4 Shape-memory Polymer Blends

4.1 Introduction

Shape-memory polymers (SMP) have received increasing attention in recent years on account of their interesting properties and potential applications. Such applications include medical devices, actuators, sensors, artificial muscles, switches, smart textiles and self-deployable structures [1–4]. Increasing numbers of scientists and engineers are turning to the design of new SMP for more extensive and in-depth applications.

According to the mechanism of action of shape-memory, the features of SMP should include a transition that can be used to fix the secondary shape at low temperatures and trigger shape recovery at high temperatures, elasticity for shape recovery above the transition temperature, and ability of fixing the temporary shapes [1]. Based on the concept, SMP can be divided into four main classes [2], as described below.

1. **Covalently crosslinked glassy thermoset networks** are the simplest type of SMP. The rubbery elasticity derived from covalent crosslinks elicits excellent shape recovery, which is tunable through adjustment of the extent of covalent crosslinking. However, the covalently fixed primary shape makes it difficult to reshape thereafter once processed.

2. **Covalently crosslinked semi-crystalline networks**: The melting transition of semi-crystalline networks can also be employed to trigger shape recovery as well as the glass transition.

3. **Physically crosslinked glassy copolymers**: In this system, crystalline or rigid amorphous domains, in the form of phase-separated block copolymers, act as physical crosslinks providing the super-glass transition temperature ($T_g$) elasticity required for shape-memory effects (SME).

4. **Physically crosslinked semi-crystalline block copolymers**: The soft phase of some block copolymers crystallises and their melting temperature ($T_m$) values function as the transition temperature instead of the $T_g$. Thus, the secondary shapes are fixed by crystallisation of the soft phase.

It has been suggested that the shape-memory ability of SMP is dominated by the
thermal and mechanical properties of polymer networks. The precise design of polymer networks seems to be necessary to achieve the desired SME. However, synthesising and characterising new types of SMP is complicated and inconvenient [5–8]. Hence, polymer blending methods (which simplify the technology, lower the cost, and make it possible to reprocess or recycle these materials easily [2, 3]) have been proposed as ideal methods for preparing novel SMP systems and improving the shape-memory properties of conventional SMP.

Based on the miscibility of the blend components, this chapter will throw light on the preparation and characteristics of miscible/immiscible SMP blends. Blending and post-crosslinking polymer components to form polymer networks such as interpenetrating networks (IPN) are also introducing as promising strategies to fabricate novel SMP.

4.2 Miscible Polymer Blends

Blending miscible polymers is an attractive method to prepare new SMP because the fabrication strategy is simple and applicable. Miscible amorphous/crystalline polymers blends can be used to create new shape-memory materials with one polymer forming the fixing phase and the other the reversible phase. Miscible SMP/crystalline polymer blends can be used to ‘tune’ or improve the properties of available SMP.

4.2.1 Shape-memory Polymer/Polymer Blends

Utilising a thermoplastic SMP as one component and a miscible polymer as the other to prepare binary SMP blends is an effective method to lower the costs as well as to adjust switch temperatures and mechanical properties while maintaining a certain level of SME of SMP.

Polyurethane (PU) is one of the most familiar SMP and has received increasing attention due to its excellent shape-memory properties [4]. Jeong and co-workers developed a novel SMP blend by means of thermoplastic polyurethane (TPU) and phenoxy resin [5]. The soft segment of TPU acted as a reversible phase and was miscible with phenoxy resin at any composition in the blends, whereas the hard domain was utilised as the fixed phase. The switching temperature could be tuned between the \( T_g \) of the soft segment of the TPU and phenoxy resin. Jeong and Song reported on the miscibility and shape-memory properties of TPU/polyvinyl chloride (PVC) blends [6]. PVC was miscible with the poly(\( \epsilon \)-caprolactone) (PCL) segment in TPU, and the switching temperature of the miscible amorphous domain varied smoothly with composition. They observed that permanent deformation was fixed by the hard segment domain in TPU, and that recoverable deformation of the reversible
phase was formed by the miscible PVC/PCL segment domain.

Ajili and co-workers reported on the SME of PU/PCL blends [7]. A PU copolymer based on a PCL diol was partially miscible with PCL. It was shown that all PU/PCL blends except for PU/PCL (80/20) showed SME and that the recovery temperatures were around the melting temperature of PCL. The shape recovery response of the PU/PCL blends was strongly influenced by the deformation temperature (melting or solution temperature) and shape fixing temperature (transition temperature). When a deformation was made above the $T_m$, shape recovery took place over a wide temperature range from the temperature at which secondary crystallites melts ($T_{m,s}$) to the temperature at which primary crystallites melts ($T_{m,p}$). This happened because primary and secondary crystalline entities were formed (Figure 4.1a). However, when the deformation was made between $T_{m,s}$ and $T_{m,p}$, steep recovery curves and almost complete recovery ratios could be obtained in the range of $T_{m,s}$. This phenomenon occurred while the temporary shape was fixed by formation of secondary crystals (Figure 4.1b).

