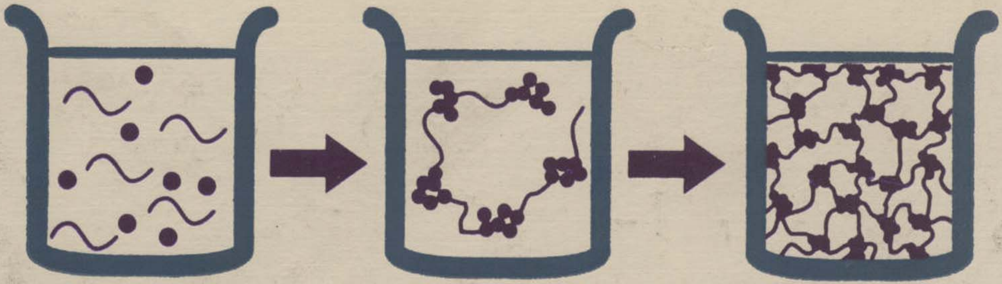
Hybrid Organic–Inorganic Composites



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Hybrid Organic–Inorganic Composites

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ACS Symposium Series

M. Joan Comstock, *Series Editor*

Foreword

THE ACS SYMPOSIUM SERIES was first published in 1974 to provide a mechanism for publishing symposia quickly in book form. The purpose of this series is to publish comprehensive books developed from symposia, which are usually "snapshots in time" of the current research being done on a topic, plus some review material on the topic. For this reason, it is necessary that the papers be published as quickly as possible.

Before a symposium-based book is put under contract, the proposed table of contents is reviewed for appropriateness to the topic and for comprehensiveness of the collection. Some papers are excluded at this point, and others are added to round out the scope of the volume. In addition, a draft of each paper is peer-reviewed prior to final acceptance or rejection. This anonymous review process is supervised by the organizer(s) of the symposium, who become the editor(s) of the book. The authors then revise their papers according to the recommendations of both the reviewers and the editors, prepare camera-ready copy, and submit the final papers to the editors, who check that all necessary revisions have been made.

As a rule, only original research papers and original review papers are included in the volumes. Verbatim reproductions of previously published papers are not accepted.

M. Joan Comstock
Series Editor

Preface

THE UNIQUE PROPERTIES OF ORGANIC AND INORGANIC materials can be synergistically combined in a number of ways. The purpose of the March 1994 symposium on hybrid organic–inorganic composites and this resulting book was to illustrate some of these ways. Most of the chapters in this book are based on contributions to the symposium, but two of the chapters (6 and 13) were commissioned separately to improve the balance in the subject matter.

The chapters in this book cover a wide range of topics, as can be seen from the overview chapter, which previews some of the contents of the book. The variety of topics is certainly desirable and stems in part from the various backgrounds of the people working in this area. Contributors include inorganic chemists, organic chemists, physical chemists, polymer scientists and engineers, chemical engineers, and materials scientists.

We hope that this book will be of use to these various constituencies and to others in related disciplines. Although our primary goal was to report on the status of the rapidly expanding area of organic–inorganic composites, there is also much discussion of unsolved problems that should inspire readers to enter and contribute to this area as well.

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Chapter 1

Some General Trends in the Area of Organic–Inorganic Composites

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This overview chapter first reviews the sol-gel process as it is being used by ceramists, and then describes how it is being modified by the incorporation of organic materials. Six general topics involving the organic-inorganic composites resulting from these new approaches are then illustrated using examples chosen from the chapters of the present book.

The Sol-Gel Process in General

Most organic-inorganic hybrid composites are prepared by introducing polymeric components into the sol-gel technology which is now much used to prepare ceramic materials. It is therefore appropriate to first describe how this sol-gel approach has been used by ceramists to prepare ceramics having unusually attractive properties[1-9]. In this technology, organo-silicates, -titanates, -aluminates, etc. are typically hydrolyzed to multi-hydroxy compounds which then condense into gel-like structures that can be dried and fired into ceramic coatings, foams, or monolithic objects. The classic example is the reaction of tetraethoxysilane (TEOS) [$Si(OC_2H_5)_4$] to yield silica (SiO_2), and ethanol as a volatile and easily-removed byproduct. A variety of acids and bases, and even some salts, greatly catalyze the process.

There are a number of advantages to this new technique for preparing ceramic materials. First, the high purity of the chemical reactants insures higher ceramic purities than can generally be obtained in the usual melting of minerals such as common sand. The temperatures involved are very much lower than those required to melt typical ceramics, and this encourages the incorporation of organic phases. In some cases, the porous ceramic precursors formed as intermediates can be pervaded by polymers (such as a polysilane) that can be converted into reinforcing phases (such as β silicon carbide) during a subsequent firing process. Also, it is much easier to imagine placing a thin coating of silica onto a surface to be used as part of a wave-guide by this technique, than by a dipping process involving molten silica! Finally, co-hydrolysis of different organometallics can be used to obtain ceramic "alloys" that are essentially unobtainable by the usual ceramic technologies.

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The Sol-Gel Process in the Preparation of Organic-Inorganic Composites

One indirect advantage of including polymers in this technology is facilitation of the processing techniques involved. Of greater interest, however, are attempts to obtain synergistic effects, specifically to produce materials that have an optimized combination of the best properties of polymers with the best properties of ceramics[10-29]. A general example would be to maintain some of the best properties of a ceramic material but to improve its mechanical strength. This could be done by having a tough polymer present to provide an additional mode for absorbing impact energy, thereby reducing brittleness.

