TRABAJO FIN DE MASTER

Tuning the shape memory effect of PLLA with the addition of low molecular weight PEG for minimal invasive surgery applications

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0 Thanking

I would like to express my gratitude to INSA Lyon Engineering School and UPV Bilbao Engineering University for the opportunity to work on this interesting topic during my exchange semester in Bilbao. I would like to thank Ester ZUZA HERNANDEZ, my tutor, for her advice and help during and after the TFM. I would also like to thank all the colleagues of the laboratory who welcomed me in the friendliest way and helped me whenever they could. And finally, I would like to thank Xabier LARRAÑAGA, the PhD student I assisted on this project, who was always there to help, support and guide me throughout this semester. Eskerrik asko denoi.

1 Abstract

Poly(ʟ-lactic acid) (PLLA) is an interesting polymer for the engineering and medical field because of its high elastic modulus, good tensile strength and sustainability. The only major obstacle for these applications, like the shape memory effect, is its brittleness. In this study, a series of poly(L-lactic acid) polymers are blended with different percentage of polyethylene glycol (PEG) plasticizer of molecular weight of 600 g/mol. We investigated the effect of PEG percentage on the shape memory behaviour, the mechanical and thermal properties of the polymer through DSC, ATG, DMTA and tensile tests. We then determined the right concentration of PEG needed to maximize the shape memory effect for medical application. The experimental results reveal that introduction of appropriate PEG content improves the shape memory behaviours, by reducing the glass transition temperature and the brittleness of PLLA.

El ácido poli(ʟ-láctico) (PLLA) es un polímero interesante para la ingeniería y la medicina por su elevado módulo elástico, su buena resistencia a la tracción y su sostenibilidad. El único obstáculo importante para estas aplicaciones, al igual que el efecto de memoria de forma, es su fragilidad. En este estudio, se mezclan una serie de polímeros de ácido poli(L-láctico) con diferentes porcentajes de plastificante de polietilenglicol (PEG) de masa molar 600 g/mol. Se investigó el efecto del porcentaje de PEG en el comportamiento de la memoria de forma y en las propiedades mecánicas y térmicas del polímero mediante ensayos de DSC, ATG, DMTA y tracción. A continuación, determinamos la concentración adecuada de PEG necesaria para maximizar el efecto de memoria de forma en aplicaciones médicas. Los resultados experimentales revelan que la introducción de un contenido adecuado de PEG mejora los comportamientos de memoria de forma, reduciendo la temperatura de transición vítrea y la fragilidad del PLLA.

Azido poli(ʟ-laktikoa) (PLLA) polimero interesgarria da ingeniaritzarako eta medikuntzarako, bere modulu elastiko handiagatik, trakzio erresistentzia onagatik eta iraunkortasunagatik. Aplikazio hauen oztopo nagusi bakarra, forma memoriaren efektua bezala, hauskortasuna da. Azterketa honetan, azido poli(L-laktiko) polimero batzuk nahasten dira 600 g/mol masa molar duen polietilenglikol (PEG) plastifikatzeko ehuneko ezberdinekin. PEG-aren ehunekoak forma-memoriaren portaeran eta polimeroaren propietate mekaniko eta termikoetan duen eragina ikertu da DSC, ATG, DMTA eta trakzio-saiakuntzen bitartez. Ondoren, medikuntza aplikazioetan forma-memoria efektua maximizatzeko behar den PEG kontzentrazio egokia zehaztu dugu. Emaitza esperimentalek agerian uzten dute PEG eduki egoki bat sartzeak forma-memoriaren portaerak hobetzen dituela, beira-trantsizio-tenperatura eta PLLAren hauskortasuna murriztuz.

Key words : Polymer, shape memory, PLLA, PEG, blend

2   List of tables, graphs and acronyms

PLLA : Poly(ʟ-lactic acid) (PLLA)

PEG : Polyethylene glycol

Tg : Glass transition temperature

Tm : Temperature of fusion

Tcc : Temperature of cold crystallization

DSC : Differential Scanning Calorimetry

TGA : Thermogravimetric analysis

DMTA : Dynamic Mechanical Thermal Analysis

MW : Molecular weight

TFM : Trabajo Fin de Master

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3   Introduction

Shape memory behaviour refers to a phenomenon where a material is able to return to its original shape, after being deformed, under the effect of a stimulus, most often temperature. This effect has been explored in recent years, particularly through shape memory polymers (SMPs) and their potential applications in the field of medicine. This is the objective of this TFM. Indeed, the shape memory effect provides a very interesting solution in the context of surgery. It allows the surgeon to make a smaller incision during an operation to replace part of a bone for example. The polymer, previously programmed into a compressed form, can then be placed in the patient's body. When heated by a magnetic field, the polymer will return to its intended shape. This allows for less dangerous interventions and each implant can be tailored to the individual needs and constraints of the patient. In addition, the scar from the operation will be less visible, providing aesthetic comfort to the person operated on.

In this TFM, we will focus on the effect and shape memory behaviour of poly(L-lactic acid) polymer (PLLA) with added polyethylene glycol (PEG) of low molecular weight. PLLA is a biodegradable bio-based polymer. It is also non-toxic which makes it relevant for application in the field of medicine. PLLA has an elastic modulus of 3-3.5 GPa, a tensile strength of 50-70 MPa with an elongation at break of 2-10%. Its glass transition temperature is 60-65°C and its melting temperature is 173-178°C[4]. It is produced from (L)-lactic acid (LLA), which is extracted from plants containing sugars and/or starch such as corn, beetroot, etc.
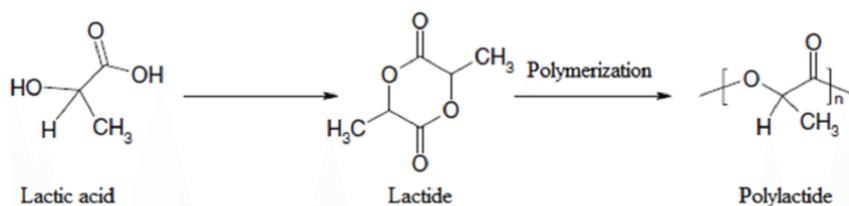
Figure 1 : PLA polymerization

