

## 1

## Surface Modification of Nanomaterials for Application in Polymer Nanocomposites: An Overview

*Muthukumaraswamy Rangaraj Vengatesan and Vikas Mittal*

## 1.1

### Introduction

In recent years, advanced nanocomposite materials have been widely used in a large number of commercially valuable industrial applications such as in automobile, marine coatings, aerospace, and construction industries. The nanocomposites are made up of organic polymers and inorganic nanomaterials using different processing techniques. For example, metal, metal oxide, and carbon-based nanomaterials have been widely used in the preparation of hybrid polymer nanocomposites. The nanocomposites are a new class of advanced materials exhibiting excellent properties compared to those of virgin polymers [1]. Nanomaterials have the ability to improve the properties of polymeric materials. In order to avoid agglomeration and insufficient dispersion of nanomaterials in polymer matrices, the surfaces of the nanomaterials are modified with some organic functionalities. Without surface modification, the unmodified nanomaterials reduce the properties of polymer nanocomposites [2, 3].

Owing to the excellent interfacial interaction between the surface of the nanomaterials and polymers, Surface-modified nanomaterials (SMNs) have attracted a great deal of attention compared to unmodified nanomaterials [4]. The surface functionalization of nanomaterials is carried out with a variety of organic functional groups such as alcohols, thiols, sulfonic, carboxylic acids, and amines. Numerous methods have been employed in the process of surface modification of nanomaterials, which is based on (i) copolymerization of functional organosilanes, macromonomers, and metal alkoxides, (ii) functionalization of organic components within sol-gel-derived silica or metallic oxides, (iii) organic functionalization of nanotubes, nanoclays, or other compounds with lamellar structures, and so on [5].

SMNs that have been reinforced into polymer matrices result superior hybrid nanocomposites, which possess light weight and high strength. The SMNs enhance the mechanical, rheological, optical, electrical, thermal, and flame retardancy properties of the polymer matrices [6, 7]. SMN-reinforced polymeric

nanocomposites are widely used in the form of photonic crystals, coatings, adhesives, pharmaceutical, biomedical, and cosmetic formulations [8–14].

This review is focused on SMNs for the application of polymer nanocomposites. The synthesis, classification, and surface modification of nanomaterials have been summarized and the effects of SMNs on the properties of the polymer matrices are also discussed.

## 1.2

### Types of Nanomaterials

Nanomaterials can be classified on the basis of the number of dimensions, but this is not confined to the nanoscale range. The nanomaterial can be classified into following types:

- 1) Zero-dimensional (0D) nanomaterial
- 2) One-dimensional (1D) nanomaterial
- 3) Two-dimensional (2D) nanomaterial
- 4) Three-dimensional (3D) nanomaterial.

#### 1.2.1

##### Zero-Dimensional (0D) Nanomaterial

The dimension of the material is measured within a nanoscale range, that is, less than 100 nm, which has no dimension. The 0D nanomaterials are commonly represented as nanoparticles. Recently, numerous physical and chemical methods have been adopted for the fabrication of 0D nanomaterials. A lot of research work has been focused on the synthesis of well-controlled dimension of 0D nanomaterials such as quantum dots [15, 16], hollow spheres [17], core–shell nanospheres [18, 19], and nanocluster [20, 21]. The 0D nanomaterials have been synthesized from metal, metal oxides, and carbon-based materials, and are widely used in applications of nanomedicine [20, 21], display [22], energy [23], and so on.

#### 1.2.2

##### One-Dimensional (1D) Nanomaterials

The 1D nanomaterials have two physical dimensions in the range of 1–100 nm and lead to a needle-like structure. These materials have been focus of intense interest in both academic research and industrial applications because of their potential as building blocks for other structures [24]. Researchers have classified 1D nanomaterials into four types: nanotubes [25], nanowires [26], nanorods [27], and nanobelts [28], all of which are widely used for the fabrication of electronic and optoelectronic devices in nanoscale dimensions. 1D nanomaterials have a significant impact on applications in electronics, display and devices, composite materials, catalysis, and energy [29–35].

### 1.2.3

#### **Two-Dimensional (2D) Nanomaterials**

The 2D nanomaterials have two dimensions beyond the nanometric size in range and are not confined to the nanoscale [36]. They exhibit plate-like shapes such as nanodisks [37], nanoplatelets [38], nanowalls [39], nanoprisms [40], and nanosheets [41]. These nanomaterials are widely used in applications in the fields of energy [39], sensors [40], and catalysis [41].

### 1.2.4

#### **Three-Dimensional (3D) Nanomaterials**

The 3D materials are the bulk nanomaterials which are not confined to be nanoscale in any dimension. These materials thus possess three arbitrary dimensions above 100 nm and have nanocrystalline structures. The bulk nanomaterials have a multiple arrangement of nanosize crystals with different orientations. The 3D nanomaterials can contain dispersions of nanoparticles, bundles of nanowires, and nanotubes as well as multiple nanolayers. It is well known that the application of 3D nanomaterials mainly depends on sizes, shapes, dimensionality, and morphologies [36]. The 3D nanomaterials are mainly used in applications in the fields of catalysis [42], biomedicine [43], and energy [44].

## 1.3

### **Synthetic Methodologies of Nanomaterials**

Nanomaterials are prepared via physical or chemical methods. A variety of physical and chemical methods are available for synthesis and fabrication of 0D, 1D, 2D, and 3D nanomaterials. The synthetic methodologies for the preparation of nanomaterials are presented in Tables 1.1 and 1.2.

## 1.4

### **Surface Modification of Nanomaterials and Their Advantages in Polymer Composites**

Numerous methods have been employed for the surface modification of nanomaterials. Among these, the silane grafting, polymer grafting, and surfactant-assisted modification methods are the more predominant and effective methods for functionalization of nanomaterials.

### 1.4.1

#### **Silane Grafting**

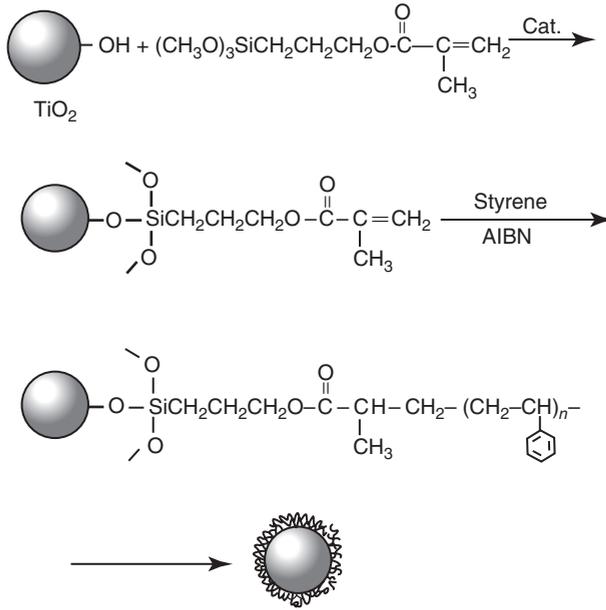
Silane is a very useful coupling agent for the modification of a variety of nanomaterials. The polar surfaces of the inorganic nanomaterials are modified by

