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Molecular weight influence on shape memory effect of shape memory polymer blend (poly(caprolactone)/ styrene-butadiene-styrene)

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Abstract

The shape memory effect (SME) does not only concern the macroscopic structure. It concerns also the polymer structure at morphological, macromolecular, and molecular scales. This effect may depend on different physicochemical properties like morphology heterogeneity, chain rigidity, steric hindrance, chain polarity, free volume, cross-linking or entanglement density, molecular shape and weight, and so on. Hence, finding the relationship between the SME and these properties is very important. This can help to obtain the knowledge about the phenomenon origin and mechanism. One of the basic polymer properties, which can have direct SME, may be the molecular weight (M_w). The question here is: If the M_w of a shape memory polymer (SMP) changes, for different reasons like degradation, what will be the effect of this change on its SME. In order to answer to this question, the investigation is focused on an SMP blend of 40% poly(ϵ-caprolactone) (PCL) and 60% styrene-butadiene-styrene (SBS). Then, enzymatic hydrolysis is performed on this blend to change its M_w. It is shown that this change is only related to the variation in the M_w of PCL. After that, different samples with a distinct average M_w are prepared and characterized by various experimental methods. Shape memory tests are performed on these blends, and the recovery rate (R_r) for each of them is determined. It is found that when M_w of PCL decreases, its degree of crystallinity, its glass transition, and its melting temperatures, corresponding to the PCL phase, increase. However, the elongation at break of the blend declines with the reduction in M_w. The tests show that the alteration in the blend's M_w influences its SME. Indeed, R_r of the (PCL/SBS) mixture drops with the decrease in M_w of PCL.

KEYWORDS

degradation, mechanical properties, stimuli-sensitive polymers, thermal properties, blends

1 | INTRODUCTION

Shape memory polymers (SMPs) constitute a range of smart materials. They have the capacity to deform to a temporary shape and to recover their permanent shape when exposed to a specific stimulus such as temperature.[1,2] This behavior applies to a wide range of SMP applications. For instance, SMPs are essentially used in

the design of biomedical devices, like sutures and microactuators.[3] In addition, these polymers are used in manufacturing self-deployable equipment in spacecraft,[4] smart textiles,[5] heat shrinkable packages, tubing, sensor, and actuators.[6,7]

For thermal trigging, the shape memory effect (SME) is obtained under the application of a specific cycle. This cycle consists of heating, deformation, relaxation, fixing, and recovery.[8]

At the microstructural scale, the SME is caused by the variation in the molecular mobility in the polymer structure. When the SMP is in its permanent shape, when the temperature is low, the chains are stable with a very low molecular motion. At high temperatures, the mobility of chains increases. Then, by applying an external force, the arrangement of these chains varies, leading to a decrease in the entropic state of the polymer, followed by a change in its shape. By cooling down the material, this entropic state is blocked, which allows the fixation (or freezing) of a temporary form. Now, if the SMP is reheated, the mobility of chains is activated again, leading to the increase in the entropy of the SMP. As a result, the SMP returns to its original form.[7] The ability of a thermosensitive SMP to change from a permanent shape to a temporary one and vice-versa could be explained by the presence of two different phases: hard and soft, with different mechanical properties. The hard segments represent the regions with high intermolecular adhesion and ensure the shape stability, hence maintaining the original form. However, the soft segments represent the switch, thus ensuring the shape change.[7]

For a shape memory blend, two immiscible polymers, one representing the hard phase and another representing the soft one, can be mixed to form a new polymer with SME.[9,10] For example, poly(ϵ-caprolactone) (PCL), which is a semicrystalline biodegradable aliphatic polyester, can be blended with styrene-butadiene-styrene (SBS) to form a new polymer with an SME. In this case, PCL represents the hard segments and SBS represents the soft ones.

Recent research[8,11] on SMPs has shown that the SME might be related to the irreversible microstructure alterations. Accordingly, even the SMP retains its SME, it will lose its initial properties, depending on its microstructure. In fact, the SME is one of the properties of SMPs which may be related to some other properties like the heterogeneity of the polymer morphology, viscoelasticity, degree of physical and chemical cross-linking, free volume fraction, and so on. In macromolecular and molecular scales, it depends on the chain structure, the molecular weight (M_w), the chain rigidity and the chain polarity, etc. It is then very important to find these properties and to investigate on this relationship. This investigation can help to find the origin of the SME and to understand its mechanism.

Between different polymer properties, the role of the M_w is very specific because many other properties depend on it. The question is what will be the relationship between this parameter and the SME?

Several studies on SMPs[12–14] have revealed that the variation in the M_w influences their mechanical and viscoelastic properties, and hence their shape memory properties, particularly in recovery and fixing steps. For example, Retna and Karger-Kocsis[6] verified that a better SME was obtained for thermoplastic shape memory polyurethane with a percentage of hard segments between 35% and 40%.

