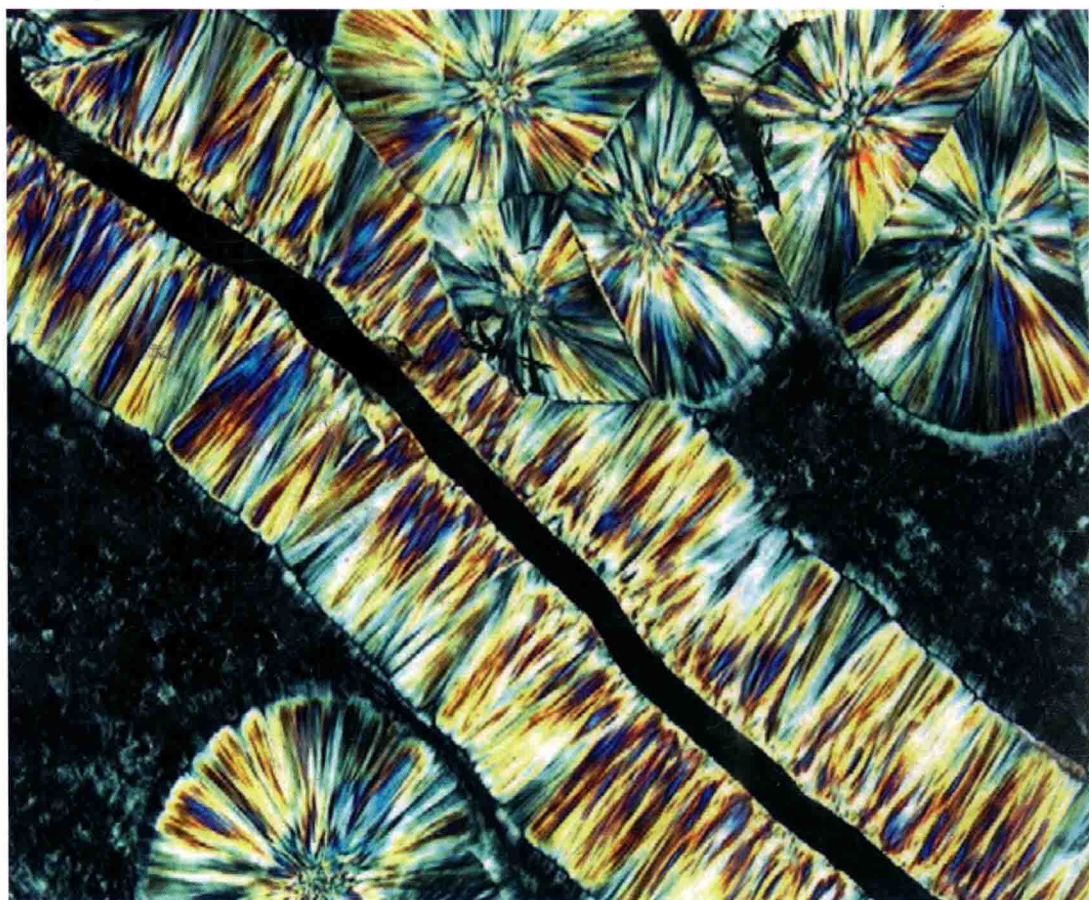


Sie Chin Tjong

 WILEY-VCH

# Polymer Composites with Carbonaceous Nanofillers

Properties and Applications



*Sie Chin Tjong*

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## Preface

Carbon nanotubes and graphene sheets exhibit unique and extraordinary electrical, mechanical, and thermal properties rendering them attractive fillers for reinforcing polymers to form functional and structural composite materials of high performance. The performance of the polymer nanocomposites relies on the inherent properties of carbonaceous nanofillers, and on optimizing the dispersion, interfacial interaction, and nanoscale exfoliation of those fillers within the polymer matrix. Designing smart polymer nanocomposite materials with the appropriate processing-structure-property relationships for biomedical, electronic, electromagnetic interference shielding, and chemical sensing as well as structural engineering applications is challenging. In recent years, one-dimensional carbon nanotubes have been incorporated into various types of polymeric materials for achieving these purposes. However, the high cost, tedious purification and high tendency of agglomeration of carbon nanotubes hurdle the development of nanotube/polymer composites in engineering applications. The recent successful synthesis of two-dimensional graphene layers from graphite oxide via chemical and thermal reduction techniques has sparked enormous interest in their properties, functions, and applications. The low cost and ease of fabrication of graphene offer tremendous opportunities for chemists and materials scientists to explore and develop novel graphene/polymer nanocomposites with excellent biological, mechanical, and physical properties. This book focuses exclusively on the latest research related to the synthesis and property characterization of one- and two dimensional carbonaceous nanomaterials and their polymer nanocomposites, and addresses potential applications of these materials to bipolar plates of fuel cells, electrocatalysts, human orthopedic implants and scaffolds, electromagnetic interference shielding materials, and gas-, pressure- and temperature sensors. This book serves as a valuable and informative reference to scientists, engineers, medical technologists, and practitioners engaged in the teaching, research, development, and use of functional polymer composites with carbonaceous nanofillers.

