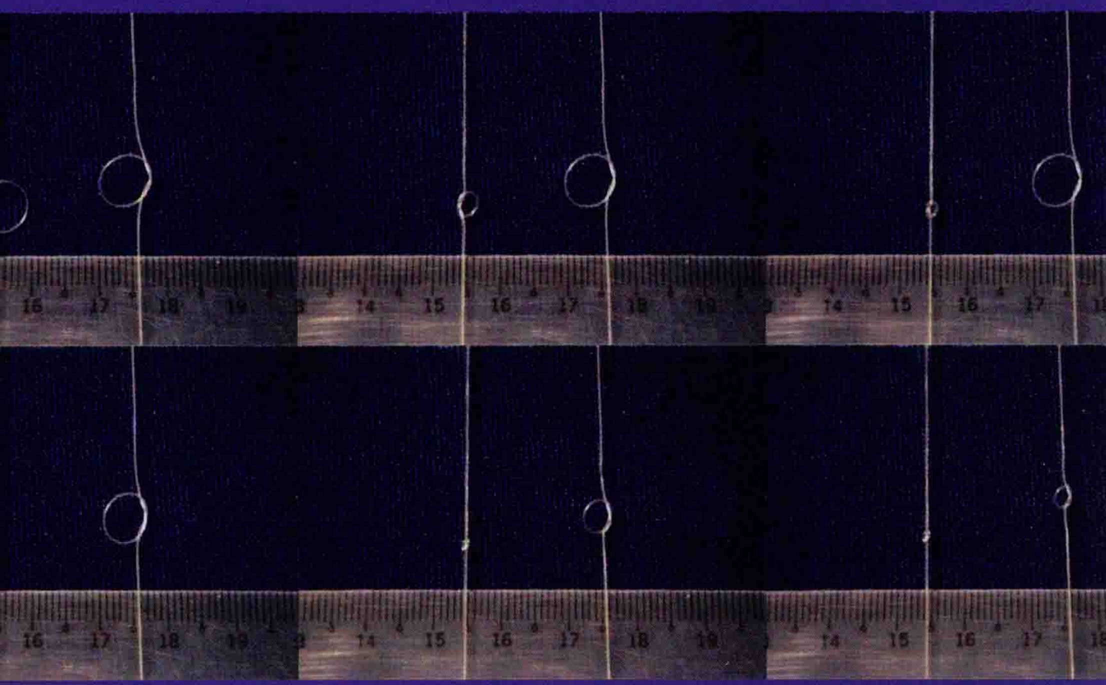
Polyurethane Shape Memory Polymers



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Forewords

This book, *Polyurethane Shape Memory Polymers*, authored by Dr. Wei Min Huang, Dr. Bin Yang, and Dr. Yong Qing Fu, is the first book dedicated to polyurethane shape memory polymers—some of the most important types of shape memory polymers in existence. As a senior researcher with more than two decades of experience in this field, I am very happy to see the publication of this book by CRC Press/Taylor & Francis Group.

This book is suitable not only for macromolecule engineers and researchers working on developing new shape memory polymers and improving the performances of existing ones, but also for students studying polymer chemistry to acquire a good understanding of the fundamentals of shape memory polymers. On one hand, this book is a useful reference for research and development; on the other, it serves as a perfect introduction for anyone who is interested in learning more about this fantastic material.

The content of this book is carefully structured with plenty of application examples. I am sure that readers will be fascinated by the wonderful world of shape memory polymers.

Dr. Shunichi Hayashi
SMP Technologies, Inc.
Japan

In recent years, intelligent or smart materials have attracted worldwide attention. One of the main types that stimulated research into intelligent materials is the shape memory alloy. The polyurethane shape memory polymer, in particular, also has been applied practically in a wide variety of fields. Dependence of the elastic modulus and yield stress on temperature in a shape memory polymer is quite the opposite of the principle of a shape memory alloy. The very large volume change of a shape memory polymer foam makes this material valuable for inflatable structures in the aerospace field. The gas permeability of the shape memory polymer thin film varies significantly above and below the glass transition temperature—a property with many applications in the medical and textile fields. If both of these outstanding qualities of the shape memory alloy and the shape memory polymer are combined, it becomes possible to develop a shape memory composite that exhibits completely new high-performance functions.

