EFFECT ON COMPATIBILITY AND GRAPHENE ON SHAPE MEMORY AND TENSILE PROPERTIES OF POLYLACTIC ACID (PLA)/ ETHYLENE VINYL ACETATE (EVA) BLENDS

NURULJANNAH BINTI RAHMAT

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by

NURULJANNAH BINTI RAHMAT

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled “Effect on Compatibility and Graphene on Shape Memory and Tensile Properties of Polylactic Acid (PLA)/ Ethylene Vinyl Acetate (EVA) Blends”. I also declared that it has not been previously submitted for the award for any degree or diploma or other similar title of this for any other examining body or University.

Name of Student: Nuruljannah binti Rahmat Signature:
Date: 17/8/2022

Witnessed by:
Supervisor: Dr. Arjulizan binti Rusli Signature:
Date:

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

$	American dollar
%	Percentage
$\theta_0, \theta_1, \theta_2$	Angle
°C	Degree Celsius
°C min^{-1}	Degree per minute
ΔH_{cc}	Enthalpy heat of cold crystallization
ΔH_m	Enthalpy heat of fusion
ΔH_m^o	Enthalpy heat of fusion for 100% of crystalline polymer
g	Gram
g/cm^3	Gram per centimeter cube
g/10min	Gram per 10 minutes
GPa	Gigapascal
J/g	Joule per gram
kN	kilonewton
µm	Micrometer
mm	Millimeter
mm/min	Millimeter per minute
mW	Milliwatt
MPa	Megapascal
N_2	Nitrogen gas
psi	Pound per square inch
rpm	Revolutions per minute
R_f	Shape fixity ratio
R_r	Shape recovery ratio
s	Second

S/m	Siemens per meter
tan δ	Loss angle
T_{cc}	Cold crystallization temperature
T_c	Crystallization temperature
T_g	Glass transition temperature
T_m	Melting temperature
T_d	Deformation temperature
T_f	Fixing temperature
T_r	Recovery temperature
T_{perm}	Thermal transition temperature
t_d	Deformation time
t_f	Fixing time
t_r	Recovery time
wt%	Weight percentage
$Wm^{-1} K^{-1}$	Watt per meter Kelvin
X_c	Degree of crystallinity

LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
CNT	Carbon nanotube
DSC	Differential Scanning Calorimetry
EVA	Ethylene co-vinyl acetate
EVA19	Ethylene co-vinyl acetate with 19 wt% of VA content
EVA40	Ethylene co-vinyl acetate with 40 wt% of VA content
EVA 206	Ethylene co-vinyl acetate with 206 wt% of VA content
EVA 328	Ethylene co-vinyl acetate with wt% of VA content
GNP	Graphene nanoplatelet
HDPE	High density polyethylene
LCE	Linear crystalline elastomer
LCP	Liquid crystalline polymer
MFI	Melt flow index
PE	Polyethylene
PEEAMA	Poly (ethylene-co-ethyl acrylate-co-maleic anhydride)
PLA	Polylactic acid
PLLA	Poly-L-lactide
PDLA	Poly-D-lactide
PDLLA	Poly-DL-lactide
PTFE	Polytetrafluoroethylene
PU	Polyurethane
SBS	Styrene-butadiene-styrene
SCP	Shape changing polymer
SEM	Scanning Electron Microscopy
SMA	Shape memory alloy
SME	Shape memory effect
SMP	Shape memory polymer
SMPC	Shape memory polymer composite
TPU	Thermoplastic polyerethane
VA	Vinyl acetate

KESAN PADA KESERASIAN DAN GRAPHENE PADA MEMORI BENTUK DAN SIFAT TEGANGAN PADA CAMPURAN ASID POLILAKTIK (PLA)/ ETILENA VINYL ASETAT (EVA)

ABSTRAK

Dalam kajian ini, sifat-sifat termoresponsif dan tegangan campuran poli(asid laktik) (PLA)/etilena ko-vinil asetat (EVA) berhubung dengan keserasian pelbagai komposisi adunan dengan kandungan vinil asetat (VA) yang berbeza dan penggabungan pengisi nanoplatelet graphene (GNP) yang bersifat konduktif haba yang tinggi telah dikaji. Pertamanya, pelbagai komposisi adunan telah diadun lebur menggunakan pengadun dalaman dan kemudian, adunan itu diacu mampatkan ke bentuk yang dikehendaki. Sifat ingatan bentuk seperti nisbah ketetapan bentuk (R_f) dan nisbah pemulihan bentuk (R_r) telah disiasat menggunakan ujian bengkokan yang mudah. Kedua-dua R_f dan R_r meningkat dengan peningkatan EVA manakala pada kandungan EVA yang sama, adunan dengan kandungan VA 40% (EVA40) menunjukkan R_f yang lebih tinggi and R_r yang lebih rendah. Kekuatan tegangan dan modulus berkurang manakala pemanjangan takat putus meningkat dengan peningkatan kandungan EVA dengan EVA 40 menunjukkan peningkatan yang lebih tinggi disebabkan keserasian yang lebih baik. Selepas itu, 1% berat hingga 5% berat GNP telah ditambah kepada 70PLA/30EVA dengan kandungan VA yang berbeza. Campuran PLA dengan EVA19 menunjukkan peningkatan R_f, R_r, kekuatan tegangan dan pemanjangan takat putus dengan 1 wt% dan 3 wt% pengisi GNP A 19 disebabkan interaksi yang bagus di antara campuran dengan GNP. Manakala tiada tren yang ketara bagi R_f dan R_r dan pengurangan berterusan kekuatan tegangan dan pemanjangan takat putus dengan peningkatan kandungan GNP dalam campuran dengan EVA 40 disebabkan pengurangan interaksi antara fasa. Kehadiran kandungan graphene yang rendah mempunyai kesan yang lebih besar terhadap

sifat-sifat tegangan dan ingatan bentuk bagi 70PLA/30EVA19 yang kurang serasi berbanding 70PLA/30EVA40 yang lebih serasi.