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## Abbreviations

AC	alternating current
AFM	atomic force microscopy
AIBN	2,2'-azobisisobutyronitrile
ARTP	atom transfer radical polymerization
BIB	$\alpha$ -bromoisobutyryl bromide
BP	benzoyl peroxide
CB	carbon black
CF	carbon fiber
CMG	chemically modified graphene
CNF	carbon nanofiber
CNT	carbon nanotube
CS	chitosan
CTAB	hexadecyltrimethylammonium bromide
CTE	coefficient of thermal expansion
CVD	chemical vapor deposition
DBP	dibutyl phthalate
DC	direct current
DGEBA	diglycidyl ether bisphenol-A
DENT	double-edge-notched tension
DMA	dynamic mechanical analysis
DMAc	<i>N,N</i> dimethylacetamide
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
DSC	differential scanning calorimetry
DWNT	double-walled carbon nanotube
EG	expanded graphite
ECM	extracellular matrix
ECSA	electrochemically active surface area
EDS	energy dispersive spectroscopy
EMI	electromagnetic interference
EVA	ethylene vinyl acetate
EWf	essential work of fracture
FGS	functional graphene sheet

FMWNT	functionalized multiwalled carbon nanotube
GIC	graphite intercalation compound
GDL	gas diffusion layer
GNP	graphite nanoplatelet
GO	graphene oxide
HA	hydroxyapatite
HDPE	high-density polyethylene
HDT	heat deflection temperature
HEK	human epidermal keratinocyte
HiPCo	High-pressure carbon oxide disproportionation
HOPG	highly oriented pyrolytic graphite
HOR	hydrogen oxidation reaction
iGO	isocyanate-treated graphene oxide
LDPE	low-density polyethylene
LEFM	linear elastic fracture mechanics
LLDPE	linear low-density polyethylene
MA-g-PP	maleic anhydride-grafted polypropylene
MD	molecular dynamics
MEA	membrane electrode assembly
MMT	montmorillonite
MTS	3-(4,5-dimethylthiazol-2-yl)-5(3-carboxymethoxyphenol)-2-(4-sulphophenyl)-2H-tetrazolium
MTT	3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide
MWNT	multiwalled carbon nanotube
ORR	oxygen reduction reaction
PA	polyamide
PAA	poly(acrylic acid); polyallylamine; polyamic acid
PC	polycarbonate
PCL	polycaprolactone
PDMS	poly(dimethyl siloxane)
PE	polyethylene
PECVD	plasma-enhanced chemical vapor deposition
PEDOT	poly(3,4-ethylenedioxythiophene)
PEEK	poly(etheretherketone)
PEMFC	proton exchange membrane fuel cell
PEN	poly(ethylene-2,6-naphthalate)
PEO	poly(ethylene oxide)
PET	polyethylene terephthalate
PGMA	poly(glycidyl methacrylate)
PI	polyimide
PLA	polylactic acid
PmPV	poly( <i>m</i> -phenylene vinylene)
PMMA	poly(methyl methacrylate)
PS	polystyrene
PSF	polysulfone

PTC	positive temperature coefficient
PTT	polytrimethylene terephthalate
PU	polyurethane
PVA	poly(vinyl alcohol)
PVC	polyvinyl chloride
PVD	physical vapor deposition
PVDF	polyvinylidene fluoride
PVP	polyvinyl pyrrolidone
P3HT	poly(3-hexylthiophene)
rGO	reduced graphene oxide
RBM	radial breathing mode
SAED	selected-area electron diffraction
SAN	styrene-acrylonitrile
SBR	styrene-butadiene rubber
SDBS	sodium dodecylbenzenesulfonate
SDS	sodium dodecyl sulfate
SE	shielding efficiency
SEM	scanning electron microscopy
SENB	single-edge-notched bending
SGF	short carbon fiber
SIP	surface-initiated polymerization
sPS	syndiotactic polystyrene
SR	silicone rubber
SWNT	single-walled carbon nanotube
TEA	triethylamine
TEGO	thermally expanded graphene oxide
TEM	transmission electron microscopy
TETA	triethylenetetramine
$T_g$	glass-transition temperature
TGA	thermogravimetric analysis
THF	tetrahydrofuran
TLP	tissue culture plate
TPU	thermoplastic polyurethane
TRG	thermally reduced graphene
VGCNF	vapor-grown carbon nanofiber
VLS	vapor-liquid-solid
WST-1	2-(4-iodophenyl)-3-(4-nitrophenyl)-5-(2,4-disulfophenyl)-2H-tetrazolium
XRD	X-ray diffraction