The composition and crystallisation conditions of PU/PCL blends clearly influenced the switching temperature. Hence, tuning shape recovery to the range of body temperature for the blends was challenging. PU/PCL blends showed great biocompatibility as evaluated by human bone-marrow mesenchymal stem cells, and might be a potential SMP as a stent implant.

Behl and co-workers examined the shape-memory properties of binary copolymer blends of poly($p$-dioxanone) (PPDO)/PCL blends [8]. The hard segment PPDO and switching segment PCL were immiscible, but the polyalkylene adipate mediator segment was incorporated in both multiblock copolymers to improve the miscibility of PPDO/PCL blends. The switching temperature was dependent upon the switching domains and the $T_m$ of PCL. Shape-memory properties were excellent at all weight ratios of the two blend components, and the mechanical properties could be varied systematically. The binary blend system had several advantages (biodegradability, economically efficient, variation of mechanical properties, and a switching temperature around body temperature) making it a suitable candidate for biomedical applications.

Madbouly and co-workers developed a degradable PU/soybean protein (SP) blend which was synthesised using an environmentally friendly aqueous dispersion method [9]. The SP and PCL segment of PU were miscible at the entire range of compositions investigated. The $T_m$ decreased with increasing SP content in the binary miscible blend due to the decreasing hard domain of PU. Figure 4.2 shows the scanning electron micrographs of PU/SP foams of different blend compositions. Porous structures were fabricated by the scCO$_2$ foaming method. The degree of porosity reached 85% at the wt% of soybean protein in PU/SP blend ($w_{SP}$) = 0.4 and decreased with increasing

Shape-memory Polymer Blends
SP content, whereas no porous structure could be obtained at $\omega_{SP} = 0.4$ owing to the decreasing stability of the foams. The polymer films and foams obtained from the PU/SP blends which possessed hydrolytic degradability and shape-memory capability could be utilised as potential biomedical materials.

**Figure 4.1** Molecular mechanism of SME for PU/PCL blends (schematic): (a) deformation above the $T_{m,p}$; and (b) deformation temperature between $T_{m,s}$ and $T_{m,p}$. Reproduced with permission from S.H. Ajili, N.G. Ebrahimi and M. Soleimani, *Acta Biomaterialia*, 2009, 5, 5, 1519. ©2009, Elsevier [7]
Shape-memory Polymer Blends

Figure 4.2 Scanning electron micrographs for the porous structure of PU/SP blends of different concentrations generated using the scCO₂ method at a foaming temperature of 35 °C, 100 bar, and 30-min saturation time. Reproduced with permission from S.A. Madbouly and A. Lendlein, Macromolecular Materials and Engineering, 2012, 297, 12, 1213. ©2012, John Wiley & Sons [9]

Erden and co-workers reported on TPU/polybenzoxazine (PB) blends [10]. It was shown that benzoxazine/PU prepolymer formed miscible blends, and that some degree of reaction between the phenolic –OH groups of PB and isocyanate groups of PU took place, during the thermal curing of benzoxazine. The PU/PB blends showed excellent shape-memory properties and higher shape recovery forces, faster shape recovery, and greater shape recovery ratio than shape-memory polyurethanes (SMPU).

A novel miscible blend with shape-memory-assisted self-healing (SMASH) properties was reported by Rodriguez and co-workers [11]. The blend was prepared by blending a crosslinked PCL network (n-PCL) and linear PCL (l-PCL) (Figure 4.3a). l-PCL interpenetrated the crosslinked PCL network. The blend exhibited a combination of shape-memory response from the network component (n-PCL) and SH capacity from the linear component (l-PCL). The blend containing n-PCL exhibited excellent shape-memory responses owing to the recovery of strain by rubber elasticity in the network and fixing of strain by PCL crystallisation [12, 13]. As the l-PCL content increased from 20 to 70 wt% in the blend, the fixity ratio ($R_f$) increased from 74.1% to 80.9% and the recovery ratio ($R_r$) decreased from 92.7 to 69.1%. The l-PCL chains could diffuse through the n-PCL network and could ‘heal’ the cracks by molecular diffusion above the $T_m$. The authors envisioned that the healing process could take
place over five stages (Figure 4.3b). Figure 4.3c shows the ‘snapshots’ of the self-healing process. The healing was nearly complete for samples with l-PCL content >25 wt%. Remarkably, the high R, could increase the probability of SH because this recovery would assist in the closing of cracks. Such SMASH blends could be utilised for self-healing bladders, inflated membranes, and architectural building envelopes.