**Table 1.1** Synthetic methodologies of nanomaterials through physical methods.

S. No.	Types of nanomaterials	Method	Examples with reference
1.	Nanoparticle (0D)	Sputter deposition	(i) Ag nanoparticles in TiO <sub>2</sub> matrix [45] (ii) Sintered TiO <sub>2</sub> [46]
2.	Quantum dots (0D)	Evaporation	Self-assembled ZnO nanodots are grown by electron beam evaporation [47]
3.	Nanoclusters (0D)	Ultra-high vacuum ion beam evaporation	Ge nanoclusters embedded in Al <sub>2</sub> O <sub>3</sub> and ZrO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> matrix [48]
4.	Nanowires (1D)	Thermal evaporation	Silver nanowires [49]
5.	Nanorods (1D)	Radiofrequency magnetron sputtering	ZnS nanorods [50]
6.	Nanotubes (1D)	Thermal chemical vapor deposition	Carbon nanotubes [51]
7.	Nanoplatelets (2D)	Spray pyrolysis	ZnO nanoplatelets [52]
8.	Nanodiscs (2D)	Thermal evaporation	ZnO nanodiscs [53]
9.	Nanowalls (2D)	Chemical vapor deposition	Carbon nanowall [54]
10.	Nanoflower (3D)	Thermal evaporation	ZnO nanoflowers [55]
11.	Aligned nanocluster (3D)	Thermal evaporation	Aligned Cu nanocluster on Si substrate [56]

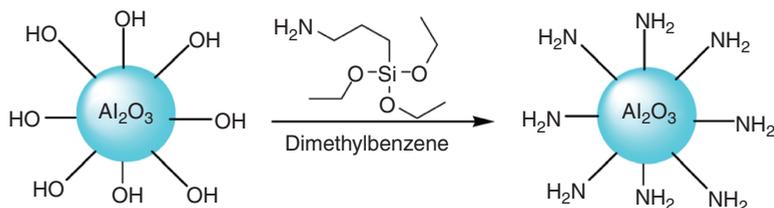
**Table 1.2** Synthetic methodologies of nanomaterials through chemical methods.

S. No.	Types of nano materials	Method	Examples with reference
1.	Nanoparticle (0D)	(i) Chemical reduction (ii) Sol–gel	(i) Ag nanoparticle [57] (ii) ZnO nanoparticle [58]
2.	Quantum dots (0D)	Wet chemical synthesis	CdS quantum dots [59]
3.	Nanoclusters (0D)	Hydrothermal	Silver nanocluster [60]
4.	Nanowires (1D)	Wet chemical synthesis	Silver nanowires [61]
5.	Nanorods (1D)	Solvothermal	TiO <sub>2</sub> nanorods [62]
6.	Nanotubes (1D)	Electrochemical	TiO <sub>2</sub> nanotubes [63]
7.	Nanoplatelets (2D)	Wet chemical synthesis	Amphiphilic graphene platelets [64]
8.	Nanosheets (2D)	Solvothermal	ZnO nanosheets [65]
9.	Nanodiscs (2D)	Hydrothermal	Fe <sub>3</sub> O <sub>4</sub> nanodiscs [66]
10.	Nanoflower (3D)	Solvothermal	CuS flower-like nanostructure [67]
11.	Hierarchical (3D)	Hydrothermal	Anatase TiO <sub>2</sub> hierarchical [68]



**Figure 1.1** The modification of nano  $\text{TiO}_2$  particles with 3-(trimethoxysilyl) propylmethacrylate (MPS) and the formation of the polystyrene- $\text{TiO}_2$  particles via free radical polymerization [70].

grafting silane coupling agents to improve dispersion ability in various organic media. Plueddemann *et al.* [69] first reported the surface modification of nanoparticles using silane coupling agents. They found that the SMN improves the compatibility of particle and polymer surfaces, which subsequently improves the properties of composite materials. Rong *et al.* [70] modified the surface of  $\text{TiO}_2$  nanoparticles using 3-(trimethoxysilyl)propylmethacrylate (MPS) (Figure 1.1) and carried out the *in situ* polymerization of styrene with modified  $\text{TiO}_2$  nanoparticles. Tuan *et al.* [71] functionalized the surface of  $\text{TiO}_2$  by using 3-glycidoxypropyltrimethoxysilane (GPS), which they used as a nanofiller for the high-density polyethylene (HDPE) composites. Prabakaran *et al.* [72] synthesized amine-functionalized  $\text{TiO}_2$  using 3-aminopropyltrimethoxysilane (APTMS) and  $\text{TiO}_2$  nanoparticles and studied the influence of amine-functionalized  $\text{TiO}_2$  on the dielectric properties of polyvinylidene fluoride-*co*-hexafluoropropylene (PVDF) composites. Duraibabu *et al.* [73] modified the surface of alumina nanoparticles using APTMS (Figure 1.2) and the modified alumina nanoparticles reinforced into epoxy matrix. Mandhakini *et al.* [74] studied the tribological properties on the influence of surface-modified alumina in bismaleimide/epoxy blend. The surface of alumina was modified using GPS. Chena *et al.* [75] developed a colloidal silica through sol-gel process and the surface of silica was modified using different types of silane coupling agents such as methyltriethoxysilane (MTES), octyltriethoxysilane (OTES), vinyltriethoxysilane (VTES), and methacryloxypropyltrimethoxysilane (MATMS). They studied the surface



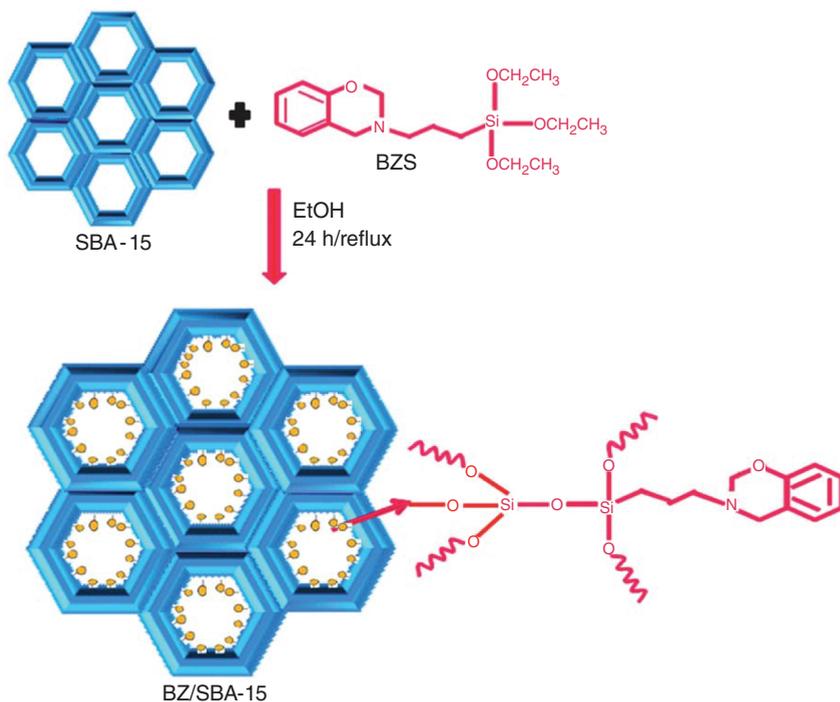
**Figure 1.2** The surface modification of alumina nanoparticles with 3-aminopropyltriethoxysilane [73].

