1

Introduction of Polymer Nanocomposites

Teng Li[1]*, Guanglong Ding*[2]*, Su-Ting Han*[1]*, and Ye Zhou*[2]

[1] *Shenzhen University, Institute of Microscale Optoelectronics, Room 909, Shenzhen, Guangdong 518060, China*
[2] *Shenzhen University, Institute for Advanced Study, Room 358, Shenzhen, Guangdong 518060, China*

1.1 Introduction

Polymers have been one of the most important components in almost every area of human activity today. Nowadays, polymers as multifunctional materials gradually replace metals, glass, paper, and other traditional materials in various applications due to its lightweight, flexibility, and low cost [1]. In most of their applications, the applied materials are not composed of a single chemical component but mixture systems of multiple components with polymers and other additives. By incorporating different additives, such as metal, minerals, or even air, a wide variety of materials with unique physical properties and competitive production costs can be produced. For example, glass fiber-reinforced plastics are composite materials manufactured by laminating unsaturated polyester resin with glass fiber and filler, which can increase mechanical strength and heat resistance [2].

In addition, scientific research shows that the size of filling material in fiber reinforced composites has a great influence on the material properties, since the size of the filling particles largely determines the surface interactions of adhesion, particle movement, dispersion, and bonding between the surface and matrix [3]. With the particle size of the filler that gradually reduces to the nanoscale, some properties depending on the interface have undergone great changes, such as gas adsorption, chemical activity, electrical properties, and catalytic activity. Examples of different sizes of materials are shown in Figure 1.1, and a hydrogen atom is about 0.1 nm in size, while a human hair is 10^4 nm in diameter. Among them, nanomaterials are employed to describe the materials that have at least one dimension in the size range from approximately 1 to 100 nm [4]. Different from the bulk and microscale materials, nanomaterials are unique in that they have many unusual, useful, and interesting properties. For example, bulk gold is a very stable precious metal in golden color, which can be kept for a long time under atmospheric environment, so it is used as the initial currency by people. Unlike bulk gold, gold nanoparticles dispersed in water will show different colors according to the size of nanoparticles,

Polymer Nanocomposite Materials: Applications in Integrated Electronic Devices, First Edition.
Edited by Ye Zhou and Guanglong Ding.

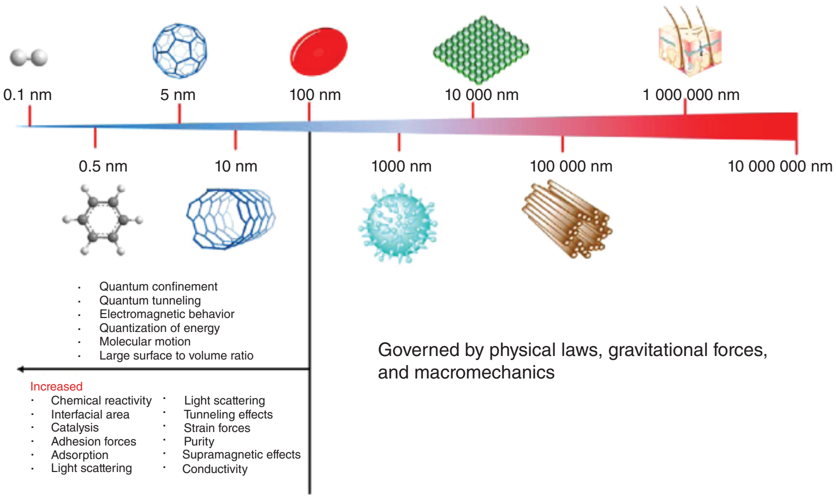


Figure 1.1 Nanomaterials peculiarities of size scale.

and they have high reactivity that can even be used as catalyst at low temperature [5]. Since most of the properties of nanomaterials depend on their size, shape, and surface structure, their ultrafine size always tends nanomaterials to aggregate into bulk materials, especially without proper stabilization in their formation and application [6]. This is because the agglomeration process makes the high surface energy and activity of nanomaterials decrease to a more stable state. Therefore, in order to preserve the properties of nanomaterials, it is necessary to distribute them uniformly in matrices to prevent from aggregating into bulk materials [7].

Polymer nanocomposites (PNCs) are the mixture of polymers and nanomaterials, having at least one-dimensional structure and one component material in the nanometer regime of less than 100 nm. Combining nanomaterials into the polymer matrix not only makes it possible to produce a new class of properties provided by uniformly dispersed nanomaterials, but also greatly improves most of expected properties of the original polymer, such as mechanical properties, heat resistance, biodegradability, and so on [8]. As early as 1970, the term “nanocomposites” was first proposed by Theng [9], and PNCs began to develop in commercial research institutions and academic laboratories in the late 1980s [10, 11]. Over the past decade, PNCs have made great progress in various fields, which is reflected by the exponential growth of publications from their inception (Figure 1.2). The existence of nanomaterials in polymer matrix changes the surface chemical and physicochemical properties of PNCs, where the geometry, surface chemistry, aspect ratio, and size of nanomaterials are the key parameters to regulate these performances. Therefore, PNCs are a new class of materials with unique properties, which are far superior to traditional doped and composite polymer systems. The large interface interaction between nanomaterials and polymer matrix surfaces and the difference of nanoscale fundamentally distinguish PNCs from the traditional system. The development of nanomaterials and polymer science and technology

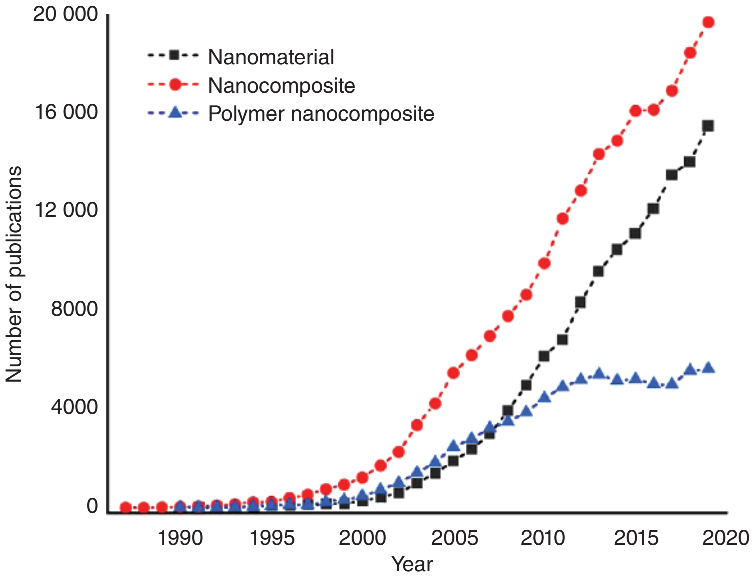


Figure 1.2 Number of publications per year on "nanomaterials," "nanocomposites," and "polymer nanocomposites," according to SciFinder Scholar on 30 April 2020.

has promoted many applications of PNCs, which cover almost all fields of polymer material application fields, such as microelectronics, magnetic electronics, biological materials, sensor, energy storage, and so on [12]. Therefore, the chapters include unique perspectives of different experts with their knowledge and understanding of PNCs in this book.