For a PCL/SBS blend, under study, some samples with different molecular weights have been prepared with accelerated enzymatic hydrolysis, which represents the principal degradation mechanism of aliphatic polyesters such as PCL which is a biodegradable polymer.[15] The enzymatic hydrolysis of PCL starts with a water absorption step followed by the hydrolytic fractionation of the ester bonds. This leads to molecular fragmentation and chain splitting. As a result, the M_w of PCL drops due to this enzymatic hydrolysis.[15–19] Different tests have been performed on these samples. It has been shown that the hydrolytic degradation of PCL generates the alteration of its transition and melting temperatures and of its crystallinity degree (X_c).[20–22] This degradation causes also the alteration of its mechanical properties such as the Young modulus, the tensile strength, and the strain at break.[20,23-25] It has been also demonstrated that the change in the M_w can modify the SME of this blend. Based on these results, the relationship between the SME and the M_w has been discussed.

2 | MATERIALS AND METHODS

A blend of (40%) PCL and (60%) SBS is studied. By preliminary studies, it is shown that this mixture with this proportion between the components has a 100% SME.

PCL used for this study is CAPA 6800 PCL and is supplied by Perstrop Limited UK. This polymer is a semicrystalline biodegradable thermoplastic with a glass transition temperature of −40°C and $X_c$of nearly 50%. It has a relatively low melting point between 58°C and 61°C. The SBS, provided by Sinopec Group, is an amorphous block copolymer whose chain is formed by butadiene groups in the middle and styrene groups in both sides. SBS is an elastomer with a glass transition temperature of −80°C. Forty percent of PCL and sixty percent of SBS are initially extruded through a twin-screw extruder machine (Brabender, Duidburg Germany). For

mechanical and shape memory tests, the extruded pellets are introduced into an injection machine to get final specimens with a gauge size of $25 \times 4 \times 2$ mm^3.

To determine the average M_w and to characterize the molecular weight distribution (MWD) of polymer chains, gel permeation chromatography (GPC) is carried out using a Waters GPC machine. GPC can measure a wide range of molecular weights including the number average molecular weight (M_n), the M_w, and the polydispersity index (I).[26,27] For this study, we use tetrahydrofuran (THF) since PCL can easily be diluted in THF. GPC is a relative method that requires calibration using the M_w curve of a standard polymer. Therefore, polystyrene, with known molecular weights, is used as the standard.

In order to measure the crystallization and the melting temperatures (T_c and T_m), differential scanning calorimetry (DSC) tests are performed using a DSC machine, Q1000 V9.0 Build 275TA Instruments, at a constant ramp of 5°C/min. T_c, T_m, ΔH_c, and ΔH_m are determined from the first heating / cooling and the second heating curves. Parameter X_c presents the degree of crystallinity and it is given by the following equation:

$$X_c = \frac{\Delta H_m}{\Delta H_{m0}} \times 100, \quad (1)$$

where ΔH_m is the melting enthalpy from DSC tests, and ΔH_{m0} is the enthalpy of pure crystalline (100%) PCL which has the value of 142 j/g.[28]

Dynamical mechanical analysis (DMA) experiments are carried out, using a DMA Q800 TA Instruments type machine, to investigate the glass transition temperature (T_α) of the blend. All DMA tests are performed with a temperature range between −100°C and 100°C, a heating ramp of 5°C/min, and a frequency of 1 Hz.

The mechanical properties of the blend are evaluated via uniaxial tensile tests using an Instron testing 5566-type machine with a load cell of 10 KN. The tests are performed at room temperature with a deformation rate of 6 mm/min. This tensile machine is equipped with a camera to measure the deformation of the sample. The stress as a function of the strain is then recorded.

To investigate the SME of the blend (40% PCL/60% SBS), shape memory tests has been performed. A typical shape memory cycle consists of the following steps: (a) heating the sample until 50°C; (b) extending to a certain strain; (c) fixing the shape at this deformation by cooling down the sample from 50°C to the room temperature; (d) unloading the sample to zero stress and then recording the strain; and (e) recovery test, which means heating up again the unloaded sample to a temperature of 58°C and then recording the strain (recovery test).

In order to have different samples with various molecular weights, enzymatic hydrolysis is carried out on this blend. For that, the samples of the PCL/SBS blend are immersed in a solution of distilled water, phosphate buffered saline (PBS) and amano lipase from pseudomonas fluorescence (2.5 μg/mL). To preserve the enzyme activity, the solution is changed twice a week. The pseudomonas enzyme and PBS are provided by Sigma Alderich. At specific periods of time, specimens are removed and dried under vacuum.

3 | RESULTS AND DISCUSSIONS

3.1 | Materials characterization before hydrolysis

GPC tests are carried out to evaluate the M_w, using THF as a solvent. Knowing that only PCL can be dissolved in THF, GPC then will give the MWD diagram (Figure 1) to determine M_n, M_w, and I of PCL in the blend using the following equations (Table 1):

$$M_n = \frac{\sum N_i M_i}{\sum N_i}, \quad (2)$$

$$M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}, \quad (3)$$

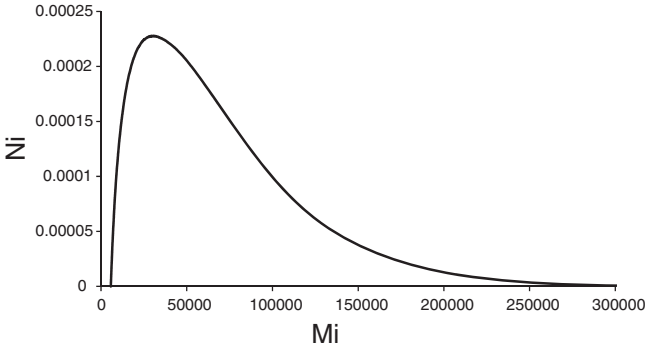

FIGURE 1 MWD curve of PCL. MWD, molecular weight distribution; PCL, poly(ϵ-caprolactone)

