Recent Developments in Temperature Responsive Shape Memory Polymers

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Abstract: Shape memory polymer is an important area of interest in the polymer science research because of its many applications in industry such as biomedical, smart textiles, actuations and so on. Among the shape memory polymers, temperature responsive shape memory polymers are gaining much attention to the scientist as their transition temperature for shape memory behavior could be easily tailored by engineering the polymer structure prior to polymer synthesis. An attempt has been taken in this review paper to review the research and development in temperature responsive shape memory polymers. This review is not intended to be comprehensive, but provides an overview of the temperature responsive shape memory polymers. The mechanisms of temperature responsive shape memory behaviors has been discussed. The review was also covers various temperature responsive shape memory polymers viz. shape memory polyurethane, shape memory copolymer, network polymer structure with shape memory property and shape memory hydro gel. Finally, the paper was concluded with some of the prospective applications of temperature responsive shape memory polymers in various segments.

Key Words: Copolymer, hydrogel, polyurethane, shape fixity, shape memory, shape recovery.

1. INTRODUCTION

Shape memory polymers are stimuli-responsive polymeric materials that can change their shape as a consequence of an external stimuli, such as variations of temperature [1,2], light [3,4], electric field [5,6], or any other external stimuli. In any instance stimuliresponsive effects of stimuli responsive polymers on the molecular level are converted into macroscopic movement, whereby generally two different moving behaviors have to be differentiated for polymerbased materials: the shape-memory effect and the shape-changing capability [7]. The development of shape memory polymers (SMPs) is currently of great interest [8] because of their light weight, high shape recovery, ease in manipulation and low cost as compared with shape-memory alloy. Among the shape memory polymeric materials, thermoresponsive shape memory polymers (SMP) have recently drawn great interest because of their high recovery ability at relatively low temperatures and easy to tailor the transition temperature of shape memory behavior for application in various purposes. As a class of novel smart materials, temperature responsive shape memory polymers (SMPs) can deform enormously above a transition temperature (T_{trans}) and can mostly be fixed in a temporary shape by cooling below T_{trans} . After reheating above T_{trans} , they can automatically recover to their original shape [9]. The stress generated by shape recovery is a function of the energy absorbed during deformation at a high temperature; thus, high energy to failure is a necessary condition for good shape-memory materials. Shape memory polymers have two phases structure viz. fixed phase and reversible phase. The fixed phase could arise from the entanglement of polymeric chain or the chemical or physical cross-linked points and the reversible phase (or the switching phase) is constituted by physical phenomenon like crystallization, H-bonding etc of the polymer segments. In the thermoresponsive SMP, the reversible phase is softened by heating. Driving forces for contraction come from the oriented chains, and only oriented or extended chains can be contributive to the recovery of deformation; these extended chains involve both crystalline and amorphous segments. The recovery process in shape memory behavior was noticed to be deorientation of oriented chains due to thermodynamic entropy effect [10,11]. Therefore, shape memory characteristics can be tuned by the way of structural modification of the polymer backbone. An attempt has been taken in this article to review some of the recent developments of temperature responsive shape memory polymers and their shape memory mechanism, and applications in various segments.