In order to develop shape memory polymer elements, it is also important to understand the thermomechanical properties of these materials. The thermomechanics of shape memory polymers are very complex because they depend on hysteresis. The most basic and important properties of the polyurethane shape memory polymer are introduced in this fine book that is certain to be of interest for researchers, students, and engineers in numerous fields of materials science and engineering.

Professor Hisaaki Tobushi
Aichi Institute of Technology
Toyota-city, Japan

Shape memory polymers (SMPs) are some of the most important and valuable new materials developed in the last 25 years. The ability to respond and recover a large deformation with the application of a particular external stimulus such as heat, light, or moisture is of great scientific and technological significance. Furthermore, these materials exhibit enormous innovation potential. Because of their novel properties and behavior, they can be utilized in a broad range of applications and address challenges in advanced aerospace, commercial, and biomedical technologies. In addition, SMPs have advantages over their older shape memory alloy cousins—their light weight, high strain and shape recovery ability, ease of processing, low cost, and other properties may be tailored for a variety of applications.

Although the focus of this book is on one commercially available thermoplastic polyurethane SMP, the main features, mechanisms, and applications discussed here are largely applicable to other SMPs. Based on the remarkable properties of SMPs and their great potential, technologists have developed many applications ranging from outer space exploration to the interior of the human body. As a result of their considerable shape memory effects (SMEs), SMPs are in the process of reshaping our thinking, approaches, and design methods in many ways that conventional materials and traditional approaches do not allow.

In the aerospace arena, SMPs formed as foams, composites, and hybrid structures used with cold hibernated elastic memory (CHEM) technology have the potential to provide innovative self-deployable space structures with significantly better reliability, lower cost, and simplicity than other expandable and deployable structures. Some advanced SMP space concepts represent a new generation of deployable structures. If developed, these innovative technologies will introduce a new paradigm for defining configurations for space-based structures and future mission architectures.

The unique attributes, biocompatibility, and other properties make polyurethane SMP technology viable for self-deployable stents and other medical products. Recently developed SMP foams combined with CHEM processing expand their potential medical applications even further. SMP materials will significantly and positively impact the medical device industry. They have unique characteristics that will revolutionize the manufacture of medical devices and usher in an era of simple, low-cost, self-deployable medical devices.

This book provides a comprehensive discussion of SMPs from a brief introduction to SMPs and their position in the world of materials, through the details of shape memory behavior, fabrication, and characterization of composites, fabrication of porous materials and their applications, investigation of SMEs at micro and nano scales, biomedical applications, fundamentals of multi-SMEs, and the future of polyurethane SMPs.

Dr. Witold M. Sokolowski
California Institute of Technology
Pasadena, California

Shape memory polymers (SMPs) belong to a novel class of intelligent ("smart") polymers introduced in the mid-1980s in Japan that have gained much attention in Japan and in the United States. SMPs are stimuli-responsive polymers that function by changing their moduli and shapes on exposure to external stimuli such as heat, light, and chemicals. This class of polymers developed rapidly in the past two decades, and many articles about various aspects of SMPs have been published in recent years including review articles focusing on material systems. Since then, continuous development efforts by various organizations and university groups have expanded the applications of SMPs into diverse fields such as morphing aircraft structures, textiles, and biomedical devices.

Among various classes of SMPs reported to date, polyurethane-based SMPs are the most extensively investigated; they were also the first SMPs to be commercialized. The scientific knowledge revealed by investigation of their molecular architectures and structure–property relationships provided a sound foundation for the understanding of the unique functionalities of these materials. The translation of such knowledge into the development of new capabilities will lead to innovations that will benefit society.