TABLE 1 M_w and I of PCL in SBS/PCL blend

Material	M_w [g/Mol]	M_n [g/Mol]	I
SBS (60%) / PCL (40%)	71,220	41,970	1.69

Abbreviations: PCL, poly(ϵ-caprolactone); SBS, styrene-butadiene-styrene.

$$I = \frac{M_W}{M_n}, \tag{4}$$

where N_i is the number of macromolecules, and M_i is the M_w.

According to GPC results, PCL has M_w of 71,220 g/mol and M_n of 41,970 g/mol. M_n is associated to the colligative characteristics of materials. M_w is associated to the bulk and physical properties of materials. When we refer to $M_w$in terms of polymer, we actually refer to the length of individual chains. PCL used in this study has a relatively high M_w, which is associated to longer chains and higher degrees of entanglement.[29] The M_w to M_n ratio determines I which represents the width of the distribution of the molecular range. For PCL, I is equal to 1.69. This outcome means that PCL has a medium width distribution as its I is between 1.2 and 2.

Practically, the average molecular weights (M_w and M_n) and the molecular distribution have a significant impact on the polymer viscoelastic and physical-mechanical properties like toughness, elasticity, and transition temperature. The mechanical properties of polymers (modulus of elasticity, resistance, and maximum deformation) are influenced by the MWD, by the weight average M_w and by the polydispersity index. Different researchers and research teams have demonstrated this impact. For example, Shinozaki et al.,[30] reported that the tensile strength and Young's modulus increase with M_w for poly(vinyl chloride) (PVC). In another study on polyethylene, G. Capaccio et al.,[31] showed that the elastic modulus rises with the increase of the polydispersity.

At the microstructure scale, the relationship between the M_w and the mechanical properties can be shown by the following formula[32]:

$$G_c = RT\rho/M_E \tag{5}$$

with G_c = shear modulus, M_E = molecular weight between entanglement, T = absolute temperature, ρ = density.

Concerning the viscoelasticity of polymers, the effect of M_w on the viscosity is also very important. This relation is given by a power law of type:

$$\eta = K.M^a \tag{6}$$

with h = viscosity, M = weight average M_w and K and a = constants.

DSC experiments are carried out in a temperature range between room temperature and 70°C, according to the procedure explained before determining the thermal properties of the materials. The results are presented in Figure 2.

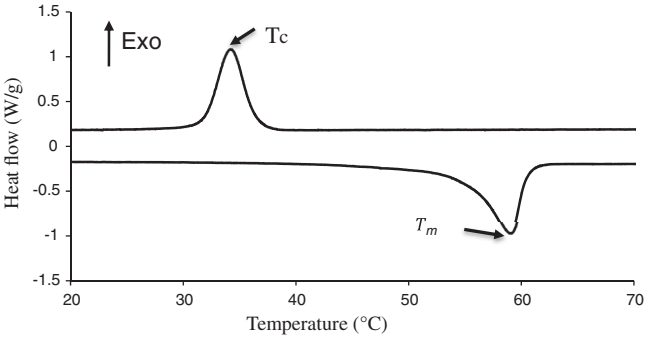

FIGURE 2 DSC curve of blend. DSC, differential scanning calorimetry

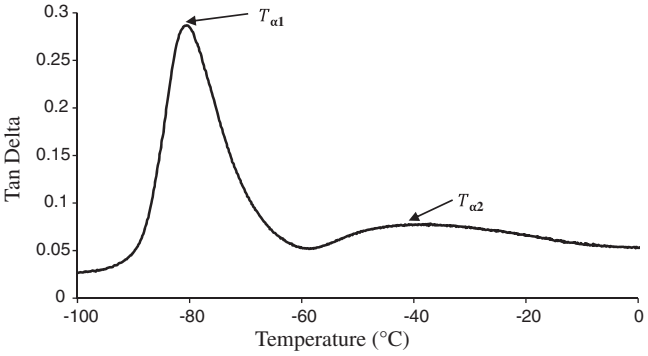

FIGURE 3 DMA results of blend. DMA, dynamical mechanical analysis

According to these results, during heating, the peak presented at 59°C corresponds to the melting point T_m of PCL and during cooling; the peak at 34 represents its crystallization temperature T_c. Actually, X_c of the blend is calculated from Equation (1) and is almost 51.4%. It is important to mention that as SBS is an amorphous elastomer, it does not dispose of crystallization or melting temperatures. Also, the ratio of SBS in the blend is not considered in calculation of the blend X_c. Thus, T_c, T_m, and X_c of the blend are only related to the PCL phase.[33]

Then, DMA tests are performed on a virgin blend. Figure 3 illustrates tanδ versus temperature of the blend. The peak on this curve gives directly the value of T_α which correspondas to the glass transition temperature of polymers in the blend.

