

Chapter 1

Introduction

Tomoko Sano, Charles L. Rando and Chang-Soo Kim

Abstract In the past decade, hybrid and hierarchical composites have come into focus for their ability to be property-specific solutions to design problems that cannot be solved by homogeneous materials. Significant advances have been especially made in the more established areas of organic–inorganic hybrids, and bioinspired and biomimetic hierarchical composites have led the development in the hierarchical composite research areas. Because of this, numerous review articles and books have been written on each of these topics (Buehler et al., *Eur J Inorg Chem* 2012(32):5091–5420, 2012; Sanchez et al., *Chem Soc Rev* 40(2):453–1152, 2011; Studart, *Adv Mater* 24(37):5024–5044, 2012; Chen and Pugno, *J Mech Behav Biomed Mater* 19:3–33, 2013; Fratzl and Weinkamer, *Prog Mater Sci* 52(8):1263–1334, 2007; Qian et al., *J Mater Chem* 20(23):4751, 2010; KICKELBICK, *Hybrid materials: synthesis, characterization, and applications*, Wiley-VCH Verlag, Weinheim, 2007; Gomez-Romero and Sanchez, *Functional Hybrid Materials*, Wiley-VCH Verlag, Weinheim, 2004; Su et al., *Hierarchically structured porous materials: from nanoscience to catalysis, separation, optics, energy, and life science*, Wiley-VCH Verlag, Weinheim, 2011; Zhang and Wei, *Advanced hierarchical nanostructured materials*, Wiley-VCH Verlag, Weinheim, 2014) with some focused on specific material class or application. However, few have focused on the nanoscale contributions and linkages of these composites. The goal of this book is to cover a broad range of current nano-lengthscale hybrid and hierarchical composite research, including the processing, properties, modeling, and applications of these composites, for a technical audience interested in learning more about these subject areas.

T. Sano (✉)

US Army Research Laboratory, RDRL-WMM-F, Aberdeen Proving Ground,
Aberdeen, MD 21005, USA
e-mail: tomoko.sano.civ@mail.mil

C. L. Rando

US Army Research Laboratory, RDRL-WMP-D Aberdeen Proving Ground,
Aberdeen, MD 21005, USA

C.-S. Kim

Materials Science and Engineering, University of Wisconsin-Milwaukee,
3200 N Cramer St., Milwaukee, WI 53211, USA

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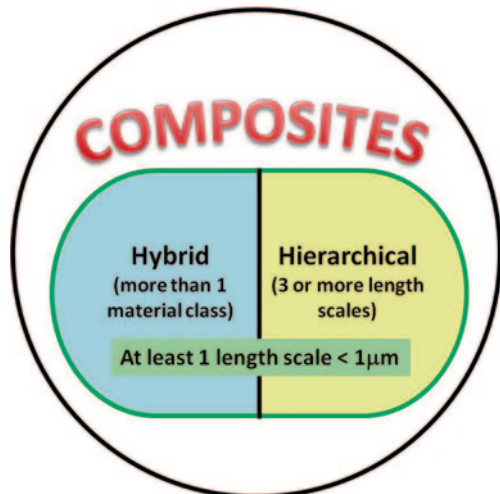
1.1 Introduction

There are a variety of definitions used in the field of hybrid and hierarchical composites. In this work, material class definitions, in a manner similar to Ashby (Ashby and Brechet 2003), are used in defining hybrid composites and hierarchical composites. We will specifically consider the following material classes in this work: organic polymers, inorganic polymers, molecular arrangements, and elemental groups (e.g., carbon nanotubes, metal oxides), metals, and ceramics and clays.

A hybrid composite is a system composed of (at least) two different material classes with length scales for at least one of the materials on the order of one micron or less. A hierarchical composite is a composite with an additional, smaller length scale component (e.g., a composite of a composite), which is a composite that consists of three or more critical length scales. Some hierarchical composites could be considered a hybrid composite with an additional component that adds another level of functionality. We will be considering hybrid and hierarchical composites with at least a single length scale on the order of one micron or less (e.g., a hierarchical composite with nanograin reinforcement). Although metal matrix composites (MMCs) are hybrid composites, we will not consider MMCs in this work due to the large volume of work published in this subject area. Figure 1.1 schematically shows the hybrid and hierarchical systems, a subset of all composites, that will be covered in the following chapters.