Figure 4.3 (a) Preparation blends containing n-PCL and l-PCL by UV-initiated thiol-ene polymerisation in the presence of non-reactive l-PCL. (b) Schematic of the five stages of healing. (c) Snapshots of crack closure and crack rebonding when the sample was unclamped from the Linkam tensile stage and heated to the temperatures shown above (stereo micrographs scale bar: 500 μm). UV: ultraviolet. Reproduced with permission from E.D. Rodriguez, X. Luo and P.T. Mather, ACS Applied Materials & Interfaces, 2011, 3, 2, 152. ©2011, American Chemical Society [11]
4.2.2 Amorphous Polymer/Crystalline Polymer Blends

Amorphous/crystalline polymer blends are completely miscible with a single phase and the $T_g$, whereas the crystalline phase acts as the fixing phase to keep a permanent shape above the $T_g$ but below the $T_m$. The $T_g$ and shape-memory properties of the blends can be manipulated by changing compositions.

Mather and co-workers reported on the miscible amorphous/semi-crystalline polymer blend systems of amorphous polyvinyl acetate (PVAc)/semi-crystalline polylactide (PLA) and amorphous polymethyl methacrylate (PMMA)/semicrystalline polyvinylidene fluoride (PVDF) [14]. The polymer blends of both systems were totally melt miscible within the experimental ranges, and formed only one single $T_g$ for all blend ratios. PVAc and PMMA were totally amorphous, but PLA and PVDF each showed semi-crystalline features and had a degree of crystallinity of $\approx 50\%$. According to the blend ratio, the rubbery modulus could be governed by a degree of crystallinity of the blends that varied from 0 to 50\%, and the crystals served as physical crosslinks. The $T_g$ of the amorphous phase worked as the critical temperature for triggering the shape recovery, and could be tailored between the $T_g$ values of the two homopolymers.

Recently, You and co-workers reported on the shape-memory performance of miscible amorphous/crystalline polymer blends of PVDF/acrylic copolymer (ACP) which could be reused readily many times [15]. They showed that simple melt-mixed PVDF/ACP blends with $40\text{–}50\text{ wt}\%$ PVDF demonstrated good shape-memory performance. The shape-memory properties are depicted schematically in Figure 4.4a. The small PVDF crystals acted as the fixed phase and the amorphous phase between the PVDF crystals acted as the switching phase. Shape recovery properties were affected by tie molecules between the fixing PVDF crystal phases. This was because there was a loose and elastic network of PVDF crystals connected by tie molecules which prevented molecular slip upon deformation (Figure 4.4b). Blends containing 50 wt\% PVDF in which a small amount of tie molecules formed a deformable elastic network possessed the best shape-memory recovery properties. Conversely, when there were few or many tie molecules in the blends, the blends exhibited relatively low shape-memory performance owing to slipping of the amorphous molecules or the large fibrillar crystal structure during deformation.
**Figure 4.4** Schematic diagrams for (a) the shape-memory properties of PVDF/ acrylic copolymer blends; and (b) the molecular mechanism. TM: Tie molecules. Reproduced with permission from J. You, W. Dong, L. Zhao, X. Cao, J. Qiu, W. Sheng and Y. Li, *The Journal of Physical Chemistry B*, 2012, 116, 4, 1256. ©2012, American Chemical Society [15]
Furthermore, You and co-workers also investigated the crystal morphologies and shape-memory properties of PVDF/ACP (50/50) blends at different cold crystallisation temperatures [16]. Blends cold crystallised at high temperature exhibited a low shape recovery ratio value due to large spherulites and high crystallinity, whereas high fixity and high shape recovery ratio could be achieved when tiny crystals (100 nm in length) produced at low cold crystallisation temperature acted as the effective fixed phase in the blends. The switching temperature of the obtained blends could be tuned at ≈5 °C by cold crystallisation. Such SMP could be utilised for biomedical applications because the switching temperature could be very close to body temperature.

4.3 Immiscible Polymer Blends

Polymers are immiscible if polymers are not mixed at the molecular level. Immiscible blends show a phase-separated structure. The phase-separated morphology influences the shape-memory properties and other properties of immiscible polymer blends. Alternatively, incorporating the same mediator segment type in both multiblock copolymers is an effective way to promote miscibility.

4.3.1 Elastomer/Polymer Blends

In elastomer/polymer blends, there are two immiscible components: one is an elastomer and the other is a switch polymer that can demonstrate good shape-memory properties. The elastomer can be any rubber or thermoplastic elastomer. The switch polymer can be any amorphous or crystalline polymer. The shape-memory properties of elastomer/polymer blends can be optimised by controlling the phase morphology of the two components.

Zhang and co-workers prepared novel immiscible styrene-butadiene-styrene tri-block copolymer (SBS)/PCL blends with different compositions [17]. They investigated the shape-memory properties of SBS/PCL blends. The shape-memory mechanism was classified into four series with different phase morphologies (Figure 4.5). In the immiscible blends, the SBS elastomer provided the stretching and recovery performances, and the switch polymer provided the fixing and unfixing performances. Shape-memory properties were largely influenced by the phase morphology. When the SBS elastomer formed a major continuous phase and the PCL segment formed a minor continuous phase, the best SME could be attained through careful design of the morphology of the immiscible phase.