Due to its semi-crystallinity and high reactivity, due to the high percentage of ester groups, PLLA is a polymer capable of being deformed and returning to its initial state, a phenomenon that we will explain later. The two main obstacles for a shape memory effect applied to the medical field are its fragility and its glass transition temperature (Tg) which is too high for the human body, 60°C. The cells of the human body cannot withstand a temperature higher than 40°C. To overcome these problems, we added polyethylene glycol (PEG) to PLLA. As these polymers have very similar solubility parameters (approximately $(20 \text{ cal/cm}^3)^{0,5})$[2], they have a good affinity and will therefore form a homogeneous phase during mixing. This polymer, from the polyether family, improves the ductility of PLLA by decreasing the nucleation density and increasing the growth rate of spherulites. This increase in the ductility of the polymer chains will have the effect of decreasing its Tg, with the aim of reaching a glass transition temperature of the PLLA/PEG mixture between 37°C and 40°C. To determine the optimal amount of PEG to inject into the PLLA, we carried out various thermal tests, such as DSC, ATG and DMA, and mechanical tests by means of tensile tests at human body temperature.

4 State of the art

The phenomenon of shape memory is due to both the chemical composition and network structure of the material as well as the method of processing it, known as "programming". Shape memory is possible due to the presence of two phases in the polymer. A rigid phase which is the nodes of the network, and a "soft" or switching phase consisting of the long polymer chain segments located between the shape fixing parts[6], Figure 2. The latter are stretched and deform to respond to the external stimulus, only if the polymer is raised above its glass transition temperature. The nodes of the network can be chemically cross-linked, via covalent bonds, or formed by physical entanglement due to strong non-covalent intermolecular interactions. This allows for better thermodynamic stability and therefore better shape memory performance. Covalent bonds can be achieved by appropriate cross-linking chemistry, while physical cross-links require a morphology consisting of at least two distinct phases, which is the case for PLLA.

The shape memory of this polymer is possible due to its semi-crystallinity. The crystalline phase acts as the rigid phase, through lattice points that are responsible for the permanent shape of the polymer. The amorphous phase is the switching phase[1]. This phase stores elastic energy during deformation and releases it when conditions are right for the materials to recover. It can be seen as a recoil of the polymer chains from the deformed state to the original state. The shape memory effect is therefore determined by the energy absorbed in the amorphous phase. The aim of the programming step is to activate the shape memory behaviour of the polymer. To do this, the polymer is first deformed at a temperature above its glass transition temperature in order to provide enough energy for the polymer chains to slip and for the switching phase to deform. Once this has been achieved, the temperature of the polymer is lowered below its Tg, while keeping a constant load applied to the material. This allows the polymer to be frozen in its temporary deformed state. In order for the material to return to its original shape, a stimulus, in this case thermal, must be applied. It is necessary for the polymer to be heated to a temperature above its Tg. The energy accumulated during the deformation will then be released to return the sample to its original stable shape. This process can be time consuming and expensive, so Ping et al. developed a method for cold stretching thermoplastic shape memory polymers.
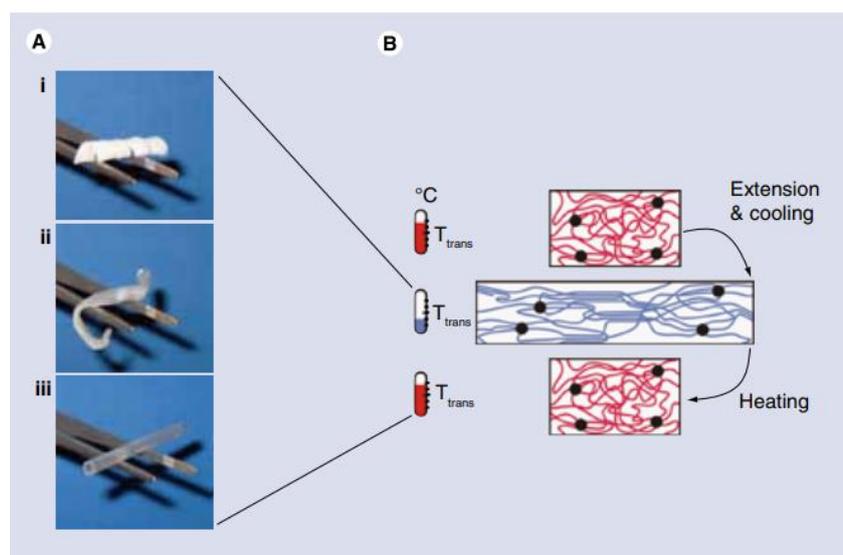
Figure 2 : Shape memory effect

The effect of PEG plasticiser on the thermal and mechanical properties of PLLA has been extensively studied. In a scientific paper, Bajardo et al[3]. demonstrated that the variation of the glass transition temperature of the PLLA/PEG blend was strongly dependent on the average molecular weight and the amount of PEG. Blends with a high MW of PEG had a lower Tg than those containing a low MW PEG. They showed that Tg varied in a linear decreasing manner with the amount of PEG inserted. They also revealed that low molecular weight PEG had better miscibility and plasticization efficiency in the PLA matrix. Xu et al.[5] studied the crystallisation behaviour of PLLA. They found that the addition of PEG decreased the nucleation density and increased the growth rate of spherulites. The team of Younes et al. studied the impact of MW and the amount of PEG on the melting temperature of PLLA. They observed that PLLA/PEG mixtures had a slight decrease in melting temperature, with the addition of low molecular weight PEG resulting in a greater decrease in the Tm of the mixture. Choi et al.[5] analysed the elongation at break of PLA. They showed that pure PLA had 17 times lower elongation at break than a blend of PLA and 9% PEG.

