Trends and Applications in Advanced Polymeric Materials
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Martin Scrivener (martin@scrivenerpublishing.com)
Phillip Carmical (pcarmical@scrivenerpublishing.com)
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Today, polymers rule the world with their diverse range of applications, fulfilling requirements ranging from the domestic to industrial and defense sectors. The changing world has seen a revolution created by polymers, the most versatile material ever discovered by human kind, owing to their lightweight, ease of processing and manufacturing, moldability into intricate shapes, and cost-effectiveness. They can easily be filled with a range of reinforcing agents like fibers, particulates, flakes and spheres in micro/nano sizes and compete with conventional materials in terms of performance, properties and durability. Polymers have become a multidisciplinary brand which is equally sought after by chemists, physicists, engineers, scientists, doctors and industrialists. More and more research is being carried out to further explore the material and modify it to meet the increasing demand.

“The more important reason is that the research itself provides an important long-run perspective on the issues that we face on a day-to-day basis.” These words of Ben Bernanke, the former U.S. Federal Reserve Chairman, have inspired us to discuss and share research on many advanced but widely used applications of polymers with techno-socio-economic importance.

Presented herein are the trends in polymer research and applications of many novel technologies. The chapters in this book feature major original works of young researchers along with a few reviews on innovative techniques and utilities. Primarily, use of polymers for advanced applications like coatings, solar energy harvesting, conducting polymers, sensors, electrolytes, drug delivery, hydrogels, batteries and high-barrier polymers has provided a framework in which to design the contents of this book. The chapters are well crafted with an abstract, introduction to the specific topic, theoretical and experimental techniques wherever necessary, a discussion of detailed results and a concise conclusion about the findings.
To start with, Chapters 1 and 2 on polymer nanocomposite coatings describe the potential of coatings beyond aesthetics. Specialized coatings are discussed wherein polymer matrices are reinforced with nanofillers for imparting specified properties like scratch/barrier resistance, electrical/thermal conductivity, as well as mechanical strength/durability. In Chapter 3, the book proceeds with a discussion of low smoke materials made for polymer nanocomposites from an industrial point of view. The authors describe the effect of various additives on the flame retardancy and smoke tolerance of the nanocomposites in detail. Polymer nanocomposites for solar energy harvesting, a topic of huge interest, is discussed in Chapters 4 and 5. While Chapter 4 deliberates the usefulness, challenges and current status of organic solar cells in the form of a review, Chapter 5 highlights the photocatalytic activities of highly efficient metal nanocrystals embedded in polymer matrix. The electrical sensitivity of various conducting polymer nanocomposite formulations, which are mainly used in sensors, is described in Chapters 6 through 8; and the luminescent characteristics are described in Chapter 9. A discussion on the gas transport phenomena in polymeric membranes filled with nanoparticles is incorporated as Chapter 10, which explains the underlying aspects and factors affecting the mobility of gas molecules through the membranes. Furthermore, the mechanism of ion transport across the membranes and the effect of nanomaterials in developing a continuous conducting path are elucidated in Chapter 11. The development of biocompatible hydrogels for drug delivery application is dealt with in Chapters 12 and 13. Factors like drug entrapment, release rate, compatibility with biological systems, etc., are clearly explained. Chapter 14 presents the advanced use of siloxane modified multilayered polyethylene for oxygen barrier packaging application. The improvement in oxygen diffusion for enhanced shelf life of packaged food items is discussed in detail. Finally, Chapter 15 highlights the advantages and opportunities in the field of rechargeable batteries, with specific emphasis on lithium-based batteries with polymer electrolyte membranes.

This book thus proposes to unveil the research prospects of polymers for indigenous development. The research discussed herein is resourceful in terms of its contents because the selected chapters cover the most recent developments and societal demands. We hope our venture will expressly encourage young people to streamline their research, industrialists to invest in advanced developments, and academicians and scientists to take their research further.

