New Polymeric Composite Materials
Environmental, Biomedical, Actuator and Fuel Cell Applications

Edited by
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Polymeric and composite materials are in high demand and their continuing development is making our life style more comfortable.

This book, ‘New Polymeric Composite Materials - Environmental, Biomedical, Actuator and Fuel Cell Applications’ brings together and broadly explores the latest developments and applications of polymeric and composite materials in the areas such as shape memory polymers, green composites for artificial organs, geomembranes for the safe disposal of waste, removal of heavy metals and dyes, adhesives, sensors and actuators, fuel cells, membrane and environmental sustainability, etc.
New Polymeric Composite Materials
Environmental, Biomedical, Actuator and Fuel Cell Applications

By

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Foreword

Polymeric and composite materials are in high demand and their use and development continually ads to make our lifestyle more comfortable. Some examples for the uses of polymeric and composite materials include their use in biomedical and environmental applications, sensors and actuators and fuel cells technologies.

This book, ‘New Polymeric Composite Materials: Environmental, Biomedical, Actuator and Fuel Cell Applications’ brings together and broadly explores the latest developments and applications of polymeric and composite materials in the areas such as shape memory polymers, green composites for artificial organs, geomembranes for the safe disposal of waste, removal of heavy metals and dyes, adhesives, sensors and actuators, fuel cells, membrane and environmental sustainability, etc.

The book is the result of significant contributions from experts from various interdisciplinary fields of science. It broadly explores the most ample, in-depth, and up-to-date research and reviews. We are thankful to all the contributing authors/coauthors for their valued contributions. We would also like to thank all publishers, authors, and others who granted permission to use their figures, tables, and schemes.

Chapter 1: Shape-memory polymers (SMPs) provide an attractive insight into material science, opening unexplored horizons and giving access to unconventional functions mainly in polymer materials, and thus SMPs play a vital role in the field of biomedical engineering and clinical applications. This chapter includes different functionality polymers and their structural approaches, types of different stimuli responsive shape-memory polymers and their applications in the biomedical field. At the end, future prospects and challenges related to clinical research are discussed in detail.

Chapter 2: Presently, the concept of ‘Green Chemistry for Sustainable Development’ is a guiding source for development of next generation materials, known as composite green polymers. The present chapter represents various applications of green composite polymers in medical technology with focus on the development of artificial organs.

Chapter 3: The increasing consumerism has resulted in massive waste generation. The proper disposal of this waste is a real challenge and lots of research is going on around the world to develop new techniques or to improvise the existing to face this challenge. Landfill liners or geomembranes are one of the most important components of landfilling which ensure the safe disposal of wastes. This article summarizes the various physical, chemical, thermal and mechanical factors that affect the performance of a geomembrane. It provides supportive information for the selection of proper geo-membrane material with respect to exposure conditions, expected life and available resources.
Chapter 4: Nowadays, the amount of implantable devices with lots of applications has increased the need for supplying the required energy to sense, monitor, vibrate, pump and report the collected data of such devices. Such a power source should have a long life time and be of ecofriendly nature. It should be capable of producing energy directly from the living organisms’ fluids or organic matter. These required properties, light up the idea of using enzymatic biofuel cells (EBFCs). Unfortunately, EBFCs suffer from short life time and poor electron transfer from the enzyme active site to the electrode surface. This issue can be overcome by using certain biocompatible mediators and some enzyme immobilization techniques such as: physical adsorption, electrostatic attraction, covalent coupling and entrapment.

Chapter 5: In this chapter the synthesis of surfactant based sodium dodecyl sulphate zirconium phosphate (SDS-ZrP) intercalated cation exchange material is discussed.

Chapter 6: The two most popular artificial intelligence (AI) techniques namely, artificial neural networks (ANN) and support vector machines (SVM) are applied for predicting the removal efficiency of heavy metals like copper (II), arsenic (III), lead (II), etc. in an adsorption process using low cost biosorbents.

Chapter 7: In this chapter, the usefulness of aqueous microwave assisted methodology has been discussed in respect of synthesis of alginic acid grafted polyacrylamide.

Chapter 8: The synergy between organic and inorganic materials offers the possibility for the development of new generation innovative organic–inorganic composites with diversified applications such as catalysis, photocatalysis, separation technology, energy storage and drug delivery. The present chapter discusses the scientific and technical advancements in the development of organic polymer based TiO₂ nanocomposite membranes for water treatment.

Chapter 9: Electrochemical biosensors have benefited extensively from advances in nanomaterials (e.g., metal nanoparticles, carbon nanotubes and graphene). Among the various biomolecules, cholesterol has aroused considerable interest in recent years on account of its being an important marker in clinical diagnosis. This chapter highlights the recent advances in the field of enzymatic and non enzymatic cholesterol sensors with the use of nanotechnology.