effect of silica nanoparticle on the properties of acrylic-based polyurethane/silica composites. Ariraman *et al.* [76] synthesized the zirconia ( $ZrO_2$ ) nanoparticle through sol-gel process and the surface of the nanoparticle was modified with GPS. They incorporated the modified  $ZrO_2$  into cyanate ester/azomethine blends and studied the effect of nanoparticles on the dielectric constant of the nanocomposites. Kanimozhi *et al.* [77] modified the surface of mullite fibers using GPS and studied the effect of surface-modified mullite fibers on the properties of epoxy nanocomposites. Selvi *et al.* [35] modified the multiwalled carbon nanotubes (CNTs) using benzoxazine functional silane. They developed multiwalled carbon/polybenzoxazine (PBZ) nanocomposites using modified CNTs. Yu *et al.* [78] functionalized the graphene nanosheets (GNs) using 3-mercaptopropyl trimethoxysilane (MTS) and developed graphene nanocomposites through thiol-ene photo polymerization method. Iqbal *et al.* [79] carried out edge functionalization on thermally reduced graphene oxide (TRG) using APTMS and studied the solvent effect for the silane grafting on the TRG. They found that the organic solvent increases the grafting yield of silane in TRG. Wang *et al.* [80] prepared amine-functionalized GNs using graphene oxide (GO) with 3-aminopropyl triethoxysilane (APTES) and used amine-functionalized GNs as a nanofiller for the epoxy composites. Vengatesan *et al.* [81] grafted the benzoxazine functional silane on to SBA-15 and developed the PBZ/SBA-15 nanocomposite. They found that the benzoxazine functional silane was perfectly grafted on the walls of the SBA-15 (Figure 1.3) and resulted in a homogenous dispersion into the PBZ matrix. Devaraju *et al.* [82] prepared glycidyl functional SBA-15 using GPS through simple post-grafting method. The glycidyl-modified SBA-15 has been used as nanofiller for the development of cyanate ester nanocomposites. Ariraman *et al.* [83] modified the surface of FMCM-41 silica using GPS via post-grafting method and used this as nanofiller for the preparation of cyanate ester silica nanocomposites.

#### 1.4.2

##### Polymer Grafting

The grafting of polymers for the surface modification of nanomaterials can be done in two ways, namely, (i) grafting of the end-functionalized polymers, which react with the appropriate surface and (ii) by growing polymer chains from an



**Figure 1.3** The surface modification of mesoporous SBA-15 with benzoxazine functional silane [81].

initiator-terminated, self-assembled monolayer. A high yield of grafting percentage of polymer-grafted nanomaterial has been obtained by initiating the graft polymerization from the surface of the nanomaterials with polymer initiating groups [84–86]. The polymerization process consists of radical, anionic, and cationic polymerization methods, involving propagation of the grafted polymers from the surface of the particle [87]. Zhang *et al.* [88] successfully modified the surface of zinc oxide nanoparticles with methyl methacrylate acetate (ZnMAAc) and developed ZnO/poly (methyl methacrylate) (ZnO/PMMA) nanocomposite films via free-radical polymerization between methyl methacrylate (MMA) and ZnMAAc. Arrachart *et al.* [89] functionalized the surface of TiO<sub>2</sub> nanoparticles with undecenylphosphonic acid and prepared TiO<sub>2</sub>/PMMA nanocomposite using modified TiO<sub>2</sub> and MMA via *in situ* bulk copolymerization. Fresnais *et al.* [90] modified the surface of iron nanoparticles with polyacrylic acid via a H-bonding interaction and studied the coating properties of the nanoparticles for the applications of pollutant dye removal. Kos *et al.* [91] developed PMMA/ZnO nanocomposites by the hydrolysis of Zn precursor. They prepared PMMA-block-PMMA-*co*-(zinc methacrylate acetate), as a polymeric precursor for the formation of ZnO nanoparticles through the reversible addition fragmentation chain transfer (RAFT) polymerization process. Hojjati *et al.* [92]

coated the PMMA chains on  $\text{TiO}_2$  spherical surfaces by RAFT polymerization using supercritical carbon dioxide ( $\text{scCO}_2$ ) as the green solvent. Hu *et al.* [93] modified the surface of zirconia using MMA and prepared transparent PMMA/ $\text{ZrO}_2$  nanocomposites using MMA-grafted  $\text{ZrO}_2$  and MMA through *in situ* bulk polymerization. Wu *et al.* [94] successfully modified the surface of iron oxide ( $\text{Fe}_3\text{O}_4$ ) nanoparticles with maleimide and prepared PBZ magnetic nanocomposite using modified iron oxide nanoparticles and benzoxazine through *in situ* Diels–Alder polymerization. Ou *et al.* [95] functionalized the surface of  $\text{TiO}_2$  nanoparticles with toluene-2,4-diisocyanate (TDI) and used this as a nanofiller for the polypropylene/polyamide blend. Wu *et al.* [96] modified the surface of  $\text{TiO}_2$  nanotubes using phenyl dichloro phosphate and incorporated this into the polystyrene (PSt) matrix through *in situ* bulk polymerization. Zhou *et al.* [97] developed a core–shell nanostructure using single-crystalline lanthanum hydroxide nanowires and a soft shell of PSt brushes. The PSt brush was grown on the surface of lanthanum hydroxide nanowires using atom transfer radical polymerization (ATRP). Ejaz *et al.* [98] grafted polyglycidyl methacrylate (PGMA) and PSt on the surface of boron nitride nanotubes (BNNTs) through the surface-initiated ATRP method (Figure 1.4). Gu *et al.* [99] modified the active surface of phosphazene nanotubes using epichlorohydrin. The epoxy-modified phosphazene nanotubes were used as nanofiller for the epoxy resin. Zhang *et al.* [100] carried out the covalent modification of GO with polynorbornene by surface-initiated ring-opening metathesis polymerization. Kumar *et al.* [101] grafted PMMA onto the surface of high-density functionalized GO through controlled radical polymerization (CRP). Mamaqani *et al.* [102] successfully grafted PSt on the surface of graphene platelets with various graft densities via the ATRP method from the edge of carboxyl groups. Gonçalves *et al.* [103] modified the surface of GO with PMMA via the ATRP method and used PMMA-*g*-GO as a nanofiller for the PMMA matrix. Cheng *et al.* [104] grafted the poly(vinyl)alcohol (PVA) on the surface of GO via a simple condensation reaction and used this as a nanofiller for the PVA matrix. They found that the mechanical properties