5 Experimental

5.1 Materials

In this study, we used poly(ʟ-lactic acid) L175 from the supplier Total-Corbion, with a molar mass of 175,000 g/mol and a density of 1.24. Its melting temperature is 175°C and its glass transition temperature is 60°C. It has a Young's modulus of 3,500 MPa, a tensile strength of 50 MPa and an elongation at break of less than 5%.

The poly(ethylene glycol) (PEG) used in the mixture has a molecular weight of 600 g/mol and was supplied by Sigma-Aldrich. The melting temperature of the PEG is 20-25°C.

5.2 Samples manufacturing

The samples were manufactured using an injection moulding machine (Xplore Micro Compounder) and an Xplore micro moulder.

Figure 3 : Xplore Micro Compounder

Figure 4 : Xplore Micro moulder

The protocol follows the following steps: PLLA was stored in an oven at 40°C and 50 mbar. The injection molding machine and the micro-moulder were heated to 200°C, the pressure in the micro-moulder was set at 15 bar. Pure PLLA is incorporated into the micro compounder beforehand, in order to have PLLA on the walls of the extrusion machine.

Figure 5 : PLLA injection in the DSM

Then 10 mg of PLLA was put into the extrusion machine and 6 or 8 or 10% PEG was added, using a syringe.

Figure 6 : Injection of PEG in the DSM

A certain amount of the PLLA/PEG mixture was injected into a gun and put into the micro-moulder. At the end, we collected the samples. For the rest of the study, we will distinguish the samples with different percentages of PEG according to the following notation: PLLA6PEG means that there is 6% PEG in the PLLA/PEG blend, the same for PLLA8PEG and PLLA10PEG.

5.3 Samples programming

For the programming of the samples, we used an INSTRON 5565 tensile testing machine. The temperature was set at 50°C for 10 minutes. The specimen was then placed in the tensile testing machine and stored for 8 minutes before programming, to ensure that the sample was at the correct temperature. It was then deformed to a certain percentage of deformation. Throughout the study, we applied deformations of 50%, 75% and 100%. It was then cooled to freeze its deformed state and removed from the control box of the tensile machine.

Figure 7 : Tensile test machine and control box

5.4 Characterization

5.4.1 DSC

To determine the thermal properties, such as glass transition temperature, melting temperature, cold crystallisation temperature or crystallinity of the PLLA/PEG blend samples, we used the TA Instruments Q200 differential scanning calorimeter. We measured the differences in heat exchange between the PLLA/PEG blend and a platinum reference as a function of temperature. For the tests, we used a standard aluminium mould with a mass between 5 and 10 mg. To erase the thermal memory of the sample, we performed a first scan from -20°C to 220°C, with a heating rate of 5°C/min, and then another heating scan to determine the actual thermal properties of the PLLA/PEG blends.

Figure 8 : DSC TA instruments Q200

5.4.2 TGA

TA Instruments Q50 thermogravimetric analysis is used to determine the degradation temperature of different PLLA/PEG blends, by measuring the change in polymer mass with temperature. For the test, we used a platinum pan and a 10-13 mg piece of sample. Once the sample and pan were placed and tared in the TGA, we applied a heating sweep from 0 to 400°C.
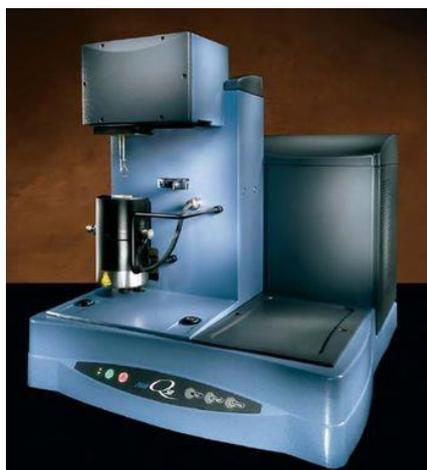

Figure 9 : TGA TA Instruments Q50

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5.4.3 DMTA

In the METTLER TOLEDO dynamic mechanical analysis, we examined the storage modulus E', the loss modulus E'' and the loss factor tan delta, in order to determine an accurate Tg of PLLA/PEG blends. The viscoelasticity of the PLLA/PEG polymer was measured, i.e. the response of the material to oscillatory deformation as a function of temperature. In the tests, the samples were cut into thin pieces of 10 mm length, cooled to 0°C, and when the temperature is equilibrated to 0°C, the temperature rise takes place. Measurements are taken from approximately 6°C to 70°C.

Figure 10 : DMTA Mettler Toledo

5.4.4 Tensile test

For the tensile tests we used an INSTRON 5565 tensile testing machine, with a temperature control box purchased from INSTRON, at 37°C. The applied strain rate is 5 mm/min.

5.4.5 Recovery

For free recovery, we used two different ovens to store the programmed samples, one to recover at 37°C and one at 40°C. The samples were left in the ovens for 24 hours. After this time, we measured their dimensions in order to compare them with their initial and programmed size.

For constant strain recovery, we used the tensile testing machine with a temperature control box. We placed the programmed specimens in the tensile testing machine at room temperature. We then heated the samples and measured the stress applied by the polymers to recover their original shape. When the stress began to stabilise, we stopped the test.

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5.5   Task description

My TFM was divided into several parts:

Firstly, the PLLA/PEG blend samples had to be made using an injection moulding machine and a micro-moulder. PLLA samples with 6, 8 and 10% PEG content were made.

Some of the samples were programmed with 100% deformation. Their mechanical properties were tested on the tensile machine to evaluate the differences in properties between the different percentages of PEG. This was done in order to find out the influence of the low molar mass PEG step on the mechanical characteristics of the PLLA/PEG blend.

Samples were selected to be tested by DSC, ATG and DMTA. We could then observe the thermal characteristics of these blends and again determine the differences between the 6, 8 and 10% PEG.

Finally, the other programmed samples were placed in two ovens at 37°C and 40°C to visualise the shape memory effect and whether it allowed the samples to recover their original dimensions.

After all these tests were carried out, we analysed the results. It was decided to carry out these tests again, but this time with samples programmed with 50% and 75% deformation, in order to study the impact of the deformation during the programming stage on the shape memory behaviour of the PLLA/PEG blend.