Chapter 10: Retention behaviour of twenty four synthetic dyes on plain and tri-n-butylamine (TBA) impregnated silica gel-G and starch layers in aqueous alcohol media has been studied. Compact and sharp spots led to some useful separations of dyes, having similar chromophore groups on the basis of their differential solubilities and preferential adsorption on these layers.
Chapter 11: The chapter deals with the basic information regarding to the materials and their types used for manufacturing ionic polymer metal composites (IMPCs) actuators using various fabrication processes under optimum experimental parameters and possible applications. Among the variety of electro active polymers recently developed, IPMCs are good candidates for use in bio-related, robotics and aerospace applications because of their biocompatibility. Several fabrication processes, their performance and mechanical characteristics, a number of recent applications of IPMCs have been reported in this chapter.

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CHAPTER 1

Shape Memory Polymers in Biomedical Applications

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Abstract
Shape-memory polymers (SMPs) provide an attractive insight into material science, opening unexplored horizons and giving access to unconventional functions mainly in polymer materials, and thus SMPs play a vital role in the field of biomedical engineering and clinical applications. The shape-memory polymers are able to recover fully under load and generate high levels of stress during recovery. When activated under a programmed thermo-chemical cycle, the materials demonstrate excellent shape-fixity and reach complete recovery on re-heating. In view of different structural approaches, a large number of polymers of medical applications are anticipated from resulting shape-memory polymers. Some of the devices are already being utilized in the medical field and others are under examination. One of these potential applications is the removal of a clot in a blood vessel using a laser-activated shape-memory polymer. This chapter includes different functionality polymers and their structural approaches, types of different stimuli responsive shape-memory polymers and their applications in the biomedical field. At the end, future prospects and challenges related to clinical research are discussed in detail. To compile this chapter and to provide adequate information to the readers, we have explored all possible ways including research articles, books, reviews and search engines such as google.com.

Keywords
Shape Memory, Polymers, Biomedical Applications, Polyrotaxanes

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1. Introduction

Shape-memory polymers belonging to a class of stimuli responsive materials can be deformed and fixed into temporary shape under specific stress conditions [1]. These materials subsequently recover their original shape upon external stimuli, such as temperature, pH, light, magnetic or electric field and analytes of interest (e.g., ions and bioactive molecules) [1,2]. As shown in Fig. 1, a closed flower (temporary shape) made of shape memory polymer (SMP) is fixed at a lower temperature and recovers from the closed state to an open flower (original shape) when the temperature is increased above its switchable temperature. For instance, a bold imagination is also shown in Fig. 2, where a lady who treated her face using shape-memory polymers when she was young so the young face can be remembered. Thus, as her age passes, she could recover her face using stimulus [3].
Fig. 1. Shape recovery of SMP (flower made of SMP opens its petals at high temperature). (Reproduced with consent from Ref. [4], Elsevier Publication 2010)

Fig. 2. Appearance recovery in magic mirror (an old woman recovers her young face in a magic mirror). (Adopted with consent from Ref. [3], Elsevier Publication 2010).
Understanding the mechanism of shape-memory polymers, a significant interest has been created during the past two decades in both academia and industry [3]. This has resulted in promising applications in the biomedical field for delivery systems, tissue engineering scaffolds, cell culture supports, bio-separation devices, sensor or actuator systems [5]. To explore these applications, a variety of polymers have been examined as SMP materials, such as polyurethanes, polyacrylates, polynorbornenes, polycaproloctones, polylactides and polyrotaxanes [6-12]. These polymers are capable of exhibiting required properties like biodegradability, biocompatibility, mechanical strength etc. for the use of switchable biomedical devices.

This chapter focuses on shape-memory polymers with special reference to biomedical applications, their classification and future prospects including challenges.

1.1 Historical Background of SMPs

The term “Shape-Memory” was first proposed by Ver-noon in the year 1941 [3]. The term “Shape-Memory Polymer” became better known as shape-memory poly(norbornene), developed by the French Company CDF-Chimie, was commercialized in Japan by Nippon Zeon Company in 1980s under the brand name of Norsorex [6]. However, the industrial applications of the shape-memory polymers were started in 1950s when a chemist named Paul Cook, Founder of Raychem Corporation, invented heat shrink tubing using radiation-crosslinked polyethylene [2]. Although, further efforts to develop SMPs began in the late 1980s, significant progress was made only in the last two decades [3].