EFFECT ON COMPATIBILITY AND GRAPHENE ON SHAPE MEMORY AND TENSILE PROPERTIES OF POLYLACTIC ACID (PLA)/ ETHYLENE VINYL ACETATE (EVA) BLENDS

ABSTRACT

In this study, the thermo-responsive and tensile properties of polylactic acid (PLA)/ethylene co-vinyl acetate (EVA) blends were examined in relation to the compatibility of various blend compositions with varying vinyl acetate (VA) content and the incorporation of thermally conductive graphene nanoplatelet (GNP) fillers. Firstly, various compositions of PLA/EVA blends were melt blended with an internal mixer and then the blends were compression molded into the desired shapes. The shape memory properties such as shape fixity ratio (R_f) and shape recovery ratio (R_r) were investigated using a simple bending test. Both R_f and R_r increased with increasing EVA while at fixed amount of EVA, blend with VA content of 40% (EVA 40) showed higher R_f but lower R_r. Tensile strength and modulus decreased while elongation at break increased with increasing EVA content with EVA 40 blend indicated higher values due to better compatibility. After that, 1 wt% to 5 wt% of GNP were added to 70PLA/30EVA of different VA contents. PLA with EVA 19 blend showed in showed improvements in R_f, R_r, tensile strength and elongation at break of EVA 19 with 1 wt% and 3 wt% of GNP filler due to good interaction of the blend with GNP. Meanwhile, no significant trend of R_f and R_r and continuous reduction of tensile strength and elongation at break with increasing GNP content in the blend with EVA 40 due to reduction of interphase interaction. The presence low amount of graphene has greater effect on improvement in the tensile and shape memory properties of less compatible 70PLA/30EVA19 compared with more compatible 70PLA/30EVA40.

CHAPTER 1

INTRODUCTION

1.1 Overview

Shape memory polymer (SMP) can immediately change their shape from a temporary to their original, permanent shapes under suitable stimuli such as temperature, light, electric field, magnetic field, pH, particular ions or enzymes. Thermal sensitive SMPs with a physical cross-linking structure, crystalline or amorphous hard phase, or chemical cross-linking structure and a low temperature transition of crystalline, amorphous, or liquid-crystal phase as a switch are the most commonly investigated and used SMPs. However, SMP blends typically have two goals which are to modify or improve the properties of existing SMPs such as switch temperature, mechanical properties, and shape memory properties, and to create new shape memory materials with one polymer forming the fixing phase and the second polymer forming the reversible phase (Meng and Hu, 2009). One of the thermally sensitive SMPs is a poly (lactic acid) (PLA) and poly (ethylene vinyl acetate) (EVA) blend that consists of biodegradable PLA, which can be used as an alternative to conventional plastic materials, and EVA, which is known for its compatibility with PLA and exhibits both rubbery and resin characteristics that leads to improve the toughening properties of PLA (Sangeetha *et al.*, 2018).

Generally, the morphological properties of the PLA/EVA blend have a clear phase separation when the VA content is low in the blend, which shows the blend immiscibility whereas the sea-island morphology presents as the PLA content increases. When the EVA content is at 15 wt%, there are many smaller voids present on the surface of the PLA/EVA blend, which indicates good interphase interaction between the PLA and EVA phase whereas when the EVA content is at 30 wt%, the formation of sea-island morphology started to appear, which specifies the poor interaction of the interphase of PLA and EVA components (Lim *et al.*, 2021). Similarly, Sangeetha et al. (2018) also reported that as the EVA loading increases in the PLA matrix, the crystallization temperature of PLA/EVA blends decreases, which indicates good compatibility between EVA and PLA matrix. Nevertheless, the tensile strength, tensile modulus, flexural strength and flexural modulus decrease as the EVA content increases in the PLA matrix. The main reason of the decreasing in mechanical properties can be due to an increase in flexibility caused by EVA content in the PLA matrix that leads to a reduction of stiffness of the PLA/EVA blends. However, there is little research on the effect of compatibility between PLA and EVA blends on shape memory properties as many researches have been limited to only one type of EVA compositions instead of two types of EVA compositions.

Other than that, SMPs have various drawbacks in engineering applications, including poor mechanical characteristics, recovery stress, and thermal conductivity. They are inappropriate for structural applications due to their weak stiffness, strength, and recovery stress, and their poor thermal conductivity might create a long thermally induced response time for thermally active SMPs (Lei *et al.*, 2019).

To enhance the shape memory behavior of the blend, incorporation of thermally conductive fillers such as graphene can be done. Graphene is suitable to be the conductive filler due to its excellent properties such as electrical conductivity of 10^6 S/m and thermal conductivity of 5000 Wm^{-1} K^{-1} in which can improve the thermal and shape memory behavior greatly for the PLA/EVA blends. The use of graphene as the filler can bring a great difference in thermal conductivity, which can directly impact the thermal properties and shape memory behavior for PLA/EVA blends (Wang *et al.*, 2018).

Furthermore, Wang et al. (2018) reported that the incorporation of graphene improves the thermal stability of the graphene/epoxy resin matrix. Also, the graphene can homogeneously disperse in the epoxy-cyanate ester as the graphene content is less than

1.6%. Nevertheless, as the graphene content increased, the surface of the nanocomposites became rougher due to the formation of agglomerates. The bending strength of the graphene/ester-epoxy composites increases at graphene content of 1.6 wt% and slightly decreases at graphene content of 2.4 wt%, which can be due to uneven graphene dispersion in the matrix. However, Wang et al. (2018) only studied from 0 wt% to 2.4 wt% of graphene content in the epoxy-based SMP in which causing the properties of different graphene loadings at higher than 2.4 wt% are still cannot be understood completely.

In addition, Lotfi Mayan Sofla et al. (2019) reported the properties of electroactive shape memory polyurethane (PU) and graphene nanocomposite. The compatibility of the PU and graphene can be observed through their morphology and tensile properties of the blends. For the morphology, the surface of the nanocomposites becomes rougher as the graphene nanosheets were added into the PU matrix, which shows a proper dispersion of graphene nanosheets. Next, the Young's modulus of the nanocomposites increases as the graphene content increases. However, the elongation at break of the nanocomposites decreases as the graphene content increases, which can indicate poor interfacial interactions between graphene and PU matrix.

Although considerable research has been devoted to graphene as conductive filler in SMP blends rather less attention has been focused on the graphene in different compositions of ethylene vinyl acetate of the PLA/EVA blends.

1.2 Problem Statement

For thermally-induced SMPs, in order to achieve SME, two types of structures are currently used which are a reversible switching unit and a highly elastic polymer network. The reversible switching unit is in charge of the form fixation process, which is influenced by the glass transition temperature, T_g, while the extremely elastic polymer network is critical for the shape recovery process (Zhang *et al.*, 2015).