Zhang and co-workers reported another immiscible blend SMP by blending SBS and poly(D,L-lactic acid) (dl-PLA) [18]. The shape-memory effect was dominated by the formation of bicontinuous structures. These bicontinuous structures showed much higher shape recovery and fixing ratios than the blends beyond the bicontinuous range. Compared with SBS/PCL blends, the shape recovery was notable even if the elastic SBS became an isolated domain in the SBS/dl-PLA blends. The SBS/PLA blend system proved to be an example of a dual-domain shape-memory system.

Weiss and co-workers designed a type of SMP by blending an elastomeric ionomer with low molar mass fatty acids and their salts [19]. Nanophase separation of the ionomer was used to develop a crosslinking network and fatty acids (salts) were used to produce a $T_m$ as the switch. However, the interactions between FA crystals and polymers were not strong enough to provide a robust crosslink without the ionomer. The switch temperature of this type of SMP was varied readily by choosing fatty acids with different melting points.
Luo and Mather prepared a shape-memory elastomeric composite (SMEC) by means of infiltrating an electrospun PCL mat with liquid Sylgard and curing below the $T_m$ of PCL [20]. Although the two components in SMEC were not blended in a melted or solution state, the new design strategy of SMEC by infiltrating two components could be regarded as a specific blending method to prepare SMP. Figures 4.6a and b show that the SMEC exhibited a two-phase morphology in which semi-crystalline PCL was present as a non-woven fabric distributed evenly in a continuous Sylgard matrix. The SMEC exhibited excellent shape-memory performance, with Sylgard providing a stationary phase and PCL serving as a $T_m$-based switching segment (Figure 4.6c). This new design strategy for SMEC is versatile and has broad applicability due to no specific chemical or physical interactions. Furthermore, it is possible to tune the shape-memory behaviour and material properties by controlling the properties of the individual components.

Figure 4.6 SMEC: (a) Composite structure (schematic); (b) scanning electron micrograph image showing bulk composite morphology; and (c) a series of photographs showing the recovery form affixed, in the temporary shape and permanent shape on a hot-plate at 80 °C. Reproduced with permission from X. Luo and P.T. Mather, Macromolecules, 2009, 42, 19, 7251. ©2009, American Chemical Society [20]
By following the same design strategy, Luo and Mather also developed a series of triple-shape polymeric composites (TSPC) based on the fibre/elastomeric matrix composite approach [21]. During fabrication of TSPC, an epoxy-based copolymer chemically composed of an aromatic diepoxide (diglycidyl ether of bisphenol-A), an aliphatic diepoxide (neopentyl glycol diglycidyl ether), and a diamine curing agent (polypropylene glycol (bis(2-aminopropyl)) was prepared. Then, a piece of PCL fibre mat was immersed into the liquid resin mixture, which could wet the mat readily due to its low starting viscosity. The TSPC also exhibited excellent shape-memory performance, with an epoxy-based copolymer providing a stationary phase and PCL serving as switching phase. The TSPC could fix two independent temporary shapes and recover sequentially from the first to the second temporary shape and eventually to the permanent shape upon continuous heating. One can control the transition temperatures by simply selecting different polymers for the fibres and matrix, or functionalising them separately to achieve other novel functions (in addition to triple-shape), such as controlled drug delivery or reversible adhesion.

### 4.3.2 Other Types of Immiscible Blends

Immiscible SMP/polymer blends, immiscible crystalline/amorphous polymer blends, and immiscible crystalline polymer blends can also demonstrate shape-memory behaviour.

Kurahashi and co-workers reported an immiscible polymer blend based on TPU and crystalline polyoxyethylene (POE) [22]. The soft segment in PU acted as the reversible phase, and the crystallisation and solidification phases of POE were used to fix the temporary shape. The PU/POE blend showed good shape-memory properties, and the shape-memory mechanism is represented in Figure 4.7. The molecular weight of POE did not have a remarkable influence on the SME of the blend. The $R_f$ below the crystallisation temperature had a sharp rise of nearly 100% and the $R_r$ above the $T_m$ grew much slower with increased POE content in the blend.

To improve the SME of PLA, Lai and co-workers prepared a bio-based PLA/TPU blend through melt-blending and investigated its shape-memory properties [23]. The $R_f$ of the PLA/TPU (50/50) blend showed a significant increase (up to 93.5 ± 0.4%) with the introduction of TPU compared with that of PLA at the pre-deformation temperature of 25 °C. The blend had enhanced shape-fixing ability with increase in pre-deformation temperature, which was contrary to the trend of shape-recovery ability. Furthermore, upon heating under full-strain constraint, the recovery stress for all samples pre-deformed at different temperatures showed a maximum peak with increasing temperature.