We are thankful to all the authors who have contributed and shared their expertise. Credit also goes to all members who have directly or indirectly
helped us in the process of compiling this book. Special thanks go to Wiley-Scrivener for providing us with the opportunity to publish our book. Last, but not the least, we bow before the Almighty, without whose blessings we would not have been able to frame this book.

Sanjay K Nayak
Smita Mohanty
Lakshmi Unnikrishnan
Bhubaneswar, India, August 2017
Polymer Nanocomposites and Coatings: The Game Changers

Gaurav Verma

Dr. Shanti Swarup Bhatnagar University Institute of Chemical Engineering and Technology (formerly Department of Chemical Engineering & Technology), Panjab University, Chandigarh, India
Centre for Nanoscience and Nanotechnology (U.I.E.A.S.T), Panjab University, Chandigarh, India

Abstract

In recent years, polymer nanocomposites and coatings have caught the attention of the research world due to their versatile properties and widespread applications. The availability of new nanoscale fillers and additives provide polymer scientists with materials and a lot of options to modify the properties of the polymeric matrix and hence widen the ambit of their applications. Increasing usage of polymer nanocomposites and their exploration for more potential applications lead to game-changing solutions to many engineering and technological problems. The issue with nanoscale fillers is their stability and compatibility with polymeric matrix. A lot depends on the processing protocols used for fabricating the nanocomposites. This chapter provides an overview of the structure-property-processing relationship for polymer nanocomposites and coatings.

Keywords: Polymer, nanoscale fillers, structure-property-processing, performance

1.1 Introduction

Polymer nanocomposites are composed of a polymeric matrix and a nanoscale filler which have at least one dimension in the nanometer range (usually 1–100 nm is accepted but nowadays many fillers up to a size of 500 nm have also been considered as nanofiller). The wide variation in
shapes and sizes of these nanoscale fillers accounts for wide ranging structural and property modifications of the polymeric matrix, as shown in Figure 1.1. Although polymers themselves are versatile materials and can be easily tailored to imitate metals, natural materials and even biomaterials,

![Figure 1.1](image)

**Figure 1.1** (Top) Different shapes and types of typical nanoparticles (nanoscale fillers) used to reinforce polymeric matrices. (Bottom) Particle shapes and surface area/volume (A/V) versus aspect ratio (a) variation for nanoscale structures which can reinforce polymer matrices [1].
the ever widening scope of new materials has yet to catch up with the latest technology, thus requiring constant research and updating.

Depending on how many dimensions of the particles are in nanometer range, nanoparticles are mainly categorized into three types. In the first type, called isodimensional nanoparticles, all dimensions are in the order of nanometers (0D) (e.g., spherical silica nanoparticles, some nanoclusters, etc.). In the second type, called nanotubes or nanowhiskers, two dimensions of the particles are in the nanometer range and the third one is larger, usually forming an elongated structure (1D) (e.g., carbon nanotubes, cellulose nanowhiskers). The third type of nanoparticles is characterized by only one dimension in the order of nano range (2D). In this case the particles are present in the form of sheets one to a few nanometers thick to hundreds to thousands of nanometers long (e.g., layered silicates [LS]).

The 21st century applications are far reaching, as scientists have started to explore more of outer space, planets and other celestial bodies. Aspirations on earth are also much more technologically advanced as compared to a decade ago. Better materials are needed to fabricate new types of automobiles like driverless cars, flying drones or supersonic aircrafts. There are two options for making materials to cater to these needs. One is to invent or discover totally novel materials with distinct properties, new structure and hence new properties. This approach is promising but may not be that helpful as there are shortcomings in a single material. Getting the best property and structural combinations is usually possible by modifying materials. So the second approach is to use nanoscale fillers to tailor materials with better property combinations without compromising their inherent characteristics.