Today, a wide range of potential biomedical applications based on SMPs have already emerged and are currently being pursued. The first biomedical application based SMP was demonstrated by Hayashi and colleagues [13], who developed SMP-based catheters, which would soften at body temperature, potentially reducing the risks for soft tissue/organ injuries during their surgical delivery. Maitland et al. [14] designed thermoset polyurethane based micro actuator for treating strokes. Similarly, biodegradable SMPs pertaining to self-expanding and drug eluting stents, self-deployable intragastric implants for treating obesity, self-fitting vascular and coronary grafts, patient-specific customized orthopedic devices, tissue engineering scaffolds and dynamic cell culture substrates have also been developed. This is how, biomedical applications based SMPs have been developed and explored widely in the past few decades [6].
2. Classification of Shape-Memory Polymers

Different types of SMPs have been developed for a wide range of applications [15] and these have been classified based on the type of stimuli and functionality of polymers.

2.1 Shape-Memory Polymers Based on Stimuli Responses

2.1.1 Temperature Sensitive Shape-Memory Polymers

Thermo responsive polymers belonging to a class of shape-memory polymers have been the most investigated SMPs due to their ability to respond to a change in temperature [16,17]. In response to the variation in temperature the microstructural features of these polymers are changed [18]. To facilitate the subsequent discussions on the performance of SMPs, some of the important key terms and their meanings used to describe the properties of polymers are summarized in Table 1 [6].

<table>
<thead>
<tr>
<th>Term</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass transition temperature ($T_g$)</td>
<td>It is the temperature beyond which a polymer turns from a hard and glass-like state to a rubber-like state. In SMPs, during the transition process, $T_g$ is often defined as the median point of the glass transition range in the heating ramp [19].</td>
</tr>
<tr>
<td>Melting temperature ($T_m$)</td>
<td>It is the temperature at which a material changes from solid to liquid state. In polymers, $T_m$ is the peak temperature at which a semi-crystalline phase melts into an amorphous state.</td>
</tr>
<tr>
<td>Transition temperature ($T_{trans}$)</td>
<td>It is the temperature around which a polymer changes from one state to another. $T_{trans}$ could be either melting temperature or glass transition temperature. Above this temperature, the polymers are in their rubbery state. Below the transition temperature, the polymeric materials become brittle and hard. At this point, the rubbery state is replaced by a glassy behavior [20].</td>
</tr>
<tr>
<td>Shape deforming temperature ($T_d$)</td>
<td>It is the working temperature at which SMP is strained to a temporary shape. The relationship of $T_d$ to $T_{trans}$ (below or above) has significant impact on the performance of shape-memory polymers.</td>
</tr>
<tr>
<td>Temporary shape fixing temperature ($T_f$)</td>
<td>It is the working temperature at which the temporary shape of a deformed SMP is fixed. $T_f$ is usually lower than $T_{trans}$.</td>
</tr>
<tr>
<td><strong>Shape recovery temperature</strong> ($T_r$)</td>
<td>It is the working temperature at which an SMP is triggered to recover from its fixed temporary shape. $T_r$ is usually higher than $T_{trans}$ and is often chosen to be the same as the $T_d$ [21].</td>
</tr>
<tr>
<td>---------------------------------------</td>
<td>-------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td><strong>Shape fixing components</strong></td>
<td>It is defined as the domain or net-point, either covalently crosslinked or physically formed (e.g., via physical entanglement or H-bonding) in an SMP network that maintains the dimensional stability during the deformation and subsequent recovery.</td>
</tr>
<tr>
<td><strong>Shape switching components</strong></td>
<td>The polymeric chains in an SMP network consist of switchable units that can switch from one state to another in response to temperature change, which are responsible for the temperature dependent deformation and recovery.</td>
</tr>
</tbody>
</table>

Thermally actuated shape-memory polymers exhibit a characteristic transition temperature, ($T_{trans}$) above which they can be deformed to a secondary shape from a primary shape by application of external stress. The deformed shape can then be fixed by cooling the polymer below $T_{trans}$ and then removing the deformation stress. The primary shape can subsequently be recovered by heating the polymer above $T_{trans}$ [21].

Shape-memory properties are related to their intrinsic non-crystalline molecular structure. As the glass transition temperature characterizes the polymers. The polymers display different states depending on the temperature range within a few degrees of $T_g$. In fact, at $T_g$, significant changes in the mechanical and thermodynamical properties may be observed [20]. The shape-memory effect with respect to temperature is shown in Fig. 3. From the Fig. 3, it is observed that polymers undergo deformation below $T_g$ and then return to their original shape by heating the polymers to higher temperature than $T_g$. If the polymers are deformed above their glass transition temperature under external force, the deformation will be fixed and maintained after removal of the external force. However, a subsequent heating of the material above its $T_g$ will allow it to recover its original shape [20].