Immiscible high-density polyethylene (HDPE) and nylon 6 (PA6) were blended by Li and co-workers to prepare a shape-memory blend through melt extrusion [24]. To improve the poor SME of the blend caused by the incompatibility of both components, ethylene-octane copolymer graft maleic anhydride (POE-g-MAH), which could increase the melt viscosity of the blend at low shear rate range and decrease that at high shear rate range, was introduced into the system as a reactive compatibiliser. When POE-g-MAH content increased, phase separation could be improved and the average particle size of PA6 decreased gradually in PA6/HDPE/PA6/POE-g-MAH blends (Figure 4.8). With the increase in POE-g-MAH content, the HDPE/PA6 blend increased the shape recovery rate and speed. The optimal shape response temperature of HDPE/PA6/POE-g-MAH blend was slightly higher than the $T_m$ of HDPE.

Li and co-workers also blended HDPE with polyethylene terephthalate (PET) to prepare SMP using ethylene-butyl acrylate-glycidyl methacrylate terpolymer (EBAGMA) as a reactive compatibiliser [25]. PET was designed as the fixed phase and melted HDPE crystals above the $T_m$ acted as the reversible phase. In the same way as the HDPE/PA6/POE-g-MAH blend, addition of a compatibiliser clearly improved shape-memory properties. The blend with 5 phr EBAGMA had the best SME when the ratio of HDPE/PET was 90/10.

A novel polymer blend of polyamide (PA) and linear low-density polyethylene (LLDPE) was prepared in a modular inter-meshing co-rotating twin-screw extruder with maleated polyethylene (PE-G) as a compatibiliser by Lin and co-workers [26]. According to the shape-memory investigation, LLDPE contributed to the fixing and PA contributed to the recovery with the help of PE-G. The SME of the blend was
investigated, and the results showed that incorporation of PE-G strongly affected the tensile properties and morphology of the blend. PA content in the blend had a significant effect on the SME of the blend, which performed best with 60 wt% LLDPE, 20 wt% PA, and 20% PE-G. The optimised phase morphology of the blend could be designed to contain the major continuous-phase LLDPE and dispersion-phase PA.

Figure 4.8 Scanning electron micrographs of HDPE/PA6/POE-g-MAH blends HDPE/PA6/POE-g-MAH: (a) 80/20/0; (b) 80/20/3; (c) 80/20/5; and (d) 80/20/10. Reproduced with permission from S-C. Li and L. Tao, Polymer-Plastics Technology and Engineering, 2010, 49, 2, 218. ©2010, Taylor & Francis [24]

LLDPE was also used by Liu and co-workers and blended with polypropylene (PP) to prepare a shape-memory blend by melt-blending with moderate crosslinked LLDPE/PP blend as a compatibiliser [27]. The compatibiliser enhanced the melt strengths of the blend as well as improving compatibility. In the LLDPE/PP blend, dispersed PP particles acted as the fixed phase and continuous LLDPE acted as the switch phase. The shape-memory mechanism of LLDPE/PP/LLDPE-PP blend is presented in Figure 4.9. Bad shape fixity and recovery performances for the LLDPE/PP blend are shown in Figure 4.9A and occurred because the fixed-phase PP could not provide sufficient
restraining force to reversible LLDPE phase. With addition of the compatibiliser, there were more small PP particles which dispersed more uniformly in the matrix of LLDPE (Figure 4.9B). The blend showed the best shape fixity and recovery performances because of the enhanced interaction between the fixed phase and switch phase. However, the blend exhibited good shape recovery performance but bad shape fixity performance if the PP content was too low (Figure 4.9C). This was due to the insufficient constraining effect of the fixed phase on the switch phase. Conversely, if the PP content was too high, the switch phase was relatively low, which made the irreversible plastic deformation more likely to occur under identical conditions, leading to the bad shape recovery effect of the blend. Liu and co-workers also made a systematic investigation on the melt rheological properties of the LLDPE/PP/LLDPE-PP blend. They found that PP particles could be dispersed better and wrapped in the LLPDE matrix at a high shear rate [28]. The higher the shear rate, the smaller the temperature sensitivity of the melt viscosity of the blends would be. The die swell ratio of the blends increased with increase in shear rate.

Cui and co-workers developed a similar blend system based on PP and PET through melting extrusion using POE-g-MAH as the compatibiliser [29]. Melted PP crystals above the $T_m$ acted as the switch phase and the dispersed PET domains contributed to the fixation as the physical crosslinks. Incorporation of the compatibiliser affected the blend in various aspects. First, it improved the compatibility of the PP/PET blend, enhancing the interfacial adhesion between PP and PET phases. Second, PP particle sizes became smaller and their crystallisation properties in the blend were reduced. Third, the recovery rate and speed of the blend increased with higher recovery temperature whereas the $R_i$ value remained almost unchanged. Except for the abovementioned effects, addition of POE-g-MAH also affected mechanical and rheological properties to a certain extent.

Meng and co-workers reported on the shape-memory behaviour of chitosan/poly(L-lactide) (PLLA) blends [30]. Chitosan does not significantly affect the $T_g$ and $T_m$ of the PLLA. Pure PLLA and chitosan/PLLA composites showed SME arising from the viscoelastic properties of PLLA comprising semi-crystalline structures. The shape recovery ratio of the chitosan/PLLA blends decreased significantly with increasing chitosan content due to the incompatibility between PLLA and chitosan. Phase separation structures of the composites were observed using atomic force microscopy. To obtain good SME, the chitosan content should be <15 wt%. The blends may have biodegradability and biocompatibility, and be suitable for biomedical applications.