In PLA and EVA blends, a research has been made on variation of properties depending on different blend ratios of PLA and EVA contents. Firstly, the morphological properties of PLA/EVA blend can be observed in which the EVA15/PLA85 blend exhibited sea-island morphology in the PLA continuous phase whereas for EVA50/PLA50, the blend showed a gross separation of PLA in the EVA continuous phase that can improve the shape fixity and recovery behavior. When the EVA content is 15 wt%, many smaller voids appear on the surface of the PLA/EVA blend, indicating good interphase interaction between the PLA and EVA phases, whereas when the EVA content is 50 wt%, sea-island morphology appears, indicating poor interphase interaction between the PLA and EVA components (Lim *et al.*, 2021).

After that, the PLA/EVA blend showed an increase in tensile strength for the PLA/EVA system especially for PLA95/EVA5 and PLA90/EVA10 compositions in which exhibit higher tensile strength compared to pure PLA. However, the tensile strength decreases significantly after PLA70/EVA30 composition when compared to pure PLA (Gajria *et al.*, 1996). Likewise, Lim et al. (2021) also reported that tensile strength of PLA/EVA blends also slightly decreased with increasing of EVA content from 15 wt% to 30 wt%, which can be due to the formation of gross phase separation. Based on few researches viewed, the mechanical properties of PLA/EVA blend tend to decrease when the EVA content increases in the PLA/EVA blends. The decrease in the tensile strength of PLA/EVA blends with increasing EVA content can be due to the compatibility between PLA and EVA blends, which can be observed through its morphological properties of the blend.

Furthermore, Sangeetha et al. (2018) also reported on the influence of EVA content on mechanical and thermal characteristics of PLA blends. Based on the research, the homogeneity of the dispersed phase can determine the compatibility of the dispersed phase and matrix. It was found that the particle size of EVA dispersed as a small droplet as the EVA loading became lower in the PLA matrix. However, as the higher loading of EVA in the PLA matrix, the particle size of EVA became larger and exhibits sea-island morphology. Hence, an additional study of the compatibility of different compositions of EVAs in the PLA matrix is needed to investigate the morphology, thermal, tensile and shape memory properties of PLA/EVA blends with different compositions of EVA in different blend ratios. Since the composition of EVA content can affect the compatibility and morphology of the blends, these factors will be considered in order to obtain blends with optimum shape memory and other properties. The compositions of the EVA content in the PLA matrix used are 19 wt% and 40 wt%.

After that, the effectiveness of fillers as reinforcement or improving the shape memory properties have been reported to be affected by the types and amount of fillers. According to Meng and Hu (2009), reinforcement of SMPs can be done by using microfiber, nano clay, carbon black, inorganic filler and etc. For example, microfibers, particularly chopped and continuous microfibers, outperform micro and nano-sized particles in terms of improving the mechanical strength of SMPs. However, the shape memory effect of the SMP cannot be observed due to the high elasticity modulus of fibers. Also, SMPs with microfibers can be used spacecraft self-deployable devices and vibration control devices.

Other than that, the incorporation of graphene in the shape memory polymer is a notable way to improve shape memory effect (SME) of the polymers. Graphene has been incorporated in various SMP matrixes such as epoxy, polyurethane, polylactic acid, polyamide and polystyrene for various actuations. Generally, 0.005-0.5 wt% of graphene nanofillers is added in high performance polymer/graphene nanocomposites for the reinforcement effect to take place (Kausar, 2022). The shape memory behavior improved with addition of graphene as fillers. A research has been reported that the shape memory properties of graphene polyimide nanocomposite significantly enhanced compared to pure polyimide resin. The shape recovery rate and shape fixity rate were increased to 96% (Yoonessi *et al.*, 2012).

In epoxy/graphene nanocomposite, the tensile properties of epoxy/graphene composite increase with increasing graphene content. However, the tensile strength of the composite suddenly dropped when the graphene content is up to 3 wt%. Similarly, the elongation at break for the epoxy/graphene composite decreases with increasing graphene content. The decrease in both tensile properties and elongation at break are due to formation of graphene agglomerates as the surface energy and van der Waals force of graphene become higher (Wang *et al.*, 2016).

Thus, for this research, the SMP of PLA/EVA blend together with different filler loading of graphene will be used to study the thermal properties, tensile properties and shape memory behavior of different blend ratios of PLA/EVA blends. The use of graphene as reinforcement filler can improve shape memory behavior and deformation of the PLA/EVA blend as graphene has high thermal conductivity. However, an optimum amount of graphene in PLA is required to be determined to achieve the desired properties.

1.3 Research Objectives

The purpose of this research study is to study the thermal and shape memory behavior of the polymer blends with different blend ratios of PLA/EVA blends with different filler loadings of the conductive fillers. In this research, the polymers used are PLA and EVA whereas the conductive filler used is graphene. The specific objectives of this research are as follows:

i. To determine the effect of compatibility of PLA/EVA blends towards thermal properties, tensile properties and shape memory behavior of PLA/EVA blends.
ii. To study the effect of different filler loadings of graphene on the thermal properties, tensile properties and shape memory behavior of different blend ratios of PLA/EVA blends.

1.4 Thesis Outline

This thesis consists of five chapters that will cover:

Chapter 1	Introduction to background study, problem statement, research objectives, scope of research and thesis outline.
Chapter 2	Detailed literature reviews on SMPs, its structure, mechanism of SME, SMP blends, SMP blend composites for PLA and EVA and conductive fillers such as graphene.
Chapter 3	Details on the raw materials and equipment used for this study, blend preparation procedure employed, procedures for investigation of thermal properties, surface morphology, tensile properties and shape memory behavior and the overall research flow.

Chapter 4	Detailed discussion on the data and results obtained in this study in the form of statistical analysis on the thermal properties, surface morphology, tensile properties from universal testing machine and shape memory behavior from shape memory test.
Chapter 5	Short summary and conclusion on this research work as well as suggestions for future research.
References	List of references used in this research study.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

SMP is a smart polymer material that, when exposed to certain stimuli like heat, light, electricity, magnetism, solvent, etc., can be deformed and fixed at a particular shape before it returns to its original shape (Ji *et al.*, 2019; Wang and Deng, 2019; Behl and Lendlein, 2007). It is a developing class of polymers with a wide range of uses in everyday life. For instance, programmable fabrics, heat-shrinkable tubes for electronics or films for packaging, self-deploying sun sails in spacecraft, self-assembling mobile phones, intelligent medical devices, and implants for minimally invasive surgery (Behl and Lendlein, 2007). Additionally, SMPs have been recognized as smart materials that have tremendous potentials especially in aerospace engineering. This is because the actuations temperature of SMPs can be controlled simply, which can be applied in various applications such as biomedical stents and robotic actuators (Hong *et al.*, 2016; Xu and Song, 2011). Figure 2.1 shows the diagram of the shape memory polymers that consists of mechanism, actuation methods and its applications.