According to Figure 3, the (PCL/SBS) blend shows two distinct peaks corresponding to two various glass transition temperatures T_α: The first one appears at −80.7°C ($T_{\alpha 1}$) which corresponds to the glass transition temperature of SBS, and the second one at −39.7°C ($T_{\alpha 2}$) which corresponds to PCL. The existence of these two separate T_α evinces that the two polymers forming the blend are immiscible.[33] These outcomes are in harmony with the work of Zhang et al.[9] who demonstrated that

PCL and SBS constituted an immiscible blend that displayed two separate glass transition temperatures (T_α), noting that SBS represents the soft segments of the blend and PCL its hard segments.

The samples are submitted to tensile tests at room temperature with a deformation rate of 6 mm/min. The results are depicted in Figure 4 and Table 2.

According to these results (Figure 4 and Table 2), the blend displays a young modulus of 116 ± 3.5 MPa, and a fracture stress of 7 ± 0.5 MPa. Its tensile curve until fracture shows two different regions of deformation: The first one consists of an elastic zone (6%–8% of deformation) and the second one consists of a plastic zone (> 10% of deformation). The blend has a strain at break of 292 ± 9%. We notice that the (PCL/SBS) blend displays a ductile character since it can undergo a significant plastic deformation before rupture.[33] The high value of deformation at break and the relatively high ductility of the blend indicate that PCL and SBS are compatible in the blend. Concerning compatibility, Massardier et al.[34] reported that for the polyamide 6 (PA6) / acrylonitrile butadiene styrene (ABS) mixture, a good compatibility between the blend components would enhance its mechanical properties. They highlighted that when the compatibility of the mixture increased, the young modulus was improved and the elongation to fracture rose. This compatibility can be explained as follows:

- Although the results of DMA, PCL, and SBS are not 100% immiscible, we can suppose that it forms two phases but with a good adhesion between them at the interface thanks to a partial miscibility.
- Since the amount of PCL is high (40%), it does not form a dispersed and discontinuous phase in the SBS matrix (60%). Indeed, the two polymers constitute two continuous phases in the blend.

Shape memory tests are realized following the typical shape memory cycle: deformation (at $T > T_\alpha$), fixing (at $T = T_{room}$), and recovery (at $T > T_\alpha$).

In the first step, the tests are performed at different levels of deformation: 25%, 50%, and 100% at 40°C.

In the second step, the sample is fixed at these rates of deformation by cooling until room temperature.

During the recovery step (Figure 5), the sample is heated at 58°C, the length of the sample decreases; and due to the SME, the sample recovers its original shape.

This step is evaluated by a parameter called the recovery rate (R_r). This parameter represents the capacity of the blend to recover its initial shape, and is determined according to the following equation:

$$R_r = \frac{L_u - L_f}{L_u - L_i} \times 100, \quad (7)$$

where L_i is the initial sample length, L_u is the length after a tensile test without stress (jaws are released), and L_f is the length after recovery.

According to Figure 5, it can be notice that for all cases the blend shows a total SME; and regardless of the deformation rate, it recovers 100% of its initial shape.

In fact, when the sample is extended to a 25%, 50%, or 100% strain at 50°C (heating + deformation steps), residual stresses are introduced in the blend structure. During

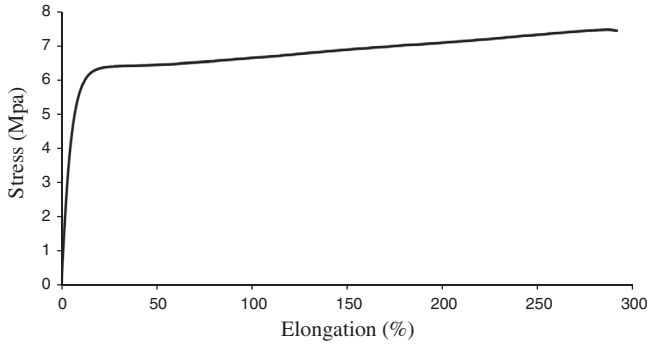

FIGURE 4 Tensile curve of blend

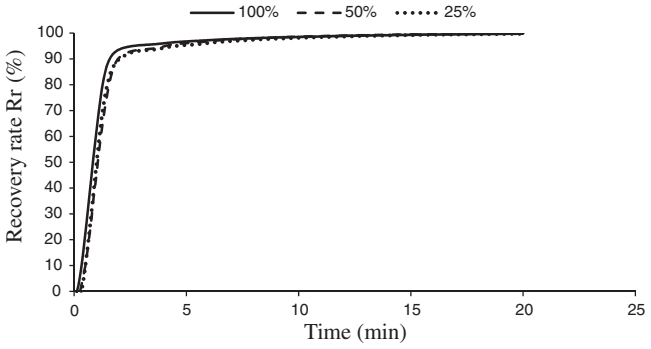

FIGURE 5 Recovery test at $T = 58°C$, for varied deformation

TABLE 2 Properties of SMP blend (40% PCL / 60% SBS)

$M_{w\,1}$ (PCL) [g/Mol]	$M_{n\,1}$ (PCL) [g/Mol]	X_c [%]	$T_{\alpha 1}$ [°C]	$T_{\alpha 2}$ [°C]	T_c [°C]	T_m [°C]	E [MPa]	ε_r [%]	R_r [%]
71,223	42,144	51.4	−80.7	−39.7	34.1	58.9	116 ± 3.5	292 ± 9.0	100

Abbreviations: PCL, poly(ϵ-caprolactone); SBS, styrene-butadiene-styrene; SMP, shape memory polymer.