Sahoo and co-workers developed a novel electro-active SMP blend consisting of polypyrrole (PPy) formed by chemical oxidative polymerisation and SMPU [31]. It was found that the conductivity of the blend increased in the presence of PPy, and high conductivity ($10^2$ S/cm) was obtained at 6–20 wt% PPy. However, the elongation at
break and tensile strength of the PU/PPy blend decreased with increase in PPy content in the blends owing to the brittle network of PPy. PU has a transition temperature near 46 °C, so the PU/PPy blends could show electro-active shape recovery by heating above the transition temperature due to melting of the PCL soft segment domain. If constant voltage (40 V) was applied, the PU/PPy blend changed spontaneously to its original shape, and a good shape recovery of 85–90% could be obtained (Figure 4.10).

Sahoo and co-workers also reported on electro-active shape-memory blends based on SMPU block copolymers, multiwalled carbon nanotubes (MWCNT) and PPy [32]. These blends also showed good conductivity and electro-active shape recovery. The shape $R_s$ of the PU/PPy/MWCNT (95/2.5/2.5) could reach 90–96% in 20 s with a bending mode if an electric field of 25 V was applied.

4.4 Blending and Post-crosslinking Polymers Networks

4.4.1 Interpenetrating Polymer Networks

Interpenetrating polymer networks (IPN) can be prepared by simultaneous polymerisation and polycondensation of low-molecular-weight monomers or macromonomers that are capable of netpoint formation. The generated netpoints of both polymer networks determine the permanent shape, whereas polymer networks contribute to the switching domains. The characteristics of IPN are dependent upon the weight ratio of the IPN components and the resulting morphology of the polymer network.

Liu and co-workers designed a PMMA-polyethylene glycol (PEG) semi-IPN which exhibited two independent shape-memory behaviours at the $T_m$ of the PEG crystals and the $T_g$ of the semi-IPN [33]. The PMMA-PEG semi-IPN were synthesised by radical homopolymerisation and crosslinking PMMA in the presence of linear PEG. For the shape-memory behaviour at the $T_m$ of PEG crystals, the fixing phase was the PMMA network and the reversible phase was the PEG crystal. For the shape-memory behaviour at the $T_g$ of the semi-IPN, the fixing phase was the chemical crosslinked point, whereas the reversible phase was the PMMA-PEG complex phase. Figure 4.11 demonstrates the shape-memory behaviour of PMMA-PEG2000 semi-IPN below and above the $T_g$ of the semi-IPN. Because of the large gap between the storage modulus below and above the $T_g$ of the semi-IPN, and a reversible order–disorder transition of the crystals around the $T_m$ of PEG, the polymer had a recovery ratio of 99 and 91%.

In accordance with the concept of PMMA-PEG semi-IPN, Liu and co-workers also prepared a novel polymer PMMA-co-(vinyl-2-pyrrolidone) (PMMA-co-VP)/PEG semi-IPN based on hydrogen bonding, which showed excellent shape-memory behaviour [34]. PMMA-co-VP/PEG semi-IPN were prepared by radical copolymerisation of 37.5–59.5 wt% methyl methacrylate and 26 wt% N-vinyl pyrrolidone in the presence of 0.5 wt% 2,2-Azo-bis(isobutyronitrile as an initiator, 1 wt% ethylene-glycol-dimethylacrylate as a crosslinker, and 15–40 wt% linear PEG. Addition of PEG to PMMA-co-VP networks not only decreased the $T_g$ and stiffness of PMMA-co-VP networks, it also altered the dynamic mechanical behaviour of PMMA-co-VP networks. Hydrogen bonding interactions between the hydroxyl group (hydrogen donor) of PEG and carbonyl group (hydrogen acceptor) of polyvinyl pyrrolidone (PVP) promoted the formation of physical networks between PVP and PEG, which partially restricted the side-chain movements of PVP and slightly increased the stiffness of PMMA-co-VP/PEG semi-IPN. For the PMMA-co-VP/PEG semi-IPN, the fixing phase was the chemical crosslinked point, whereas the reversible phase was the PEG-PVP complex phase. The recovery ratio of these polymers could reach 99%.
Figure 4.11 Shape-memory phenomena of PMMA-PEG2000 semi-IPN. The initial rod was heated to 100 °C and deformed into a spiral shape, then cooled to room temperature under constrained conditions. After withdrawing the external force, the spiral-shaped sample was put into a glass container and kept at constant temperature at 100 °C for a short time. A snapshot of the sample was captured by a digital camera. Reproduced with permission from G. Liu, X. Ding, Y. Cao, Z. Zheng and Y. Peng, Macromolecular Rapid Communications, 2005, 26, 8, 649. ©2005, John Wiley & Sons [33]