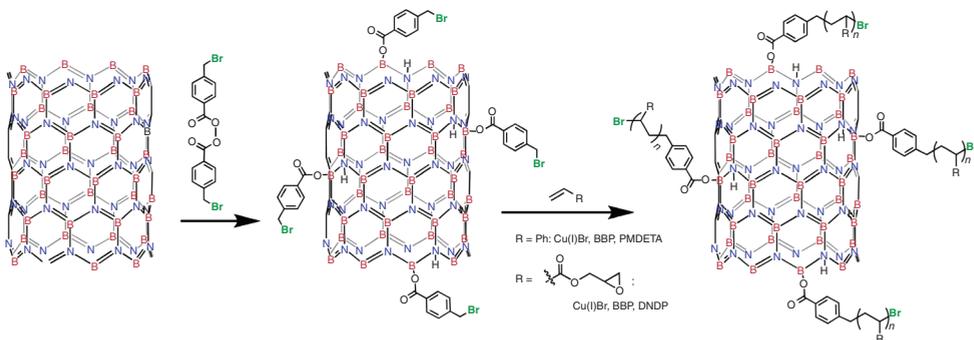


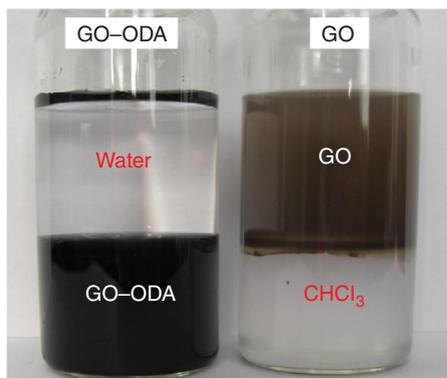
Figure 1.4 Grafting of polymer brushes in BNNTs via surface-initiated ATRP process [98].

of PVA were significantly improved by incorporation of PVA-*g*-GO. Fang *et al.* [105] modified the surface of graphene platelets using PSt chains via diazonium addition followed by the ATRP method. They found that the functionalized graphene platelets resulted in a 15 °C increase in the glass transition temperature of PSt compared to the pure polymer. Yang *et al.* [106] grafted poly(*N*-isopropyl acrylamide) (PNIPAM) on the surface of the mesoporous silica (MSN) through the ATRP method. They found that MSN@PNIPAM materials can be applied in biological systems for cellular imaging or as biosensors. Lia *et al.* [107] modified the outer surface of MSN nanoparticles using light-responsive polymers and studied the drug delivery application using surface-modified MSN. Hong *et al.* [108] developed a novel core–shell nanostructure with a mesoporous core and a polymer nanoshell by grafting the PSt chain on the exterior surface of MSNs. They reported that the thickness of the nanoshell increased with an increase in the time of polymerization. Pasetto *et al.* [109] grafted the polymer chains on the surface of ordered mesoporous silica (OMS) particles via surface-initiated atom transfer radical polymerization (SI-ATRP) using MMA or styrene. They studied and discussed the influence of the polymerization conditions on the OMS particle structure.

### 1.4.3

#### Surface Modification of Nanomaterials Using Surfactants

Physical modification of nanomaterials is usually performed with the help of surfactants or macromolecules. The polar groups in the surfactants are selectively adsorbed on nanoparticle surface as a result of electrostatic interactions. The surfactant reduces the physical forces between the nanomaterials which decrease the inter particle interaction and controlling the agglomeration, therefore the surfactant-modified nanomaterials can be used as a nanofiller for polymer matrices [110]. Zhu *et al.* [111] modified the surface of SiO<sub>2</sub> with oleic acid and used this as a nanofiller for the polylactide matrix. Nakayama and Hayashi fabricated poly(L-lactic acid)/TiO<sub>2</sub> nanocomposite films by incorporating surface-modified TiO<sub>2</sub> nanoparticles into the poly(L-lactic acid) matrix. The surface of TiO<sub>2</sub> nanoparticles was modified by using carboxylic acid and long-chain alkyl amine [112]. Rahmani *et al.* [113] modified the surface of calcium carbonate (CaCO<sub>3</sub>) with steric acid and incorporated this into polypropylene matrix. They found that influence of the surface modification was to improve the distribution and dispersion of CaCO<sub>3</sub> into the PP matrix. Zhong *et al.* [114] prepared ferromagnetic supermagnetic nanoparticles by the coprecipitation method and the surface of the nanoparticles was modified with oleic acid. The modified nanoparticles were incorporated into PSt by facile bulk polymerization and showed a uniform distribution. Mallakpour and Mani [115] modified the surface of ZrO<sub>2</sub> using 2, 3, 4, 5-tetrabromo-6-[(4-hydroxyphenyl)carbamoyl] benzoic acid as the flame-retardant material and used this as a nanofiller for poly (amide-imide) matrix. Kiskan *et al.* [116] coated the surface of iron nanoparticles with carboxylic acid functional benzoxazine monomer via the post-coating method. They developed



**Figure 1.5** Dispersion of GO and GO-ODA (20 h) in  $\text{CHCl}_3/\text{H}_2\text{O}$  mixture [119].

nanomagnetite PBZ thermosets by thermally activated ring-opening copolymerization of benzoxazine group-coated nanomagnetite with bare benzoxazine. Hana *et al.* [117] improved the lipophilicity of graphene by the addition of steric acid. They incorporated steric acid-modified graphene into a low-density polyethylene (LDPE) matrix and studied its thermal and mechanical properties. Lin *et al.* [118] modified graphene platelets with steric and oleic acid and used this as an additive for the lubricant oil. They studied the wear resistance and load-carrying capacity of the lubricant oil with the reinforcing effect of modified graphene platelets. Li *et al.* [119] carried out a simultaneous surface functionalization and reduction of GO using octadecylamine (ODA) without the use of any other reducing agents. The ODA-modified GO is well dispersed in organic solvents (Figure 1.5). They incorporated the ODA-g-GO into a PSt matrix and studied its thermal and electrical properties.

## 1.5

### Method for the Incorporation of Nanomaterials in a Polymer Matrix

The incorporation of nanomaterials into a polymer matrix has been carried out at the nanoscale level through *in situ* polymerization, reactive blending method, and sol-gel method.

#### 1.5.1

##### Sol-Gel Method

In this method, the nanomaterials incorporated into the inside of the polymer matrix in aqueous solution medium results in an interpenetration network formation between the inorganic and organic phases at mild temperatures. This method helps to improve a strong interfacial adhesion between the phases. This is very facile method for the preparation of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{ZnO}$ ,

and  $\text{TiO}_2$ -based polymer nanocomposites at a nanoscale level [120]. In this method, metal alkoxides, coupling agents, and polymer precursors have been employed for the preparation of hybrid polymer nanocomposites. Jothibasu *et al.* [121] prepared a transparent PSt-silica hybrid using maleimide-grafted PSt, tetraethoxysilane (TEOS), and APTES via *in situ* sol-gel process and utilizing the Michael-addition reaction. Selvi *et al.* [122] developed PBZ-SiO<sub>2</sub>-TiO<sub>2</sub> hybrid nanocomposites using dimethylol-functional benzoxazine monomer (4HBA-BZ), TEOS, 3-(isocyanatopropyl) triethoxysilane (ICPTS), and titaniumisopropoxide (TIPO) through an *in situ* sol-gel process followed by thermal polymerization. They found that the hybrid PBZ nanocomposites possess higher surface energy than that of pure PBZ. Devaraju *et al.* [123] prepared polybenzoxazine-silica (PBZ-SiO<sub>2</sub>) hybrid nanocomposite via *in situ* sol-gel process followed by thermal polymerization (Figure 1.6). Ivanković *et al.* [124] carried out a simultaneous polymerization and sol-gel reaction using GPS, MMA, and poly (oxypropylene)diamine. Their results showed that the hybrids have much better thermal stability than PMMA and the surface of hybrids are more hydrophilic than PMMA. Zhang *et al.* [125] developed zinc oxide quantum dots (ZnO QDs)-PMMA nanocomposite films by incorporating ZnO QDs into a transparent PMMA matrix. The results showed that 3-(trimethoxysilyl)propylmethacrylate (TPM) used as a coupling agent which bound to the surface of ZnO QDs inhibited the agglomeration of QDs and promoted the compatibility between ZnO QDs and PMMA matrix. Jung *et al.* [126] developed polyimide-organosilicate hybrids via hydrolysis and polycondensation of aminosilane with alkyl-bridged silane. Jena *et al.* [127] prepared hyperbranched waterborne polyurethane-urea/silica hybrid coating material using 3-aminopropyltriethoxysilane as a coupling agent with SiO<sub>2</sub> as a crosslinker.