To understand the shape-memory behavior, the following experiment can be performed: the sample was first immersed in a water bath at 80º C, quickly deformed to an “M” shape and quenched to 0º C by immersing in a second bath containing an ice/water mixture. After immersing into a third water bath at 40º C, the sample showed some minor recovery due to the incomplete fixing of the polymer, but a major part of the deformation was retained (since the fixity ratio (Rf) of shape b is still greater than 70%) and a temporary shape b similar to Fig. 4B was fixed. Maintaining the sample temperature at 40º C, the sample was further manipulated by winding it around a glass rod and...
immersed into the ice/water bath again. This led to fixing of the second temporary shape a as shown in Fig. 4A. After immersing the sample with shape a back into the water bath at 40º C, it quickly recovered to shape b as shown in Fig. 4B, which further recovered to its permanent shape c after immersing into the water bath at 80º C as shown in Fig. 4C [22].

![Graph](image1.png)

**Fig. 3.** Elasticity modulus versus temperature of amorphous polymer. (Adopted with consent from Ref. [20], Wiley Online Library Publication 2010).

![Images](image2.png)

**Fig. 4.** Photographs showing the sequential recovery of epoxy/polycaprolactone from temporary shape a (A), to temporary shape b (B), and to permanent shape c (C). (Adopted with consent from Ref. [22], Wiley Online Library Publication 2010).

A unique property of temperature-responsive polymers is the presence of a critical solution temperature, which is the temperature at which the phase of polymer and solution is discontinuously changed according to their composition [23]. It is important
not only from the fundamental research point of view, but also from the standpoint of practical applications [24]. If the polymer solution has one phase below a specific temperature, in other words, it becomes insoluble upon heating, due to a lower critical solution temperature (LCST). Otherwise, it is called a higher critical solution temperature (HCST) or an upper critical solution temperature (UCST) [3,25]. Generally, the solubility of most of the polymers increases with an increase in temperature. However, in the case of polymers with a LCST, the solubility decreases as temperature increases and therefore polymers shrink as the temperature increases above the LCST [23]. Thermo-responsive polymer’s structures which possess very sensitive balance between the hydrophobic and the hydrophilic groups and a small change in the temperature can create new adjustments [18]. Therefore, the change in LCST can be obtained by incorporating the hydrophilic or hydrophobic groups in a polymeric system.

The polymers with a LCST near to body temperature are the most relevant in the biomedical field. As an example of this kind of polymers, one can highlight the poly(N-substituted acrylamide) family such as poly(N-isopropylacrylamide), poly(N,N′-diethylacrylamide), poly(dimethylamino ethylmethacrylate) and poly[N-L-(1-hydroxymethyl) propyl methacrylamide]. This class of polymers reduce side effects and are therefore preferred in the biomedical field [26,27].

2.1.2 pH Sensitive Shape-Memory Polymers

pH-sensitive polymers are generally polyelectrolytes that have structures with weak acidic or basic groups that either accept or release protons in response to changes in the environmental pH [5]. The acidic or basic groups of polyelectrolytes undergo ionization just like acidic or basic groups of monoacids or monobases [16] in suitable solvents. This group of smart polymers changes their solubility by changing the electrical charges of the polymer molecules [28]. Thus, the transition from a soluble state to an insoluble state is caused due to the decrease of the electrical charge in the polymeric molecules. The electrical charge of the polymer can be decreased by decreasing its pH, neutralizing the electrical charge and reducing the hydrophilicity of the polymer [18]. Polyacidic polymers remain unswollen at low pH, due to the presence of protonated and unionized acidic groups. When the pH of the solution increases, the polymer swells due to the electrostatic repulsion of the negatively charged groups. The opposite behavior is found in case of polybasic polymers, since the ionization of the basic groups increases by decreasing the pH [5]. We have significant variation of pH in different parts of our body that can make the pH sensitive polymers ideal for biomedical applications [18]. Generally, the pH range where a reversible phase transition occurs can be modulated by employing two strategies:
(i) Selection of ionizable moiety with a matching $pK_a$ is important. This can be achieved through proper selection of polyacid or polybase for the desired application.

(ii) Incorporating hydrophobic moieties into the polymer backbone and controlling their nature, amount and distribution. When ionizable groups become neutral, electrostatic repulsive forces disappear within the polymer network through dominated hydrophobic interactions. Thus, the introduction of higher hydrophobic moiety can offer a more compact conformation in the uncharged state and a more accused phase transition. The hydrophobicity of these polymers can be controlled by the copolymerization of hydrophilic ionisable monomers with more hydrophobic monomers with or without pH-sensitive moieties. Typical examples of pH sensitive polymers with anionic groups are poly(carboxylic acids) as poly(acrylic acid) (PAA) or poly(methacrylic acid). Another kind of polyacidic polymers are the polysulfonamides (derivatives of $p$-aminobenzenesulfonamide). A few examples of cationic polyelectrolytes are poly(N,N-diakylaminoethyl methacrylates), poly(lysine) (PL), poly(ethylenimine) (PEI) and chitosan.