Zhang and co-workers incorporated polyethylene glycol dimethacrylate (PEGDMA) into poly(lactide-co-glycolide) (PLGA)/isophorone diisocyanate (IPDI) systems and achieved IPNs with good shape-memory and hydrophilic properties for biomedical applications [35]. First, a hydrophilic network was formed by irradiation crosslinking of dimethacrylate groups in PEGDMA. Second, a PU network was generated by the reaction of hydroxyl telechelic PLGA and IPDI. The chemical crosslinking points acted as the fixed phase to memorise the original shape, whereas the amorphous domains of miscible PLGA and PEG acted as the reversible phase. The crosslinking densities of PU networks could be controlled by varying the arm lengths of oligomeric PLGA. The hydrophilicity, mechanical properties and $T_{\text{trans}}$ of IPN were tuned conveniently by variation of compositions. The switch temperature of the IPN could be adjusted at around body temperature for potential clinical applications.
Feng and co-workers synthesised an elastic amorphous IPN of polyester urethane/PEGDMA by UV-photopolymerisation of PEGDMA and thermal polymerisation of poly(ε-caprolactone-co-lactide) (PCLA) with IPDI [36]. Synthesis of four-armed oligomer PCLA and IPN is represented in Figure 4.12a. Polyester urethane–PEG IPN showed good shape-memory properties with good strain fixity and strain recovery ability. In the IPN, the chemical crosslinking points of PCL acted as the fixed phase to memorise the original shape whereas the amorphous domains of PCLA and PEG acted as a reversible phase. The strain recovery rate and strain fixity rate were found to be >90%. The IPN could quickly recover to their original shape in 10 s above the $T_g$ (Figure 4.12b). The wettability, mechanical properties and $T_g$ of the polymer networks could be adjusted readily by variation of the compositions of hydrophobic PCLA and hydrophilic PEGDMA. Polyester urethane–PEG IPN had a high potential for biomedical applications such as smart implants, medical devices, site-specific controlled drug delivery systems, and stents in the treatment of cardiovascular disease.

Ratna and Kager-Kocsis synthesised a series of crystalline polyethylene oxide (PEO)/crosslinked polymethyl methacrylate (x-PMMA) semi-IPN SMP, which were prepared at various PMMA/PEO ratios using different amounts of crosslinker [37]. They observed that the recovery time increased with increasing crosslinker concentration, whereas the shape fixity tended to decrease with decreasing crosslink density for all the recovery temperatures. The shape-memory properties (shape recovery and shape fixity) of the semi-IPN could be tailored upon the x-PMMA/PEO ratio and crosslinking degree of x-PMMA. A semi-IPN having a composition of PMMA/PEO=68/32 and crosslinker concentration of 4 wt% offered the best shape-memory properties. The creep compliance of the semi-IPN was influenced primarily by the degree of crosslinking of x-PMMA without an obvious change over the compositional change in the range studied.

### 4.4.2 Crosslinked Polymer Blends

SMP with polymer network structures can be prepared through blending and radiation crosslinking. The polymer components and the density of netpoints affect blend properties. The blends could be applied to commodity devices with specific thermomechanical needs, of which the shape-memory properties can be controlled by enhancing the crosslinks with blending sensitisers in polymer networks.
Figure 4.12 (a) Synthesis of four-armed oligomeric PCLA and IPN. (b) Shape-memory photographs (A–F, 2-s interval) of polyester urethane–PEG IPN showed the transition from a temporary to permanent shape. The initial rod strip-shaped film (F) was deformed into a spiral shape in an oven at 5 °C (A), cooled to 0 °C, and the external force withdrawn. Then the deformed sample was placed in water at 50 °C and recovered its permanent shape. Poly(LA-co-CL): Polylactide-co-ɛ-caprolactone. Reproduced with permission from Y. Feng, H. Zhao, L. Jiao, J. Lu, H. Wang and J. Guo, Polymers for Advanced Technologies, 2012, 23, 3, 382. ©2012, John Wiley & Sons [36]
Zhu and co-workers reported on the SME of sensitising radiation-crosslinked PCL with polyfunctional polyester acrylate (PEA) [38]. PCL is a novel biocompatible and biodegradable material. Although radiation-crosslinked PCL exhibited SME at low temperatures, the radiation-crosslinking efficiency of pure PCL was very low [39]. By blending polyfunctional PEA with PCL, the efficiency of the radiation crosslinking of PCL was improved distinctly because the double bonds of the polyfunctional PEA were readily ‘unlocked’ by rays and participated in the crosslinking chemical reactions. The radiation crosslinking of PCL in the presence polyfunctional PEA followed the Chen–Liu–Tang relationship. It was shown that enhanced radiation crosslinking increased the heat deformation temperature of PCL and presented a higher and wider rubbery-state plateau. The shape-memory results revealed that enhanced crosslinking PCL elicited 100% recoverable deformation and a quicker recovery rate than pure PCL.