## 1.5.2

### Blending Method

The incorporation of nanomaterial into the polymer matrix has been carried out by melt blending or solution blending. This method is more convenient and simple for the preparation of polymer hybrid nanocomposites in bulk scale. The SMN has reactive and nonreactive sites and it reacts or interacts with the polymer matrix, resulting in perfect hybrid polymer nanocomposites. In this method, the SMN has the advantage that it avoids agglomeration in the polymer nanocomposites.

#### 1.5.2.1 Solution Blending Method

Charpentier *et al.* [128] prepared polyurethane/TiO<sub>2</sub> composite via the solution blending method and studied its antibacterial; self-healing properties. Selvi *et al.* [129] used solution blending of surface-modified carbon black with benzoxazine. They obtained the PBZ/carbon black composite by simple solvent evaporation followed by thermal annealing. Vengatesan *et al.* [81] utilized the solution blending method for the preparation of SBA-15/PBZ nanocomposites using benzoxazine functional silane and benzoxazine monomer. The nanocomposites were

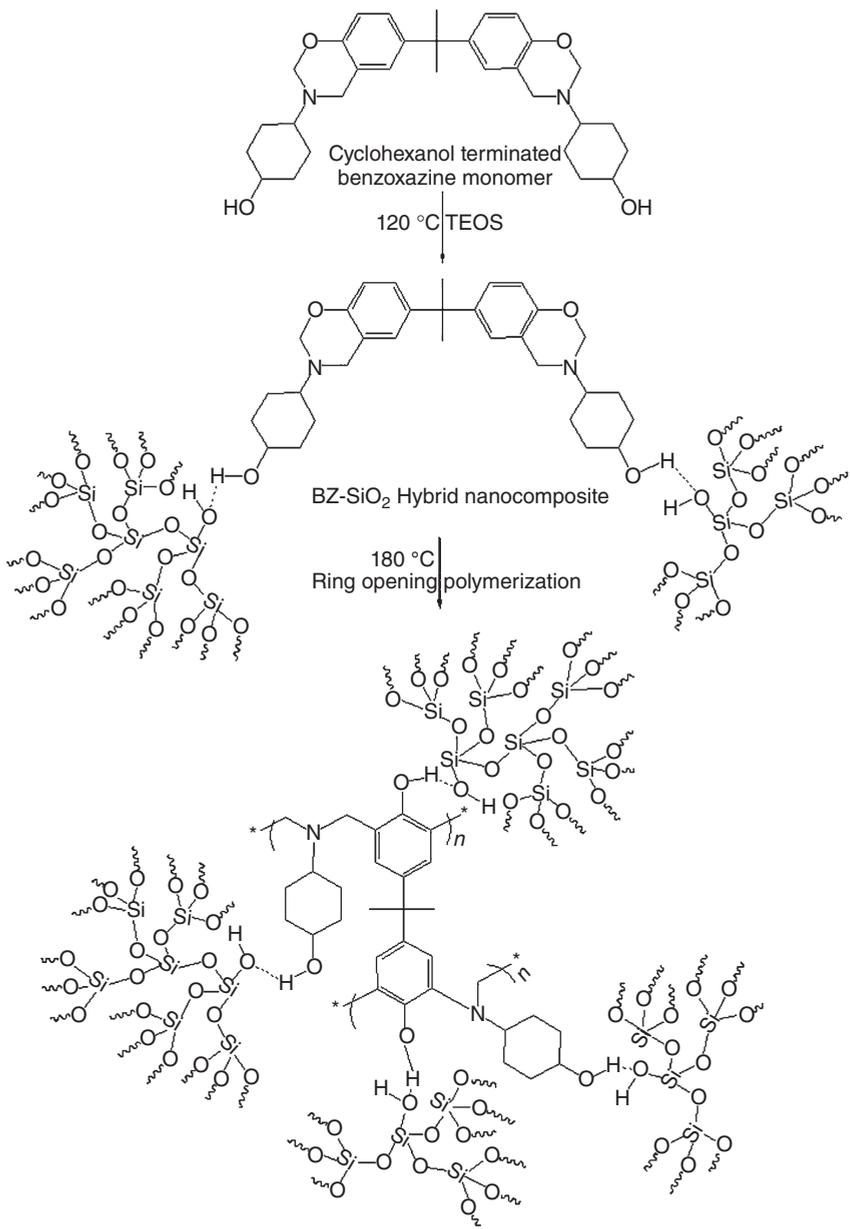


Figure 1.6 Schematic representation of polybenzoxazine-silica hybrid (PBZ-SiO<sub>2</sub>).

prepared by solvent evaporation followed by thermal annealing. Sasikala *et al.* [130] synthesized a PSt hybrid silica sphere composite using vinyl and amine-functionalized silica sphere and PSt through the solution blending method. Devaraju *et al.* [131] prepared cyanate ester-polyhedral oligomeric silsesquioxane (POSS) composites via the solution blending method. Vengatesan *et al.* [132] used the solution blending method for the preparation of PBZ–POSS nanocomposites using benzoxazine monomer and POSS derivative. Gu *et al.* [99] prepared phosphazene/epoxy nanocomposites through the solution blending method. Cao *et al.* [133] developed polyolefin–graphene nanocomposites through the solution blending method. Zeng *et al.* [134] prepared PMMA/graphene composites via a simple solution blending method. Joshi *et al.* [135] utilized the solution blending method for preparation of polyaniline-coated graphene epoxy composites [135].