With nanotechnology in mind, this book will uniquely address a broad spectrum of areas of interest in both hybrid composites and hierarchical composites. These areas of interest include recent development of processing technologies, structural designs, modern computational simulation techniques, and the relationships among processing, structure, property, and performance.

Fig. 1.1 A schematic of the hybrid and hierarchical composite subjects covered in this book



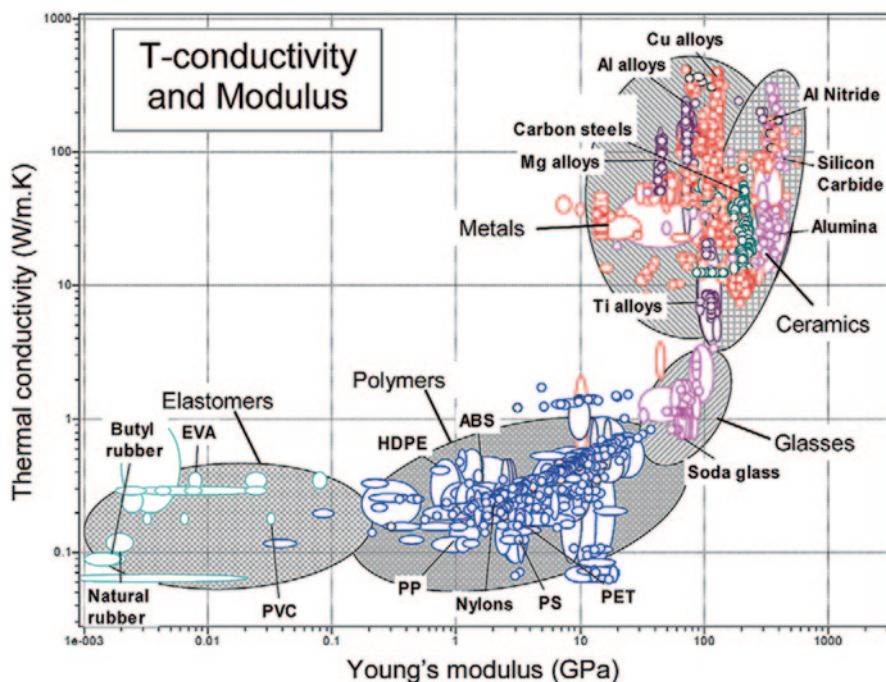


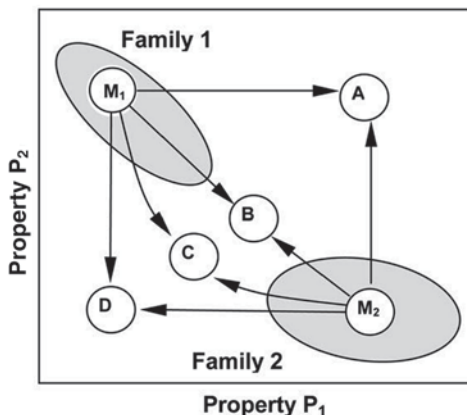
Fig. 1.2 A material property chart indicating the thermal conductivity and Young's modulus for a variety of materials. (Reprinted from Ashby and Brechet (2003), with permission from Elsevier)

1.2 Hybrid Composites

Hybrid composites are composites that combine two or more different material classes, such as an inorganic ceramic and an organic polymer. There are many classifications of hybrids. Gomez-Romero and Sanchez (2004) as well as Kickelbick (2007) distinguish hybrids with weak interactions such as van der Waals and hydrogen bonding or weak electrostatic interactions as class I. They classify class II as hybrids with strong chemical bonding between the two components. Ashby and Bréchet (2003) address hybrids from a functional classification, and Nanko (2009) classifies hybrids into three categories: structurally hybridized materials (composites), materials hybridized in chemical bond, and functionally hybridized materials. The differences in classifications depend on one's point of view. A polymer chemist could view hybrids differently than a design engineer.