1.2 The Advantage of Nanocomposites

Since the fillers of nanocomposites are nanoscale, the performances of nanocomposites can be improved by the advantages of the reduction of filler size and the increased surface area. In terms of size, the filler is 3 orders of magnitude smaller than the traditional substitute. In addition, the quantum confinement effects caused by the nanomaterials will lead to new physical phenomena, which can be applied in electrical and optical research. Many of these properties are related to the size of the polymer chain, and the polymer chain close to the fillers is affected by the interaction between the packing surface and the polymer matrix, which is different from the polymer chain far away from the interface. The size of polymer chain can be reflected the radius of gyration R_g, and the thickness of the interface regions (t) around the particle is independent of the particle size. Therefore, the volume of interface material ($V_{\text{interface}}$) relative to the volume of particle (V_{particle}) will increase with the decrease of particle size.

Figure 1.3 shows the functional relationship between the $V_{\text{interface}}/V_{\text{particle}}$ varies and the aspect ratio of particles [13]. The aspect ratio reflects the shape of the

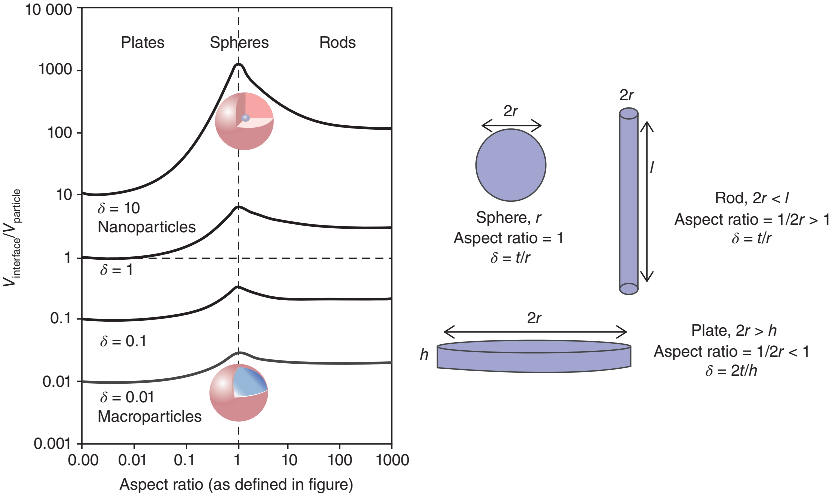


Figure 1.3 The graph on the left shows the function relationship between the ratio of interfacial volume to the particle volume ($V_{interface}/V_{particle}$) and the particle aspect ratio. The red shell represents the interface of particle, where the blue nucleus represents the particle. The graph on the right defines the particle aspect ratio and the ratio of the interfacial thickness to the particle size (δ) with different shapes (r is radius, l is length, h is height). The interface thickness (t) is considered to be independent of particle size. When the particle size is reduced to less than 100 nm, the physical properties can be controlled by the volume of the interface around the particle, which is especially obvious for the sphere and rod. Source: Winey and Vaia [13].

particles, which can be divided to plate (aspect ratio <1), sphere (aspect ratio = 1), and rod (aspect ratio >1). δ represents the size of the filler, that is, the ratio of the interface thickness t to the minimum dimension size of the particle. For spherical and rod-shaped particles, δ is equal to the t/r, but δ is $2t/h$ in plate-shaped particles. When the particle is microscale, δ is approximately equal to 0.01, and the particle volume exceeds the volume of the interface region in all shapes. As the particle size decreases, $V_{interface}/V_{particle}$ values gradually increases. When δ goes above one, $V_{interface}$ is going to exceed $V_{particle}$. When the particles reach the nanoscale ($\delta = 10$), the interface volume is more than 10 times that of the particle. Moreover, particles with different shapes have different $V_{interface}/V_{particle}$ in the same δ. The three-dimension sphere has the highest value, followed by the two-dimensional rod and the one-dimensional plate. With the decrease of particle size, the gap becomes more obvious, and even the $V_{interface}/V_{particle}$ of spherical particles is 2 orders of magnitude larger than that of plate-shaped particles. Therefore, the addition of nanoscale fillers has a great impact on the performance of polymer in PNCs. Even if the volume fraction of fillers is very small, the resulting interface region volume will be very large.

As the interaction between polymer and particle is strengthened in PNCs, the interparticle interface and coordination will be reflected in the macroscopic properties. Due to the nanoscale of particles, the secondary forming constituents have a very high aspect ratio of over 100. When the volume fraction is 1–5%, these fillers can reach the percolation thresholds, which refer to the critical value of the volume fraction of the packed particles that can mutate a certain physical property of the composite material system. Therefore, the mechanical and transport performances of PNCs can be greatly improved under the condition of low load nanoparticles. Especially for the conductive particles, when the volume fraction of these particles increases to a certain critical value in polymer, conductivity of the polymer suddenly increases sharply from insulator to conductor, and the change range is up to 10 orders of magnitude.

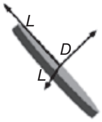
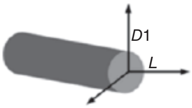
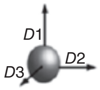
1.3 Classification of Nanoscale Fillers

So far, various types of nanomaterials have been found to be able to form PNCs with polymers. According to different applications, nanoparticles with corresponding properties can be selected into the polymer system to achieve the expected performance. In general, these nanofillers suitable for PNC applications can be mainly divided into one-, two-, and three-dimensional materials according to their different dimensions (Table 1.1).

1.3.1 One-Dimensional Nanofillers

One-dimensional nanofillers are plate-like materials with one-dimensional dimensions less than 100 nm, which are usually a few nanometers thick and relatively long sheets [14]. Most one-dimensional nanofillers have unique morphology

Table 1.1 Overview of nanomaterials classified by their nanoscale dimensions.