In addition, SMPs are a class of stimuli-responsive shape changing polymers (SCPs) in which the shape changing behavior can be programmed. Most researchers agreed that SMP possess the ability to transform from any deformed temporary shape back into its “memorized” shape or known as its original shape. This process is called programming or programmability will be further discussed in Section 2.1.3. The programmability of SMPs clearly differentiates SMPs from other stimuli-responsive SCPs (Zhao *et al.*, 2015).

Figure 2.1 Shape memory polymers that consists of mechanism, actuation methods and its applications (Xia *et al.*, 2021).

In contrast, SCPs will either undergo macroscopic changes or at least visible under microscopes and often accompanied by chain conformational changes (shape changes at molecular scale) (Zhao *et al.*, 2015). For instance, stimuli-responsive SCPs can be ranging from swelling or deswelling hydrogels to appealing reversible surface morphological changes of crystalline elastomers (LCEs). The shape shifting of SCPs cannot be manipulated externally after fabrication, which is known as non-programmable shape changing behavior (Zhao et al., 2015; Zhou and Sheiko, 2016). Figure 2.2 shows the classification of shape changing polymers (SCPs) that can be divided into two classes which are programmable and non-programmable polymers. Programmable SCPs such as one-way and two-way SMPs can be externally manipulated as the shape shifting behavior of SMPs is not present inherently in the microstructure in which causing the need of programming step to fabricate it into the desired shape. The programming step of SMPs is further discussed in Section 2.1.3. However, the non-programmable SCPs such as hydrogels and liquid crystalline elastomers (LCPs) cannot be manipulated externally, indicating the shape shifting behavior of these SCPs is inherent and non-programmable (Zhao et al., 2015; Zhou and Sheiko, 2016).

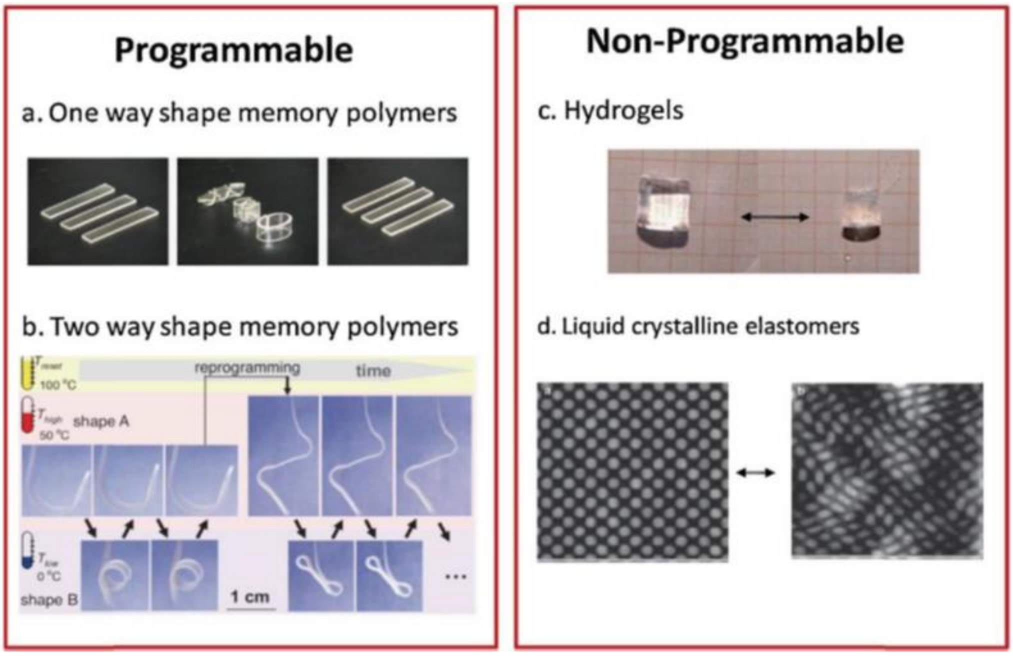

Figure 2.2 Classification for shape shifting polymers (SCPs) which can be classified as programmable and non-programmable polymers (Zhao *et al.*, 2015)

Additionally, SMP has a number of advantages over traditional shape memory alloys (SMAs) when studied by researchers, including having lower density, greater shape recovery, ease of mass production and lower price per pound (Zare *et al.*, 2019; Lei *et al.*, 2019; Razzaq *et al.*, 2007). The comparison of both SMPs and SMAs can be seen in Table 2.1. Furthermore, many SMPs are biocompatible and biodegradable materials in which making them suitable for biomedical applications (Lei *et al.*, 2019).

Nevertheless, the unreinforced SMPs relatively have some limitations such as low shape recovery stress, low mechanical strength, low elastic modulus, low stiffness and longer shape recovery time. However, these drawbacks can be resolved by adding suitable fillers into the SMPs, so that it can improve the thermomechanical properties of the polymer matrix (X. J. Zhang *et al.*, 2020; Xu and Song, 2011).

Table 2.1 Comparison between SMP and SMA (Liu *et al.*, 2007).

	SMP	SMA
Density (g/cm^3)	0.9-1.1	6-8
Elongation at break (%)	Up to 800%	<8%
Elastic modulus at T< T_{trans} (GPa)	0.01-3	83 (Nitinol)
Elastic modulus at T> T_{trans} (GPa)	$(0.1\text{-}10) \times 10^{-3}$	28-41
Deformation stress (MPa)	1-3	50-200
Recovery stress (MPa)	1-3	150-300
Critical temperature (°C)	-10 -100	-10 – 100
T_{trans} (°C)	10-50	5-30
Recovery time	<1s – several minutes	<1s
Thermal conductivity ($W\ m^{-1}\ K^{-1}$)	0.15-0.30	18 (Nitinol)
Biocompatibility and biodegradability	Biocompatible and/or biodegradability	Some are biocompatible (e.g: Nitinol) but do not biodegradable
Processing parameters	<200°C at low pressure	>1000°C at high pressure
Chemical resistance	High	High
Price (per pound)	< $10	~ $250

2.1.1 Classification of Shape Memory Polymers

Next, the classification of SMPs can be made based on their shape recovery behavior which can be found in one-way, two-way and multiple SMPs. For the one-way SMPs, it indicates the shape recovery is irreversible which means the shape shifting during shape recovery is only achievable from a temporary shape to a permanent shape but not the other way around. For one-way SMPs, it has two structures which are the switchable segments that can affix the temporary shape and the net points that can define the permanent shape. The softening and hardening of the transition phase in the polymer enable the lock and unlock of the temporary shape which can be done by direct or indirect heating. By using direct or indirect heating, this can ensure the polymer has to change phase activity and make sure enough enthalpy for shape changes (Xia *et al.*, 2021; Zhao *et al.*, 2015).