Using nanoscale fillers to modify conventional materials like polymers is an up-and-coming and very promising technique. By using only a very small quantity of nanoscale fillers like less than 10 weight percent, huge property benefits can be achieved. In comparison to conventional microscale filled composites, the reduction in weight percentage of the filler used is about 10 times or more, while the property improvements almost double. Sometimes the properties which couldn’t be imbibed in conventional composites (Figure 1.2) can now be easily induced in nanocomposites. These advantages and other structural, morphological and physical improvements have led to increased interest in scientific and commercial communities. The only issue facing the use of nanocomposites is the ultimate control over nanofiller size, which still needs to be attained. Processing of nanocomposites, especially coatings, is also a far cry from realization; hence; the objective of this chapter is to instigate the research world into formalizing the processing protocols. By using examples of
polymer-based nanocomposites and coatings, this chapter presents useful information on structure-property-processing of nanocomposites. Some of their applications will also be briefly discussed.

1.2 Polymer Nanocomposites

1.2.1 Types of Polymer Nanocomposites: Processing

The possibility of combining nanoscale fillers with polymers is enormous, as polymers themselves are a huge class of materials with versatility in their chemistry and physical structure. The tunability of polymeric structures results in various forms like hard plastics, soft foams, coatings and even cellular structures and biomaterials. Inspired by many natural structures and composites like bone, teeth and nacre, many hierarchical structures of polymer nanocomposites have been built. Depending upon the use of either thermoplastic or thermosetting polymers, various processing techniques are adopted to fabricate these materials. For example, commercially developed large-scale thermoplastic composites of polymers can be processed using melt processing mechanical methods like extrusion and injection molding (Figure 1.3). Composite processing machines ranging from lab-scale customized extruders to pressurized plunger-type injection-molding machines are sometimes well suited for thermoplastic polymer and 1D nanofillers like nanotubes and nanofibers. Although these nanofibers/nanotubes significantly depend on their orientation in the shear developed during melt processing, many times a solution or solvent precasting with polymer is done for blending them with certain matrices. Shear is generated through twin-screw extruding for some matrices like polyether ether ketone (PEEK) in some cases to disperse nanofibers up to 1 weight percent (wt%) [2, 3]. The intrinsic viscosity of thermoplastic polymers contributes to the high shear which is generated inside the barrel.
during processing and helps in dispersing the carbon nanotubes/carbon nanofibers (CNTs/CNFs). The orientation of the fibers can be an issue when using such techniques. Certain composites may require directional properties, others might not. Depending upon the requirement of the product, the suitability of the technique may be decided. Some scientists have also used preprocessing or a precursor technique like ball milling or sonication prior to final or intermediate processing to achieve better aspect ratio of the nanofillers [4].

Thermosetting polymers like epoxy and polyurethane and their variants have to undergo a solution/solvent-based processing protocol when reinforced with nanofillers like carbon nanotubes (CNTs) (Figure 1.4). Solvent-based processing requires separate dispersion or dissolution of CNTs directly in polymer mixture and then casting into a given mold, unlike thermoplastic processing techniques of extrusion, where in-situ mixing of nanofillers are carried out.

But the new nanoscale fillers demand greater technological advancements for dispersing and homogenizing them into polymer matrices. As
needs have changed, an upgrade of conventional processing equipment used in the polymer and rubber industries is required. Parameters like stability and control over shape, particle size and surface area can only be attained if the equipment in use caters to their manipulation and alteration. New designs may soon be entering the industry for commercialization and large-scale production of polymer nanocomposites. Till that time, small batches may be produced with prototypes being used at laboratory and research scale. Shown in Figures 1.5–1.7 are three such essential types of equipment used by our laboratory to produce polyurethane-clay nanocomposite coatings [5–10].

![Figure 1.5](image)

**Figure 1.5** (a) View of ultrasonic bath used for sonication with time control. (b) Schematic representation of the deagglomeration of particles by sonication with the help of cavitation.