Plate	**Rod**	**Sphere**
		
• Montmorillonite clays (MMT)	• Carbon nanofibers (CNFs)	• Nano-silica (n-silica)
• Nanographene platelets (NGPs)	• Carbon nanotubes (CNTs)	• Nano-alumina (n-Al_2O_3)
• Layered double hydroxide (LDHs)	• Halloysite nanotubes (HNTs)	• Nano-silver (n-Ag)
	• Nickel nanostrands (NiNs)	• Nano-titanium dioxide (n-TiO_2)
	• Aluminum oxide nanofibers (Nafen)	• Nano-silicon carbide (n-SiC)
		• Nano-zinc oxide (n-ZnO)
		• POSS

characteristics, such as nanoplate [15], nano-disk [16], nano-wall [17–23], etc., which play an important role in functional nano-devices [24, 25]. Recently, the widely studied materials are montmorillonite clays (MMT) [26], nanographene platelets (NGPs) [27, 28], ZnO nanosheets [29–31], Fe_3O_4 nanosheets [30], and so on, which have excellent electrical, optical, and magnetic properties [32], and are widely used in the fields of micro–nano electronics, biosensors, and chemical engineering [33]. The one-dimensional nanofillers are common nanomaterials in electronic and thermal devices due to their shape characteristics.

1.3.2 Two-Dimensional Nanofillers

Two-dimensional fillers are the materials with two dimensions less than 100 nm, and they are mostly in the form of rods [14]. The typical two-dimensional nanomaterials are carbon nanofibers (CNFs), carbon nanotubes (CNTs), halloysite nanotubes (HNTs), nickel nanostrands (NiN_S), and aluminum oxide nanofibers (Nafen). In addition, the most common two-dimensional nanofillers in PNCs are nanotubes [34], plant fibers [35–39], nanowires [40], carbon fibers [41–44], oxides [45–55], graphene [56, 57], molybdenum disulfide (MoS_2) [58], and hexagon boron nitride (h-BN) [59]. Compared with one- and three-dimensional fillers, two-dimensional fillers have better flame retardancy and striped characteristic, resulting in wide applications in the fields of catalysis, electronics, optics, sensing, and energy [3, 26, 60–62].

1.3.3 Three-Dimensional Nanofillers

Three-dimensional nanofillers are nanomaterials with three dimensions on the nanometer scale, so they are mostly spherical or cube-shaped [63], which is also commonly referred to zero-dimensional particles. The most common three-dimensional fillers are polyhedral oligomeric silsesquioxane (POSS), nanosilicon, nanometal particles, nanometal oxides, and quantum dots (QDs) [33, 64]. Among them, metals and metal oxide nanoparticles have the advantages of high stability, catalytic activity, and easy preparation, and they are often used in the fields of catalysis [65], purification [66–69], coatings [70–74], and biological fields [75, 76], together with various polymers. One-, two-, and three-dimensional nanofillers all have various special properties, and will ultimately promote the remarkable performance of PNCs by loading in compatible polymers.

1.4 The Properties of Polymer Nanocomposites

In PNCs, many properties of the original polymer can be greatly improved, as well as new properties resulting from the addition of nanoparticles. As shown in Figure 1.4, the main properties of PNCs are listed, covering physical, chemical, and biological areas. In general, the improvement level of properties is determined by the size,

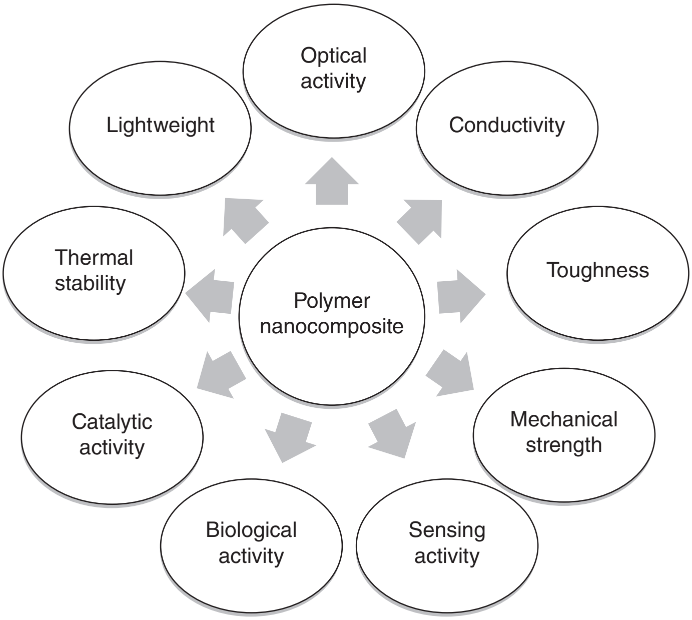


Figure 1.4 Significant properties of polymer nanocomposites.

loading capacity, aspect ratio, dispersion uniformity, and interface interactions of the nanofillers with polymer matrix [4].

For example, most polymers don't possess conductivity except some conducting polymers, which is due to the covalent bonding of polymers and the lack of electron channels or ion migration. Interestingly, new PNCs formed by adding conductive nanofillers to insulating polymers exhibit many electrical properties. As early as 1994, Ajayan et al. used CNTs as reinforcement materials to prepare PNCs [77]. Since then, there have been a lot of researches on using CNTs as fillers to improve the electrical properties of PNCs. Only a small volume fraction of such fillers is needed to improve the electrical properties of polymers by several orders of magnitude effectively [78].

1.5 Synthesis of Polymer Nanocomposites

In the synthesis of PNCs, it is necessary to uniformly distribute the fillers into matrix in order to realize the functions of fillers. However, due to the fact that the fillers are nanoscale, the uniform dispersion is much different from that of the microscale fillers, which is mainly manifested in the following aspects. First, if the filling operation is carried out according to the volume fraction, much more nanometer fillers than the microfillers are required at the same volume fraction. Therefore, the nanoparticles in matrix are very crowded with greater van der Waals and electrostatic interactions between the particles, making it difficult to distribute evenly. Second, the anisotropic nanofillers have a very high aspect ratio, which makes them

Table 1.2 Summary of common methods for synthesis of polymer nanocomposites.

Technique	Suitable filler	Suitable matrix	Solvent	Controlling factors
Ultrasonication-assisted solution mixing	All types	Liquid or viscous monomers or oligomers of thermosets	Required	Sonication power and time
Shear mixing	Nanosheets	Liquid or viscous monomers or oligomers of thermosets	Required	Shapes of the rotor blades, rotating speed and time
Three roll milling	Nanosheets and nanotubes	Liquid or viscous monomers or oligomers of thermosets	Not required	Speed of roller, gap between adjacent roller
Ball milling	All types	Liquid or solid thermoplastics and thermosets	Not required	Time of milling, ball size, rotating speed, ball/nanofiller ratio
Double-screw extrusion	All types	Solid thermoplastics	Not required	Processing temperature, screw configuration, rotation speed
In situ synthesis	All types	Liquid or viscous monomers or oligomers of thermosets	Required	Chemical reaction conditions, temperature, condensation rate

more prone to agglomerate. For example, monolayer graphene has aspect ratio of about 10^4, so they tend to reduce their surface energy by π–π stacking. Third, a large amount of nanofillers with huge surface area is loaded in the polymer matrix, which will produce a large interface area and change the overall performances of the PNC. Therefore, the decisive step in the synthesis of PNCs is the uniform dispersion of nanofillers in polymer matrix. As shown in Table 1.2, the common methods to disperse nanofillers and prevent the aggregation of nanoparticles by using external energy are summarized.

