



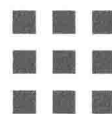
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CLAY-CONTAINING POLYMER NANOCOMPOSITES

FROM FUNDAMENTALS TO REAL APPLICATIONS



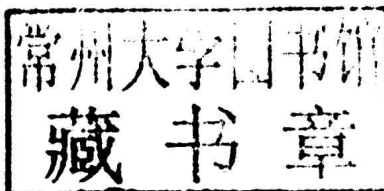
Suprakas Sinha Ray



Clay-Containing Polymer Nanocomposites: From Fundamentals to Real Applications

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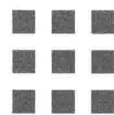
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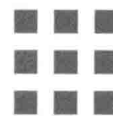
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Dedicated to my family



Preface

Since the end of the last decade, much research and development effort has emerged in addressing hybrid organic–inorganic systems; particular attention has been given to those systems in which nanofillers are dispersed in polymer matrices. This class of materials called *polymer nanocomposites*, shows unique value-added properties that are completely absent in neat matrices and conventional composites. Researchers believe that the interaction between the filler and matrix at the nanoscale is the basis for new and unique properties of the nanocomposites, as opposed to conventional composites.

Nanofillers can be made from a wide range of materials, the most common being clays (or layered silicates), carbon nanotubes, polyhedral oligomeric silsesquioxanes, metals, metal-oxide ceramics, and metal-nonoxide ceramics. Recently, other materials have been used for nanofillers, such as polymers and compound semiconductors. However, the former class of materials is used for the majority of polymer nanocomposite applications.

During the past few years, all types of nanofillers have been used for the preparation of composites with almost all types of polymer matrices. However, clay-containing polymer nanocomposites (PNCs) have attracted great interest in today's materials research, because these substances can significantly enhance nanocomposite properties, especially when compared with those of a neat polymer [1–4]. These improvements may include high moduli; increased strength, flexibility, and heat resistance; decreased gas permeability and flammability; increased rate of crystallization; and enhanced rheological properties.

The most generally used clays for the preparation of PNCs belong to the general family of phyllosilicates, that is, layered or sheetlike structures more commonly referred to as *layered silicates*. In this subclass, rings of tetrahedrons are linked by shared oxygen atoms to other rings in a two-dimensional plane that produces a sheetlike structure. The best-known member in this family is montmorillonite (MMT), a natural phyllosilicate extracted from bentonite. Therefore, this book focuses on PNCs based on layered-silicate-type clays.

The mixing of clay particles with polymer matrices to form nanocomposites appears to have begun in the late 1940s [5], with a resurgence in the early 1960s with the patent application from Nahim and Backlund [6]. During the same period, the first research articles appeared on this topic [7–9]. In the early 1990s, two major findings stimulated the revival of great interest in these materials: First, a Toyota research group studying Nylon 6–MMT nanocomposites [10, 11] reported that very small amounts (~5 vol %) of organically modified MMT loadings resulted in pronounced improvements in mechanical, thermal, and barrier properties; second, Vaia, Ishii, and Giannelis [12] reported that it is possible to melt mix polymers with clay without the use of organic solvents. Today, efforts are being conducted globally, using almost all types of clays and polymer matrices.

One could argue that PNCs are part of a boom that includes other areas of nanoscience and nanotechnology, but there is more work to be conducted [13]. Not every physical mixture of polymer and clay leads to the formation of a PNC. The fundamental understanding of the interfacial interaction between a polymer chain and clay surface at the nanoscale has tremendous implications for the performance and final properties of the obtained nanocomposite material. Therefore, the study of PNCs is not simply about capturing the buzz from nanoscience and

nanotechnology; it is about understanding the associated interfacial science and structure–property relationships at the molecular and macromolecular level [13].

During PNC formulation, the nanolevel dispersion of clay particles is the single most important characteristic to achieve to generate a high interfacial or surface area for polymer–clay interactions, improved cooperative phenomena among dispersed particles, and a strong confinement effect. In the case of nonpolar polymer matrices, the primary challenge is to find the right chemistry to provide the best thermodynamic driving force to disperse clay platelets at the nanolevel. To this end, researchers are currently using two approaches. One approach involves the incorporation of functionality into a polymer matrix by grafting, copolymerization, or blending with other polymers. Another approach is the functionalization of clay surfaces to improve compatibility with polymer matrices. Moreover, in the case of nanoclays that have a layered structure, researchers are using ion-exchange chemistry to decrease the inherent van der Waals forces among silicate layers and thereby improve the delamination of silicate platelets in polymer matrices.

Among the preparation methods currently being used, melt blending or melt extrusion is considered a promising approach for the fabrication of PNCs due to its versatility, compatibility with current polymer processing equipment, and environmental friendliness, because no solvents are used. However, to optimize melt-processing conditions, it is essential to have a nanolevel dispersion of clay platelets. Additionally, the processing method and regime should have minimal adverse effects on the polymer matrix or surface-modified clay; that is, the degradation of both components should be avoided.

Furthermore, to establish a structure–property relationship, a certain qualitative measure of the degree of clay platelet dispersion in the polymer matrix is necessary. However, researchers face challenges when analyzing the true dispersion state of clay platelets in PNCs. Therefore, a qualitative understanding of the dispersion state of clay platelets in a PNC is very important.