2. MECHANISM OF TEMPERATURE RESPONSIVE SHAPE MEMORY BEHAVIOR

The shape-memory effect of shape memory polymer is not a specific polymer property; however, it is results of a combination of the polymer chemical structure, morphology and various intra and/or inter molecular interaction forces between the polymer chains, and applied processing and programming technology during shape memory testing [11]. The temperature responsive shape memory behavior is schematically shown in Fig. (1). The material deformed into a temporary shape by applying force (F) at few degree above the "transition temperature" ($T_S + \Delta T_1$), in order to make sure that the material is in rubbery state. After that material cooled below the transition temperature $(T_S - \Delta T_2)$ without removing applied force (not shown in Fig. (1)) and at this point, after removal of force, the material can not return to its original shape at $(T_S - \Delta T_2)$. Hence admirable deformation has been stored in the polymer structure at the molecular level. Therefore, above and below the "transition temperature" the temporary shape is, respectively, formed and fixed. The material recovers almost to its original shape when the deformed material reheated at few degrees above the transition temperature $(T_S + \Delta T_3)$. In order to display thermally induced shape memory behavior, polymers should possess at least two phases with two distinct thermal transitions, viz. a fixing phase, constituted by physical or chemical cross-links that impart dimensional stability to the material, and a reversible phase that provides elastomeric properties to the polymeric materials [12,13]. The shape memorizing phase may consists of physical (crystallinity, glassy phase, ionic, hydrogen bonding or van der Waals interactions etc) and/or chemical (covalent bonding) crosslinking in the polymer, which allows the SMP to remember the primary (original) shape. The shape fixing phase can be amorphous (glassy state) or semicrystalline (thermal transition of crystal melting) polymer matrix [11].

The transition temperature for shape memory behaviour should be relevant to the particular application of the shape memory polymers. The permanent shape will internally store in the temporary shape, and the material exhibits shape memory behavior when heat up few degree above the transition temperature (T_{trans}). The transition temperature for shape memory property of SMP could be glass transition (T_g) or melting (T_m) temperature. Mechanism of the temperature responsive shape memory behavior of shape memory polymers are well explained by researchers [11, 14]. The polymer shows shape memory behaviour as a whole act as crosslinked network structure which could be a physically crosslinking or covalently crosslinking netpoints. Therefore, the deformed polymer matrix which is under external stress, to be reversibly prevented from reshaping by the introduction of reversible netpoints as the molecular switches [14]. Physical interactions or covalent bonds could act as reversible net-

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Fig. (1). Schematic representation of the thermally induced shape-memory effect of shape memory polymers.

points. Physical crosslinking may be obtained by hydrogen bonding, or vitrification or crystallization of polymer matrix, and the reversible covalent cross-linking is obtained by attaching functional groups in the polymer chains. To induce shape memory behaviour, these physical crosslinking netpoints or covalent bonds must be able to interact each other reversibly in presence of specific external stimuli. Shapememory behavior can be observed for many polymers that may differ significantly in their chemical compositions [11] and morphologies.

3. VARIOUS TEMPERATURE RESPONSIVE SHAPE MEMORY POLYMERS

3.1. Shape Memory Polyurethane

Most prominent shape memory polymer is shape memory polyurethane (SMPU) [11]. Structurally they consist of hard and soft segments [15]. Di-isocyanate and chain extender form hard segment, on the other hand the long chain polyol is soft segment. Phase separation takes place in shape memory polyurethanes due to the thermodynamic incompatibility between the hard and the soft segments. The polymer would form separate soft and hard domain regions. The hard micro phase is a hard segment-rich micro domain, which is generally semi-crystalline and imparts stiffness and reinforces to the material. The soft-segment-rich micro phase, which is responsible for the elastic behaviour of polyurethane's, is usually amorphous with a glass transition temperature (T_{g}) below room temperature. Shape memory behaviour of SMPU could be engineered in the molecular level by properly selecting the hard and soft segments from wide range of raw material available for polyurethane synthesis. Shape memory behaviour of SMPU could also control by tailoring their composition i.e. proportion of hard and soft segments. The shape memory effect of the segmented polyurethanes could changes by changing with hard segment content (HSC). Experimental results revealed that the shape fixity decreased with the increase of HSC. When $HSC \leq 35\%$ the polyurethanes showed over 94% of shape fixity while when HSC \geq 40% the shape fixity decreased rapidly. The shape recovery of the segmented polyurethanes was determined by the physically crosslinked network maintained in the course of shape memorization. The segmented polyurethanes with $15\% \le HSC \le 40\%$ showed over 90% of shape recovery. However, as HSC increased to 45% and 50% the shape recovery dramatically dropped to 83% and 75% respectively. This decrease of shape recovery should results from the hard-segment phase changing from isolated to interconnected states [9].