1.5.1 Ultrasonication-assisted Solution Mixing

The most widely used approach to produce PNCs is ultrasonication-assisted solution mixing [79–83]. In this method, the nanofillers and polymer are initially dissolved in a solution. Then the nanofillers are evenly distributed in the matrix in assistant of the ultrasound. Afterwards, the PNCs are obtained by evaporation of the solvent.

The nanoparticles are separated from the agglomeration state to the smaller units by the ultrasonic energy, which is higher than the energy of interaction between the nanomaterials in the aggregates. With the increase of ultrasonic time, the aggregates of nanofillers are broken down into smaller ones, and even become individual nanoparticles independent of other nanoparticles in the polymer. In addition, this process often occurs at a high temperature, which can initiate in situ polymerization of reactive monomers or their soluble prepolymers with nanomaterials to enhance interfacial interactions [84].

Due to the simple operation and stable performance, the ultrasonic-assisted solution mixing method has been widely used in the researches of new nanocomposites. However, due to the poor effect of ultrasound in high viscosity solution, most of the polymers need to be dissolved in a high boiling point solvent and maintain a low concentration, which will affect the process of solvent removal and ultimately reduce the quality of the nanocomposites. Therefore, when using this method, it is important to pay attention to the choice of solvent.

1.5.2 Shear Mixing

Compared with the ultrasonic-assisted method, shear mixing is a much more common and simple method, which only requires the stirring process and has the potential for industrial mass production [85]. In the process of stirring, the shear force generated by stirrer rotating is used to separate the aggregates of nanofillers. Due to the low strength of the shear force, the nanoparticles will be separated under stirring and then aggregated again, so it is generally necessary to increase the speed of the agitator to complete the separation. This method generally does not destroy the structure of nanofillers; therefore it is suitable not only for separating loosely bound nanoaggregates, but also for stripping off some layered nanosheets. In addition, this method needs to be carried out in low viscosity solvent just like ultrasonic assisted method.

1.5.3 Three Roll Milling

Three roller milling is a method of dispersing nanofillers by the shearing force between rolls in high viscosity matrix, such as ink, paste material, coating, etc. The machine of three roll milling is composed of three cylindrical rollers with different rotating speeds, and the adjacent rollers rotate in the opposite direction. The particle size distribution and uniformity of the packing can be well controlled as the speeds of the rollers and the gap between them are adjustable. In addition, the shearing force generated between the rollers is higher than that generated by stirring, so the method can be applied to high viscosity materials, and carried out under the condition of little or no solvent. Therefore, this method is often used to disperse some anisotropic nanofillers, such as CNTs [86–89], graphene nanosheets [90–92], nanoclays [93–95], and so on.

However, it should be noted that the distance between adjacent rollers should be at least 1 μm, so the dispersion effect of nanospheres with three-dimensional direction less than 100 nm will not be good. The aggregates of nanospheres can only be turned into smaller units, not broken into individual particle. On the other hand, the rotation of the roller requires the addition of viscous materials, and nanofillers can only be dispersed in the thermosetting matrix but not in the thermoplastic matrix.

1.5.4 Ball Milling

Ball milling is widely used in metallurgy and mineral processing industry [96]. The principle of ball milling is to grind and mix powders in a closed space by using the huge shear force and compression force produced by hard ball collision. In the synthesis of PNCs, this method can disperse CNTs [97], graphene nanoparticles [98–101], silica nanoparticles [102], and BNs [103, 104] into thermoplastic and thermosetting polymers. The high shear force produced by ball milling can peel off some two-dimensional nanostructures, such as graphene, MoS_2, and BNs, but may not separate the interlayer structure connected by ionic bonding [105–110]. In addition, ball milling is not only suitable for solvent-free conditions but also solvent-free conditions, so nanofillers can be directly dispersed in some solid thermoplastic matrix, such as polyethylene (PE) [101, 111], polyphenylene sulfide [104, 112], and polymethyl methacrylate (PMMA) [102].

1.5.5 Double-screw Extrusion

Double-screw extrusion disperses nanofillers in thermoplastic matrix by huge shear force generated by high speed rotation of double-screw at high temperature [113, 114]. This method has been widely used in industry due to the advantages of solvent-free and environment-friendly technology. With this method, the fillers can be dispersed into the polymer in a high content way to achieve the well-controlled performance, and applied to different sizes of nanoparticles, such as graphene sheets [115], CNTs [116], and silicon dioxide [117]. This method needs higher temperature, which is helpful to reduce the viscosity of polymer and load more nanofillers, but also has the risk of decomposing polymers and nanofillers. The reason is owing to the existence of low thermal stability functional groups in the materials. When the temperature is too high, the fracture will occur, resulting in the deterioration of the performance of PNCs [118]. Moreover, the gap between the screws is too large to keep some aggregates of nanofillers evenly, which will not achieve the uniform monodispersing of nanofillers. So, it is necessary to combine other technologies to further improve the performance [119, 120].

1.5.6 In Situ Synthesis

In addition to the aforementioned methods of dispersing prepared nanofillers into polymers, another important synthesis strategy is in situ synthesis, which directly generates nanoparticles in polymers through molecular precursors [121]. This method can be divided into chemical and physical in situ synthesis [122]. Chemical in situ synthesis is used to synthesize nanoscale fillers by chemical reaction, such as the hydrothermal method and sol–gel method [123, 124]. The physical in situ synthesis is transforming the precursor of gas phase into inorganic nanoparticles through plasma action, and then condensing the organic compounds on the surface of inorganic particles to cover the polymer shell to form PNCs [125].

1.6 Conclusions and Future Outlook

In this chapter, the basic principles, properties, and synthesis methods of PNCs are clearly described. The composite material has unique structure and performance, and has a wide range of applications in many fields. The particle size, orientation, shape, dispersion, and volume dispersion of nanofillers affect the properties of PNCs. Most of the physical, chemical, and mechanical properties of PNCs depend on the interface interaction between the filler and the matrix. Therefore, the uniform dispersion of nanofillers is the most important consideration in the synthesis of PNCs. PNCs have recently become part of modern technology, but these areas are still in the early stage of development. With more and more scientists and engineers contributing to the understanding of PNCs, these functional materials will be applied in more and more fields.