6   Results and discussion

6.1   Thermal behaviour

To understand the shape memory behaviour of the PLLA/PEG blend, it is necessary to look at its thermal characteristics and in particular at the glass transition temperature, which is the fundamental parameter. Indeed, it indicates the threshold at which the polymer chains will be able to slide between each other. It therefore represents the shape memory temperature.

Using DSC analysis and TA Universal Analysis software, we can determine the main thermal characteristics of a material, namely its glass transition temperature, melting temperature and cold crystallisation temperature. We start our analysis with PLLA6PEG, PLLA8PEG and PLLA10PEG samples, programmed with 100% strain. The averages are shown in the Figure 11. We compare these polymers to determine the influence of PEG 600mg/mol on PLLA.
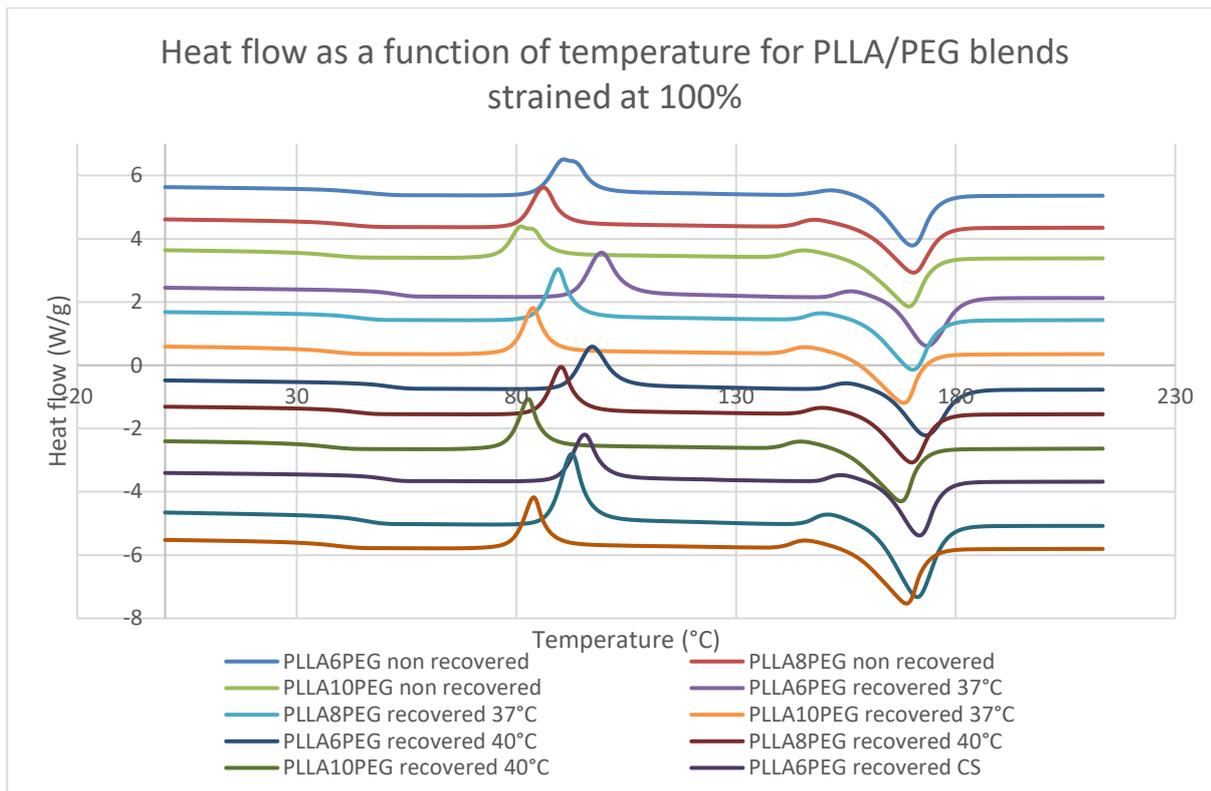
Figure 11 : DSC thermogram of PLLA/PEG blends strained at 100%

A trend can be seen that corroborates the studies previously cited in the state of the art. The T_g of the polymer blend decreases proportionally with the increase of the percentage of PEG. Indeed, for PLLA6PEG we have a T_g of about 49,13°C, for PLLA8PEG it is about 43,16°C, but this remains above the expected temperature range for our application. Only PLLA10PEG falls within this range with a T_g of about 37,71°C, see Table 1 in Annex I. This variation can also be observed in the cold crystallisation peak. A smaller decrease in the melting temperature of the PLLA/PEG mixture can be seen.
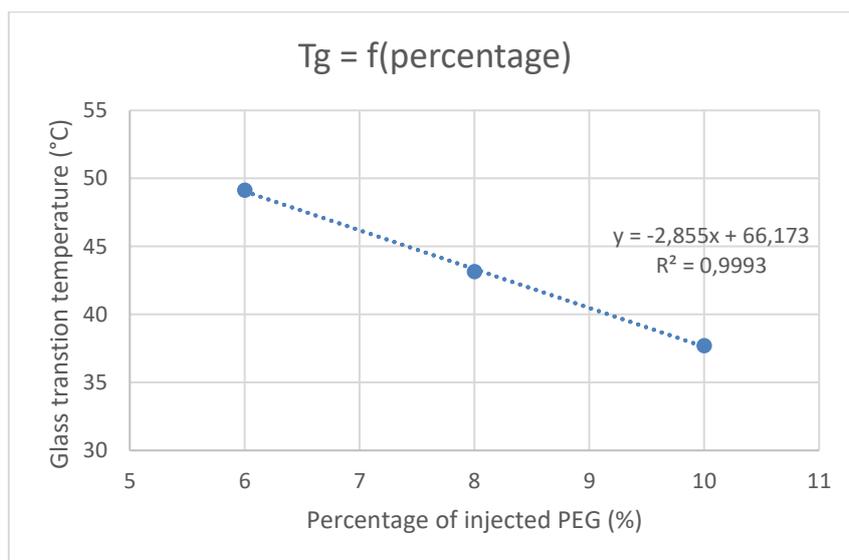