The shape memory effect of shape memory polyurethane fiber is schematically shown in Fig. (2). In Fig. (2), the soft segments of polyester are shown as being coiled or folded on themselves. The schematic section length of the zig-gag line corresponds to one repeating unit within the polyol. The isocyanate is shown as solid circle. The hard segments are set in space but have a tendency to adhere each other through strong hydrogen bonding. When the fiber is heated above transition temperature (T_{trans}) , the soft segment phases are melted. If they are stretched, the soft segment phases are extended. When the temperature is cooled below T_{trans} and the fiber is kept at constant strain, the soft segment phases crystallize. As a result, the internal stress is stored in the fiber and the associated deformation is fixed temporally. When it is reheated to above T_{trans} , its soft segment phase becomes flexible. It resumes to the folded configuration because of the internal stress stored between hard segments. As a result, the fiber recovers to its original shape [16].

Depending on the type of transition temperature, shape memory polyurethanes could be divided by glass (T_{σ}) or crystal melting (T_{m}) transition type shape memory polyurethanes. Characterization of the shape memory effect in polyurethane (PU) films suggests that the $T_{\rm m}$ type films generally show higher shape fixities than the T_{g} -type films [17]. In addition, this shape fixity decreases with increasing molecular weight (M_n) in the T_g -type SMPU, but the shape recovery increases with M_n in both types of SMPU. The shape recovery temperature, in contrast, decreases with M_n as suggested by the result of their thermal strain recovery. The higher molecular weight $(M_n > 200\ 000$ g mol⁻¹) is a prerequisite for SMPUs to exhibit higher shape recovery at a particular temperature. The $T_{\rm m}$ -type SMPU shows higher shape fixity, close to 100%, due to the good crystallizability of the soft segments at ambient temperature (Fig. 3(A)), while the shape fixity of the T_g -type SMPU is less than 88% (Fig. 3(B)). The difference between the second cycle and the third cycle for $T_{\rm m}$ -type SMPU is smaller, which implies that the crystal structure is easier to be reformed with little energy loss in the cyclic tensile test [17].

The shape memory behavior of SMPU could be improved by structural modification of polyurethane. Oxazolidone-incorporated PU exhibits 100% shape recovery even after 5 cycles [Ratio of moles



Permanent Shape

Fig. (2). Schematic representation of the molecular mechanism of the shape memory effect of the SMF, zig-zag represents coiled or folder chains of polyols, circles represent isocyanate groups (Reproduced with permission, Meng, Q.H.; Hu, J.L.; Zhu, Y.; Lu, J.; Liu, Y. Polycaprolactone-based shape memory segmented polyurethane fiber. *J. Appl. Polym. Sci.*, 2007, *106* (4), 2515 [©] 2007 Wiley Periodicals, Inc. [16]).



Fig. (3). Cyclic tensile behavior of (A) T_m -type SMPU and (B) T_g -type SMPU (Reproduced with permission, Chen, S.J.; Hu, J.L.; Liu, Y.Q.; Liem, H.M.; Zhu, Y.; Meng, Q.H. Effect of molecular weight on shape memory behavior in polyurethane films. *Polym. Int.*, **2007**, *56* (9), 1128 [©] 2007 Society of Chemical Industry (SCI) Permission is granted by John Wiley & Sons Ltd. on behalf of the SCI.: [17]).