2.1.3 Dual Stimuli-Responsive Shape-Memory Polymers

Polymers simultaneously sensitive to dual stimuli are dual stimuli-responsive shape-memory polymers. It is possible to obtain polymers sensitive to both temperature and pH by the simple combination of ionisable and hydrophobic (inverse thermosensitive) functional groups. This has been achieved mainly by the copolymerization of monomers bearing these functional groups, combining thermo-sensitive polymers with polyelectrolytes [semi-interpenetrating network (SIPN) and interpenetrating network (IPN)] or by the development of new monomers that could respond simultaneously to both stimuli [29]. Particularly, polymers responsive to both temperature and pH are gaining a considerable attention recently for their advantages in biotechnological and biomedical applications. In this respect, Leung and coworkers [30] have prepared smart core-shell polymeric microgels based on poly(N-isopropylacrylamide) (PNIPAAm), N, N’-methylenebisacrylamide (MBAAm) and chitosan. These materials exhibited a well-defined core shell structure consisting of temperature-sensitive cores and pH-sensitive shells, made of cationic water-soluble polymers. Kuckling et al. [31] prepared copolymers of N-isopropylacrylamide with acrylamide derivatives bearing carboxylic groups attached to spacers with different chain length, and studied the influence of both temperature and pH on their properties. Sun et al. [32] reported chitosan-based hydrogel films having both temperature and pH sensitivity, by blending chitosan with temperature sensitive poly(N-isopropylacrylamide) and poly(ethylene glycol) (PEG). Hiruta et al. [29] synthesized the dual pH- and temperature-responsive fluorescent terpolymer system ($L_{42}D_{50}S_{8}$-FL) consisting of PNIPAAm, N,N-dimethylacrylamide (DMAAm) and
sulfamethazineacrylamide (SMZ), followed by activation of terminal carboxyl groups with N-hydroxysuccinimide and reaction with 5-aminofluorescein which were applied for the selective imaging of acidic tumor micro-environments.

2.1.4 Other Stimuli-Responsive Shape-Memory Polymers

In addition to, temperature variation or change in pH, there are many other ways to drive the shape recovery in polymers. Other stimuli [33] that can release the stored elastic energy in the elastic component of the polymer to drive recovery of shape are described below:

2.1.4.1 Light Induced Shape-Memory Polymers

The shape memory polymers which have photo sensitive groups are activated by light. These groups act as molecular switches and such polymers are stretched and illuminated by a light of wavelength greater than a fixed wavelength. The photo sensitive groups form crosslinks by which, the polymer is locked in the new shape and retains the temporary shape even after releasing the stress. When this is illuminated by light of lower frequency, the crosslinking cleaves and allows the material to go back to its original state [34].

The incorporation of light sensitive groups as molecular switches in the polymer network enabled the development of light induced SMPs. In this type of SMPs, instead of increasing the sample’s temperature, light of different wavelength ranges can be used for the fixation of the temporary and recovery of the permanent shape. Photo-isomerization can also be used to draw out a shape-memory (SM) response. For instance, azobenzene in particular has been extensively studied to convert light into mechanical motion [35]. Here, azobenzene isomerizes from the thermodynamically stable trans state to the meta-stable cis configuration when irradiated with UV light, and it returns to the trans state when irradiated with visible light or heated [36]. In 2005, Lendlein and co-workers [34] demonstrated the use of light as a trigger for temporary crosslinking for SM using the photo-reversible [2+2] cycloaddition of cinnamic groups. Cinnamates, along with similar groups like coumarin, form dimers when irradiated with $\lambda > 260$ nm light and dissociate when irradiated with $\lambda < 260$ nm light as shown in Fig. 5 [35,37]. The authors programmed a temporary shape by mechanical deformation coupled with irradiation to form cinnamic dimer crosslinks; and the restoration of the original shape was achieved using a lower wavelength light to reversibly break the crosslinks. The kinetics of shape fixing was relatively slow, taking an hour of irradiation to achieve 30-50% shape fixity. However, the work represented a dramatic move forward and an important proof-of-concept, showing the potential of light to be used as a stimulus for SMPs. More recently,
several researchers have developed new light-active SMPs. Wang et al. [38] developed hyperbranched, highly-entangled polycoumarates with the ability to hold multiple shapes that respond to both light and temperature stimuli.

Lendlein et al. [34] reported two photo-responsive shape-memory polymers, one was the grafted polymer obtained by copolymerization of n-butylacrylate (BA), hydroxyethyl methacrylate (HEMA) and ethyleneglycol-1-acrylate-2-cinnamic acid (HEA-CA) with poly(propylene glycol)-dimethacrylate as crosslinker. In the second polymer, an interpenetrating network was created from BA with poly(propylene glycol)-dimethacrylate as crosslinker. The permanent network was star-poly(ethylene glycol) containing cinnamylidene acetic acid (CAA) terminal groups (SCAA), under the influence of light, SCAA molecules can be reversibly crosslinked, fixing the temporary shape by interpenetrating the permanent network.