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## 1

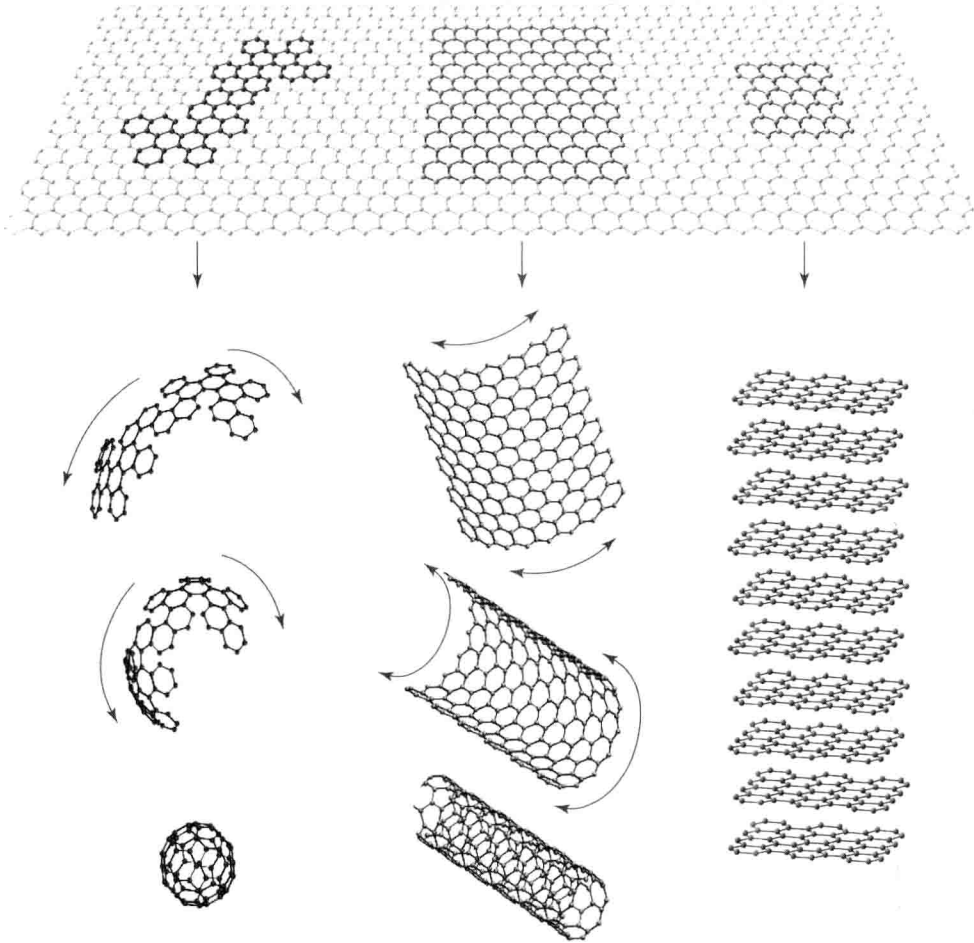
## Introduction

### 1.1

#### Graphene-Based Nanomaterials

Carbon exists in many forms including buckyballs, diamond, nanotubes, and graphite. It is naturally abundant as coal and natural graphite. Two-dimensional (2D) graphene, a new class of carbon nanostructure, has attracted tremendous attention in recent years since the successful isolation of graphene by micromechanical cleavage of highly oriented pyrolytic graphite (HOPG) [1, 2]. Graphene is a single atomic layer of  $sp^2$  hybridized carbon atoms covalently bonded in a honeycomb lattice. It is a building block for carbon materials of different dimensionalities, including 0D buckyballs, 1D nanotubes, and 3D graphite (Figure 1.1). It shows great potential for technological applications in several areas such as electronics, optoelectronics, nanocomposites, sensors, batteries, and so on [3–7]. Graphene sheets stack together to form graphite with an interlayer spacing of 0.34 nm, showing strong in-plane bonding but weak van der Waals interaction between layers. By virtue of this layered structure, large efforts have been tempted to exfoliate graphite into individual atomic layers. It is difficult to obtain a fully separated sheet layer of graphene because freestanding atomic layer is widely considered to be thermodynamically unstable. A lack of an effective approach to exfoliate graphite into individual, pure graphene sheet in large quantities remains a major obstacle to exploiting its full potential applications.