On the contrary, the two-way SMPs can be referred to as a reversible shape shifting between a temporary meta-stable shape and a permanent shape that can intermittently change shape upon stimulus changes. Accordingly, two-way SMPs have received more attention compared to one-way SMPs based on their ability to change shapes in response to external stimuli (Xia *et al.*, 2021; Zhao *et al.*, 2015). In the same way, a multi SMP, step wise SMP or multi shaped SMP suggests that the shape shifting occurs in more than one temporary shape with one permanent shape. For instance, triple-shape SMP indicates that the shape shifting occurs in two different temporary shapes and one permanent shape (Sabzi *et al.*, 2017). Figure 2.3 shows the comparison between dual shape and triple shape SMP.

Other than that, SMP can also be categorized into two different systems which are cross-linking system and blending system that can be shown in Figure 2.4. For cross-linking systems, it can be divided into chemical cross-linking and physical cross-linking, which can be in amorphous or crystalline polymers. Chemical cross-linking refers to covalent bonds such as disulphide bond that influenced the shape recovery of SMP (Wang *et al.*, 2014; Zhao *et al.*, 2015; Liu and Mather, 2004), whereas the physical cross-linking with a similar function refers to weaker interactions made of crystalline, glassy hard domains, hydrogen bond, ionic interactions or physical entanglements (Zhao *et al.*, 2015).

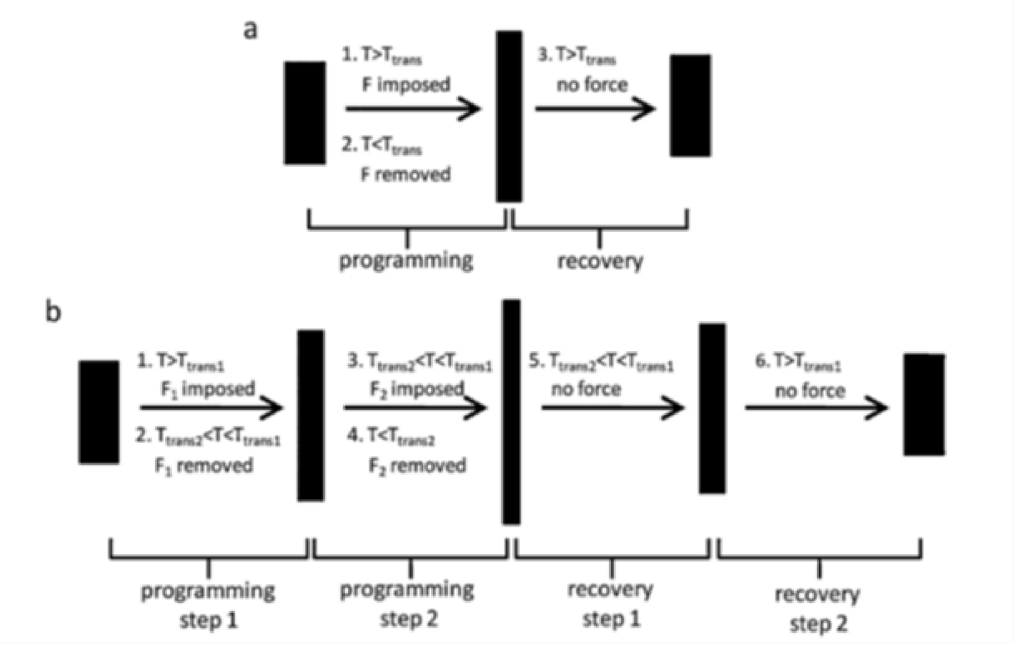

Figure 2.3 Programming step for (a) dual-shaped SMP and (b) triple-shaped SMP (Zhao *et al.*, 2015).

Meanwhile, there is another category for SMP which is blend system that acts as to tune or enhance the thermo-responsive behavior of SMPs as well as to form new kinds of SMP with different materials that have different microstructures and properties (Meng and Hu, 2009). The use of SMP blends for this research is due to its simpler ways to produce SMPs and also to improve the properties of the SMPs such as thermal and tensile properties (Wang *et al.*, 2014). Additionally, the particulates or fiber materials can be incorporated into the polymer in order to enhance the properties of SMP or to create multi-functional SMP where the SMP is sensitive towards indirect heating by other non-thermal stimuli for the purpose of remote actuation (Behl *et al.*, 2010).