Figure 12 : proportionality between percentage of PEG and Tg

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The results obtained are supported by the DMTA tests performed, Figures 13, 14 and 15. These tests allow us to measure the conservation modulus E', the loss modulus E'' and the tan(δ). The conservation modulus represents the amount of energy that the polymer can store when its temperature increases under a slight oscillation. This is the elastic characteristic of the polymer. On the other hand, the loss modulus represents the amount of energy lost when the polymer heats up, which is its viscous characteristic. When the storage modulus decreases and the loss modulus increases, this means that the material becomes viscous, the chains relax and start to move together, so we are around the glass transition temperature. We can determine this Tg from the tan(δ). The latter represents the fraction of energy dissipated by the material, its maximum being the glass transition temperature.
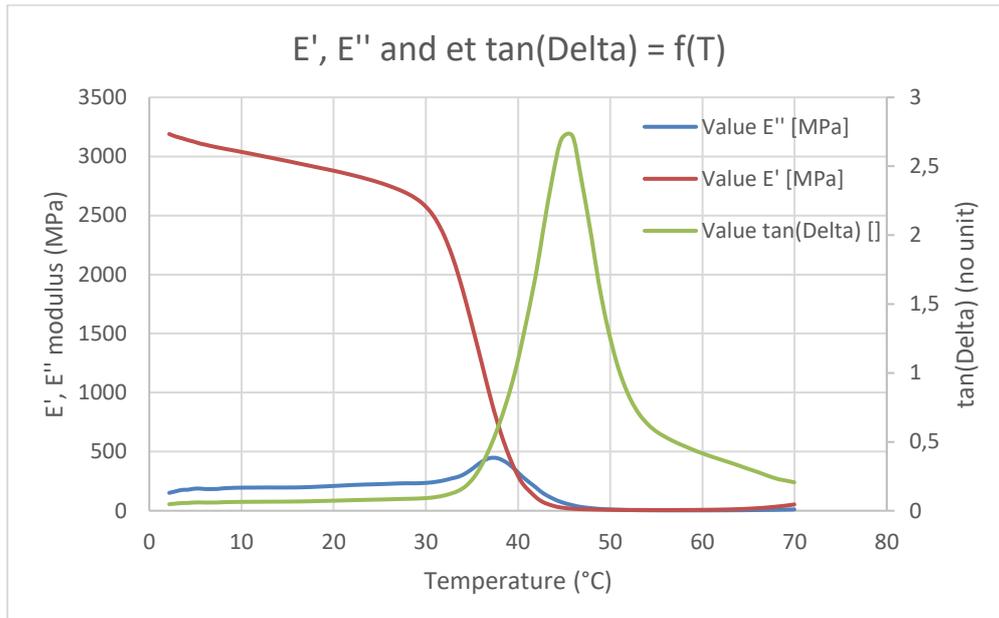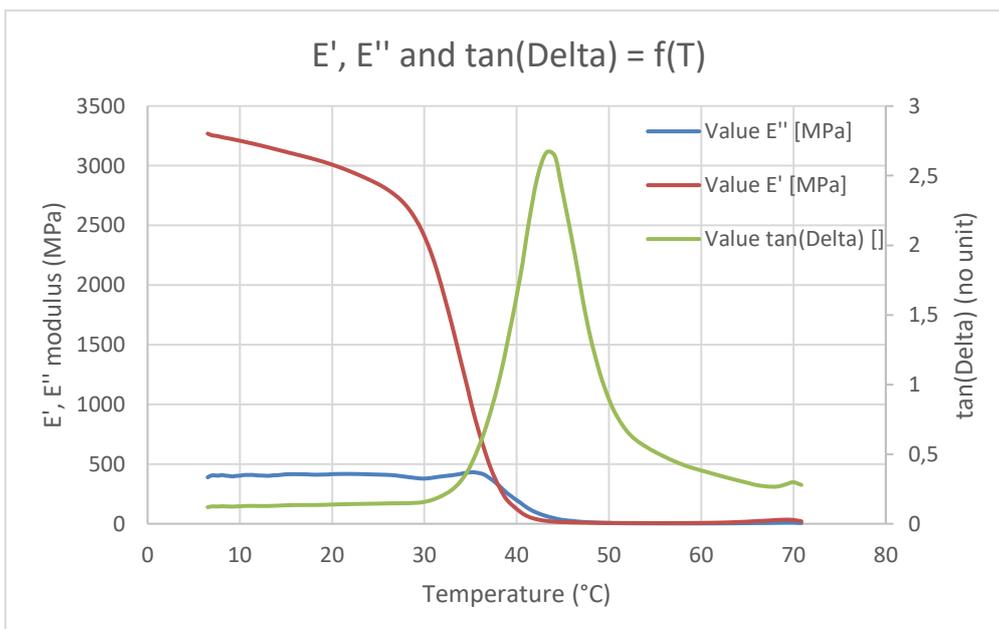