Using an analogous approach, Zhu and co-workers improved the radiation efficiency of PCL by blending it with polymethyl vinyl siloxane (PMVS) before radiation crosslinking [40]. PMVS is a highly flexible material with a breaking elongation ratio as high as 1500%. Like PCL, PMVS is biocompatible and nontoxic. The double bond of PMVS is sensitive to irradiation crosslinking. Owing to the addition of PMVS (which decreased the gelation dose and ratio of degradation to crosslinking), the radiation crosslinking efficiency of PCL/PMVS blends was significantly higher than that of pure PCL. The crosslinked PCL/PMVS blends exhibited better SME such as narrower switch temperature, higher heat sensitivity, and higher recovery speed in comparison with pure PCL.

Ware and co-workers prepared a radiation crosslinked SMP based on blending and irradiating a system of polymethyl acrylate (PMA) and polyethylene glycol diacrylate (PEGDA) in various ratios. PEGDA is miscible in PMA and sensitises the radiation crosslinking of PMA [41]. The extent of crosslinking increased with an increase in the molar concentration of PEGDA of a constant number average molecular weight. Although longer PEGDA molecules were more effective for sensitising crosslinking at a given molar ratio of sensitisier to PMA, shorter PEGDA molecules were more effective at sensitising crosslinking at a given weight ratio. Figure 4.13 demonstrates the shape-memory properties of PMA/PEGDA blends at 50 kGy. There was a greater increase in stress with increased molar ratio of PEGDA and lower residual strains after a full shape-memory cycle in steps 1 and 2. PMA/PEGDA showed a more rapid and uniform recovery with an increased molar ratio of PEGDA in step 4. The shape fixity was >99% for the PMA/PEGDA blend. Shape recovery over one cycle was between 97% and 99%, and increased with increasing molar ratio of PEGDA (Figure 4.13).
A SMP network composed of carboxylated telechelic PCL and epoxidised natural rubber (ENR) was prepared by Chang and co-workers. This network was formed by the reaction between the reactive groups of PCL and ENR during thermal moulding. In the ENR/PCL blends, the degree of crosslinking and crystalline melting transition temperatures were influenced by the blend compositions and molecular weight of the PCL segment [42]. If there was an adequately high degree of crosslinking for the crystalline melting transition, the recovery temperatures were well matched with the crystalline melting temperature of each sample, and the ENR/PCL blends showed good shape fixation and shape recovery.

Figure 4.13 Shape-memory cycle of blends of PMA and PEGDA 258 irradiated at 50 kGy as a (a) stress–temperature relationship; (b) stress–strain relationship; and (c) strain–temperature relationship. Step 1 is isothermal loading; step 2 is cooling at constant load; step 3 is isothermal unloading; and step 4 is shape recovery upon heating. Reproduced with permission from T. Ware, W. Voit and K. Gall, *Radiation Physics and Chemistry*, 2010, 79, 4, 446. ©2010, Elsevier [41]
Kolesov and Radusch synthesised peroxidic crosslinked binary and ternary blends based on linear HDPE and two ethylene-1-octene copolymers (EOC) through medium and high degrees of branching [43]. HDPE/EOC blends were prepared by mixing HDPE and EOC with 2 wt% of liquid peroxide 2,5-dimethyl-2,5-di-(tert-butylperoxy)-hexane at 190 °C through melt blending. The average crosslink density of HDPE/EOC blends was dependent upon the component ratios and temperature. HDPE/EOC blends showed multiple shape-memory behaviours which appeared only at consequent stepwise application of convenient programming strains and temperatures. All binary and tertiary HDPE/EOC blends except the HDPE/EOC (50/50) blend exhibited triple and quadruple SME because of the large amount of poorly separated peaks formed during multiple melting of these blends. HDPE/EOC blends could be used as functional materials that gradually changed the sample geometry with low thermally induced recovery strain rate.

4.5 Conclusions

In this chapter, a comprehensive overview of recent progress in SMP blends was presented. The design strategy of blending polymers can not only improve shape-memory properties and mechanical properties while maintaining the SME of SMP, they can also create new polymer/polymer blends possessing SME. Constructing binary SMP/polymer blends using a thermoplastic SMP as one component and a commodity polymer as the other component was an effective method to lower costs as well as to adjust shape-memory properties and mechanical properties. SMP can be obtained by blending polymers which have no shape-memory properties on their own. The shape-memory properties of SMP can be tuned via changing the ratio of components, adding a compatibiliser, or selecting a blending method. It is also possible to synthesise novel SMP with IPN or crosslink networks by means of blending and post-crosslinking commodity polymers. This type of SMP could be used as functional materials that gradually change sample geometry with low thermally induced recovery strain rate because shape-memory properties such as shape recovery ratio can be tuned via changing crosslinking methods and the density of netpoints. The strategies presented here are an effective avenue for SMP with remarkable characteristics. SMP prepared by blending appropriate polymers could have shape stability, excellent recovery stress and strain, biocompatibility, and biodegradability.

References