2.1.4.2 Magnetically Induced Shape-Memory Polymers

A magnetic field can be used to trigger the shape recovery of SMPs filled with magnetic particles. In comparison with direct or electrical heating, inductive heating by alternating the magnetic field has more advantages especially in medical applications [39]. For thermally-adaptive SMPs, energy is used from the direct heating to trigger the shape change, where as in inductive heating approach, recovery of SMPs is by indirect heating, through the selection of suitable ferromagnetic particle as filler, using this method one can eliminate the problem of overheating. Generally, magnetic responsive SMPs can be produced by employing ferromagnetic fillers which include metal particles,
ferromagnetic particles, like iron oxide particles, NdFeB particles, Ni-Mn-Ga single crystals and nickel powders [3, 39-40]. Figure 6 represents the shape-memory polymer (black strip) changing to its permanent shape in the presence of an alternating magnetic field [41]. The magnetic field adaptive shape-memory effect is more advantageous compared to pH and temperature. Thermo-magnetically and electromagnetically-induced shape-memory effects are of great interest for medical applications, because the embedded SMP devices can be actuated by an externally applied magnetic field through a non-contact remote mode. Other promising applications include smart implants, on demand drug delivery, etc. [39]. As these materials are originally proposed for biomedical applications, the SMP matrices are mostly biodegradable and biocompatible polymers, such as poly(D,L-lactide), crosslinking poly(ε-caprolactone), a copolymer, poly[p-dioxanone-co-(ε-caprolactone)], crosslinking oligo(ε-caprolactone)dimethacrylate/butylacrylate, and grafting polymerpoly(ε-caprolactone) diisocyanatoethyl methacrylate (PCLDIMA) and poly(ethylene glycol) monomethylether-mono-methacrylate (PEGMA) [39].

Fig. 6. Sequence of photographs showing the shape-memory polymer (black strip) changing to its permanent shape in the presence of an alternating magnetic field. (Adopted with consent from Ref. [41], Copyright (2006) National Academy of Sciences, U.S.A.).

2.1.4.3 Phase Sensitive Smart Polymers

Other types of smart polymers, suitable for the biomedical field are phase sensitive smart polymers. These can be used to develop biocompatible formulations for controlled delivery of proteins in a conformationally stable and biologically active form. These smart polymeric systems have many advantages over other systems which require less stressful manufacturing conditions for sensitive drug molecules and have a high loading capacity [42].
This category of polymers employs water insoluble biodegradable polymers. Polymers such as poly(D, L-lactide), poly(D,L-lactide-co-glycolide) and poly(D,L-lactide-co-ε-caprolactone), when dissolved in pharmaceutically acceptable solvent to which a drug is added, forms a solution or suspension. After injection of the formulation in the body, the water-miscible organic solvent dissipates and water penetrates into the organic phase. This causes phase separation and precipitation of the polymer forming a depot at the site of injection [42].

2.1.4.4 Water/Moisture Activated Shape-Memory Polymers

Although various external stimuli can be used as a recovery trigger, the most widely studied are thermally induced SMPs, which are not always suitable for biomedical applications, because their switching temperature does not fall completely within the range of room temperature to body temperature. Thus, water-induced SMPs may be used to resolve this issue due to the lower transition temperature exhibited by the polymers with water in the polymer matrix. Water-induced SMPs have been found more suitable for biomedical applications, because their shape recovery occur upon exposure to body fluid and consequently, these polymers have received great attention in recent years [42]. In 2005, Huang et al. [43] first observed water or solvent-driven shape recovery effects in many SMPs having glass transition as the switching transition. Water or solvent molecules may penetrate into the amorphous areas of polymers [39], and thereby increase the flexibility of polymer chains due to a plasticizing effect. As a result, the glass transition temperature of the SMPs may drop to a temperature below the room temperature, which leads to the shape recovery of a deformed SMP [39]. One of the methods to obtain an outstanding water-active shape-memory effect is filling a hydrophilic or water soluble ingredient in SMPs [39]. Chen et al. [44] reported a water sensitive biodegradable stent made of chitosan films crosslinked with an epoxy compound. Based on this idea, Luo et al. [45] prepared cellulose nanowhisker/shape-memory polyurethane (SMPU) nanocomposites with outstanding water-active shape-memory effect (SME). The cellulose nanowhisker in SMPUs did not affect the intrinsic thermal-active SME of the SMPU, but enabled the SMPU water-active SME. The water-active SME is tailorable by changing the content of the cellulose nanowhiskers. The water-active SMPUs require hours to lower the glass transition temperature for recovery; while the water-responsive cellulose nanowhisker/elastomer composite needs only 10 min for recovery which is much faster. The water-active cellulose nanowhisker/elastomer composites have several advantages over water-active SMPU based its dropping glass transition temperature [46].
2.1.4.5 Electricity Responsive Shape-Memory Polymers