Figure 13 : DMTA thermogram of PLLA6PEG

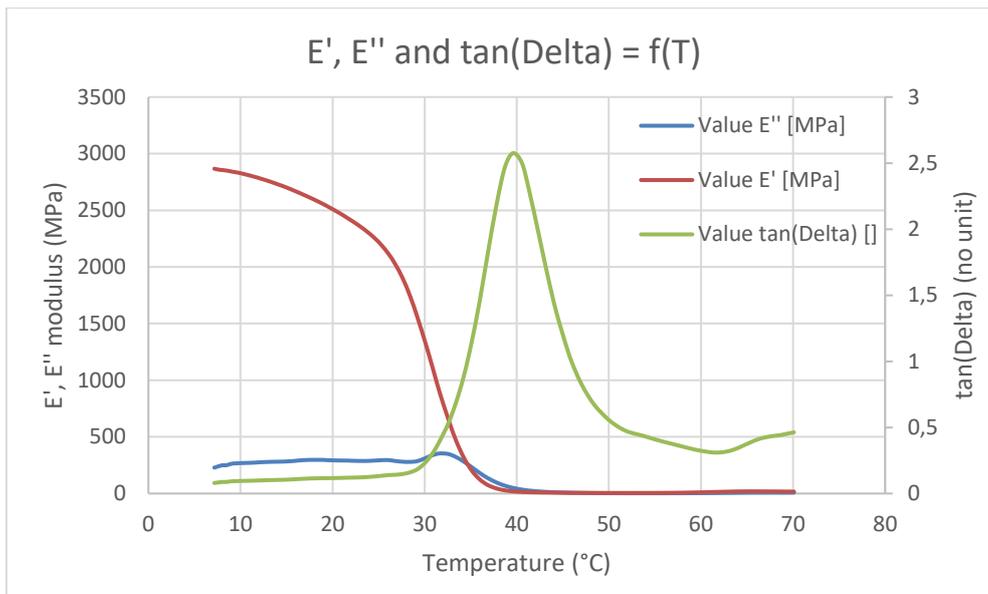Figure 14 : DMTA thermogram of PLLA8PEG

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Figure 15 : DMTA thermogram of PLLA10PEG

First of all, we notice that E' is 10 times higher than E'', so the material tends to keep its mechanical strength before the Tg. Because of this difference between the two moduli, it can be considered that its behaviour tend to be elastic. The modulus of conservation remains similar for PLLA6PEG and PLLA8PEG, even though the PLLA8PEG has a lower tan(δ). On the other hand, it decreases for the 10%, which informs us of a decrease in the elasticity of the material in favour of the viscosity. The deformation of the material will be more rapidly irreversible. It can be seen in Figures 13, 14 and 15, that the tan(δ) decreases well with increasing percentage of PEG in the mixture, the trend is similar to the results obtained with DSC. For PLLA6PEG we have a Tg of about 46°C, for PLLA8PEG the Tg is about 43°C. As with DSC, only PLLA10PEG is in the desired temperature range, despite a higher value close to the limit, at about 39.5°C.

The ATG test allows us to corroborate our deductions but this time on the degradation temperature of the PLLA/PEG mixture, as shown in Figure 16. As PEG has a lower degradation temperature than PLLA, as the PEG content increases, the decay temperature will irreversibly decrease.
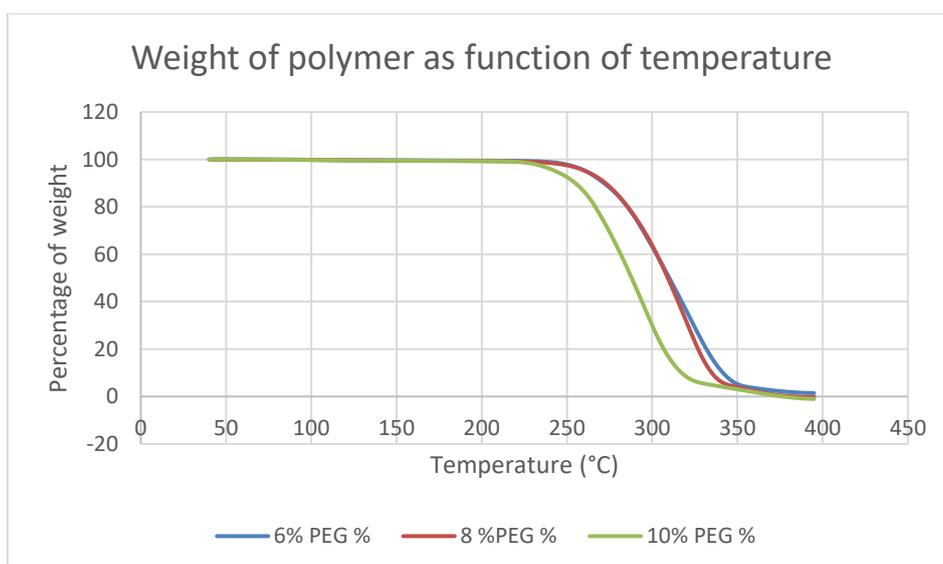

Figure 16 : TGA comparaison of influence of PEG in the PLLA/PEG blends

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Another interesting parameter to consider is the crystallinity of the mixture. From the DSC tests we can determine the crystallinity levels of the different PLLA/PEG blends. For this we use the following equation:

$$X_c = \frac{\Delta H_m - \Sigma \Delta H_{cc}}{\Delta H°_m}$$

With : $\Delta H°_m$ = 106 J/g

It can be seen in the Table 2, in Annex I and in the Figure 17, that the degree of crystallinity increases proportionally with the amount of PEG added to the PLLA polymer. When the PEG particles are inserted between the PLLA chains, they will have the effect of facilitating the movement of the chains between them, resulting in a lower Tg. This will also result in the chains being able to rearrange themselves more easily and therefore crystallise more easily. This is why the higher the PEG content, the more crystallised the polymer will be.
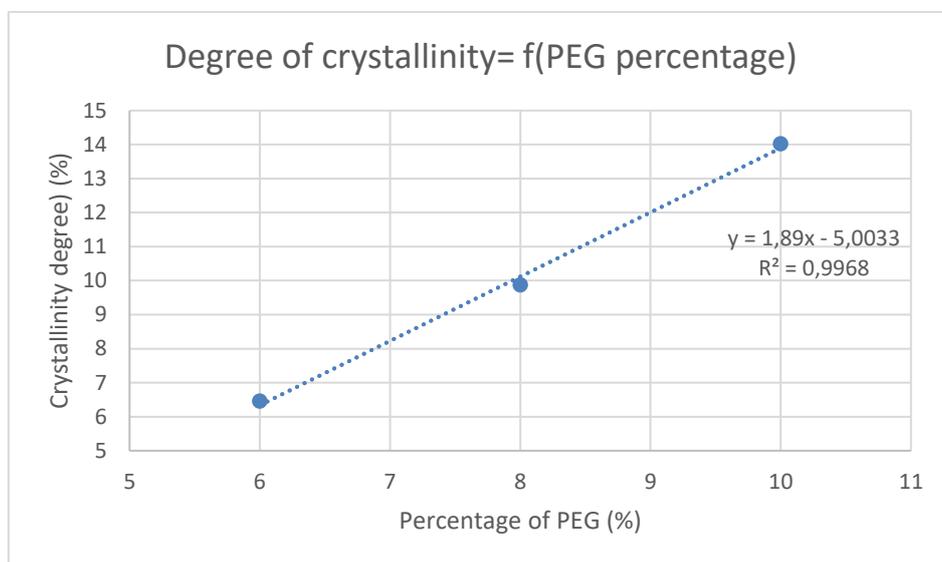