Hydrolysis time [days]	M_w (PCL) [g/Mol]	M_n (PCL) [g/Mol]	I
0	$M_{w\,1} = 71{,}220$	$M_{n\,1} = 42{,}144$	1.69
7	$M_{w\,2} = 68{,}760$	$M_{n\,2} = 39{,}291$	1.75
15	$M_{w\,3} = 66{,}480$	$M_{n\,3} = 34{,}093$	1.95
21	$M_{w\,4} = 647{,}340$	$M_{n\,4} = 35{,}767$	1.81
25	$M_{w\,5} = 62{,}800$	$M_{n\,5} = 31{,}879$	1.97

TABLE 3 M_w and M_n values depending on hydrolysis time

Abbreviation: PCL, poly(ϵ-caprolactone).

fixing, the material is cooled down and these stresses are stored in the SMP structure. Next, at the recovery step, when the sample is heated again, these internal stresses are released and the material recovers its initial shape due to its shape memory property. As the temperature increases, the chains become more flexible and their mobility grows, which facilitates shape recovery. For this SMP blend, PCL, which represents the hard segments, ensures shape stability, and SBS, which represents the soft segments, ensures shape changes.

The SME can be explained by the variation in the molecular mobility inside the polymer. Indeed, while the SMP is in its permanent shape, the chains are in a stable thermodynamic state. However, at a high temperature, the chains become more flexible; and by applying an external stress, the chains arrangement varies and causes a reduction in the entropic state of the polymer followed by a change in its form. By cooling down the material, this entropic state is blocked and allows the fixation of the temporary shape. Finally, by heating again the SMP blend, the mobility of the chains is reactivated, and the polymer regains its initial shape.[35]

To evaluate M_w and MWD of the PCL and to determine the influence of these properties on the viscoelastic and physical-mechanical properties of the blend, GPC, DSC, DMA, and tensile experiments are performed according to the procedure explained before. These experiments are followed by shape memory tests in order to examine the SME of the blend. All results are recapitulated in Table 2. The existence of two separate glass transition temperatures,$T_{\alpha 1}$ corresponding to the SBS phase and $T_{\alpha 2}$ corresponding to the PCL phase, confirms the immiscible or weak partial immiscible character of polymers in the blend. This immiscibility can be explained also by high X_c of the blend. The results of tensile tests indicate that the blend displays a ductile character. Usually, a high M_w means an elevated degree of entanglement in the amorphous phase.[36] These entanglements permit the polymer to be stretched more before the rupture of chains. This could be explained by the fact that a raised degree of entanglement implies that there are more polymer bonds that need to be broken, which allows the polymer to absorb more energy before fracture.

In addition, DSC experiments reveal that T_c and T_m of the blend corresponds to the PCL phase, which confirms the mixture compatibility. This compatibility can explain the good recovery of the permanent shape. Furthermore, according to Table 3, PCL used in the blend has a relatively high molecular weight ($M_w \simeq 71\ Kg/mol$). Generally, this parameter is related to longer chains of hard segments and the existence of intermolecular hydrogen bonds.[36] This provides more stability of physical crosslinks, leading to high R_r. Shape memory tests confirm this outcome as the (SBS/PCL) blend under study has a recovery rate of 100%. Moreover, longer chains are more flexible and their deformation is easier at $T > T_{\alpha 2}$. As a result, the SMP exhibits a better SME.

3.2 | Change in PCL M_w by enzymatic hydrolysis

In order to change the M_w of PCL and to get blend samples with varied M_w of PCL, enzymatic hydrolysis[33] is performed according to the protocol described in the previous section. Multiple samples, aged at different time, are obtained in this way. Virgin and aged samples are then tested by GPC according the procedure explained above. Figure 6 outlines the MWD curves of PCL before and after 25 days of hydrolysis, and Table 3 shows the values of M_w, M_n, and I obtained by GPC tests.

According to these results, one can notice an enlargement of the PCL MWD, which means the increase in I and the decrease in M_w during hydrolysis. M_w passes from 71,220 to 66,480 g/mol after 15 days. After 25 days of hydrolysis, it has the value of 62,800 g/mol. At the same time, I rises from 1.69 to 1.97 at the end of hydrolytic degradation. This polydispersity growth is associated to an enlargement of the MWD curves of PCL. The decrease in M_w could be explained by the scission of

chains due to hydrolysis, as M_w gives an indication of the length of chains. In fact, enzymatic hydrolysis starts with hydrolytic fractionation of ester bonds, which induces a molecular fragmentation. This chain splitting leads to the decline in entanglement density within the PCL structure. The reduction in chain entanglement may have a consequence on the mechanical properties of polymers. Tsuji and Ishizaka[37] realized the enzymatic hydrolysis of pure PCL and PCL/PLLA (Poly-L-Lactide) mixture using a lipase from *Rhizopus arrhizus*. They noted that the hydrolysis of pure PCL was more significant than that of the PCL/PLLA mixture. They also reported that the MWD of PCL is slightly widened and its M_w decreases after 15 days of enzymatic hydrolysis.