### 1.5.2.2 Melt Blending

In this method, the SMNs are well dispersed into the polymer matrix using extrusion, internal mixing, and two-roll milling at elevated temperature. This method is more convenient and common method for the preparation of polymer hybrid nanocomposites on a large scale. Wong *et al.* [136] used melt extrusion for the preparation of ZnO QDs/PMMA nanocomposites. Murariu *et al.* [137] developed high-performance polylactide/ZnO nanocomposites using surface-modified ZnO and unmodified ZnO via the melt blending method. They found that the silane-treated ZnO nanoparticle-reinforced nanocomposites have good mechanical properties compared to those of unmodified nanoparticles. Ou and Li [138] prepared nanocomposites by incorporating the TDI-functionalized TiO<sub>2</sub> nanoparticles into the PP/PA6 blend via the melt blending method. Xu *et al.* [139] developed polyamide 6/SiO<sub>2</sub> nanocomposite by melt mixing of polyamide 6 and surface-modified SiO<sub>2</sub>. They found that crystallization temperature and crystallization rate of PA6/SiO<sub>2</sub> nanocomposites were lower than that of neat polyamide 6. Reddy and Das [140] prepared high-pressure low-density polyethylene (HPLDPE)/organic functionalized SiO<sub>2</sub> nanocomposites using the melt blending method. They reported that the organic modification onto the SiO<sub>2</sub> surface led to an increase in thermal stability, elastic modulus, and toughness of the nanocomposite. Zubair *et al.* [141] prepared poly(styrene-*co*-MMA)/graphene nanocomposites via the melt blending method and irradiated the nanocomposites using microwave at different time intervals. Ryu and Shanmugharaj [142] prepared polypropylene-modified GO nanocomposites via the melt blending method and studied its crystallization, mechanical, and electrical properties.

## 1.5.3

### *In Situ* Polymerization

In this method, nanoparticle dispersion and polymerization occurs simultaneously. Abdul Kaleel *et al.* [143] synthesized polyethylene (PE)/TiO<sub>2</sub> nanocomposites using ethylene, metallocene catalysts, and titanium (IV) oxide through *in situ* polymerization. Rong *et al.* [70] developed PSt/TiO<sub>2</sub>



**Figure 1.7** TEM analysis of 15 wt% of  $ZrO_2$  dispersed in PMMA/ $ZrO_2$  nanocomposite [145].

nanocomposites using styrene monomer and MPS-modified  $TiO_2$  *in situ* radical polymerization. Liu and Su [144] successfully prepared PMMA/ $ZnO$  nanocomposites using MMA and oleic acid–modified  $ZnO$  nanoparticles (OA- $ZnO$ ) with 2,2'-azobis(isobutyronitrile) through *in situ* solution radical polymerization. Hu *et al.* [145] prepared PMMA/ $ZrO_2$  nanocomposites using MMA-functionalized  $ZrO_2$  nanoparticles and MMA via *in situ* bulk polymerization. Transmission Electron Microscopy (TEM) analysis results show that the nanoparticles are well dispersed in PMMA matrix (Figure 1.7). Milani *et al.* [146] prepared isotactic polypropylene (iPP)/GNs nanocomposites by the *in situ* polymerization method using metallocene complex ( $rac\text{-Me}_2\text{Si(Ind)}_2\text{ZrC}_{12}$ ) and methylaluminoxane (MAO) as cocatalyst. Huang *et al.* [147] developed highly conductive polypropylene/graphene composites via *in situ* Ziegler–Natta polymerization.

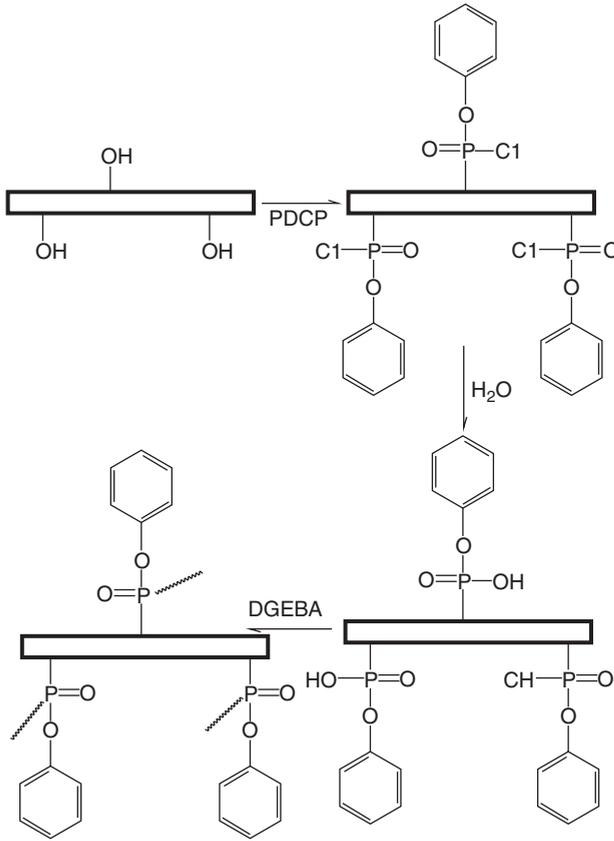
## 1.6

### Influence of Surface-Modified Nanomaterials on the Properties of Polymer Nanocomposites

#### 1.6.1

##### Thermal and Flame-Retardant Properties

The incorporation of SMNs into the polymer matrix, results in a large influence on the crystallization behavior and glass transition temperature of the resultant composite material. The SMNs improves the thermal stability and flame-retardant property of the polymer matrix by acting as a superior thermal insulator and as a mass transport barrier to the volatile products generated during decomposition [148]. Patra *et al.* [149] studied the thermal degradation behavior of oleic acid-capped  $TiO_2$  nanorods/PMMA nanocomposites. They reported that the thermal stability of the nanocomposites improved with increasing in filler loading and the nanorods prevent rapid heat diffusion and limit further degradation of the PMMA matrix. Wu *et al.* [150] fabricated  $TiO_2$  nanotube–epoxy composites



**Figure 1.8** Schematic representation of formation of phenyl dichlorophosphate modified TiO<sub>2</sub>/epoxy nanocomposites [150].

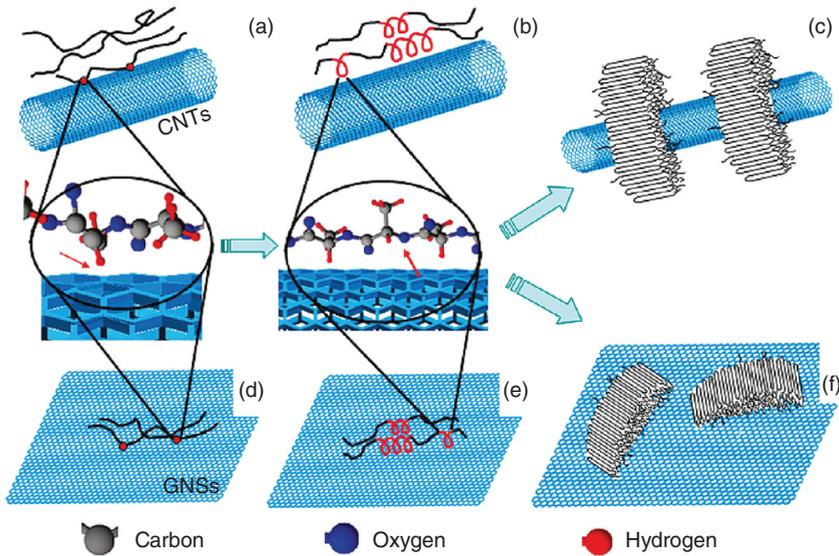
using phenyl dichlorophosphate–modified TiO<sub>2</sub> nanotubes (Figure 1.8) and epoxy resin. They found that the modified TiO<sub>2</sub> nanotubes were able to improve the thermal stability and combustion behavior of the epoxy matrix due to their flame-retardant behavior. Gao *et al.* [151] studied the intumescent flame-retardant behavior of polypropylene (IFR-PP) with the reinforcing effect of polysiloxane and silane-modified SiO<sub>2</sub>. They found that the polysiloxane more effectively enhances the thermal stability of the IFR-PP at high temperature and increases the char residue and markedly reduces the flammability parameters of PP. Ash *et al.* [152] studied the glass transition behavior of alumina/PMMA nanocomposites. They reported that the 0.5 wt% of surface-modified alumina reduces the glass transition temperature of PMMA by 25 °C. Nikje and Tehrani [153] prepared polyurethane rigid foam/modified nanosilica composite. They found that the functional groups on the nanosilica affected the stoichiometry and reduced the hard phase formation in bulk polymer and also decreased the glass transition temperature. Selvi *et al.* [154] developed cyclophosphazene