Figure 17 : Proportionnality between degree of crystallinity and percentage of PEG

We have demonstrated the relationship between the amount of PEG in the PLLA polymer and the variation of its glass transition temperature. When testing the recovery of the polymer samples in the 37°C and 40°C ovens, we noticed a surprising behaviour from the samples. For the 37°C oven, there was no shape memory effect from the samples. In the 40°C oven, PLLA6PEG recovered its size very weakly, whereas according to the Tg of the latter this should not have been possible. Even more surprisingly, PLLA8PEG and PLLA10PEG recovered less than the one with 6% PEG. This could be explained by the fact that the 40°C oven did not remain at a constant temperature throughout the recovery, it was observed to oscillate up to 45°C. It was at this point that the shape memory effect was activated for PLLA8PEG, its glass transition temperature being 43°C. The oven could have risen above this value and activated the reaction of PLLA6PEG. However, this does not explain why the latter had the most significant shape memory effect. A possible hypothesis is that the cause of the poor shape memory effect, for the PLLA8PEG and PLLA10PEG, is that the samples crystallises when stretched to 100%. These numerous fixed zones in the material block the switching zones from returning to their initial state. The polymer is therefore locked in its deformed state. In order to verify this hypothesis, we decided to test different deformations when programming the PLLA/PEG blend. We arbitrarily decided to perform the same tests for 50% and 75% deformations. We will see the results later on.

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Comparing the three different programming deformations, we note that the 75% and 100% deformations have very similar characteristics. On the other hand, the samples deformed at 50% during the programming show surprisingly weird results. This is because the data is from the first DSC run and is therefore wrong. It was probably forgotten to program a second cycle during this 50% deformed sample run. Nevertheless, one can think that the results should correspond to the other two percentages in PEG.
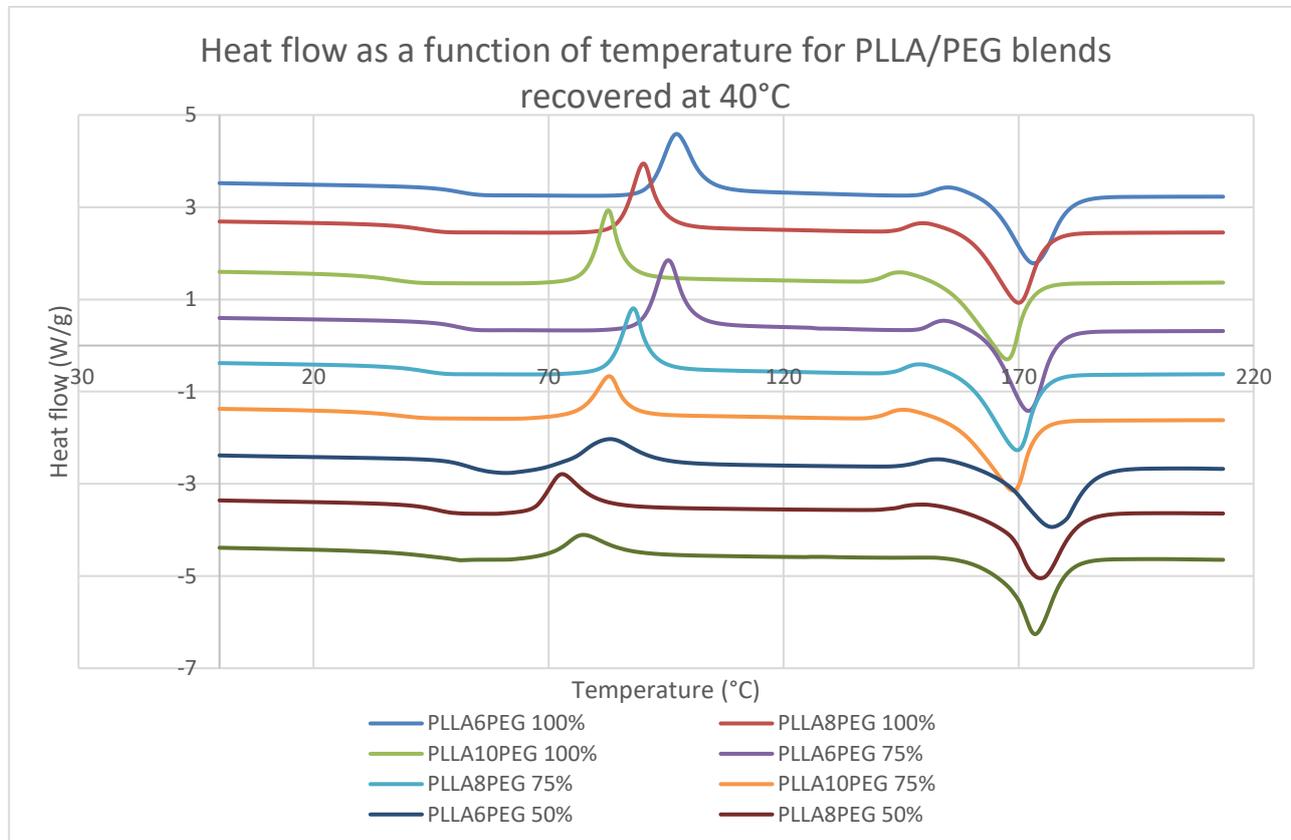
Figure 18 : Comparison between DSC thermogram of PLLA/PEG of 50-75-100% strain and recovered at 40°C

We have shown that increasing the 600g/mol PEG content in PLLA resulted in a proportional decrease in its Tg. This allowed us to achieve a glass transition temperature of approximately 38°C for PLLA10PEG, which is within the temperature range required for the intended medical application. However, the increase in the ductility of the material, due to the PEG plasticizer, will lead to a decrease in certain mechanical properties. We will therefore study, in a second part, the impact of the quantity of low molar mass PEG on the mechanical properties of the PLLA/PEG blend.