In 2004, Geim and coworkers of the Manchester University (United Kingdom) prepared single layer of graphene using the cohesive tape method through repeated peeling of graphite and deposited onto a Si/SiO<sub>2</sub> substrate [1, 2]. This is often referred to as a *scotch tape* or *drawing method*. Optical microscopy was initially used to distinguish individual graphene layers followed by their identification in an atomic force microscope (AFM). Geim and Novoselov received the Nobel Prize in Physics for 2010 for their pioneering work in the fabrication and physical characterization of graphene. Such novel preparation of graphene has opened up a new era in nanotechnology and materials science and prompted much excitement in these fields. This technique can only produce low-yield, high-purity graphene for research purposes, and insufficient for practical applications. Moreover, it is hard to control the number of layers for peeled off pieces.



**Figure 1.1** Graphene is a 2D building material for carbon materials of different dimensionalities. It can be wrapped up into 0D buckyballs, rolled into 1D nanotubes, or stacked into 3D graphite. (Source: Reproduced with permission from Ref. [3], Nature Publishing Group (2007).)

As an alternative, graphene can be grown directly on solid substrates using two different approaches. The first involves graphitization of single-crystal silicon carbide substrate through thermal desorption of silicon in ultrahigh vacuum at high temperatures (circa above  $1300^{\circ}\text{C}$ ). Consequently, excess carbon is left behind on the surface. The carbon-enriched surface then undergoes reorganization and graphitization to form graphene under proper control sublimation conditions. This process yields epitaxial graphene with dimensions dependant on the size of SiC substrate [8, 9]. The shortcomings of this process are the use of high processing temperature, the formation of atomic scale defects in the graphene lattice and

the difficulty of achieving large graphite domains with uniform thickness. The second approach involves epitaxial growth of graphene on metal carbide (e.g., TaC, TiC) or metallic substrates (e.g., Ni, Cu) via chemical vapor deposition (CVD) of hydrocarbons at high temperatures. This is commonly followed by chemical etching and transfer printing to arbitrary substrates [10–14]. For example, Kim *et al.* [11] prepared patterned graphene film on thin nickel layer using a gas mixture of CH<sub>4</sub>, H<sub>2</sub>, and Ar, followed by transferring the printing film onto target substrates. The growth of graphene on nickel with higher carbon solubility (>0.1 at%) occurs by the diffusion of the carbon species into the metal surface before segregating and precipitating to the surface on fast cooling. Ni can dissolve more carbon atoms and thus it is difficult to obtain uniform graphene films due to precipitation of extra C during fast cooling. In contrast, the graphene growth on low carbon solubility Cu substrates occurs by means of surface adsorption process [13]. CVD graphene generally exhibits lower electron mobility than mechanically exfoliated graphene because of its higher concentration of point defects, smaller grain sizes, and residual impurities from the transfer or growth processes [14]. The transfer-printing process is also difficult to scale up for industrial applications. Accordingly, wet chemical processing through oxidation of graphite into graphene oxide (GO) followed by reduction appears to be a cost-effective method for mass-producing graphenelike materials.

### 1.1.1

#### Graphite Intercalation Compound

Apparently, high-yield production processes for graphene sheets are necessary for practical applications as conductive films and nanofillers for composite materials. Hence, chemical conversion from graphite offers significant advantages over physical approaches and the CVD process for preparing graphene for large-scale applications. This approach converts natural graphite into graphite intercalation compound (GIC) by reacting with electron-donor agents such as alkali metals and electron-acceptor agents such as halogens and acids [15]. Because of its layered structure, acid molecules and alkali metal can penetrate within the gallery spaces of graphite. The layers of graphite interact with the guest molecules through charge transfer process. For example, potassium can be inserted into graphite galleries to yield both first stage and higher stages of intercalation. Stage implies the number of graphite host layers divided by the number of guest layers that occur periodically in the galleries. In the case where every carbon layer in graphite is intercalated, a stage I compound forms, while intercalating on average every other layer yields a stage II compound [16a]. The first-stage intercalation compound, KC<sub>8</sub>, has a larger d-spacing (0.541 nm) compared to that of graphite. The second-stage compound, KC<sub>24</sub>, and the third-stage material, KC<sub>36</sub>, have a spacing of 0.872 and 1.2 nm, respectively (Figure 1.2). KC<sub>8</sub> generally forms by heating graphite with potassium under vacuum at 200 °C [16b]. The KC<sub>8</sub> compound then reacts with ethanol to yield potassium ethoxide and hydrogen gas, which aid in separating the graphitic sheets