nanotube (PZT) reinforced poly (benzoxazine-*co-e*-caprolactum) nanocomposites and studied its thermal and flame-retardant behaviors. They reported that 1.5 wt% of PZT nanocomposites show a low oxygen index (LOI) value of 31.4. Baoqing *et al.* [155] studied the effect of oleic acid–modified  $\text{CaCO}_3$  on the crystallization behavior of PP. They found that the addition of modified  $\text{CaCO}_3$  nanoparticles significantly increased the crystallization temperature, crystallization degree, and crystallization rate of PP and also led to the formation of  $\beta$ -crystal PP. Wu *et al.* [96] studied the thermal and combustion behavior of surface-modified  $\text{TiO}_2$ -reinforced PSt nanocomposites. They observed that the addition of nanotube reduces the heat release rate and improves the thermal stability of the PSt matrix. Mallakpour and Zeraatpisheh [156] developed  $\text{ZrO}_2$ -reinforced chlorinated poly(amide-imide) nanocomposites and studied their flame-retardant behavior. The surface of the  $\text{ZrO}_2$  was modified with APTES. They reported that the addition of  $\text{ZrO}_2$  nanoparticles enhances the thermal stability and flame-retardant behavior of the polymer matrix. Jose *et al.* [157] studied the nucleation and nonisothermal crystallization kinetics in cross-linked PE/ZnO nanocomposites with the aid of theoretical estimation. The surface of the ZnO was modified with trimethoxyoctyl-silane. They found that the addition of surface-modified ZnO accelerates the overall crystallization process and possesses a heterogeneous nucleating ability in the cross-linked PE matrix. Shehzad *et al.* [158] synthesized HDPE/graphene nanocomposites via *in situ* polymerization using metallocene catalyst and MAO as cocatalyst. They studied the nonisothermal crystallization behavior of the nanocomposites and found that the graphene nucleates the crystallization of HDPE in addition to increasing the crystallization onset temperature ( $T_{\text{on}}$ ). Xu *et al.* [159] carried out a comparative study of isothermal crystallization behavior of poly(L-lactide) (PLLA) with GNs and CNTs. They observed that both the CNTs and GNs could serve as nucleating agents that accelerate the crystallization kinetics of PLLA. They found that the crystallization ability of CNT is stronger than that of GNs (Figure 1.9). Liao *et al.* [160] prepared a flame-retardant reduced graphene oxide (rGO) via *in situ* reduction and functionalization on the surface of GO using 9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO). The DOPO-functionalized reduced GO (DOPO-rGO) was used as nanofiller for epoxy matrix. They studied the flame-retardant behavior of the epoxy nanocomposites and reported that 10 wt% of DOPO-rGO significantly increases the char yield and LOI value of epoxy nanocomposites.

### 1.6.2

#### Mechanical Properties

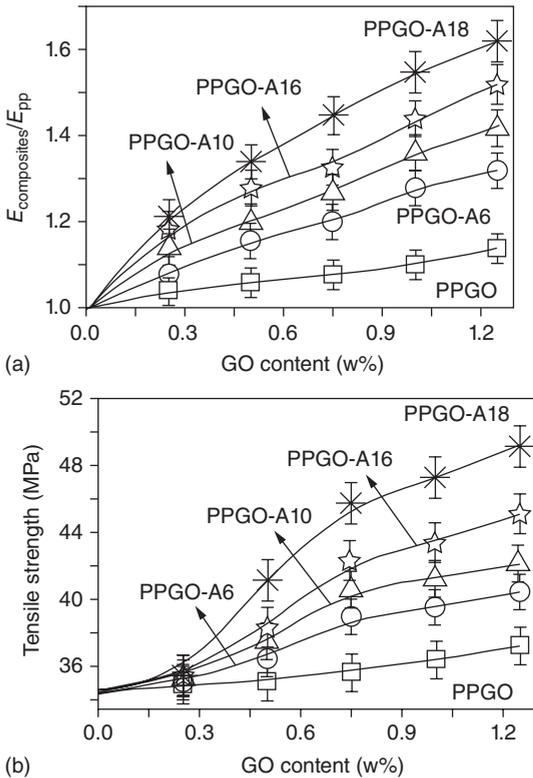
The mechanical properties of polymeric materials are an important parameter for advanced industrial and engineering applications. Virgin polymer materials have relatively low mechanical properties compared to hybrid polymer nanocomposites. The polymeric materials are hybridized with SMNs to enhance the mechanical properties via reinforcement mechanisms [2]. Ma and Zhang [161]



**Figure 1.9** Schematic representation of conformational ordering and crystallization of PLLA in the presence of CNTs (a–c) and GNSs (d–f) [159].

studied the mechanical properties of waterborne polyurethane nanocomposites using surface-modified flower-like ZnO nanowhiskers (f-ZnO). They found that the tensile strength of composite films increased significantly with increase in f-ZnO up to the optimum value (1.0 wt%). Gao *et al.* [162] developed the rubbery block copolymer-grafted SiO<sub>2</sub> nanoparticle-toughened epoxy nanocomposites and studied its mechanical properties with the effect of grafting density and molecular weight of the polymer in SiO<sub>2</sub> nanoparticle. They found that the ductility (maximum 60% improvement), fracture toughness (maximum 300% improvement), and fatigue crack growth resistance of the epoxy matrix enhanced with the incorporation of copolymer-grafted SiO<sub>2</sub> nanoparticles. They also reported that the nanocomposites with SiO<sub>2</sub> containing lower graft density and larger molecular weight of the polyhexylmethacrylate (PHMA) block show simultaneous improvements in fracture toughness and tensile modulus. Shukla *et al.* [163] prepared epoxy/alumina composites using surface-modified and unmodified alumina and studied their mechanical and fracture properties. They reported that unmodified alumina platelets increase the elastic modulus and fracture toughness of epoxy nanocomposites and decrease the tensile strength at higher volume. They observed that the surface-modified alumina platelets enhanced the tensile strength of epoxy nanocomposites, also retaining the improvements in elastic modulus and fracture toughness. Palimi *et al.* [164] studied the mechanical properties of polyurethane/Fe<sub>2</sub>O<sub>3</sub> nanocomposites. They reported that surface-modified nanoparticles show a significant improvement in the mechanical properties of the polyurethane coating. Zhou *et al.* [165] prepared surface-modified silica-hybridized CdTe QDs/PMMA hybrid nanocomposite film