In the past decade, several researches have conducted the experiments on the mechanism of shape recovery and electrical properties of SMP filled with conductive filler, and their corresponding applications. One of the approaches to make shape recovery triggered, more conveniently by passing an electrical current through SMP composite by employing typical conductive fillers like carbon black (CB) nanoparticle and short carbon fiber (SCF) [47]. Electricity as a stimulus enables resistive actuation of shape-memory polymer filled with fillers. In this way, external heating, which may be unfavorable for specific applications, is used to stimulate conventional shape-memory polymers, can be avoided. The electric triggering of shape-memory polymer composites enlarges their technological potential. Smela [48] reported electrically actuated polymeric materials known as electro-active polymers (EAPs). These are mostly conjugated polymers, useful in regeneration of tissues, biosensors, etc. The devices made of these polymers find applications in the biomedical field as artificial muscle, a technology for biomimetic actuation [48,49].

2.2 Shape-Memory Polymers Based on Functionality

The approaches for designing different shape-memory functions have become more abundant as scientists better understand the SME mechanism of SMPs and their increasing diversification. Thus, the development of shape-memory functions of SMPs is growing rapidly. The shape-memory functionality of SMPs is illustrated in Fig. 7 [3].

Moreover, two and even three different types of shape-memory functions can be achieved simultaneously in the same SMP material [50,52]. An example of this is an SMP network mainly composed of star-shaped hydroxy-telechelic poly(ω-pentadecalactone) (PPD) and poly(ε-caprolactone) (PCL), herein named the PDCL network, that shows one-way, two-way and triple SMEs under different programming [3].

SMPs may adopt one (dual-shape), two (triple-shape) or several (multi-shape) stable temporary shapes and recover their permanent shape (or other temporary shapes in case of multi-shape versions) upon the action of an external stimulus [53].

If the shape-memory behavior of SMPs is typically recognized as a nonreversible feature, as the external stimulus activates the only changes from a temporary to a permanent shape. This is a so-called “one-way” shape-memory behavior. This type of shape-memory function allows one to satisfy the requirements of a wide variety of applications. By contrast, the development of polymers featuring a reversible shape shifting on the basis of an on-off stimulus are the so called “two-way” shape-memory behavior, which
may fulfill the requirements of applications such as sensors and actuators, or as artificial muscles [9, 50-53].

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<th>Dual Shape</th>
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<th>Two-Way Shape Memory Effect</th>
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Fig. 7. Illustration of the shape–memory functionality of SMPs. (For one-way SME, once the stimulus is terminated, the temporary shape is retained, while for two-way SME, the temporary shape can be recovered to the initial shape when the stimulus is terminated) (Reproduced with consent from Ref. [3], Elsevier Publication 2014).

### 2.2.1 One-Way SME and Two-Way SME

Scientists thought that one-way SMEs were not good enough for many applications because they were the most simple and common SMEs of SMPs, and thus they began to explore two-way SMEs of polymers. Research on smart materials with two-way SMEs has attracted considerable attention as these materials are capable of changing their geometries when exposed to an external stimulus.

However, as more and more programming protocols have been devised and reported in the literature, one-way SMPs have been found to be much more flexible, versatile and applicable than the two-way SMPs, because two-way SMEs are difficult to program. One-way SMEs have their original shapes predefined in the manufacturing process, while
temporary shapes can be varied based on different shape–memory programming processes [3].