3.3 | Effect of molecular weight on blend properties and on its SME

3.3.1 | Effect of molecular weight on some blend properties

Different blend samples with different M_w are submitted to various experiments. DSC, DMA, and tensile tests are performed, following the same protocols described in section 2.

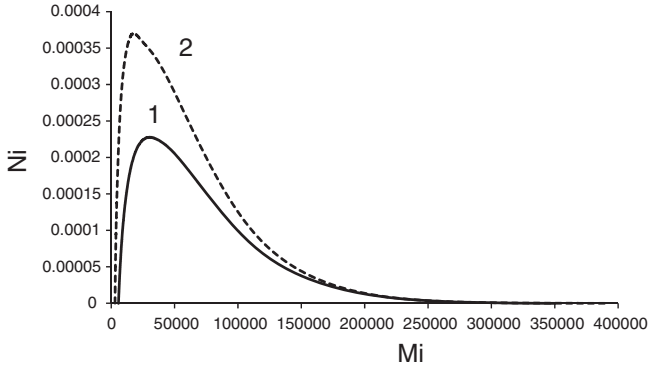

FIGURE 6 MWD curve of PCL: Before hydrolysis (1) and after 25 days (2). MWD, molecular weight distribution; PCL, poly (ϵ-caprolactone)

Table 4 summarize the evolution of the blend's physical and mechanical properties depending on M_w of PCL.

From these results, we can have the following comments:

- The glass transition temperature of SBS remains relatively constant; that is, SBS is not affected by enzymatic aging. Only PCL is hydrolyzed, and its glass transition temperature ($T_{\alpha 2}$) changes from −39.7°C to 33.1°C. As a result, the gap between the two transition temperatures goes up and consequently the heterogeneity of blend constituents rises.
- The relationship between the M_w and the glass transition temperature may be given by the Fox Flory equation:

$$T_\alpha = T_{\alpha\infty} - \frac{K_{ff}}{M_n} \tag{8}$$

Figure 7 shows the variation in T_α versus $1/M_n$. With a correlation coefficient far from 1 ($R^2 = 0.91$), it is difficult to say that this variation follows a straight line. The deviation of this variation from the Fox Flory equation may be explained by the presence of SBS in the structure

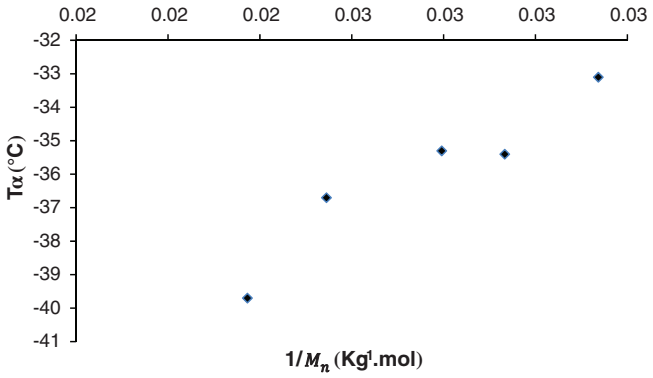

FIGURE 7 Variation in T_α versus $1/M_n$ [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 4 Dependence of blend properties on M_w

M_w [g/Mol]	M_n [g/Mol]	$T_{\alpha 1}$ [°C]	$T_{\alpha 2}$ [°C]	T_m [°C]	T_c [°C]	X_c [%]	ε_r [%]	E [MPa]
$M_{w\,1} = 71{,}220$	$M_{n\,1} = 42{,}144$	−80.7	−39.7	58.9	34.1	51.4	292 ± 9.0	116 ± 3.5
$M_{w\,2} = 68{,}760$	$M_{n\,2} = 39{,}291$	−81.8	−36.7	59.0	35.7	61.0	294 ± 9.0	144 ± 4.5
$M_{w\,3} = 66{,}480$	$M_{n\,3} = 34{,}093$	−79.7	−35.4	59.2	35.9	66.1	123 ± 4.0	141 ± 4.5
$M_{w\,4} = 64{,}740$	$M_{n\,4} = 35{,}767$	−80.5	−35.3	59.4	36.0	67.7	75 ± 2.5	219 ± 7.0
$M_{w\,5} = 62{,}800$	$M_{n\,5} = 31{,}879$	−79.9	−33.1	59.6	36.1	69.7	61 ± 2.0	187 ± 6.0

of the blend and the effect of its amorphous morphology on PCL.