Regardless of terminology used, the purpose of hybridizing is to obtain combined properties, such that the hybrid is an improvement compared to each of the parent materials. For example, a solution to an engineering problem might require a new material with a higher Young's modulus and a lower thermal conductivity. Figure 1.2 presents a typical property chart to show the relationship between the thermal conductivity and Young's modulus for a variety of materials (Ashby and

Fig. 1.3 Hybridization property map scenarios. (Reprinted from Ashby and Brechet (2003), with permission from Elsevier)



Brechet 2003). Examining Fig. 1.2, one might decide to combine a polymer with a metal to obtain a hybrid composite with these desired properties. However, the processing technique, the volume percentages, the choice of catalysts, etc., can play an important role in the hybrid's homogeneity, interfaces, bonding, and the resulting structure and properties. An idealization of such a process is shown in Fig. 1.3, where the combination of Material 1 (M_1) and Material 2 (M_2) results in the hybrid A, with its improved synergistic properties. In the figure, hybrid B would be a combination that follows the “rule of mixtures,” hybrid C is the combination that has one improved property, and hybrid D would be the worst case scenario with no benefit to hybridization.

In the following hybrid chapters, the various successful combinations of hybrid composites will be introduced and discussed in detail. Chapter 2 covers the synthesis of organic–inorganic polymer hybrids and provides an overview of their applications. In Chap. 3, the emerging field and potential applications of particle brushes, or polymer-tethered inorganic nanoparticle hybrids, are discussed. Chapter 4 details the engineering of multiferroic and magnetoelectric hybrids, as well as the properties, processing, and modeling and simulation of these hybrid systems. In Chap. 5, the last chapter in the hybrid composites area, the types, processing, properties, and modeling work of clay–polymer nanocomposites will be discussed.

1.3 Hierarchical Composites

The simplest form of a composite consists of a two-phase structure. As described earlier, a hierarchical composite is a composite with an additional, smaller length scale component that is part of one of the phases. For example, a structural hierarchical composite might contain a structural component possessing its own unique substructure (Lakes 1993). As another example, one of the most notable biological hierarchical composite is bone. As shown in Fig. 1.4, at the macroscopic scale, bone is made up of osteons, which consist of haversian canals that surround nerves and