References

1 Karak, N. (2019). *Fundamentals of Nanomaterials and Polymer Nanocomposites*. Elsevier.

2 Brunner, G. (2014). *Supercritical Fluid Science and Technology*, vol. 5 (ed. G. Brunner). Elsevier.

3 Pradhan, S., Lach, R., Le, H.H. et al. (2013). Effect of filler dimensionality on mechanical properties of nanofiller reinforced polyolefin elastomers. *ISRN Polym. Sci.* 2013: 1–9.

4 Jordan, J., Jacob, K.I., Tannenbaum, R. et al. (2005). Experimental trends in polymer nanocomposites-a review. *Mater. Sci. Eng., A* 393: 1–11.

5 Xiao, J. and Qi, L. (2011). Surfactant-assisted, shape-controlled synthesis of gold nanocrystals. *Nanoscale* 3: 1383–1396.

6 Koo, J. (2015). *An Overview of Nanomaterials*. Cambridge University Press.

7 Vigneshwaran, N., Ammayappan, L., and Huang, Q. (2011). Effect of Gum arabic on distribution behavior of nanocellulose fillers in starch film. *Appl. Nanosci.* 1: 137–142.

8 Hussain, F., Hojjati, M., Okamoto, M., and Gorga, R.E. (2006). Review article: polymer-matrix nanocomposites, processing, manufacturing, and application: an overview. *J. Compos. Mater.* 40: 1511–1575.

9 Theng, B.K.G. (1970). Interactions of clay minerals with organic polymers. some practical applications. *Clays Clay Miner.* 18: 357–362.

10 Usuki, A., Kawasumi, M., Kojima, Y. et al. (1993). Swelling behavior of montmorillonite cation exchanged for ω-amino acids by ∈-caprolactam. *J. Mater. Res.* 8: 1174–1178.

11 Kojima, Y., Usuki, A., Kawasumi, M. et al. (2011). Mechanical properties of nylon 6-clay hybrid. *J. Mater. Res.* 8: 1185–1189.

12 Ray, S.S. and Bousmina, M. (2007). *Polymer Nanocomposites and Their Applications*. American Scientific Publishers.

13 Winey, K.I. and Vaia, R.A. (2011). Polymer nanocomposites. *MRS Bull.* 32: 314–322.

14 Verdejo, R., Bernal, M.M., Romasanta, L.J. et al. (2018). Reactive nanocomposite foams. *Cell. Polym.* 30: 45–62.

15 Nieto, A., Lahiri, D., and Agarwal, A. (2012). Synthesis and properties of bulk graphene nanoplatelets consolidated by spark plasma sintering. *Carbon* 50: 4068–4077.

16 Schmidt, F.P., Ditlbacher, H., Hohenester, U. et al. (2012). Dark plasmonic breathing modes in silver nanodisks. *Nano Lett.* 12: 5780–5783.

17 Jung, S.-H., Oh, E., Lee, K.-H. et al. (2008). Sonochemical preparation of shape-selective ZnO nanostructures. *Cryst. Growth Des.* 8: 265–269.

18 Siril, P.F., Ramos, L., Beaunier, P. et al. (2009). Synthesis of ultrathin hexagonal palladium nanosheets. *Chem. Mater.* 21: 5170–5175.

19 Dong, X., Ji, X., Jing, J. et al. (2010). Synthesis of triangular silver nanoprisms by stepwise reduction of sodium borohydride and trisodium citrate. *J. Phys. Chem. C* 114: 2070–2074.

20 Nayak, B.B., Behera, D., and Mishra, B.K. (2010). Synthesis of silicon carbide dendrite by the arc plasma process and observation of nanorod bundles in the dendrite arm. *J. Am. Ceram. Soc.* 93: 3080–3083.

21 Vizireanu, S., Stoica, S.D., Luculescu, C. et al. (2010). Plasma techniques for nanostructured carbon materials synthesis. a case study: carbon nanowall growth by low pressure expanding RF plasma. *Plasma Sources Sci. Technol.* 19: 34016.

22 Mann, A.K.P. and Skrabalak, S.E. (2011). Synthesis of single-crystalline nanoplates by spray pyrolysis: a metathesis route to Bi_2WO_6. *Chem. Mater.* 23: 1017–1022.

23 Tiwari, J.N., Tiwari, R.N., and Kim, K.S. (2012). Zero-dimensional, one-dimensional, two-dimensional and three-dimensional nanostructured materials for advanced electrochemical energy devices. *Prog. Mater Sci.* 57: 724–803.

24 Kim, K.S., Zhao, Y., Jang, H. et al. (2009). Large-scale pattern growth of graphene films for stretchable transparent electrodes. *Nature* 457: 706–710.

25 Bae, S., Kim, H., Lee, Y. et al. (2010). Roll-to-roll production of 30-inch graphene films for transparent electrodes. *Nat. Nanotechnol.* 5: 574–578.

26 Isitman, N.A., Dogan, M., Bayramli, E., and Kaynak, C. (2012). The role of nanoparticle geometry in flame retardancy of polylactide nanocomposites containing aluminium phosphinate. *Polym. Degrad. Stab.* 97: 1285–1296.

27 Shen, J., Hu, Y., Li, C. et al. (2009). Synthesis of amphiphilic graphene nanoplatelets. *Small* 5: 82–85.

28 Li, B. and Zhong, W.-H. (2011). Review on polymer/graphite nanoplatelet nanocomposites. *J. Mater. Sci.* 46: 5595–5614.

29 Umar, A. and Hahn, Y.B. (2006). ZnO nanosheet networks and hexagonal nanodiscs grown on silicon substrate: growth mechanism and structural and optical properties. *Nanotechnology* 17: 2174–2180.

30 Bai, W., Zhu, X., Zhu, Z., and Chu, J. (2008). Synthesis of zinc oxide nanosheet thin films and their improved field emission and photoluminescence properties by annealing processing. *Appl. Surf. Sci.* 254: 6483–6488.

31 Mani, G.K. and Rayappan, J.B.B. (2014). A simple and template free synthesis of branched ZnO nanoarchitectures for sensor applications. *RSC Adv.* 4: 64075–64084.

32 Li, B.L., Setyawati, M.I., Chen, L. et al. (2017). Directing assembly and disassembly of 2D MoS_2 nanosheets with DNA for drug delivery. *ACS Appl. Mater. Interfaces* 9: 15286–15296.

33 Vengatesan, M.R. and Mittal, V. (2016). *Nanoparticle- and Nanofiber-Based Polymer Nanocomposites: An Overview*. Wiley-VCH.

34 Yang, J., Zhang, Z., Friedrich, K., and Schlarb, A.K. (2007). Creep resistant polymer nanocomposites reinforced with multiwalled carbon nanotubes. *Macromol. Rapid Commun.* 28: 955–961.

35 Fahmy, T.Y.A., Mobarak, F., Fahmy, Y. et al. (2005). Nanocomposites from natural cellulose fibers incorporated with sucrose. *Wood Sci. Technol.* 40: 77–86.