of poly(tetramethylene oxide) (PTMO): epoxy: tolylene diisocyanate (TDI) = 1:1:2]. The PU without oxazolidone exhibited only 92% shape recovery. The important factor leading to enhanced shape recovery of poly(urethane–oxazolidone) (PUOs) is its enhanced crystal-linity. On enhancing the hard segment concentration by way of incorporation of oxazolidone moiety, shape recovery increases. Thus, the

higher hard segment content, the better is the shape memory property [18]. A new family of crosslinked polyurethanes was synthesized and characterized as shape-memory polymers [19]. Three-arm network junctions are provided by 1,1,1-trimethylol propane with an isocyanate group on each arm. Three diisocyanates are used: 4,4'-methylene bis(phenyl isocyanate), toluene diisocyanate, and 4,4'-dibenzyl diisocyanate. The variation in crosslink density arises solely from change in length of the soft segment macrodiol (MD) chains. When they are end linked to the extended network junctions, through relatively less mobile diisocyanate (DII) segments, their mobility is highly restricted, lengthening their retardation times. In addition there is an increase in volume fraction of the DII-rich regions of reduced mobility. The width of the shape-recovery temperature window ΔT was found to decrease with decreasing MD chain length [19].

3.2. Crosslinked Polymer Structure Showing Shape Memory

The supramolecular polymer network could be formed by crosslinking. A molecular design of supramolecular crosslinking network structure is shown in Fig. (4) and involves three polymerizable components: butyl acrylate (BA) monomer, a tri-functinal crosslinker (Trimethylolpropane trimethacrylate, TMP-TMA), and the ureidopyrimidinone (UPy)-substituted ethyl methacrylate monomer (UPy-EMA) [20]. BA was chosen as the primary component because it is a tacky, amorphous polymer and exhibits a low glass transition temperature (Tg \approx -64 °C) that should not interfere with thermomechanical studies above -20 °C. The lightly crosslinked polymer network that is easy to synthesize and contains only a small fraction (ca. 2 mol%) of UPy pendent side-groups. These new elastomers exhibit shape memory effects arising from reversible hydrogen bond association that H-bond lifetimes are long enough such that the rate of H-bond dissociation dominates elastomeric creep and shape recovery. Thermo-mechanical cycling resulted in strain fixity of about 90% and strain recovery of about 100%. The excellent strain recovery indicates that the new material memorizes its shape well, while the lack of complete strain fixity is due to the elasticity of the material itself [20]. Shape memory could be induced in low-density polyethylene (LDPE) by crosslinking with dicumyl peroxide (DCP) and their shape memory behavior could be study by a heatingstretchng-cooling cycle [21]. With increasing of crosslinking content the onset of recovery decreased, whereas the recovery constant showed different effects at these two stretching temperatures. These differences in the recovery behavior could be reasonably explained by



Fig. (4). Synthesis of lightly crosslinked shape-memory polymers (SMPs) containing pendent ureidopyrimidinone side-groups (Reproduced with permission, Li, J.H.; Viveros, J.A.; Wrue, M.H.; Anthamatten, M. Shape-memory effects in polymer networks containing reversibly associating side-groups. *Adv. Mater.*, 2007, *19* (19), 2851 [©] 2007 Wiley-VCH Verlag GmbH & Co. KGaA [20]).

the observed changes in the thermal properties which were attributed to the differences in crystalline structures and mechanism of crystal formation during the heating-stretching-cooling process [21].