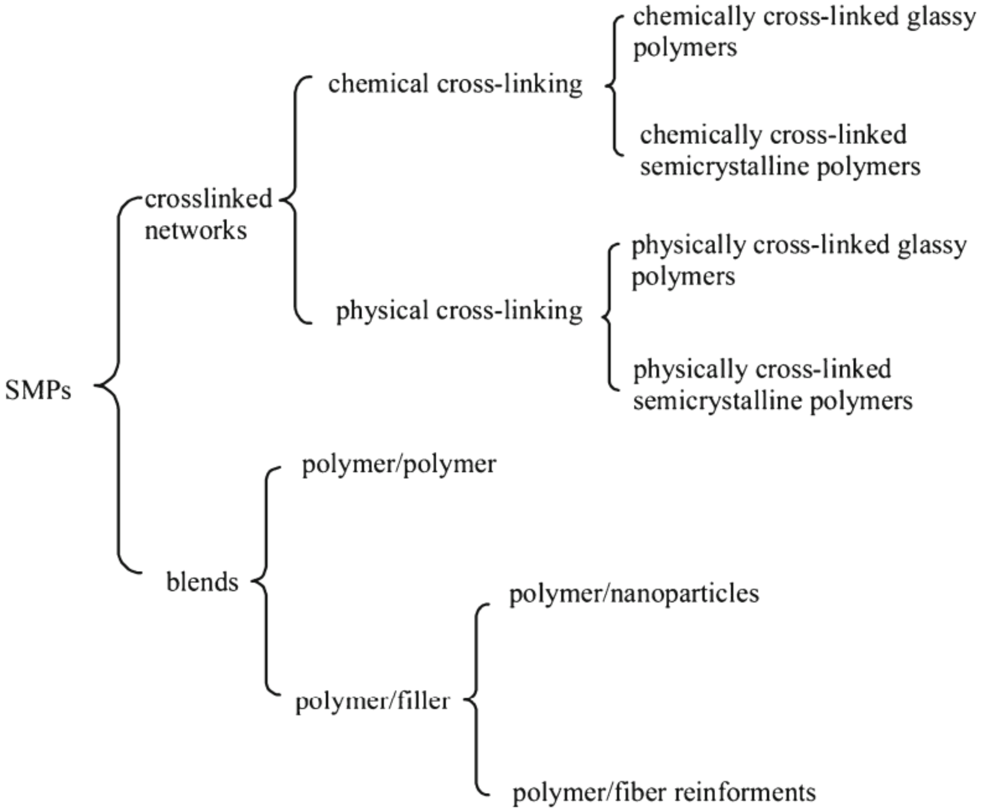

Figure 2.4 Classification for SMP system which consists of crosslinked SMPs and SMP blends (Wang *et al.*, 2014).

On the other hand, the SMP can also be grouped by different switching mechanism which are in thermal phase transition or molecular switches (Xia *et al.*, 2021). For the thermal phase transition, it relies on changes in molecular mobility due to thermal changes whereas the molecular switches work on changes in chemical structure upon stimuli especially for both thermal and non-thermal changes (Zhao *et al.*, 2015). The feasible switching transitions for thermal phase transition include the crystallization or melting transition and the vitrification or glass transition, where exposure to temperatures above these transition points results in less restriction on the molecular mobility of the macromolecules (Meng *et al.*, 2013).

Simultaneously, the reversible covalent bonds, such as disulphide bonds, Diels-Alder reactions, and acylhydrazone bonds, and reversible non-covalent physical bonds, such as multiple hydrogen bonds, metal-ligand coordination, and supramolecular recognition, are involved in the switching transitions of molecular switches as shown in Figure 2.5.

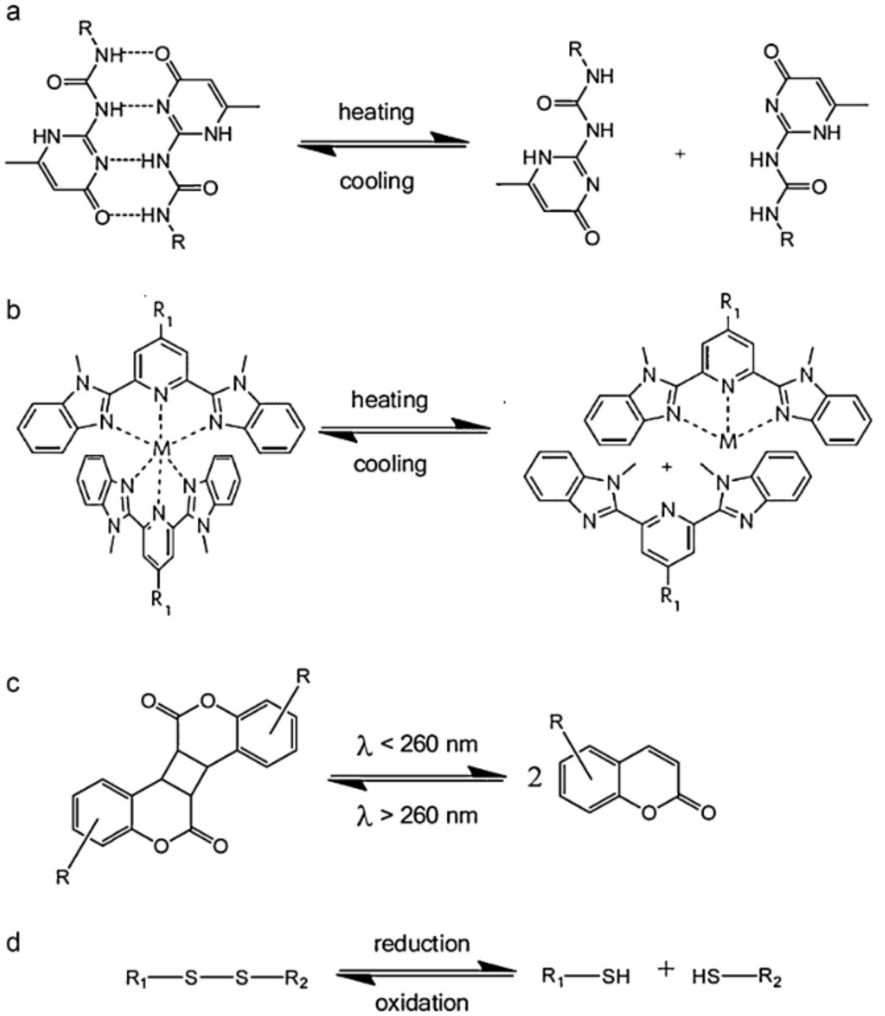

Figure 2.5 Examples of molecular switches: (a) ureidopyrimidinone (UPy) coupling (b) Metal–ligand coordination bonding (c) Coumarin [2 + 2] cycloaddition (d) Disulphide bonding (Zhao *et al.*, 2015).

2.1.2 Structure of Thermally Induced SMPs

As the shape of the polymer changes due to the change in temperature, it is called thermally induced shape memory polymers or thermo-responsive shape memory polymers. The shape memory effect (SME) of thermally induced shape memory polymers can be achieved because of its structure. This type of SMPs consists of two-phase structures which are stationary phase and reversible phase, which are responsible for shape memory properties of these polymers. Firstly, the stationary phase mainly includes cross-linked polymers with partially crystalline winding structure of ultra-high molecular chain that acts as “memory effect” for the initial shape of the polymeric structure. This phase will show the highest thermal transition temperature (T_{perm}) that acts as the physical crosslink in which responsible for its permanent shape. When the stationary phase is heated above its thermal transition temperature, it can be undergoing conventional processing method such as extrusion or injection molding (Ji et al., 2019; Lendlein and Kelch, 2002; Zhang et al., 2015; Zhou and Sheiko, 2016).

Next, the reversible phase is a partial crystalline phase that can have reversible transformation between softening and curing under the change of external stimulus. This phase acts as a molecular switch in which provides the fixation of the temporary shape. In order to fix the switching segments into temporary shape, the glass transition temperature or melting temperature will be used and subsequently, the temporary shape will be fixed by cooling the polymer below the switching temperature. However, the physical cross-links in the switching segments will be separated when the polymer is heated above transition temperature (Ji *et al.*, 2019; Lendlein and Kelch, 2002; Zhang *et al.*, 2015; Zhou and Sheiko, 2016a).