![Figure 1.6](image)

**Figure 1.6** (a) Oblique and (b) front view of high shear homogenizer and (c) its stator-rotor.
Equipment and Processing

For preparation and processing of polymer-nanomaterial/nanofiller nanocomposites and coating formulations, a combination of three different types of equipment can be used. Table 1.1 is a concise list of the types of equipment and their functions.

The ultrasonic apparatus (Figure 1.5a) disperses and deagglomerates the nanomaterial/nanofiller using the principle of ultrasonic cavitation (Figure 1.5b). The sound waves that propagate in the liquid (organic solvents and binder) result in alternating high-pressure (compression) and low-pressure (rarefaction) cycles. This applies mechanical stress on the attracting electrostatic forces (e.g., van der Waals forces) between the individual particles.

Ultrasonic cavitation in liquids causes high speed liquid jets of up to a maximum of 1000 km/h. Such jets press liquid at high pressure between the particles and separate them from each other. Smaller particles are accelerated with the liquid jets and collide at high speeds, thus effectively milling the micron-size and sub-micron-size particles, as shown in Figure 1.5b.

Table 1.1 Equipments and its specifications.

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Function</th>
<th>Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultrasonic bath</td>
<td>Breaks down agglomerates</td>
<td>Branson 3510; 240V; 40kHz</td>
</tr>
<tr>
<td>High shear homogenizer</td>
<td>Homogenizes, dispenses</td>
<td>Fluka FA-25; 500W; 220V; 50Hz</td>
</tr>
<tr>
<td>Mechanical stirrer</td>
<td>Mixes and blends</td>
<td>Perfit; 220V, 250 rpm</td>
</tr>
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</table>
The high shear homogenizer consists of a high speed rotor housed inside a fixed stator (Figure 1.6). The high speed rotation of the rotor generates strong centrifugal force by which materials are sucked into the narrow gap between the precision-engineered stator chamber and rotor from the top and bottom end of the agitator (Figure 1.7c,d). With the intense mechanical and hydraulic shear generated in the narrow gap between the stator and rotor, material is dispersed and emulsified in the first step (Figure 1.7a,b). With the function of high linear velocity (min = 15 m/s; max = 40 m/s) generated by the high speed rotating rotor, strong hydraulic shearing force (Equation 1.1) and other mechanical forces, the material is completely dispersed, emulsified and homogenized.

The final material is ejected from the slanted slot in the stator (Figure 1.7b). Material is continuously ejected at high speed from the slanted slots, while it faces internal material friction and wall resistance. Meanwhile, the flow direction of material is changed with the strong suction force of the high speed rotating rotor and a vortex motion is generated (Figure 1.7c,d). After several cycles, materials are thoroughly dispersed, emulsified and homogenized.

The shear stress exerted on the nanomaterials/nanofillers as per Cao et al. [11] can be calculated using Equation 1.1:

\[ \tau = \mu \dot{\gamma} \]  

(1.1)

where \( \tau \) is the shear stress, \( \dot{\gamma} \) is the shear rate, and \( \mu \) is the solution viscosity. The shear rate of the homogenizer is calculated by Equation 1.2:

\[ \dot{\gamma} = 2\pi (OD)R/(ID - OD)60 \]  

(1.2)

where \( OD \) is the outside diameter of rotor, and \( ID \) is the internal diameter of the stator, as shown in Figure 1.8. \( R \) is the revolutions per minute of the stator-rotor system of the homogenizer.

The equipment discussed in the above section is effective for small-sized laboratory samples but may need a constant scale-up to cater to industrial needs.