- It is seen that T_m is almost the same for all samples with different molecular weights, and the change in T_c is negligible, but the variation in X_c is relatively important. According to Table 4, X_c of the blend increases with the decrease in M_n of PCL. For instance, X_c passes from 51.4% to 69.7% when M_w of PCL falls from 71,220 g/mol to 64,740 g/mol. Indeed, lower M_w means shorter PCL chains. The latter display more end groups that rise molecular mobility. Consequently, increasing chain mobility facilitates reorientation and recrystallization. Also, the growth of T_{α}, as explained before, could be associated to the rise in X_c and the improvement of the cohesion forces in the structure. The buildup of intermolecular interactions, which depict the cohesive forces between materials chains, could be explained by the development of crystallinity. In fact, the increase in crystallinity engenders the reinforcing cohesion of the polymer.
- The growth of X_c engenders the decline in the blend phase's compatibility. Moreover, we remark that the strain at break ε_r of the mixture drops with the decrease in the M_w ratio of PCL. For example, ε_r goes down from 292%, for PCL M_w equal to 71,220 g/mol, to 61%, for PCL M_w equal to 62,800 g/mol. The drop of PCL M_w causes the reduction in the ductility of the blend. This embrittlement can be explained by the fact that when M_w falls, the degree of chain entanglement decreases too. An elevated degree of entanglement means that there are more bonds that need to be broken, which permits the polymer to absorb more energy before rupture. This outcome is in coherence with the work of B. Fayolle et al.[29] reported that for an amorphous or semicrystalline polymer, the embrittlement of the structure is related to the decline in the M_w under a critical one due to the reduction in the degree of entanglement. Moreover, the decrease in the elongation to fracture of the blend could be explained by the narrowing of interlamellar spacing due to the elevation of X_c.[38] Furthermore, results show two different zones, connected by a transition zone. For the sample with high M_w (>70 Kg/mol), the samples are significantly ductile. But for the low M_w (<65 Kg/mol), the samples become less ductile (brittle). There is a ductile-brittle transition zone between these two zones.
- Table 4 presents also the values of the Young modulus, E of the samples under study. By decreasing M_w from 71,220 to 62,800 g/mol, we can see the increase in E from 116 MPa to 187–219 MPa. The growth of the rigidity of the polymer is essentially caused by the rise in X_c. Generally, the amorphous phase is less compact, less rigid, and less impermeable than the crystalline phase. In contact with water, the amorphous phase undergoes degradation (hydrolysis) because water can diffuse into this phase more easily. Due to this degradation, the molar mass decreases. This reduction in the molar mass leads to the increase in chain mobility and promotes the formation of more crystalline zones. It engenders also the increase in the rate of crystallinity. The rise in the elastic modulus E is essentially due to this increase in crystallinity. On the other hand, it can be noted that the strain at break decreases with the decline in the molar mass. The conclusion pinched from this is that as the M_w decreases, X_c rises, leading to an increase in stiffness and tensile strength.[39] Our outcome is in accordance with the study of Margolies[40] who indicated that that stiffness was a function of the crystallinity degree. While M_w of polyethylene decreases, X_c and hence stiffness increases. Stiffness continues to rise with the decrease in M_w or the increase in crystallinity.

3.3.2 | Molecular weight and SME alteration

To investigate the effect of the decrease in the M_w on the shape memory property of the SMP blend (SBS/PCL), shape memory tests are carried out on the blend with different M_w PCL samples. All tests are performed while respecting the following steps: heating until 50°C, 25% of deformation, fixing the sample, and recovery at 58°C. Figure 8 presents the R_r curves for varied M_w.

According to Figure 8, the reaction of the blend to thermal heating during the recovery step differs with variable M_w. R_r decreases when M_w of PCL drops. Table 5 denotes the R_r evolution depending on M_w.

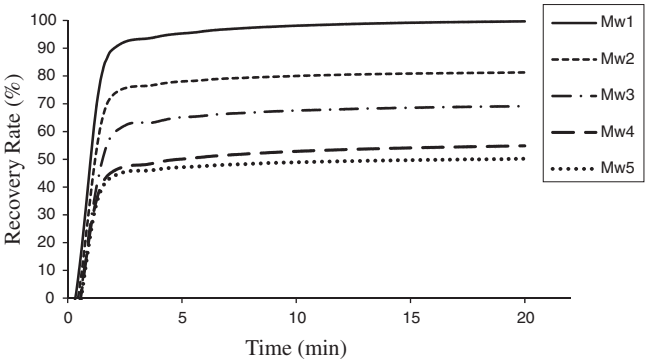

FIGURE 8 R_r curves for different molecular weights

TABLE 5 R_r depending on M_w

M_w [g/Mol]	R_r [%]
$M_{w\,1} = 71{,}220$	$R_{r\,1} = 100$
$M_{w2} = 68{,}760$	$R_{r\,2} = 81$
$M_{w\,3} = 66{,}480$	$R_{r\,3} = 69$
$M_{w\,4} = 64{,}740$	$R_{r\,4} = 55$
$M_{w\,5} = 62{,}800$	$R_{r\,5} = 50$

The results indicate that R_r decreases with decreasing M_w. It means that the initial 100% SMP becomes a partial SMP.[41] It passes from 100%, for PCL M_w of 71,220 g/mol, to 69%, for M_w of 66,481 g/mol. For M_w equal to 62,800 g/mol, R_r is equal to 50%. When the M_w of PCL passes from 71,220 g/mol to 62,802 g/mol, the (PCL/SBS) blend with a total SME (TSME) becomes a blend with a partial SME (PSME). The alteration of R_r, due to the drop of PCL M_w, can be explained by various phenomena.