36 Garcia de Rodriguez, N.L., Thielemans, W., and Dufresne, A. (2006). Sisal cellulose whiskers reinforced polyvinyl acetate nanocomposites. *Cellulose* 13: 261–270.

37 Fahmy, T.Y.A. and Mobarak, F. (2008). Nanocomposites from natural cellulose fibers filled with kaolin in presence of sucrose. *Carbohydr. Polym.* 72: 751–755.

38 Lee, K.-Y., Bharadia, P., Blaker, J.J., and Bismarck, A. (2012). Short sisal fibre reinforced bacterial cellulose polylactide nanocomposites using hairy sisal fibres as reinforcement. *Compos. Part A: Appl. Sci. Manuf.* 43: 2065–2074.

39 Ibrahim, I.D., Jamiru, T., Sadiku, E.R. et al. (2016). Impact of surface modification and nanoparticle on sisal fiber reinforced polypropylene nanocomposites. *J. Nanotechnol.* 2016: 1–9.

40 Lonjon, A., Laffont, L., Demont, P. et al. (2010). Structural and electrical properties of gold nanowires/P(VDF-TrFE) nanocomposites. *J. Phys. D* 43: 345401.

41 Xu, Y. and Hoa, S.V. (2008). Mechanical properties of carbon fiber reinforced epoxy/clay nanocomposites. *Compos. Sci. Technol.* 68: 854–861.

42 Pozegic, T.R., Anguita, J.V., Hamerton, I. et al. (2016). Multi-functional carbon fibre composites using carbon nanotubes as an alternative to polymer sizing. *Sci. Rep.* 6: 37334.

43 Ulus, H., Şahin, Ö.S., and Avcı, A. (2016). Enhancement of flexural and shear properties of carbon fiber/epoxy hybrid nanocomposites by boron nitride nano particles and carbon nano tube modification. *Fibers Polym.* 16: 2627–2635.

44 Ye, G. (2017). Preparation of poly(7-formylindole)/carbon fibers nanocomposites and their high capacitance behaviors. *Int. J. Electrochem. Sci.* 12: 8467–8476.

45 Lu, X., Chao, D., Chen, J. et al. (2006). Preparation and characterization of inorganic/organic hybrid nanocomposites based on Au nanoparticles and polypyrrole. *Mater. Lett.* 60: 2851–2854.

46 Subedi, D.P., Madhup, D.K., Sharma, A. et al. (2012). Retracted: study of the wettability of ZnO nanofilms. *Int. Nano Lett.* 2: 1.

47 Ślosarczyk, A., Barełkowski, M., Niemier, S., and Jakubowska, P. (2015). Synthesis and characterisation of silica aerogel/carbon microfibers nanocomposites dried in supercritical and ambient pressure conditions. *J. Sol–Gel Sci. Technol.* 76: 227–232.

48 Dhandapani, S., Nayak, S.K., and Mohanty, S. (2016). Compatibility effect of titanium dioxide nanofiber on reinforced biobased nanocomposites: thermal, mechanical, and morphology characterization. *J. Vinyl Add. Technol.* 22: 529–538.

49 Ma, J.-L., Chan, T.-M., and Young, B. (2016). Experimental investigation of cold-formed high strength steel tubular beams. *Eng. Struct.* 126: 200–209.

50 Saranya, M., Ramachandran, R., and Wang, F. (2016). Graphene-zinc oxide (G-ZnO) nanocomposite for electrochemical supercapacitor applications. *J. Sci. Adv. Mater. Devices* 1: 454–460.

51 Shehata, N., Gaballah, S., Samir, E. et al. (2016). Fluorescent nanocomposite of embedded ceria nanoparticles in crosslinked PVA electrospun nanofibers. *Nanomaterials* 6: 102.

52 Shehata, N., Samir, E., Gaballah, S. et al. (2016). Embedded ceria nanoparticles in crosslinked PVA electrospun nanofibers as optical sensors for radicals. *Sensors* 16: 1371.

53 Sunny, A.T., Vijayan, P.P., Adhikari, R. et al. (2016). Copper oxide nanoparticles in an epoxy network: microstructure, chain confinement and mechanical behaviour. *Phys. Chem. Chem. Phys.* 18: 19655–19667.

54 Alswata, A.A., Ahmad, M.B., Al-Hada, N.M. et al. (2017). Preparation of zeolite/zinc oxide nanocomposites for toxic metals removal from water. *Results Phys.* 7: 723–731.

55 Fambri, L., Dabrowska, I., Ceccato, R., and Pegoretti, A. (2017). Effects of fumed silica and draw ratio on nanocomposite polypropylene fibers. *Polymers* 9: 41.

56 Wang, X. and Song, M. (2013). Toughening of polymers by graphene. *Nanomater. Energy* 2: 265–278.

57 Paszkiewicz, S., Pawelec, I., Szymczyk, A., and Rosłaniec, Z. (2015). Thermoplastic elastomers containing 2D nanofillers: montmorillonite, graphene nanoplatelets and oxidized graphene platelets. *Polish J. Chem. Technol.* 17: 74–81.

58 Wang, X., Xing, W., Feng, X. et al. (2017). MoS_2/polymer nanocomposites: preparation, properties, and applications. *Polym. Rev.* 57: 440–466.

59 Ribeiro, H., Trigueiro, J.P.C., Silva, W.M. et al. (2019). Hybrid MoS_2/h-BN nanofillers as synergic heat dissipation and reinforcement additives in epoxy nanocomposites. *ACS Appl. Mater. Interfaces* 11: 24485–24492.

60 Rao, K.S., Senthilnathan, J., Ting, J.M., and Yoshimura, M. (2014). Continuous production of nitrogen-functionalized graphene nanosheets for catalysis applications. *Nanoscale* 6: 12758–12768.

61 Shahjamali, M.M., Salvador, M., Bosman, M. et al. (2014). Edge-gold-coated silver nanoprisms: enhanced stability and applications in organic photovoltaics and chemical sensing. *J. Phys. Chem. C* 118: 12459–12468.

62 Wan, J., Kaplan, A.F., Zheng, J. et al. (2014). Two dimensional silicon nanowalls for lithium ion batteries. *J. Mater. Chem. A* 2: 6051–6057.

63 Bhattacharya, M. (2016). Polymer nanocomposites-a comparison between carbon nanotubes, graphene, and clay as nanofillers. *Materials* 9: 262.

64 Kumar, A.P., Depan, D., Singh Tomer, N., and Singh, R.P. (2009). Nanoscale particles for polymer degradation and stabilization-Trends and future perspectives. *Prog. Polym. Sci.* 34: 479–515.