Some General Trends

Biomimicry and Template-Based Systems. The goal in biomimicry is to understand the structure of biomaterials to the extent that some of the same guiding principles can be used to prepare better synthetic (non-biological) materials. One approach is illustrated in this volume by the precipitation of an irorganic phase between the crystalline regions of a partially-crystalline organic polymer by Calvert et al., in a manner reminiscent of the way bone structures are produced. Another example, by Mann and coworkers, involves the generation of a ferrimagnetic phase within the constraining environment of the protein ferritin.

Since template-directed syntheses are commonplace in biosytems, there is a strong connection between these two topics. One approach involving intercalation of organic phases between layered structures is illustrated by the contributions of Clement, by Lerner et al., and by Okada et al. Some related experiments in which silica-like particles are grown within the pores of a membrane are described by Mauritz and coworkers.

New Techniques and Approaches. The complexity of many organic-inorganic composites, and the very diverse backgrounds of many of the people working in this area has encouraged a wide range of new techniques and approaches. This has occurred with regard to both synthesis and characterization. An example of a new synthetic technique is the solution to the shrinkage problem generally occurring in the preparation of some composites, by Novak et al. In their approach, alkoxide groups that would otherwise have to be removed from the reacting system are instead polymerized in-situ to give the desired organic phase. An example of a new characterization technique in this area is the extensive use of small-angle scattering measurements by Beaucage, Ulibarri, Black, and Schaefer to investigate composite structures.

Two novel ways for the generation of organic phases are then described. In the first, by Guyot and coworkers, functionalized silica is used as nucleation sites in the emulsion polymerization of a typical vinyl monomer, ethyl acrylate. In the second, Wei et al. use a photochemical polymerization to synthesize the polymeric phases in a variety of composites. The use of a different type of radiation, γ photons, to polymerize a second monomer absorbed into a composite is outlined by Brennan, Miller, and Vinocur.

Techniques for preparing organic-inorganic composites from non-aqueous sytems is the subject of one contribution, by Sharp, and the use of polymeric phases to lock regular arrays of silica particles in place is the subject of another, by Ford et al. A final example in this category, by Belfiore and coworkers, describes the thermo-irreversible gelation of diene polymers in the presence of an inorganic salt.

Bonding and Other Interactions. The two phases in these composites are very disparate and, since good miscibility is generally desirable, much attention is being paid to the nature of the interactions occurring in these materials. The chemical bonding occurring in some of these systems is discussed by Corriu and colleagaues, and a broader discussion of the structures and interactions occuring in three types of organic-inorganic composites is given by Mackenzie. A study showing how the maximum size of silica particles growing in an elastomeric matrix is controlled by the constraining effects of the stretched-out polymer chains is given jointly by the Schaefer group at Sandia and the Burns group at Dow Corning.

Ladder and Bridged Structures. A number of ionic polysiliconate and polygermylate compounds form unusual penta- and hexacovalent compounds, and these have been used to form novel ladder, bridged, and network materials. Some of this work is described in two articles by Shea, Small, and Meyers at UC Irvine collaborating with Loy, Jamison, and Assink at Sandia.

High-Temperature Polymers. Using high-performance, high-temperaure polymers as the organic phase in these composites presents several special problems. For one thing, such polymers are generally almost intractable even under the best of conditions. Second, polymers of this type are designed to be unreactive, since this is required in most of their applications. This unreactivity becomes a problem, however, in getting good bonding between the polymer phase and the inorganic, ceramic phase. Finally, there is what is likely to become part of the central dogma in the area of organic-inorganic composies: the better the properties of the polymer to begin with, the more difficult it is to achieve further improvements. Some descriptions of recent work in this area, emphasizing polymers of interest to the US Air Force, are given in three chapters by Arnold et al., and by Mark et al.

Electrical, Optical, and Interfacial Properties. The characterization of these properties is extremely active in polymer science in general, so it will come as no surprise that organic-inorganic composites are playing increasingly-important roles in this area. Examples of electrical and optical properties are the chapters on conductive polymer/superconductive bilayer systems by McDevitt and coworkers, and on composite materials in photonics by Prasad and coworkers.

The use of this technology for interfacial properties is illustrated using coatings for metals and glass by Schmidt et al., and the chemical modification of carbon fibers for composites by Wang and Quirk.

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BIOMIMICRY AND TEMPLATE-BASED SYSTEMS

Chapter 2

Organic–Inorganic Hybrids with a Crystalline Polymer Matrix

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Many nanoscale hybrids of organic and inorganic materials have now been prepared. In general the materials become stiffer but significantly more brittle as increasing quantities of the inorganic phase are introduced into the organic polymer. This behavior is similar to that found in conventional particle-reinforced polymers. The properties of bone, as a polymer reinforced with nanometer-sized ribbon-shaped crystals of mineral, are good when compared with the properties of these synthetic polymer composites. In an effort to induce more structured, and possibly elongated, precipitation of the inorganic phase in hybrids, a crystalline polymer matrix is used. It was expected that the inorganic phase would be constrained to deposit between the crystalline polymer lamellae. Titania-polypropylene composites have been studied. They show an increase in stiffness but there is a loss of strength, apparently due to segregation of the titania to the spherulite boundaries. This study also shows that melt processing of hybrids is feasible as opposed to the usual casting of films.

Bone has an elastic modulus in the range of 20-30 GPa, about 10 times that of collagen or synthetic resins, table 1 (*1,2*). This increase is achieved by reinforcement with 40-50 vol% of hydroxyapatite ribbons which have a thickness of a few nanometers and a high aspect ratio. Various theories can be used to predict composite moduli from composition (*3*) and bone seems to be in the range expected for the known component moduli, volume fraction and particle shape.

Particle-filled composites generally show a decrease in strength and a rapid decrease in toughness with increasing particle content. Fiber-filled composites get

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