3.3. Interpenetrating and Network Structure with Shape Memory Properties

Interpenetrating polymer networks (IPNs) constitute a group of components in which usually two chemically distinct networks are intimately combined. Like other multicomponent systems, IPNs exhibits phase separation, which arises from the mutual incompatibility between the constituent components in polymers. The structure of the IPNs is determined by the chemical nature of the components, and parameters such as the crosslink density and the kinetics of polymerization of each network. It is directly responsible for the different properties of the final material, and therefore a special task in preparing IPNs should be the detailed knowledge of all the reactions and side-reactions taking place during synthesis [22,23]. A novel polyesterurethane/poly(ethylene glycol) dimethacrylate (PEGDMA) interpenetrating networks (IPNs) with good shape-memory properties were synthesized using solvent casting method [24]. The star-shaped oligo[(rac-lactide)-co-glycolide] was coupled with isophorone diisocyanate to form a polyesterurethane network (PULG), and PEGDMA was photopolymerized to form another polyetheracrylate network. The good shape-memory effect of IPNs was attributed to chemical crosslinking in IPNs. The controllable T_{trans} was due to T_{g} of IPNs. The miscibility of PULG segments and PEG segments resulted in one $T_{\rm g}$. The chemical crosslinking points acts as a fixed phase to memorize the original shape, while the amorphous domains of miscible PLGA and PEG as a reversible phase. T_{trans} of the polymer networks could be conveniently regulated in wide range by adjusting the IPNs compositions. The PULG/PEGMMA IPNs showed good strain fixity and strain recovery ability in thermocyclic tensile tests. The values for strain fixity rate (R_f) and strain recovery rate (R_r) were over 93%. $T_{\rm trans}$ could be easily adjusted in the range of -23.0 to 62.8 °C. The T_{trans} of the IPNs could be adjusted in around body temperature to match the potential clinical applications by introducing 10 wt % of PEGDMA in IPNs [24].

Triple-shape materials have been introduced as a promising class of smart polymers, that can change from a first shape to a second shape and from there to a third shape. Here, the dual-shape capability of such a triple-shape polymer network system having two distinct transitions temperature. The multiphase polymer networks could be synthesized by photopolymerization from poly(ethylene glycol) (PEG) monomethyl ether monomethacrylate and poly(ɛcaprolactone) (PCL) dimethacrylate as crosslinker. Their permanent shape is determined by the chemical crosslinks formed in network structure, the two different crystallizable phases viz. $T_{\rm m}$ (PEG), and $T_{\rm m}$ (PCL) can be used to fix temporary shapes. The dual-shape memory effect is triggered by heating the material from a temperature below to a temperature above the switching temperature ($T_{\rm sw}$). $T_{\rm sw}$, which is determined in cyclic thermomechanical experiments, describes the macroscopic shape change starting from the temporary shape in which switching domains forming segments are oriented to a certain degree. For the dual-shape memory effect either a single crystallizable domain or the combination of both crystallizable domains could act as switch. It was observed that the samples return to their permanent shape as soon as $T_{\rm sw}$ is exceeded [25].

Shape-memory poly[(methyl methacrylate) (MMA)-co-(N-vinyl-2-pyrrolidone)(VP)]/poly(ethylene glycol) (PEG) semiinterpenetrating polymer networks which is stabilized by hydrogenbonding interactions is described by Liu et al. [26]. The shapememory behavior was occured by changing the operation temperature below and above the T_g (\approx 65 °C) of the P(MMA-co-VP)/PEG1000 semi-IPNs. The semi-IPNs behave as a hard domain at room temperature and the permanent shape of the polymers. If the temperature of deformed shape was raised to 85 °C the polymers quickly returned to the initial shape in 45 s with a shape recovery ratio of above 99%. This interesting phenomenon is reversible and can be repeated at least ten times. As stated earlier, a shape-memory polymer basically contains a fixing phase and a reversible phase. The fixing phase imparts a level of rigidity, dimensional stability, and thermal resistance, while the reversible phase provides the elastic properties, primary recovery and energy absorption. For the P(MMA-co-VP)/PEG semi-IPNs, the fixing phase was the chemical crosslinked point, while the reversible phase was the PEG-PVP complex phase [26].

3.4. Shape Memory Copolymer

Appropriate control of the two phases is important in determining the shape-memory behavior. Advances in the structural approach are being developed actively using methods like copolymerization, blending, and the introduction of cross-linking agent [27]. Biodegradable poly(oxyethylene-*b*-butylene adipate) ionomers (POBAis) could be synthesized by bulk polymerization of adipic acid and mixed monomers of bis(poly(oxyethylene)) sulfonated dimethyl fumarate and 1,4-butanediol. The POBAis exhibited recovery rate ranging from 81% to 95% at near body temperature, depending on the content of ionic group. It was found that the polymer is also irreversible and α -form crystal formed during recovery process does not turn back to the initial state. The recovery rate and crystallinity of POBAis increased with the times of cyclic tensile test. POBAis shows strong recovery ability with respect to its crystalline structure, depending on the ionic content [28].