65 Shifrina, Z.B., Matveeva, V.G., and Bronstein, L.M. (2020). Role of polymer structures in catalysis by transition metal and metal oxide nanoparticle composites. *Chem. Rev.* 120: 1350–1396.

66 Sotto, A., Boromand, A., Balta, S. et al. (2011). Doping of polyethersulfone nanofiltration membranes: antifouling effect observed at ultralow concentrations of TiO_2 nanoparticles. *J. Mater. Chem.* 21: 10311–10320.

67 Huang, J., Zhang, K., Wang, K. et al. (2012). Fabrication of polyethersulfone-mesoporous silica nanocomposite ultrafiltration membranes with antifouling properties. *J. Membr. Sci.* 423–424: 362–370.

68 María Arsuaga, J., Sotto, A., del Rosario, G. et al. (2013). Influence of the type, size, and distribution of metal oxide particles on the properties of nanocomposite ultrafiltration membranes. *J. Membr. Sci.* 428: 131–141.

69 Zhao, S., Yan, W., Shi, M. et al. (2015). Improving permeability and antifouling performance of polyethersulfone ultrafiltration membrane by incorporation of ZnO-DMF dispersion containing nano-ZnO and polyvinylpyrrolidone. *J. Membr. Sci.* 478: 105–116.

70 Macyk, W., Szaciłowski, K., Stochel, G. et al. (2010). Titanium(IV) complexes as direct TiO_2 photosensitizers. *Coord. Chem. Rev.* 254: 2687–2701.

71 Paz, Y. (2010). Application of TiO_2 photocatalysis for air treatment: patents' overview. *Appl. Catal., B* 99: 448–460.

72 Su, W., Wang, S., Wang, X. et al. (2010). Plasma pre-treatment and TiO_2 coating of PMMA for the improvement of antibacterial properties. *Surf. Coat. Technol.* 205: 465–469.

73 Olad, A. and Nosrati, R. (2013). Preparation and corrosion resistance of nanostructured PVC/ZnO–polyaniline hybrid coating. *Prog. Org. Coat.* 76: 113–118.

74 Wang, N., Fu, W., Zhang, J. et al. (2015). Corrosion performance of waterborne epoxy coatings containing polyethylenimine treated mesoporous-TiO_2 nanoparticles on mild steel. *Prog. Org. Coat.* 89: 114–122.

75 Di Carlo, G., Curulli, A., Toro, R.G. et al. (2012). Green synthesis of gold-chitosan nanocomposites for caffeic acid sensing. *Langmuir* 28: 5471–5479.

76 Matos, A.C., Marques, C.F., Pinto, R.V. et al. (2015). Novel doped calcium phosphate-PMMA bone cement composites as levofloxacin delivery systems. *Int. J. Pharm.* 490: 200–208.

77 Ajayan, P.M., Stephan, O., Colliex, C., and Trauth, D. (1994). Aligned carbon nanotube arrays formed by cutting a polymer resin-nanotube composite. *Science* 265: 1212–1214.

78 Mao, C., Zhu, Y., and Jiang, W. (2012). Design of electrical conductive composites: tuning the morphology to improve the electrical properties of graphene filled immiscible polymer blends. *ACS Appl. Mater. Interfaces* 4: 5281–5286.

79 Jang, J., Bae, J., and Yoon, S.-H. (2003). A study on the effect of surface treatment of carbon nanotubes for liquid crystalline epoxide–carbon nanotube composites. *J. Mater. Chem.* 13: 676–681.

80 Stankovich, S., Dikin, D.A., Dommett, G.H. et al. (2006). Graphene-based composite materials. *Nature* 442: 282–286.

81 Yousefi, N., Gudarzi, M.M., Zheng, Q. et al. (2013). Highly aligned, ultralarge-size reduced graphene oxide/polyurethane nanocomposites: mechanical properties and moisture permeability. *Compos. Part A: Appl. Sci. Manuf.* 49: 42–50.

82 Yousefi, N., Sun, X., Lin, X. et al. (2014). Highly aligned graphene/polymer nanocomposites with excellent dielectric properties for high-performance electromagnetic interference shielding. *Adv. Mater.* 26: 5480–5487.

83 Shen, X., Wang, Z., Wu, Y. et al. (2016). Multilayer graphene enables higher efficiency in improving thermal conductivities of graphene/epoxy composites. *Nano Lett.* 16: 3585–3593.

84 Yousefi, N., Lin, X., Zheng, Q. et al. (2013). Simultaneous in situ reduction, self-alignment and covalent bonding in graphene oxide/epoxy composites. *Carbon* 59: 406–417.

85 Paton, K.R., Varrla, E., Backes, C. et al. (2014). Scalable production of large quantities of defect-free few-layer graphene by shear exfoliation in liquids. *Nat. Mater.* 13: 624–630.

86 Gojny, F.H., Wichmann, M.H.G., Köpke, U. et al. (2004). Carbon nanotube-reinforced epoxy-composites: enhanced stiffness and fracture toughness at low nanotube content. *Compos. Sci. Technol.* 64: 2363–2371.

87 Thostenson, E.T. and Chou, T.-W. (2006). Processing-structure-multi-functional property relationship in carbon nanotube/epoxy composites. *Carbon* 44: 3022–3029.

88 Viets, C., Kaysser, S., and Schulte, K. (2014). Damage mapping of GFRP via electrical resistance measurements using nanocomposite epoxy matrix systems. *Composites Part B* 65: 80–88.

89 Souri, H., Nam, I.W., and Lee, H.K. (2015). Electrical properties and piezoresistive evaluation of polyurethane-based composites with carbon nano-materials. *Compos. Sci. Technol.* 121: 41–48.

90 Ahmadi-Moghadam, B. and Taheri, F. (2014). Effect of processing parameters on the structure and multi-functional performance of epoxy/GNP-nanocomposites. *J. Mater. Sci.* 49: 6180–6190.

91 Chandrasekaran, S., Sato, N., Tölle, F. et al. (2014). Fracture toughness and failure mechanism of graphene based epoxy composites. *Compos. Sci. Technol.* 97: 90–99.

92 Li, Y., Zhang, H., Bilotti, E., and Peijs, T. (2016). Optimization of three-roll mill parameters for in-situ exfoliation of graphene. *MRS Adv.* 1: 1389–1394.

93 Dalir, H., Farahani, R.D., Nhim, V. et al. (2012). Preparation of highly exfoliated polyester-clay nanocomposites: process-property correlations. *Langmuir* 28: 791–803.

94 Park, J.-J. and Lee, J.-Y. (2013). Effect of nano-sized layered silicate on AC electrical treeing behavior of epoxy/layered silicate nanocomposite in needle-plate electrodes. *Mater. Chem. Phys.* 141: 776–780.