2.2.2 One-Way Reversible SME and Two-Way Reversible SME

Zhou et al. [54] reported a general approach for enabling reversible shifting (two-way) between programmable shapes in semi-crystalline polymeric elastomer, poly(octylene adipate), with uniform chemical composition and without applying a persistent external force. These authors also developed a general strategy for reversible shape-memory (RSM) which can be applied to conventional semicrystalline polymeric elastomers. Strategy integrates three different shape-memory (SM) behaviors: conventional one-way SM, two-way RSM, and one-way RSM. Also the relative contributions of the different strains (one-way SM, two-way RSM, and one-way RSM) to aforementioned shape-memory can be tuned by controlling the respective proportions of chemical crosslinks and crystallites. For instance, the experimental demonstrations of two different RSM concepts are displayed in Fig. 8. The structure of poly(octylene adipate), a semicrystalline elastomer shown in (Fig. 8a), similarly: (i) two-way reversible shape transformation upon heating-cooling cycles (Figs. 8b–e) and (ii) one-way shape reversibility upon heating (Figs. 8f–h). In the first experiment (Fig. 8b), a straight bar of the semicrystalline elastomer was programmed as a hairpin temporary shape by deforming the sample at a temperature of 60 °C and then quenching it to 5°C. Subsequent heating to 38 °C and cooling to 5°C resulted in a reversible shape transformation of the hairpin between 115° and 155° angles, which occurred spontaneously without applying any external force. The angles of oscillations are highly repeatable. Upon consecutive heating and cooling cycles, the sample shape changed reversibly multiple times without losing memory of both angular shapes (Fig. 8e). Similar reversible behavior was accomplished for a polymer coil (Fig. 8c) and for the folding-unfolding of origami-like polymer sheets (Fig. 8d). Note that the upper temperature, 38°C, corresponds to partial melting of the crystalline phase. In the second experiment (Figs. 8f–h), a one-way reversible SM transformation was evoked in the same polymer by reprogramming the temporary shape at an elevated temperature corresponding to a partial molten state. As shown in Fig. 8f, a sample having a temporary shape of a straight rod was heated to an intermediate temperature of \( T_i = 34 \)°C (substantially below \( T_m = 41 \)°C) and manually coiled into a new temporary shape. The new coil was then fixed by quenching to \( T_0 = 5 \)°C. Subsequent heating from \( T_0 = 5 \)°C to \( T_i = 34 \)°C and then to \( T = 60 \)°C, triggered a one-way transition from coil (second temporary shape) to rod (first temporary shape) and back to coil (permanent shape) (Fig. 1f). In a similar way, an opposite shape transformation was demonstrated, i.e., rod-coil-rod using the same temperature ramp (Fig. 8g).
Fig. 8. Two-way and one-way-reversible shape memory. (a) Chemical structure of poly(octylene adipate) (POA) oligomers used for the synthesis of shape-memory elastomers. Their cross-linking density and melting temperature were controlled by varying the degree of polymerization $n$ of the oligomers and copolymerization. (b–e) Examples of two-way reversible shape memory demonstrated by polymer ($v = 200$ mol/m$^3$, $T_m = 42^\circ$C), for three different shape transformations upon heating to 38°C and subsequent cooling to 5°C. (e) Reversible oscillations of the interior hairpin angle shown in panel (b) during eight consecutive heating–cooling cycles within the 5–38°C temperature range. (f–h) One-way reversible shape transformations were observed during heating from 5 to 60°C. While the two-way transformations may be repeated multiple times, the one-way reversibility occurs only once. (h) Temperature ramp and the corresponding variations of the interior angle of a hairpin sample which was programmed to perform one-way reversible bending. (Adopted with consent from Ref. [54], American Chemical Society Publication 2014).
2.2.3 Triple-Way Shape Memory Effect

Triple-shape polymers, unlike conventional “dual-shape” SMPs which can recover from a temporary shape to a permanent shape, are capable of fixing two temporary shapes and recovering sequentially from the first temporary shape (shape 1), to the second temporary shape (shape 2), and eventually to the permanent shape (shape 3), upon stimulus [22]. Xie et al. [55] reported bilayer polymers that consist of two epoxy dual shape memory polymers which have well separated glass transition temperatures. These bilayer epoxy samples exhibited a triple shape-memory effect (TSME) with shape fixities tailorable by changing the ratio between the two layers. The triple shape fixities of the bilayer epoxy polymers can be explained by the balance of stress between the two layers. Based on this work, it is believed that the following three molecular design criterions should be considered in designing triple-shape memory polymers with optimum TSME:

I. well separated thermal transitions,

II. a strong interface, and

III. an appropriate balance.

Luo and Mather [22] developed a series of triple-shape polymeric composites (TSPCs), using a unique and broadly applicable fiber/matrix composite approach. It is a significant approach as polymer composites afford a large degree of design flexibility in designing triple-shape systems for targeted applications. For example, one can control the transition temperatures by simply selecting different polymers for the fibers and the matrix, or separately functionalize them either chemically or physically to achieve other novel functions such as controlled drug delivery or reversible adhesion. The triple-shape memory effect is demonstrated in Fig. 9 [56].

Jeon et al. [57] studied the shape-memory properties of norbornyl-POSS (POSS-cubic polyhedral oligomeric silsesquioxane, a nanoparticle) copolymers having either cyclohexyl corner groups (CyPOSS) or cyclopentyl corner groups (CpPOSS). The POSS copolymeric composites showed two stages of strain recovery or triple SME, a fast strain-recovery process related to the polynorbornene relaxation in the norbornyl matrix, and a second slow strain recovery process related to the POSS rich domains.