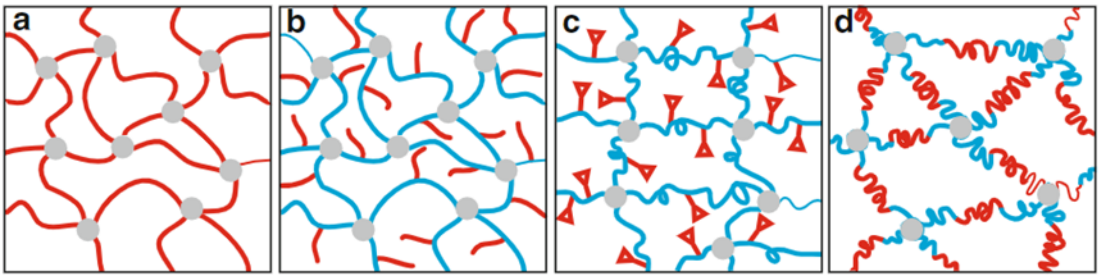

Figure 2.6 Polymer networks for SMP (red: molecular switches, grey: polymer net points): (a) switching segments linking net points, (b) side chains as switching segments, (c) functional groups as switching segments (d) ABA triblock segments linking net points (Behl *et al.*, 2009).

In addition, the SME of thermally induced shape memory polymers can also be determined through the entropic elasticity of the polymer network, which can be generated by a physical cross-linking structure, crystalline phase, chemical cross-linking, or interpenetrating polymer network structure, dictates the driving force for shape recovery in SMPs (Behl *et al.*, 2009). The switching unit is in charge of regulating shape fixity and recovery in response to heat stimuli, which can include crystallization or melting transitions and glass transitions. The cross-links points in the polymer network structure act as the anchors or “permanent entanglements” that can prevent the chains from slipping from each other. Besides the cross-link points, the polymer networks can also contain flexible components which are the amorphous segments. When the temperature is below glass transition temperature, the networks will be elastic. The entropy of elasticity will be shown, and then it can be stretched with a loss of entropy, which results in increasing distance between net points as they become oriented. Nevertheless, the SMPs will return into its original shape as the external force is removed, which causes it to gain back its lost entropy. This will be resulting in maintaining its mechanical stress in equilibrium of the polymer networks (Zhang et al., 2015; Lendlein and Kelch, 2002; Zhou and Sheiko, 2016; Liu et al., 2007).

2.1.3 Mechanism of Thermally Induced SMPs

Generally, the mechanism of SMPs as shown in Figure 2.7 can be determined through the shape programming process. The shape programming process refers to the external and physical manipulation process that can define the shape shifting pathways. This process involves shape deforming, shape fixing and shape recovery, which involves removal of external stress from the polymer. However, the polymer needs to be deformed under external stress by heating before the programming process. The programming process is an independent process for the same materials with numerous possible temporary shapes or pathways that can be done only by changing the programming settings such as deformation force. The programmability of SMPs is a clear distinguishable property of SMPs apart from SCPs (Xia *et al.*, 2021; Zhao *et al.*, 2015; Lei *et al.*, 2019).

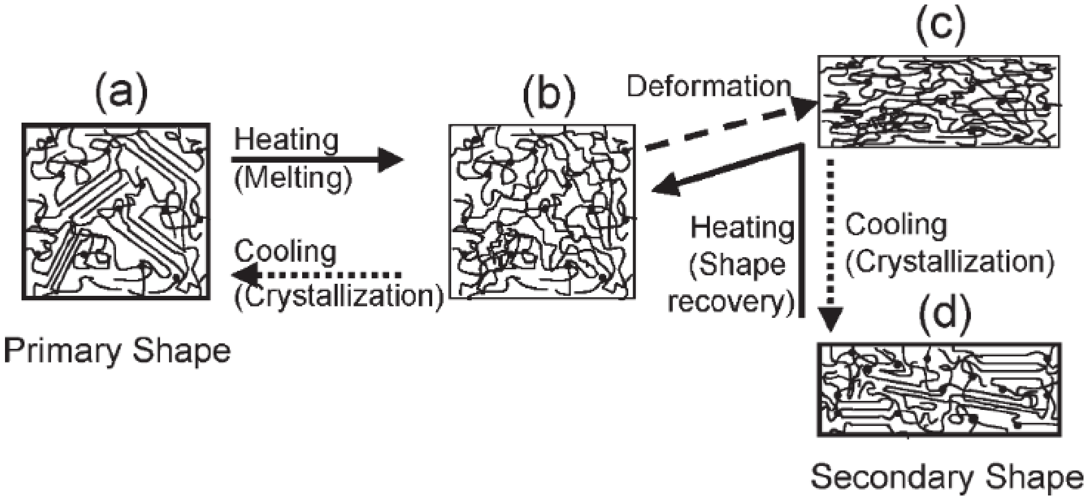

Figure 2.7 Mechanism of shape fixing and shape recovery of semi-crystalline shape memory (Liu *et al.*, 2007).

Firstly, the polymer needs to be heated to its deformation temperature (T_d) above the glass transition temperature (T_g). As the temperature increases, the entropy of the polymer will increase resulting in decreasing the energy barrier and making the molecular chain becomes more mobile in which causes the relaxation time to be gradually decreases. This makes the polymer chains easier to manipulate before it deformed into a desired temporary shape. At T_d, the polymer sample is deformed into desired shape and then, it will be cooled down to a temperature below T_g in order to fix the deformation by increasing the relaxation time.

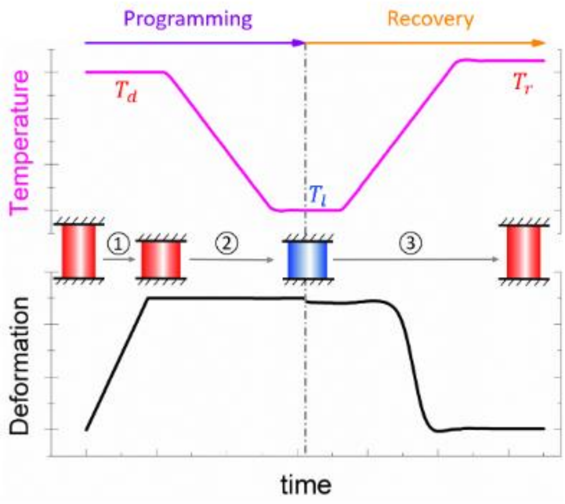

Figure 2.8 Shape memory polymer for thermally induced SMPs (Lei *et al.*, 2019)

As the temperature decreases, the temporary shape is fixed and then maintained by external stress, which includes physical and chemical changes that can avoid the movement of polymer molecular chains. The temporary shape is fixed as long as the material is kept to the temperature below T_g. To recover the permanent shape of the polymer, it can be reheated to the recovery temperature T_r above T_g in which can reduce the relaxation time (Xia *et al.*, 2021; Zhao *et al.*, 2015; Lei *et al.*, 2019).