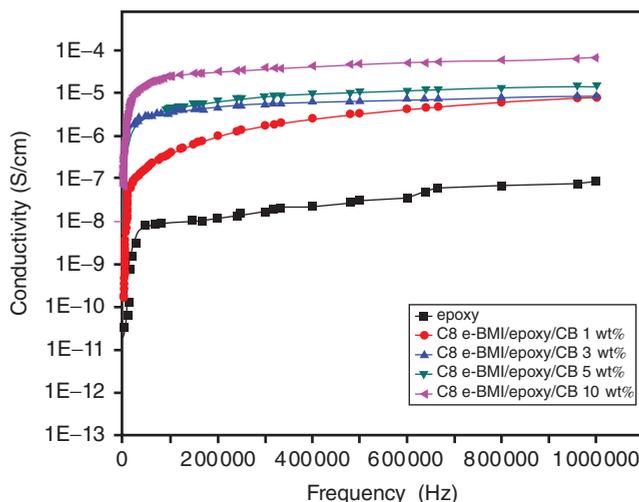
**Figure 1.11** variation of Young's modulus (a) and tensile strength (b) with the GO contents of PP nanocomposites.

the GO with different chain length of alkylated amines and used them as a nanofiller for PP matrix. They found that 1 wt% of ODA-modified GO-reinforced PP composites shows an improved Young's modulus by up to 47% and tensile strength by up to 29.4% compared to other alkylated aminemodified GO and pristine GO reinforced PP composites (Figure 1.11).

### 1.6.3

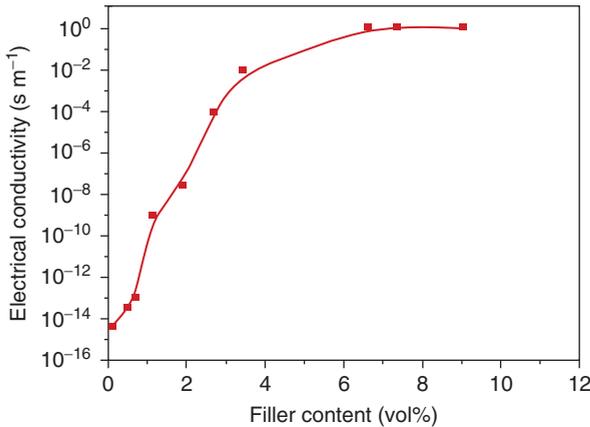
#### Electrical Properties

Polymer hybrid nanocomposites are widely used in electronic industries in the form of insulators, packaging materials, conducting devices, coating materials, and so on. Ma *et al.* [171] studied the influence of surface-modified  $\text{TiO}_2$  on the electrical behavior of PE nanocomposites. They reported that surface-modified  $\text{TiO}_2$  improved both the dielectric breakdown strength and space charge distribution of the PMMA matrix. Dang *et al.* [172] prepared surface-modified  $\text{TiO}_2$ /silicone rubber nanocomposites and studied their dielectric properties. They found that the incorporation of surface-modified  $\text{TiO}_2$  enhanced the



**Figure 1.12** Conductivity as a function of the CB loading in epoxy/bismaleimide composites [173].

electrical breakdown strength and decreased the dielectric loss of the silicone rubber material. Mandhakini *et al.* [173] prepared conductive carbon black (CB)-reinforced/bismaleimide epoxy composites and studied their electrical properties. The results show that the loading of 5 wt% carbon black improved the conductivity of bismaleimide/epoxy blends (Figure 1.12). Devaraju *et al.* [174] developed cyanate ester-silica hybrid (CE-SiO<sub>2</sub>) nanocomposites by *in situ* sol-gel method for the low *k* dielectric applications. They reported that the higher loading of silica content in hybrid composites possesses a low *k* dielectric value. Sasi Kumar *et al.* [175] synthesized lamellar-structured POSS/PBZ nanocomposites and studied its dielectric properties. They found that the composite with 30% POSS exhibited an ultra-low-*k* value of  $1.7 \pm 0.01$  at 1 MHz which is due the highly ordered lamellar network with distinct crosslinks of composites. Hong *et al.* [176] studied the dielectric properties of ZnO/LDPE nanocomposites. They examined the effect of nanofiller distribution on the dielectric constant and found that an inhomogeneous distribution of ZnO in composites contributed to an increased permittivity at frequencies up to approximately 10 kHz. Lin and Wang [177] synthesized a series of novel low-dielectric constant (low- $\kappa$ ) polyimide (PI) composite films containing the SBA-15 or the SBA-16-type MSN via *in situ* polymerization followed by thermal imidization. The results show that the incorporation of 3 wt% modified SBA-15 and 7 wt% modified SBA-16 reduced the dielectric constant of PI to about 2.73 and 2.61 respectively. Li *et al.* [178] functionalized the GO using APTES and used as this a nanofiller for the PMMA matrix. They studied the electrical properties of the composites and 10 wt% functionalized GO-incorporated PMMA composites to show surface resistivity of  $2.0 \times 10^3 \Omega$ . Tang *et al.* [179] developed a facile approach of simultaneous



**Figure 1.13** Effect of f-GO content on the electrical conductivity of rubbery epoxy/graphene composites [179].

functionalization and reduction of GO using polyetheramine. The functionalized graphene oxide (f-GO) was incorporated into rubbery epoxy resin and studied its electrical conductivity. The incorporation of 2.7 vol% of f-GO into the epoxy resin increases the electrical conductivity of the epoxy nanocomposite to about  $1.0 \times 10^{-4} \text{ S m}^{-1}$ , which is nearly 11 orders of magnitude higher than that of neat epoxy (Figure 1.13). Wang *et al.* [180] prepared two types of PVDF nanocomposites using rGO and poly(vinyl alcohol)-modified reduced graphene oxide (rGO-PVA) via the solution casting method. They studied the dielectric properties of the nanocomposites in a frequency range from  $10^2$  to  $10^7$  Hz and reported that both nanocomposites exhibited an insulator-to-conductor percolating transition with an increase of the filler content. They compared the dielectric property of both composites and reported that rGO-PVA/PVDF nanocomposites possess higher dielectric constant and lower loss factor than rGO/PVDF.

## 1.7

### Conclusion

SMNs are potentially applicable for the development of hybrid polymer nanocomposites. Surface modification improves the miscibility and interfacial interaction of the nanomaterials with polymer matrices, resulting in unique properties, such as good mechanical, optical, electronic, gas-barrier, and flame-retardance properties. Hybrid polymer nanocomposites have been prepared from SMNs and can be used in the form of adhesives, matrices, and advanced composite materials for varying range of engineering with improved longevity.

### Abbreviations

Al <sub>2</sub> O <sub>3</sub>	Alumina
Ag	Silver
CdS	Cadmium sulfide
Cu	Copper
CuS	Copper sulfide
Fe <sub>3</sub> O <sub>4</sub>	Iron oxide
GO	Graphene oxide
GNs	Graphene nanosheets
Si	Silicon
SiO <sub>2</sub>	Silica
TiO <sub>2</sub>	Titania
ZrO <sub>2</sub>	Zirconia
ZnO	Zinc oxide
ZnS	Zinc sulfide

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