This book provides a foundation for better understanding of various aspects of SMPs, including shape memory mechanisms and mechanics. In addition, various application concepts are introduced to establish a good framework for assessing the potential utility of this class of materials in modern society. The authors provide numerous examples to illustrate the unique functionalities that SMPs can bring about in engineering designs for future applications, such as the discussions on fabrication of micro- and nano-sized elements in Chapter 9, large-scale surface pattern generation in Chapter 10, and multi-shape memory effect in Chapter 12.

The material in this book is valuable for university students, research scientists, and engineers. As an active participant in the SMP technology field in the past decade, I am convinced that this book will play a valuable role in generating a greater awareness of the numerous possibilities presented by this class of unique materials. SMPs are organic polymeric materials that offer actuation, shape memory, and stimulus responsiveness enabling new capabilities for engineering design. The "smart" nature of these materials represents a new design paradigm and invites us to consider them for use in applications that are not feasible with conventional polymers.

Dr. Tat Hung Tong
Cornerstone Research Group, Inc.
Dayton, Ohio

Preface

The discovery of materials exhibiting shape memory effects (SMEs)—so-called shape memory materials (SMMs)—opened an exciting field and made a significant breakthrough in the development of materials that complement or supplant the traditional materials and approaches for a variety of engineering applications and also influenced the way many products are designed.

At present, shape memory polymers (SMPs) are undergoing rapid growth and becoming the leading members of the fantastic world of SMMs. Based on their advantages over other SMMs, in particular low cost and high versatility, SMPs are more accessible and more flexible, thus showing greater potential for numerous applications, from deployable structures in outer space to medical devices such as stents and sutures.

Although a few types of SMPs, e.g., the polystyrene SMP invented by Dr. Tat Hung Tong and now marketed by Cornerstone Research Group, are gaining in popularity, polyurethane SMPs are to date the most extensively studied. The polyurethane SMP invented by Dr. Shunichi Hayashi, and subsequently developed into a range of products by him and his co-workers, is seemingly the most successful SMP in the market at present.

This book, although focused on polyurethane, reveals the fascinating aspects of SMPs in a systematic way, from fundamentals to applications, from macro scale to submicron scale, from the history to the future. By focusing on a particular SMP that is available commercially, we are able to reveal its technical details and features. The many illustrations and vivid pictures included will help readers to instantly visualize and grasp the basic concepts and mechanisms. We hope that, after reading this book, readers will be ready to explore their own designs.

Chapter 1 introduces SMMs and SMPs and describes their mechanisms and general applications. Thereafter, the focus is on polyurethane SMPs. Chapters 2 to 5 present the thermal- and moisture-responsive features, electrically conductive composites, and thermomechanical properties of these remarkable materials. Chapter 6 elucidates the fabrication and characterization of magnetic SMP composites. A more extensive and systematic review of SMP composites can be found in Chapter 7. Chapter 8 focuses on porous and foam SMPs. Chapter 9 discusses SMEs at micro and nano scales. Chapter 10 is about wrinkling atop SMPs. Novel biomedical applications are revealed in Chapter 11. Chapter 12 explains the fundamentals of the multi-SMEs and how these effects add a new dimension to SMP applications. The concluding chapter covers the future of polyurethane SMPs.

We greatly appreciate the kind help of Dr. Shunichi Hayashi, Prof. Hisaaki Tobushi, Dr. Witold M. Sokolowski, and Dr. Tat Hung Tong in providing constructive comments and writing the Forewords. The origin of this book may be traced back more than 12 years, when Dr. Sokolowski passed a few pieces of SMP foams to W.M. Huang. We thank him for introducing us to this magic material.

W.M. Huang would like to thank all current and previous members of his research group for their support. The content of this book is largely based on their hard work over several years. It is indeed enjoyable to work with them and share both sad and exciting moments.

Last but not least, Hendra Purnawali helped edit, compile, and finalize this book. Without his help and patience, the book would not have been ready for publishing. Many big thanks to him.