The shape memory effect (SME) of thermally induced SMPs can be divided into two stages which are shape pre-deformation and recovery stages. In the pre-deformation stage, the shape of SMPs will be changed at relatively higher temperature, and then fixed at relatively lower temperature to achieve the temporary deformed shape. For recovery stage, the SMPs will be exposed into higher temperature at a certain degree, which can cause the temporary deformed shape to be reduced and the original shape of SMP will be recovered. The degree of shape recovery of SMPs can be determined through the shape recovery ratio (Zhang *et al.*, 2015).

Moreover, the characterization of SME for SMPs can be done in several methods developed by researchers. Firstly, the degree of recovery and shape fixity are measured quantitatively by determining some main parameters such as shape recovery ratio (R_r) and shape fixity ratio (R_f) (Zhang *et al.*, 2015). Nevertheless, a more specific measurement of R_r and R_f can be established by using thermo-mechanical analyzer as it can be convenient in measuring multiple cycles that includes results such as recovery stress, etc. (Zhao *et al.*, 2015). Alternatively, there are more simpler ways such as origami folding, twisting and bending methods to measure R_r and R_f in which did not require any usage of machinery (Zhou and Sheiko, 2016).

2.2 SMP Blends

2.2.1 Raw Materials Used in SMPs

2.2.1(a) Polylactic Acid (PLA)

Polylactic acid (PLA) is one of the biodegradable polymeric compounds designated as a polyester, also known as poly-lactate and polylactide. Additionally, PLA is a thermoplastic polymer with a high elasticity modulus, tensile strength, and low elongation at break. In addition, PLA can be produced from widely available renewable resources such as corns, wheats, and potatoes, all of which are plants that produce lactic acid, which will not contribute in any way to carbon gas emissions into the atmosphere. Thus, by using ring-opening polymerization or condensation polymerization of lactic acid, these plants can be transformed into PLA with a high molecular weight. Despite its good properties, PLA also has low impact strength, poor processability due to its vulnerability to hydrolysis and slow crystallization rate. Due to these issues, it can only be utilized in the thermoformed rigid packaging industry. However, when specific end-use performance is required, new grades of PLA will be used for flexible packaging. Therefore, blending method is used to achieve moderate improvement for PLA in terms of compositions, processing, compatibility levels and morphological properties.

In addition, in SMP systems, high molecular PLAs can function as structural domains or net-points due to their physical entanglement and crystallization, which are in charge of the form fixing and shape switching components. In general, shape fixing portions will maintain dimensional stability during deformation and recovery, whereas shape switching portions should consist of long polymeric chains that can store elastic energy for elastic recoiling during stimulus shape recovery (Alias and Ismail, 2019; Xu and Song, 2015; Ge *et al.*, 2012).

2.2.1(b) Ethylene co-vinyl acetate (EVA)

Poly (ethylene vinyl acetate) (EVA) is a type of thermoplastic elastomers that consist of crystalline regions of polyethylene (PE) and amorphous regions of poly (vinyl acetate) (VA). EVA is generally used in various applications such as flexible packaging, footwear, hot melt adhesives and cable sheathing. It has also been considered as one of the highly potential materials for biomedical applications due to its ease of handling, processing and biocompatibility or drug delivery capability (Wang and Deng, 2019).

Next, the physical and mechanical properties of EVA can be influenced by the crystallinity of the copolymer that can be varied due to its different compositions of vinyl acetate (VA) content. The crystalline structures can be formed due to its orderly mannered arrangements of linear polyethylene chains in EVA. Furthermore, the stereoregularity of the polymer chains will reduce as the VA content increases which proceeds in decreasing the crystallinity of PE segments. As the crystallinity of the PE segments decreases, the melting temperature and the storage modulus of EVA will also be reduced. Not only that, EVA commonly shows different microstructural and performance characteristics, which can be obtained from thermoplastics elastomer with crystalline structure to elastomer without crystallites and some EVAs are also expected to possess good memory shape behavior due to the simultaneous presence of crystalline and elastomeric regions (Zhang *et al.*, 2015; Wang and Deng, 2019).

2.2.2 PLA/EVA blend

The shape memory polymer of PLLA/EVA blends system is immiscible where the PLLA phase will exhibit a more apparent switching role compared to dispersed PLLA particles. Zhang et al. (2015) reported that PLLA/EVA samples with 20 wt% of PLLA exhibit sea-island structure as the PLLA is the dispersed phase while EVA is the continuous matrix. With increasing PLLA content up to 40 wt%, the sample still exhibits sea-island structure. On the other hand, as the PLLA content up to 50 wt%, the sample becomes a co-continuous structure. In addition, the presence of PLLA component did not apparently affect the crystalline structure of EVA component, which caused the blends to have the same crystallization temperature even with different compositions (Zhang *et al.*, 2015). Similarly, Siti Najihah and Mohamad (2015) reported about the phase morphology of the PLA/EVA blends where the particle size of EVA at 5 wt% is large and then it decreases as the EVA content increases until 10-15 wt%. The polar group of PLA and EVA may cause high interaction between them as EVA has a greater effect on enhancing the toughness for PLA.

For SMP with PLLA/EVA blends, the EVA phase acts as the “hard” segments while the PLLA phase will act as the reversible switching structure due to its amorphous state. The presence of PLLA components will increase the shape fixity ratio, R_f which denotes its amorphous glass state which can aid in the retention of the pre-deformed shape that becoming more apparent with increasing of PLLA component. This suggests that the immiscible PLLA component can help fixity form at low temperatures (23°C), and then, the time required to achieve the temporary shape will decrease greatly. The researchers also mentioned that the effect on deformation temperature (T_d) and shape fixity ratio (R_f) can be related to the activation of molecular chain mobility of PLLA and EVA (Zhang *et al.*, 2015).