Recently, the worldwide demand for PNCs has rapidly increased in advanced packaging, automotive, construction, and other industries due to superior barrier, thermal, mechanical, and other properties of PNCs. The development of industries related to PNCs possessing enhanced features and expanding research activities in the development of new PNCs are some of the factors that may drive the PNC market in the coming years (projected growth rate 56%). Currently, the most publicized applications of PNCs are those in the automotive sectors, such as timing belt covers (Toyota Motor Corporation) and exterior step assists (General Motors). Another extensive application of PNCs is in barrier materials. Though a number of PNC-based commercial products are available in the market, many of these have not yet been reported in the literature extensively.

Although structural characterization, physical and mechanical properties, processing, and commercial applications of various types of PNCs are widely published in peer-review journals, patents, conference proceedings, and edited books, to the best of our knowledge, no single book consolidates knowledge on these areas in a concise form. A single book of this nature, covering material from fundamental aspects to real applications, serves as a very useful reference for both undergraduate and postgraduate students, academic researchers, engineers, and other professionals interested in this exciting field of research. This book also helps industrial researchers and R&D managers who want to bring advanced polymer-based products into the market.

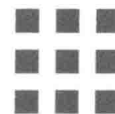
This book comprises 13 chapters that highlight recent developments in PNCs and discuss their potential applications and future outlook. Following an overview of pure and organically modified clays (Chapter 1), Chapter 2 discusses the thermodynamics, molecular modeling, and kinetics of PNC formation. Chapter 3 is dedicated to the techniques generally used to characterize the structure and morphology of PNCs and their drawbacks. PNC processing and

characterization are described in Chapter 4. Chapters 5 to 8 focus on various properties of PNCs. The effects of the incorporation of clay particles on polymer crystallization behavior and kinetics are summarized in Chapter 9, and Chapter 10 is dedicated to the melt-state rheological behavior of PNCs. A brief summary of the foam processing of PNCs is presented in Chapter 11. Chapters 12 and 13, respectively, summarize the practical uses of PNCs and provide deep insight into the future direction of the field.

I express my sincerest appreciation to all colleagues, postdoctoral fellows, and students for their valuable contributions as well as the reviewers for their critical evaluation of the proposal and manuscripts. I also thank all authors and publishers for their permission to reproduce their published works. My special thanks go to L. Hutchins, K. Marinakis, A. Koch, and R. Mohanapriyan at Elsevier Science for their cooperation, suggestions, and advice during the various phases of preparation, organization, and production of this book. Finally, I thank my wife Dr. Jayita Bandyopadhyay and my son, Shariqsrijon Sinha Ray, for their tireless support and encouragement.

References

- [1] Sinha Ray S, Okamoto M. Polymer/layered silicate nanocomposites: a review from preparation to processing. *Progn Polym Sci* 2003;28:1539–641.
- [2] Sinha Ray S, Bousmina M. Biodegradable polymers and their layered silicate nanocomposites: in greening the 21st century materials world. *Prog Mater Sci* 2005;50:962–1079.
- [3] Pavlidou S, Papaspyrides CD. A review on polymer-layered silicate nanocomposites. *Prog Polym Sci* 2008;33:1119–98.
- [4] Paul DR, Robeson LM. Polymer nanotechnology: nanocomposites. *Polym* 2008;49:3187–204.
- [5] Carter LW, Bolley DS. Elastomer reinforced with a modified clay. US Patent No. 2531396, 1950.
- [6] Nahim PG. Light weight rubber composition containing clay. US Patent No. 3084117, 1963.
- [7] Blumstein A. Étude des polymérisations en couche adsorbée. *Bull Soc Chem France* 1961;98:899–906.
- [8] Dekking HGG. Propagation of vinyl polymers on clay surfaces. I. Preparation, structure, and decomposition of clay initiators. *J Appl Polym Sci* 1965;9:1641–51.
- [9] Friedlander HZ, Frink CR. Organized polymerization III. Monomers intercalated in montmorillonite. *J Polym Sci B Polym Lett* 1964;2:475–9.
- [10] Okada A, Kawasumi M, Usuki A, Kojima Y, Kurauchi T, Kamigaito O. Nylon 6-clay hybrid. *Mater Res Soc Sympo Proc* 1990;171:45–50.
- [11] Okada A, Usuki A. Twenty years of polymer-clay nanocomposites. *Macromol Mater Eng* 2006;291:1449–76.
- [12] Vaia RA, Ishii H, Giannelis EP. Synthesis and properties of two-dimensional nanostructures by direct intercalation of polymer melts in layered silicates. *Chemf Mater* 1993;5:1694–6.
- [13] Morgan AB, Wilkie CA. Flame retardant polymer nanocomposites. Hoboken, NJ: John Wiley & Sons; 2007.



About the Author

Suprakas Sinha Ray is one of the most active and highly cited authors in the field of polymer nanocomposite materials. Recently, was rated one of the top 50 high-impact chemists in the world (February 2011, Thomson Reuter). Professor Sinha Ray is author and coauthor of 10 book chapters and 145 articles in international journals, as well as the holder of several patents.



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