W.M. Huang, B. Yang, and Y.Q. Fu

Authors

Wei Min Huang is an associate professor at the School of Mechanical and Aerospace Engineering at Nanyang Technological University (NTU), Singapore. He was awarded his PhD from Cambridge University (United Kingdom) in 1998 and has published approximately 100 journal papers, mainly in the field of shape memory materials. His current research interests include the fundamentals of the shape–temperature memory effect, shape memory materials and technologies, and their applications.

Bin Yang obtained his PhD from the School of Mechanical and Aerospace Engineering, Nanyang Technological University, Singapore, in 2007. His PhD work focused on the polyurethane shape memory polymer and its composites, under the supervision of Professor W.M. Huang and Professor C. Li. Dr. Yang is now a chief engineer at Helvoet Rubber & Plastic Technologies Pte. Ltd. (Singapore).

Richard Yong Qing Fu is a reader at the Thin Film Centre at the University of the West of Scotland in the United Kingdom. He was a lecturer at Heriot-Watt University, Edinburgh, from 2007 to 2010. He earned a PhD from Nanyang Technological University, Singapore, and then worked as a research fellow at the Singapore–Massachusetts Institute of Technology Alliance and as a research associate at the University of Cambridge. Dr. Fu has extensive experience with microelectromechanical systems (MEMS), thin films, surface coatings, shape memory alloys, smart materials, and nanotechnology. He has published a book on thin film shape memory alloys, about 10 book chapters, and more than 150 refereed journal papers.

Contents

1 Introduction

1.1 SHAPE MEMORY MATERIALS AND SHAPE MEMORY POLYMERS

There are plenty of fascinating materials in the world, and we still see many new materials invented almost every day—largely driven by the needs for new materials from a variety of engineering applications. One group of materials can respond accordingly to a particular stimulus by means of altering certain physical or chemical properties. The types of stimuli include heat (thermo-responsive); stress and/or pressure (mechano-responsive); electrical current and/or voltage (electro-responsive); magnetic field (magneto-responsive); change of pH, solvent, or moisture level (chemo-responsive); light (photo-responsive); and other factors.

Technically speaking, members of this group are known as stimulus-responsive materials (SRMs; Figure 1.1). SRMs, in particular stimulus-responsive polymers (including polymeric gels) and their composites, have become very hot topics in recent years due to a wide range of potential applications, from functional nanocomposites to controlled and targeted drug and gene delivery therapies (Zhao et al. 2009, Kostanski et al. 2009, Onaca et al. 2009, Bajpai et al. 2008, Schmaljohann 2006, Stratakis et al. 2010, Kundys et al. 2010, Huck 2008, Caruso et al. 2009, Stuart et al. 2010, Chaterji et al. 2007, Osada and Gong 1998, Thornton et al. 2004).

One group of SRMs exhibits the ability to change shape in the presence of the right stimulus (Lendlein 2010). If the shape change is spontaneous and instant when the stimulus is presented, the result is a shape change material (SCM); electro-active polymers (EAPs) and piezoelectrical materials (such as PZTs) are two typical examples of SCMs (Aschwanden and Stemmer 2006, Haertling 1999, Yu et al. 2003). A second group designated shape memory materials (SMMs) maintain their temporary shapes virtually forever until the right stimulus is applied. All SMMs are characterized by the shape memory effect (SME), defined as the ability to recover original shape in the presence of the right stimulus after severe and quasi-plastic distortion (Huang et al. 2010a).

A few major types of SMMs have been developed. Probably the most important ones at present are shape memory alloys (SMAs) and shape memory polymers (SMPs; Wei et al. 1998, Feninat et al. 2002, Hornbogen 2006, Gunes and Jana 2008). While the mechanism behind the SMEs in SMAs is the reversible martensitic transition, the dual-segment/domain system is the mechanism in SMPs (Funakubo 1987, Sun and Huang 2010a, 2010b). Probably the newest type of SMM, the shape memory hybrid (SMH) composed of at least two components and lacking SMEs as an individual compound, shares the same mechanism as SMPs (Fan et al. 2011, Huang et al. 2010a). Shape memory ceramics (SMCs) exhibit the same working principle as SMAs, i.e.,

