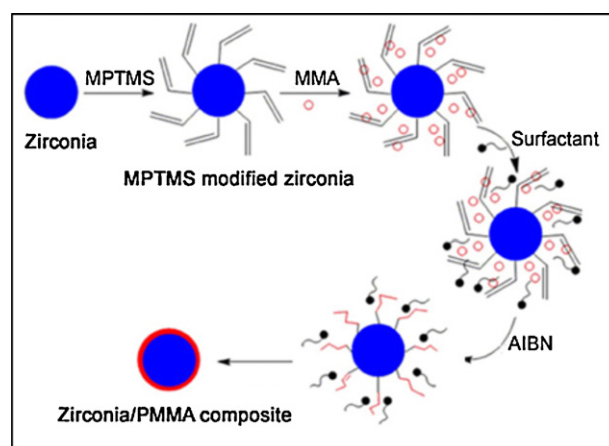Reprinted from [197] with permission from Elsevier.

Fig. 9. TEM pictures of (a) PMMA/ZrO$_2$ – 2.5%, (b) PMMA/ZrO$_2$ – 5% and (c) PMMA/ZrO$_2$ – 10% composites. Reprinted with permission from [198]. Copyright Wiley-VCH Verlag GmbH & Co. KGaA.

group present on the TiO$_2$ surface. Therefore, the morphologies of PMMA and PS composites were found to be quite different from each other.

Nguyen et al. [197] successfully prepared poly(2-hydroxyethyl methacrylate) (PHEMA) and magnetic nanoparticle (Fe$_3$O$_4$) hybrid nanocomposites by dispersion polymerization in scCO$_2$ using a copolymeric stabilizer, poly[(2-dimethylamino)ethyl methacrylate-*co*-1*H*,1*H*-perfluorooctyl methacrylate] (PDMAEMA-*co*-PFOMA). Fe$_3$O$_4$ nanoparticles were first surface-modified by the silane coupling agent MPTMS followed by copolymerization with 2-hydroxyethyl methacrylate (HEMA). The concentrations of Fe$_3$O$_4$ nanoparticles used as seeds in the composite formation were found to be 10, 20, 30 and 40% (w/w to HEMA) respectively. TEM analysis (Fig. 7) proved that the Fe$_3$O$_4$ nanoparticles were fairly dispersed in the polymer matrix. The prepared composite particles were non-spherical in shape with the average particle size of 30 nm. They observed agglomerated composite particles due to the ineffective stabilization of latex particles in CO$_2$. Magnetic property increased with the increasing amount of Fe$_3$O$_4$ nanoparticles in the composite. Fig. 8 shows the magnetization curves of composites with different amounts of Fe$_3$O$_4$ nanoparticles. The saturation magnetization increased up to 5.75 emu/g by the addition of 40% Fe$_3$O$_4$. These samples had an excellent superparamagnetic property, which was favorable for their bio-applications. Very recently, Haldorai et al. [198] synthesized zirconia (ZrO$_2$) nanoparticles of average size 200 nm by sol–gel method and formation of composites with PMMA via in situ radical dispersion polymerization in scCO$_2$ using a commercially available stabilizer poly(dimethylsiloxane)-*g*-pyrrolidone carboxylic acid (Monosil PCA). They also surface-modified the ZrO$_2$ nanoparticles by MPTMS, which was capable of copolymerizing with MMA and provided a reactive C=C bond. The TEM images of PMMA/ZrO$_2$ nanocomposites clearly showed that the core–shell morphology was successfully produced with PMMA (light color) as the shell and ZrO$_2$ as the core (dark) (Fig. 9). The nature of association between filler and the polymer component showed that almost all ZrO$_2$ particles were encapsulated by PMMA for composites with 2.5 and 5% ZrO$_2$ (Fig. 9a and b), whereas some ZrO$_2$ particles exist outside of the polymer surface in the case of composite with 10% ZrO$_2$ (Fig. 9c). This can be attributed to the fact that the percentage of grafting onto the polymer decreases with the increasing amount of ZrO$_2$ particles in the composite. For the composite with 10% ZrO$_2$, the TEM picture revealed highly agglomerated particles without a clear core–shell type image. It is clear that the particle agglomeration is directly proportional to the amount of ZrO$_2$ loaded. The possible mechanism for the synthesis of PMMA/ZrO$_2$ hybrid composite is shown in Scheme 8. In principle,

Scheme 8. Schematic representation for the synthesis of PMMA/ZrO$_2$ composite. Reprinted with permission from [198]. Copyright Wiley-VCH Verlag GmbH & Co. KgaA.

this simple and environmentally friendly synthetic procedure can be employed to prepare other metal oxide containing polymer composites.

5. Conclusions

In summary, this article provided an overview on the synthesis of polymer–inorganic filler nanocomposites in scCO$_2$ by different methods. Principally, three methods for the preparation of nanocomposites can be used: blending, sol–gel and in situ polymerizations. All the three methods were successfully investigated, and scCO$_2$ was demonstrated to be a viable alternative to the conventional solvents. By combining the attractive functionalities of both the components, the resultant nanocomposites could potentially provide many applications in various areas such as biomedical, automotive, aerospace, optoelectronics, etc. Apart from the properties of individual components in a nanocomposite, the degree of dispersion of nanoparticles in the polymer and the interfacial interaction play important roles in enhancing or limiting the overall properties of the system. Although much work has already been done on various aspects of polymer/inorganic filler nanocomposites, more research is required in order to further understand the complex structure–property relationships. As a simple and universal synthetic approach, the techniques reported here can be easily applied to synthesize other metal or metal oxide/polymers nanocomposites.

Acknowledgment

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