Progress in Polymer Science 49–50 (2015) 79–120

Contents lists available at ScienceDirect

Progress in Polymer Science

journal homepage: www.elsevier.com/locate/ppolysci

Editorial/Preface

Recent progress in shape memory polymer: New behavior, enabling materials, and mechanistic understanding

Qian Zhao [a], H. Jerry Qi [b], Tao Xie [a,*]

[a] State Key Laboratory of Chemical Engineering, Department of Chemical and Biological Engineering, Zhejiang University, 38 Zheda Road, Hangzhou, 310027 PR China
[b] The George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, 801 Ferst Drive, Atlanta, GA 30332, USA

ARTICLE INFO

Article history:
Available online 11 April 2015

Keywords:
Shape memory polymer
Smart materials
Stimuli-responsive polymer
Polymer modeling

ABSTRACT

Shape memory polymers (SMPs), as a class of programmable stimuli-responsive shape changing polymers, are attracting increasing attention from the standpoint of both fundamental research and technological innovations. Following a brief introduction of the conventional shape memory effect (SME), progress in new shape memory enabling mechanisms and triggering methods, variations of in shape memory forms (shape memory surfaces, hydrogels, and microparticles), new shape memory behavior (multi-SME and two-way-SME), and novel fabrication methods are reviewed. Progress in thermomechanical modeling of SMPs is also presented.

Contents

1. Introduction 80
2. General aspects of SMPs 82
   2.1. Programming 82
   2.2. Classification 83
   2.3. Basic molecular requirements and mechanism 83
   2.4. SMP characterization 85
3. Shape memory switches and triggers 86
   3.1. Phase versus molecular switches and thermal versus non-thermal triggers 86
   3.2. Direct/indirect trigger methods 89
4. Variants in shape memory forms 90
   4.1. Shape memory surfaces 90

Abbreviations: SCPs, shape changing polymers; LCEs, liquid crystalline elastomers; SMP, shape memory polymer; SME, shape memory effect; 2W, two-way; 1W, one-way; T_{trans}, transition temperature; T_g, glass transition temperature; T_m, melting temperature; T_{cl}, liquid crystal cleaning temperature; T_d, deformation temperature; T_f, shape fixing temperature; T_c, crystallization temperature; R_f, shape stability ratio; R_r, shape recovery ratio; T_{sw}, switching temperature; ε_{max}, maximum recoverable strain; σ_{max}, maximum recovery stress; SMC, shape memory cycle; ε_{load}, strain under load; ε, fixed strain; T_r, recovery temperature; ε_{rec}, recovered strain; V_r, strain recovery rate; $T_{\sigma max}$, temperature corresponding to σ_{max}; $T_{sw,app}$, apparent switching temperature; PCL, poly(ε-caprolactone); SMPU, shape memory polyurethane; EMU, elemental memory unit; TME, temperature memory effect; PU, polyurethane; T_i, liquid-crystal isotropic transition temperature; T_v, vitrification temperature; CIE, crystallization induced elongation; MIC, melting induced contraction.

* Corresponding author.
E-mail address: taoxie@zju.edu.cn (T. Xie).

http://dx.doi.org/10.1016/j.progpolymsci.2015.04.001
0079-6700/

4.2. Shape memory hydrogels 92
4.3. Shape memory microparticles 94
5. Multi-SMPs 95
5.1. Intrinsic multi-SMPs 95
5.1.1. General aspects 95
5.1.2. Multi-SMPs via distinct thermal phase switches 96
5.1.3. Multi-SMPs via molecular switches 98
5.1.4. Tunable multi-SMPs via a single broad thermal phase switch 99
5.2. Extrinsic multi-SMPs 102
5.3. Reprocessible multi-SMPs 103
6. Two-way SMPs 104
6.1. Quasi 2W-SME for liquid crystalline elastomers 104
6.2. Quasi 2W-SME for semi-crystalline networks 104
6.3. 2W-SME for semi-crystalline networks 105
7. Novel SMP fabrication methods 107
7.1. Electrospinning 107
7.2. Four dimension printing 107
7.3. Photo-induced shape transformation 107
7.4. Origami-inspired manufacturing 108
8. Modeling of thermomechanical behavior of SMPs 109
8.1. Thermoviscoelastic models 110
8.2. Phase evolution models 112
8.3. Models for predicting shape memory performance 112
9. Summary and outlook 113
Acknowledgments 114
References 114

1. Introduction

Active shape change in response to environment conditions is commonplace in nature [1]. In fact, this property is essential for the survival of animals and even some plants. Among numerous interesting examples are sunflowers that move with the sun to maximize light exposure, the opening and closing of Venus flytrap to capture preys, and the microscopic shape changes in the skin layers of cattlefish that enables its macroscopic color change.

Polymer materials, in their early days, were mostly studied for use as static structural parts. In the modern days, however, advanced polymer materials that exhibit special functions in response to external conditions have attracted more and more attention. Such behavior is similar to the biological intelligence observed in nature. Accordingly, such polymers are also called smart polymers, or in a more scientific term, stimuli-responsive polymers. Whereas macroscopic changes in polymer functions are often accompanied by chain conformational changes (i.e., shape changes at the molecular scale), stimuli-responsive shape changing polymers (SCPs) commonly refer to those for which shape changes are either macroscopic or at least visible under microscopes. Examples of stimuli-responsive SCPs are numerous, ranging from the well known swelling/deswelling of hydrogels [2] to the intriguing reversible surface morphological changes of liquid crystalline elastomers (LCEs) [3]. Of importance here is that, for the preceding two examples, after the materials are fabricated, the shape change can only occur between a fixed number of equilibrium shapes (often two). That is, their shape shifting cannot be manipulated externally after fabrication, a non-programmable shape changing behavior.

In contrast, shape memory polymers (SMPs) are a class of stimuli-responsive SCPs for which shape shifting behavior can be programmed. This is the single most important feature that distinguishes SMPs from other stimuli-responsive SCPs. Specifically, a typical SMP can be programmed to fix one temporary shape and subsequently recover to its permanent shape upon stimulation (typically heating), as illustrated in Fig. 1a. Here, the temporary shape is usually defined by the applied force during the shape fixing step. Accordingly, this step is also called a programming step. Since the shape memory cycle in Fig. 1a involved a total of two shapes (one temporary and one permanent), the associated behavior is called a dual-shape memory effect (dual-SME), representing the simplest and most well known behavior for SMPs.

From a molecular structure standpoint, the dual-SME is enabled by the combination of a reversible switching mechanism and a network structure [4]. Thus, the simplest (and very common) polymer systems, such as a crosslinked (chemically or physically) amorphous (or crystalline) polymer would exhibit such a behavior [5–10]. Indeed, the dual-SME has been known for quite a long time and is the basis of numerous technological innovations. Best known examples of commercial applications include heat-shrinkable tubes used in cable industry, heat-shrinkable labels used for packaging, and shrink-dink toys. Other high value-added applications, mostly in the biomedical [11–15] and aerospace fields [16–18], are also being actively explored. The vast potential to enable technological innovations highly relevant for the human society (e.g., health) has been the driving force for active research on SMPs.