At first, higher M_w is characterized by longer chains of hard segments and more intermolecular hydrogen bonds, which increases the stability of PCL physical cross linking. Additionally, when M_w is higher, the chains are longer and more flexible, so they can easily be deformed. Therefore, under thermal trigging, the mixture recovers more of its permanent shape. Xu et al.[42] studied a SMP based on polyethylene glycol (PEG), as soft segment, and diisocyanate, as hard segments. These hard segments are synthesized using the diisocyanate of biphenyl and the isophorone diisocyanate (IPDI). They stated that the elevation of the molar ratio r, of the diisocyanate of biphenyl versus IPDI in the hard phase, induces the augmentation of R_r and owing to the amelioration of interaction in the polymer structure. As a result, the SME is enhanced.

We showed that X_c of the mixture goes up while the M_w of PCL drops. This rising of the crystallinity provokes the reduction of the compatibility between the blend's phases. As a result, R_r goes down due to the lower compatibility between hard and soft segments. Lee and al.[43] reported that the crystallinity of polyols would influence the separation between hard and soft segments. Indeed, higher crystallinity engenders lower compatibility between mixture segments.

Furthermore, we reveal that $T_{\alpha 1}$, corresponding to the PCL phase, increases when PCL M_w decreases. However, $T_{\alpha 1}$, corresponding to the SBS phase, remains nearly constant. As a result, the gap between the two transition temperatures rises, hence the immiscibility and heterogeneity of the blend's component growth. Subsequently, the recovery of the SMP blend declines.

Moreover, the decrease in the blend's recovery can be associated to the morphological change in the structure, since the diminution of M_w engenders the drop of the entanglement density and the reduction in the free volume.[36] The effect of the degree of entanglement in the recovery of the SMP blend will be treated in future work.

In addition, the reduction in R_r can be associated to the augmentation of the hard phase rigidity. In fact, we remark that the Young modulus E increases with the decline of PCL M_w. This outcome means that the rigidity of the blend's hard segments rises. Since PCL is the only influenced by enzymatic hydrolysis, E related to the soft segments (SBS) remains the same. However, the SME is related to the presence of two separate phases, hard and soft, with different mechanical properties. It is important to have a compromise between the contributions of these two phases in order to have a better SME. For example, the study of[9] reported that when the rate of PCL in the blend changed, R_r changed as well. The best $R_r$was obtained for a PCL proportion between 30% and 50%. Also, according to our tests, we reveal that a rate of 40% PCL and 60% SBS gives 100% of recovery. These results mean that specific quantities of hard segments (PCL) and soft segments (SBS) should be produced to have maximal R_r. For our case, a certain and a specific rigidity of two phases should be present to have a better SME .Thus, the decline in the SME could be explained by the loss of the rigidity of hard segments, while the SBS segments remain constant. The specific influence of the Young modulus on the recovery of the SMP blend will be examined in future work.

The SME, which represents the capacity of the SMP blend to change from a permanent shape to a temporary one and vice-versa, depends on the microstructural properties of the blend components. Indeed, the drop of M_w of PCL engenders the alteration of the morphology, physico-chemical and mechanical properties of the (SBS/PCL) mixture. These changes remain: a reduction in chain lengths, a decrease in entanglement density, an increase in X_c, a drop of elongation to break, and a rise in both glass transition and melting temperatures. It is obvious that various SMPs such as (SBS/PCL) blends, with different properties, are produced. Then, via shape memory tests, it is shown that these blends have different SMEs, since R_r changes. When M_w passes from 71,220 to 62,802 g/mol, R_r is reduced from 100% to 50%. Thus, the blend is transformed from a TSME material to a PSME one. It is worth mentioning that the PSME represents an intermediate behavior between SMPs and polymers without an SME. This concept is crucial because it helps to create various SMPs in order to meet distinct and specific industrial uses. In any case, the evolution of the SME is very attractive for industry.

4 | CONCLUSION

In this paper, the influence of M_w alteration on the SME of a blend consisting of 40% PCL and 60% SBS is investigated. M_w of PCL is equal to 71,220 g/mol and its polydispersity index is equal to 1.69. It has been shown that the polymers forming the mixture are immiscible. DSC and tensile tests confirm the compatibility of the blend. In addition, this mixture displays a ductile character. Then, shape memory tests are performed. It has been revealed that, for these properties, the (40% PCL/60% SBS) blend has a TSME, as it recovers 100% of its permanent shape under thermal trigging. Afterwards, enzymatic hydrolysis is used as a proceeding to vary the M_w of PCL. M_w of PCL decreases with hydrolysis time. The diminution of the PCL M_w engenders the reduction in chain lengths, the decrease in the entanglement density, the increase in X_c, the drop of the elongation to break and the rise of both glass transition and melting temperatures. Subsequently, SM tests are carried out on blends with different values of PCL M_w, hence the different physico-chemical properties. It has been shown that the SME of the SMP mixture decreases, since R_r goes down, when M_w of PCL drops. This result could be associated to the shortening of chains, the drop of the entanglement degree, the embrittlement of the structure, and the decline in the compatibility and homogeneity of the blend components. We have reported that the SME does not only concern macroscopic changes but it results from a combination of the polymer M_w and its internal properties. We have also revealed that by varying the M_w of one of the SMP blend components, a range of new blends with different SMEs are created. The (SBS/PCL) mixture is transformed from a TSME polymer into a PSME one. The establishment of a relationship between the SMP physiochemistry and its SME will be necessary to better apprehend its evolution in order to meet specific uses and applications.

CONFLICT OF INTEREST

The authors declare no conflicts of interest.

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