---

**Figure 1.8** Schematic drawing of stator and rotor showing \( ID \) and \( OD \). Dimensions shown in mm are not to scale.
1.2.2 Polymer Property Enhancements

A variety of polymer-nanofiller combinations, such as nylon, polypropylene, polyethylene, polybutene, polyurethanes, etc., have been fabricated and tested for property improvements. After the pioneering work done by the Toyota group [12], an enormous amount of work has been carried out on preparation of polymer-based nanocomposites. Now the focus is moving towards polymer nanocomposites, which are light, possess good mechanical properties, and are eco-friendly (i.e., biocompatible/degradable), for mainly two reasons: environmental concerns and the realization that our petroleum resources are finite. In this regard, several research groups have developed different nanocomposites based on biocompatible/degradable polymers which are obtained from fossil sources as well as renewable resources. Particularly, more attention has been paid to polymers from renewable resources because they allow adding value to agricultural products, which is economically important for many countries. So far, different biocompatible/degradable polymers have been used such as poly caprolactone (PCL), poly lactic acid (PLA), poly hydroxybutyrate (PHB), poly butylene succinate (PBS), natural rubber, starch, cellulose, etc. Several researchers have also reported nanocomposites based on blends of biocompatible/degradable polymers or obtained blending of these polymers with non-degradable polymers. Usuki et al. [12] from the Toyota research group were the first to prepare commercial polymer nanocomposites by solution polymerization of caprolactam in the clay galleries. Later on, this product was marketed by UBE Industries and Bayer. Currently, these nylon 6-based nanocomposites are used to make belts for Toyota car engines and also for the production of packaging film [12].

Table 1.2 briefly lists the polymers, nanofillers and their respective property improvements. Shown at a glance are some of the common polymer-based nanocomposites and coatings.

<table>
<thead>
<tr>
<th>Sl. no.</th>
<th>Polymer</th>
<th>Nanofiller</th>
<th>Property enhancement</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Polyurethane thermoset PU coatings</td>
<td>Clays</td>
<td>Scratch resistance, Barrier resistance</td>
<td>[5–10]</td>
</tr>
<tr>
<td>2</td>
<td>PU thermoplastic</td>
<td>Clay</td>
<td>Mechanical properties</td>
<td>[13–14]</td>
</tr>
<tr>
<td>3</td>
<td>PU</td>
<td>CNT</td>
<td>Tensile Strength, Electrical</td>
<td>[15]</td>
</tr>
<tr>
<td>4</td>
<td>TPU</td>
<td>MWCNT</td>
<td>Thermal, Electrical conductivity</td>
<td>[16]</td>
</tr>
<tr>
<td>5</td>
<td>PP</td>
<td>CNT</td>
<td>Tensile modulus</td>
<td>[17]</td>
</tr>
</tbody>
</table>
1.2.3 Polymer Nanocomposite Structure and Morphology

The long-chain molecular structure of polymers undergoes transformation depending on the kind of interface of polymeric chains with the included nanofiller. There are three main material constituents in any composite: the matrix, the reinforcement (fiber), and the so-called interfacial region. The interfacial region is responsible for communication between the matrix and filler and has conventionally ascribed properties different from the bulk matrix because of its proximity to the surface of the filler [18].

Figure 1.9 depicts the expected morphology of the polymer in the presence of a 2D nanofiller like clay or graphene. If the plate-like structures are not dispersed and delaminated at nanoscale then the resulting composite is a microcomposite. If the polymer chains happen to shear past the “d-spacing” of the 2D nanofiller an intercalated nanocomposite is formed. An exfoliated nanocomposite is formed when the polymer chains not only enter into the gallery spacing of the 2D nanostructure but also are able to separate/disperse and completely delaminate the clay/graphene into single platelets. A partially intercalated and exfoliated sample forms a mixed composite (Figure 1.9). This structure of polymer-nanofiller combination affects the final properties of the nanocomposite and is also responsible for its performance.

The surface and bulk morphology is governed by the nanofiller type, size and composition. For instance, the nanoclay imbibed into thermoset two-pack polyurethane significantly changes its hard-soft segmental

Figure 1.9 Resultant morphology due to the combination of polymer 2D nanofillers like clay/graphene. The interface between polymeric chains and platelets of 2D nanofiller controls whether the morphology is intercalated, exfoliated or a mix of both.