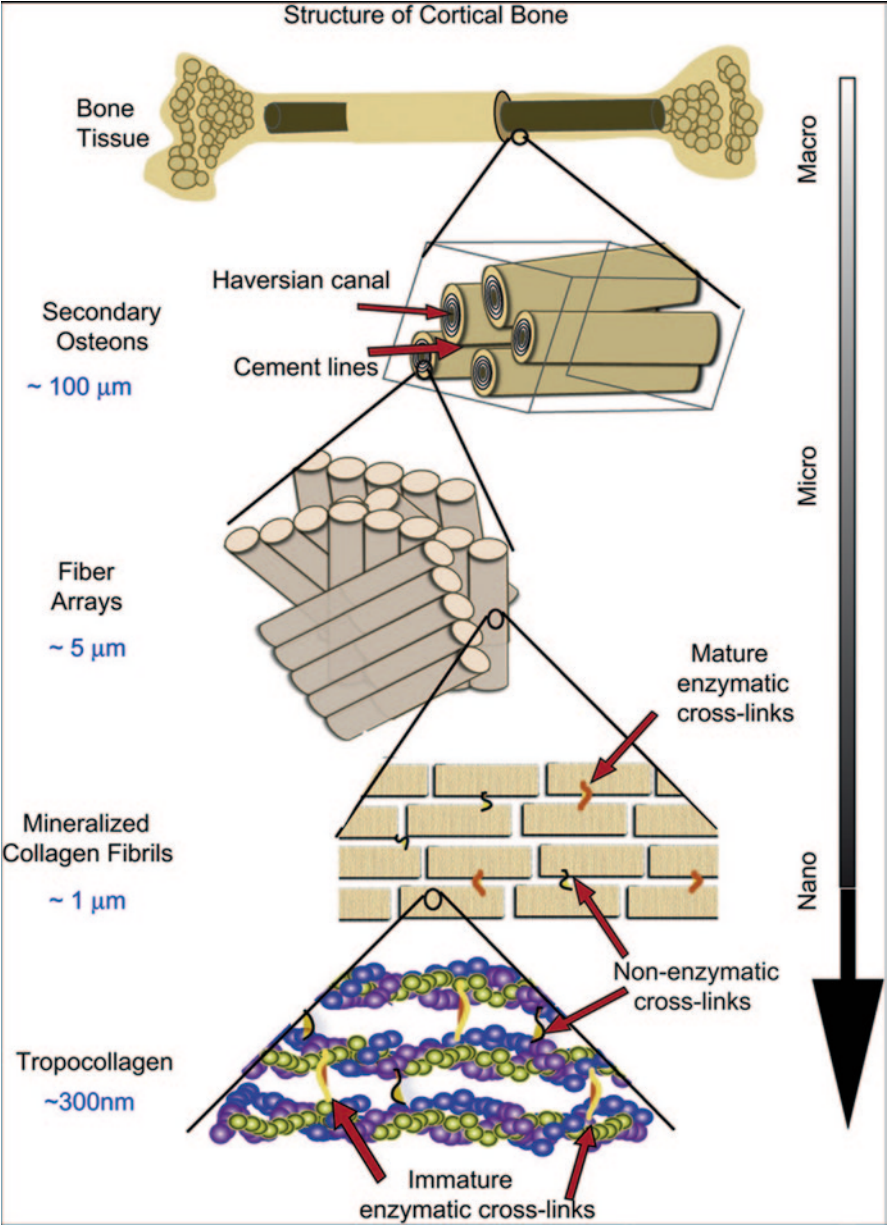


Fig. 1.4 The hierarchical structure of bone at multiple length scales. (Reprinted from Barth et al. (2011), with permission from Elsevier)

blood vessels, and cylindrical lamellae. The lamellae are made up of mineralized collagen fibers. The mineralized collagen fibers are bundles of mineralized fibrils, which in turn are made up of tropocollagen molecules (Barth et al. 2011; Vaz et al. 2011). Each of the hierarchical components and their materials play a role in the

strengthening and toughening mechanisms at multiple length scales, and contribute to the anisotropic properties of bone. By natural evolution, biological systems have combined a variety of materials with specific properties to create hierarchical composite solutions for survival.

These naturally occurring hierarchical materials have inspired the research and generation of engineered or synthetic hierarchical composites made with different classes of materials for a variety of applications (Chen and Pugno 2013; Fratzl and Weinkamer 2007; Studart 2012; Su et al. 2011; Vaz et al. 2011; Zhang and Wei 2014; Dunlop and Fratzl 2013; Launey and Munch 2009; Fratzl 2007). Hence, the goal for many synthetic hierarchical composites is to obtain better performing materials by intentionally creating material complexity by designing composites with multi-length scale property control. For example, structural hierarchical composites have been shown to provide both stiffness and damping characteristics, which are generally competing properties (Lakes, 2002).

Hierarchical composite research has broadened with the increased interest in creating hierarchical composite solutions for various applications. The multi-length scale design and creation of such hierarchical composites include advanced characterization of the material components, processing techniques that optimize the structure–property relationships, and modeling and simulations. In the second half of this book, these application-specific hierarchical composite systems and their design metrics will be described, starting with medical applications of hierarchical composites in Chap. 6. The hierarchical composite material types, their properties, and specific medical applications of the hierarchical composites are described. In Chap. 7, electrochemical hierarchical composites used for energy applications are discussed. These include mechanisms of energy storage, hierarchical composite use in batteries, energy conversion, and sensors. Chapter 8 covers bioinspired structural hierarchical composites, providing examples from nature and showing how researchers have applied a design methodology for hierarchical composites. Elements of these methodologies include reinforcements, hierarchical porosity, and hierarchical topography. In Chap. 9, various morphologies of hierarchical composites with carbon nanotube additions, their properties, and processing methods are described. Depending on the incorporation method, the carbon nanotubes can play several different roles in the matrix, such as changing the polymer mobility, or improving the mechanical properties.

1.4 Concluding Remarks

The following chapters will reveal that hybrid and hierarchical composite research has grown and will continue to grow for some time. There are new formulations, processing methods, and structure–property relationships to optimize for numerous applications. We hope this book educates the reader in some of the exciting research currently being conducted in these fields, and inspires them for further inquiry.

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