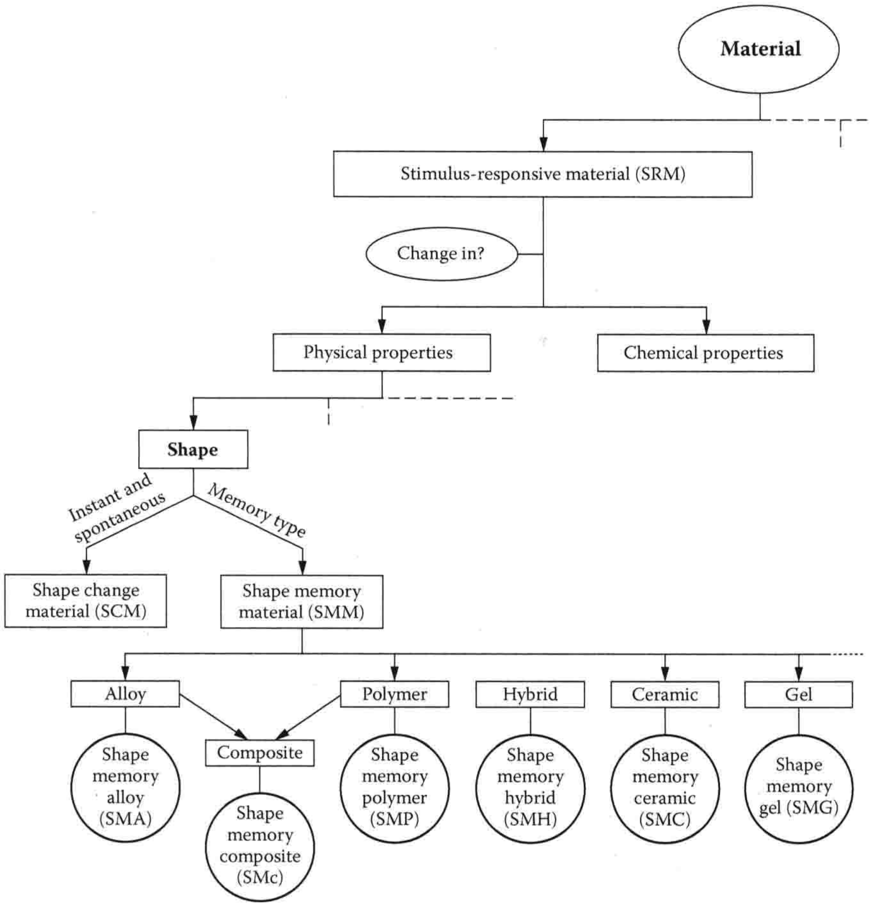

FIGURE 1.1 Location of shape memory polymers within the world of materials.

reversible phase transformation, or have multi-phase systems and are thus similar to SMPs (Wills 1977, Swain 1986, Pandit et al. 2004). Due to swelling effects and/or electrical charges, gels are normally considered typical SCMs. Some gels exhibit SMEs due to, for instance, a reversible order–disorder transition (Osada and Gong 1998, Mitsumata et al. 2001, Liu et al. 2007a, Gong 2010). It is interesting that the swelling effects have been utilized recently to actuate SMPs (Lv et al. 2008). A shape memory composite (SMc) is defined as a composite with at least one SMM (most likely SMA or SMP) as its component (Liang et al. 1997, Wei et al. 1998, Tobushi et al. 2009). From this view, SMcs do not constitute an independent subgroup of SMMs, even for shape memory bulk metallic glass composites (Hofmann 2010).

Although SMEs were found in a gold cadmium alloy as early as 1932, the attraction of this phenomenon was not apparent until 1971 when significant recoverable strain was observed in a nickel titanium alloy at the US Naval Ordnance Laboratories (Funakubo 1987). At present, a few SMA systems have been developed and are commercially available (Huang 2002). Thin film SMAs have become promising