The copolymer networks from oligo[(ɛ-hydroxycaproate)-coglycolate]dimethacrylates with M_n of the cross-linked macromonomers of at least 6900 $g \cdot mol^{-1}$ and a glycolate content of 14 mol % shows almost complete strain fixity with values for $R_{\rm f}$ above 94% [29]. The copolymer shows good to excellent shape-memory properties in between 0 and 70 °C, combining a good strain fixity rate of the temporary shape, fast attainment of a stable cyclic behavior, and only little loss of the permanent shape in the first cycles. The Ehydroxycaproate dominated segments crystallized below $T_{\text{trans.}}$. The temporary shape is fixed by the physical cross-links formed by the crystallites. With increasing M_n of chain segments, the values obtained for $R_{\rm f}$ increase, reflecting the degree of crystallinity. The $R_{\rm f}$ depends on the effective maximum strain ε_l , which is influenced by two factors: the creeping of the test specimen under constant load and temperature, and an expansion of the deformed specimen during the cooling process. With increasing $M_{\rm n}$ of the cross-linked prepolymers, ε_1 tends to increase. The temperature-dependent strain increases with increasing cross-link density. By a variation of chain segments' M_n between 3500 and 12 800 g·mol⁻¹, T_{switch} (T_{SW}) determined in air was between 23 and 37 °C [29].

Thermoplastic shape-memory co-polymers with short aramid hard segments and poly(ε -caprolactone diol) (PCL) PCL 2000, 3000 and 4000 soft segments are reported by Rabani *et al.* [30]. The polymers could be obtained by a low-temperature solution polymerization. Aramid units gave high elongations at break (800%) similar to many of their polyurethane counterparts. They also provided effective physical cross-links even at a relatively low hard segment content of about 12 wt%. Shape recovery was good, although it worsened slightly as both the number of cycles and ε_m increased. On the other hand, shape fixity remained almost constant even after seven cycles. The optimum ε_m value for obtaining the best shape-memory properties was 300%, for which a strain recovery rate of 99.5% and a strain fixity of 79% could be observed. Strain recovery generally deteriorated at a higher ε_m value, whereas a small ε_m tended to affect strain fixity [30].

Copolymer of *trans*-polyisoprene (TPI) segmented urethane shows that the recovery rates of the films depend on their TPI segment contents, while the fixity rate was measured to be close to 100% [31]. The film containing 70% TPI segments shows a recovery rate of 85%. TPI-urethane copolymer is considered as a typical shape memory polymer with the transition temperature being the melting point. The TPI segment not only serves as the switching molecule but also enables the fixation of the temporary shape. As the stretched film is cooled from the loading temperature to room temperature, TPI segments begin to recrystallize under the stress. The crystallites reformed can prevent the polymer from immediately reforming coil-like structures and from spontaneously recovering the original shape. The good shape fixity observed for the films implies that the strain-induced crystallization of TPI is important [31].

The shape memory effect could arises as a result of intermolecular H-bonding of the poly (acrylic acid-co-acrylonitrile) [poly(AA-co-AN)] copolymer gels with polytetra methylene oxide (PTMO). The shape memory property is proportional to the H-bonding complexation formed by high AA-content in the copolymer. Fixed phases are due to entanglements or cross-linked points of the polymer chain and the reversible phase can be either crystalline or amorphous and contribute to the properties of elastomers-primarily recovery and energy absorption. The reversible phase is constituted by PTMO complex. The AA content in the polymer decides the extent of complexation and the reversible phase transformation. It is the glass transition temperature of complex that trigger the shape recovery property. AN is unlikely to be involved in H-bonding with AA or with PTMO. The swelling ratio of poly(AA-co-AN) in PTMO decrease with AN content of the copolymer, as this group cannot complex with PTMO through H-bonding. With increase in swelling ratio, PTMO content increases in the complexed gel and it leads to a better shape memory property [32].