95 Kothmann, M.H., Ziadeh, M., Bakis, G. et al. (2015). Analyzing the influence of particle size and stiffness state of the nanofiller on the mechanical properties of epoxy/clay nanocomposites using a novel shear-stiff nano-mica. *J. Mater. Sci.* 50: 4845–4859.

96 Zhang, D.L. (2004). Processing of advanced materials using high-energy mechanical milling. *Prog. Mater Sci.* 49: 537–560.

97 Gupta, T.K., Singh, B.P., Mathur, R.B., and Dhakate, S.R. (2014). Multi-walled carbon nanotube-graphene-polyaniline multiphase nanocomposite with superior electromagnetic shielding effectiveness. *Nanoscale* 6: 842–851.

98 Wu, H., Zhao, W., Hu, H., and Chen, G. (2011). One-step in situ ball milling synthesis of polymer-functionalized graphene nanocomposites. *J. Mater. Chem.* 21: 8626–8632.

99 Jiang, X. and Drzal, L.T. (2012). Reduction in percolation threshold of injection molded high-density polyethylene/exfoliated graphene nanoplatelets composites by solid state ball milling and solid state shear pulverization. *J. Appl. Polym. Sci.* 124: 525–535.

100 Tang, L.-C., Wan, Y.-J., Yan, D. et al. (2013). The effect of graphene dispersion on the mechanical properties of graphene/epoxy composites. *Carbon* 60: 16–27.

101 Gu, J., Li, N., Tian, L. et al. (2015). High thermal conductivity graphite nanoplatelet/UHMWPE nanocomposites. *RSC Adv.* 5: 36334–36339.

102 Castrillo, P.D., Olmos, D., Amador, D.R., and Gonzalez-Benito, J. (2007). Real dispersion of isolated fumed silica nanoparticles in highly filled PMMA prepared by high energy ball milling. *J. Colloid Interface Sci.* 308: 318–324.

103 Donnay, M., Tzavalas, S., and Logakis, E. (2015). Boron nitride filled epoxy with improved thermal conductivity and dielectric breakdown strength. *Compos. Sci. Technol.* 110: 152–158.

104 Gu, J., Guo, Y., Yang, X. et al. (2017). Synergistic improvement of thermal conductivities of polyphenylene sulfide composites filled with boron nitride hybrid fillers. *Compos. Part A: Appl. Sci. Manuf.* 95: 267–273.

105 Lin, Y. and Connell, J.W. (2012). Advances in 2D boron nitride nanostructures: nanosheets, nanoribbons, nanomeshes, and hybrids with graphene. *Nanoscale* 4: 6908–6939.

106 Yao, Y., Lin, Z., Li, Z. et al. (2012). Large-scale production of two-dimensional nanosheets. *J. Mater. Chem.* 22: 13494–13499.

107 Lee, D., Lee, B., Park, K.H. et al. (2015). Scalable exfoliation process for highly soluble boron nitride nanoplatelets by hydroxide-assisted ball milling. *Nano Lett.* 15: 1238–1244.

108 Brent, J.R., Savjani, N., and O'Brien, P. (2017). Synthetic approaches to two-dimensional transition metal dichalcogenide nanosheets. *Prog. Mater Sci.* 89: 411–478.

109 Buzaglo, M., Bar, I.P., Varenik, M. et al. (2017). Graphite-to-graphene: total conversion. *Adv. Mater.* 29: 1603528.

110 Teng, C., Xie, D., Wang, J. et al. (2017). Ultrahigh conductive graphene raper based on ball-milling exfoliated graphene. *Adv. Funct. Mater.* 27: 1700240.

111 Gu, J., Guo, Y., Lv, Z. et al. (2015). Highly thermally conductive POSS-g-SiCp/UHMWPE composites with excellent dielectric properties and thermal stabilities. *Compos. Part A: Appl. Sci. Manuf.* 78: 95–101.

112 Gu, J., Xie, C., Li, H. et al. (2013). Thermal percolation behavior of graphene nanoplatelets/polyphenylene sulfide thermal conductivity composites. *Polym. Compos.* 35: 1087–1092.

113 Wu, C.L., Zhang, M.Q., Rong, M.Z., and Friedrich, K. (2002). Tensile performance improvement of low nanoparticles filled-polypropylene composites. *Compos. Sci. Technol.* 62: 1327–1340.

114 Fawaz, J. and Mittal, V. (2014). *Synthesis of Polymer Nanocomposites: Review of Various Techniques*. Wiley-VCH.

115 Kim, I.-H. and Jeong, Y.G. (2010). Polylactide/exfoliated graphite nanocomposites with enhanced thermal stability, mechanical modulus, and electrical conductivity. *J. Polym. Sci., Part B: Polym. Phys.* 48: 850–858.

116 Villmow, T., Pötschke, P., Pegel, S. et al. (2008). Influence of twin-screw extrusion conditions on the dispersion of multi-walled carbon nanotubes in a poly(lactic acid) matrix. *Polymer* 49: 3500–3509.

117 Zou, H., Wu, S., and Shen, J. (2008). Polymer/silica nanocomposites: preparation, characterization, properties, and applications. *Chem. Rev.* 108: 3893–3957.

118 Venugopal, G., Veetil, J.C., Raghavan, N. et al. (2016). Nano-dynamic mechanical and thermal responses of single-walled carbon nanotubes reinforced polymer nanocomposite thinfilms. *J. Alloys Compd.* 688: 454–459.

119 Moniruzzaman, M., Du, F., Romero, N., and Winey, K.I. (2006). Increased flexural modulus and strength in SWNT/epoxy composites by a new fabrication method. *Polymer* 47: 293–298.

120 Isayev, A.I., Kumar, R., and Lewis, T.M. (2009). Ultrasound assisted twin screw extrusion of polymer–nanocomposites containing carbon nanotubes. *Polymer* 50: 250–260.

121 Hanemann, T. and Szabó, D.V. (2010). Polymer-nanoparticle composites: from synthesis to modern applications. *Materials* 3: 3468–3517.

122 Caseri, W.R. (2013). Nanocomposites of polymers and inorganic particles: preparation, structure and properties. *Mater. Sci. Technol.* 22: 807–817.

123 Xiong, M., Zhou, S., Wu, L. et al. (2004). Sol–gel derived organic–inorganic hybrid from trialkoxysilane-capped acrylic resin and titania: effects of preparation conditions on the structure and properties. *Polymer* 45: 8127–8138.

124 Cao, Z., Jiang, W., Ye, X., and Gong, X. (2008). Preparation of superparamagnetic Fe_3O_4/PMMA nano composites and their magnetorheological characteristics. *J. Magn. Magn. Mater.* 320: 1499–1502.

125 Vollath, D. and Szabó, D.V. (1999). Coated nanoparticles: a new way to improved nanocomposites. *J. Nanopart. Res.* 1: 235–242.