4. APPLICATIONS OF SHAPE MEMORY POLYMERS

4.1. Biomedical Filed

The recovery temperature of deformed shape memory polymers tuned at near human body temperature would find interesting clinical applications as shape memory implants. Shape-memory materials have been proposed in biomedical device design due to their ability to facilitate minimally invasive surgery and recover to a predetermined shape in vivo [33]. The material needs to have a high shape recovery ratio when deployed at high temperature so that a small device can be inserted and navigated through the vasculature and deployed into a large device that fits the target artery. In addition, when in place at body temperature, a high modulus is desired for resistance in tension and compression. Finally, thermomechanical properties need to be stable over time. These general requirements would apply to any SMP interventional medical devices. The thermomechanical properties of these materials can be adjusted and seem to be well suited for manufacturing medical interventional devices such as thromboembolic extractors and vascular stents [34]. In the specific field of medical implants, the shape memory ability is particularly desirable in order to minimize surgical impact. In biomedical applications, shape memory materials are required to be both biocompatible and to have a recovery temperature near human body temperature [12]. Cardiovascular stents are synthetic material scaffolds used to expand and/or support blood-carrying vessels. Utilizing the shape-memory effect is a reliable way to deliver a large polymer scaffold in a minimally invasive manner. The stents can be pre-programmed to activate at body temperature, resulting in natural deployment without need for auxiliary devices [33].

Smart, biodegradable polymer materials also demonstrate promising potentials toward minimally invasive surgery. For example, the mechanical characteristics and degradability of shape-memory, multiblock copolymers can be used for the preparation of smart surgical sutures. By increasing the temperature higher than the T_{trans} , shape-memory fibers, programmed to apply the optimum force, and tighten suture knots [35].

4.2. Smart Textiles

Day-by-day consumers becoming more discerning and require additional comfort and functionality to their clothing. A smart textile materials are also called interactive textiles, because they react to changes in the temperature in either the user or their environment, in which case they try to maintain the user's temperature balance and remove perspiration from the body surface. The recent huge advancement of shape memory polymers has opened the door for many useful applications in textile field. Although relatively few structures are presently built with such materials, the potential market for the applications of these materials can be quite large. The unique properties of shape memory polymer resulting from thermally induced phase transformation has been exploited commercially to produce a variety of products [36]. Shape memory polymer can be laminated, coated, foamed, and even straight converted to fibres. Permeability (sweat transport) of SMP coated or laminated fabrics could changes as the environment and body temperature changes, which could be useful to make smart garments [37]. When the body temperature is low, the fabric remains less permeable and keeps the body heat. When the body is in a sweat condition, it allows the perspiration to escape into the environment because its moisture permeability becomes high with increasing body temperature.

Temperature responsive shape memory polymers are capable of changing their shape upon application of external stimuli such as heat. Large change in thermo-mechanical properties occurs across the transition temperature such as glass transition temperature (T_g) or soft segment crystal melting temperature (T_{ms}) of SMP. When SMP changed from glassy state to rubbery state, Young's modulus, tensile and elastic properties would vary greatly, which would be useful for garments. For example, when the polyurethane based SMP garments

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would wash at higher temperature or worn at body temperature, it could recover to the original state (wrinkle free) [38].

4.3. Other Applications

Industrial recycling is a practice of growing importance. Shape memory polymer screw could be used in electronic products to disassemble at its end of life (EOL), perhaps 5 - 10 years later, the product contains all the necessary information and mechanisms to disassemble itself following a single generic triggering event such as heat [39]. Stimuli-responsive polymers have a significant advantage over conventional microfluidic actuators owing to their ability to undergo abrupt volume changes in response to the surrounding environment without the requirement of an external power source [40]. Some of the other potential applications of SMP include embolic coil release mechanisms, thrombus extraction devices, and many more [41].

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