6.2 Mechanical properties

The second disadvantage of PLLA is its fragility. Indeed, its elongation at break of less than 5% is very low and does not allow an application in the medical field, as the polymer is supposed to be able to absorb shocks and deformation during its use. The PEG contributes its plasticizing character and should allow a better ductility of the mixture. On the other hand, the polymer must not lose too much of its mechanical strength at the risk of seeing it lose all interest in the desired application.

With the help of tests carried out with the traction machine and its control box, we will compare the mechanical characteristics of samples of PLLA6PEG, PLLA8PEG and PLLA10PEG deformed at 100%, in order to determine the influence of the plasticizer. These tests were carried out at a temperature of 37°C in order to recreate the conditions of the human body.
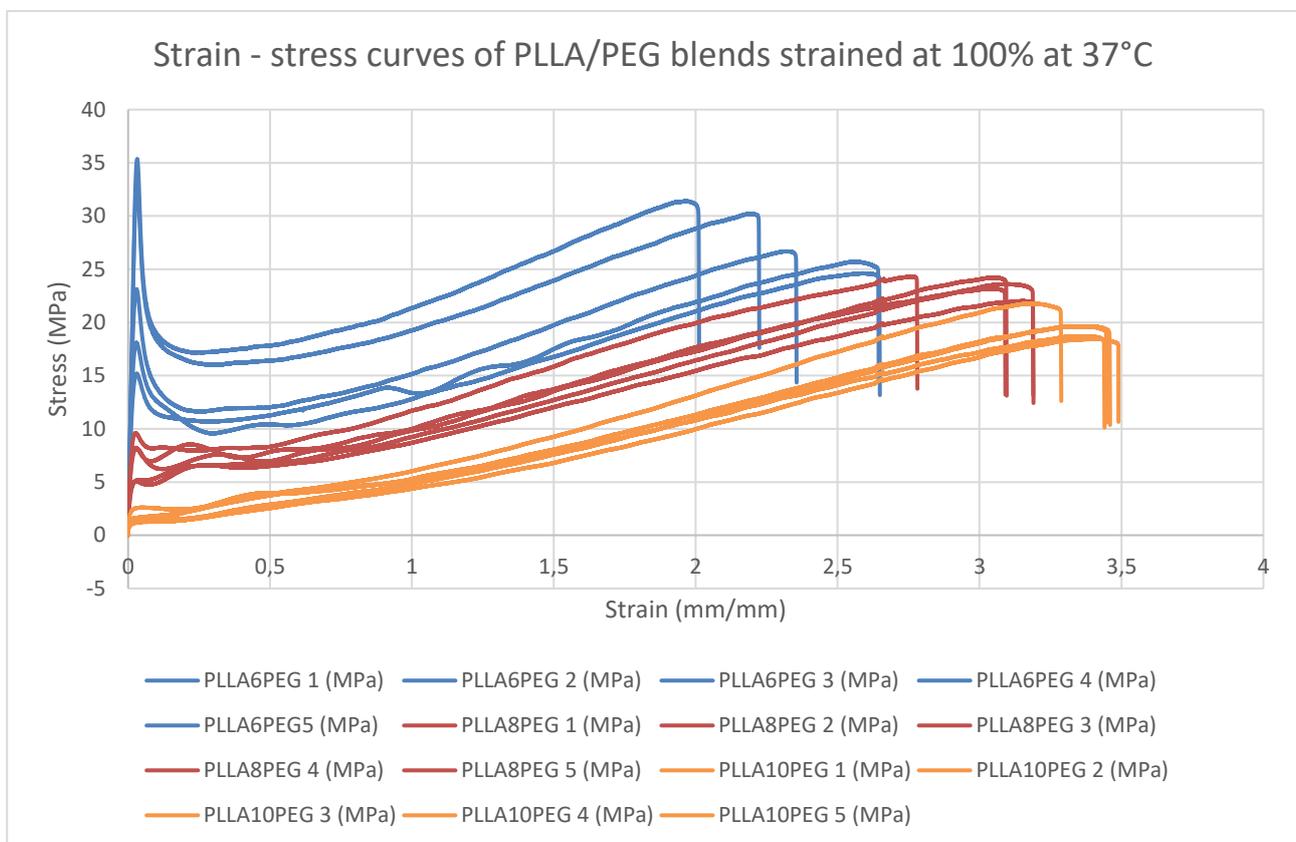

Figure 19 : Stress-strain curves of PLLAPEG blends strained at 100°C at 37°C

As mentioned in the state of the art, the plasticising effect of PEG increases the ductility of the PLLA polymer. On average, PLLA6PEG had an Rm around 22 MPa, PLLA8PEG had an Rm approximatively 10 MPa and for PLLA10PEG its Rm is 3 MPa. The elongation at break is 237% for PLLA6PEG, 306% for PLLA8PEG and 342% for PLLA10PEG. This phenomenon can be explained by the fact that the PEG particles are inserted between the chains and increase the mobility of the latter between them. On the other hand, this increased ductility of the material leads to a drop in its Rm. At present, PLLA10PEG, which is theoretically the only one with the necessary thermal characteristics, has a mechanical strength that is far too low to be used in the medical field. As the glass transition temperature is the most important parameter, the amount of PEG in the mixture cannot be reduced. A possible solution would be to introduce particles that increase the mechanical strength of the PLLA/PEG mixture.

When comparing the 50%, 75% and 100% specimens, a better tensile strength was observed for the 50 and 75% deformed specimens. However, this is still not sufficient to achieve the properties expected to replace a bone. The 50% and 75% deformed samples also have similar elongations at break.
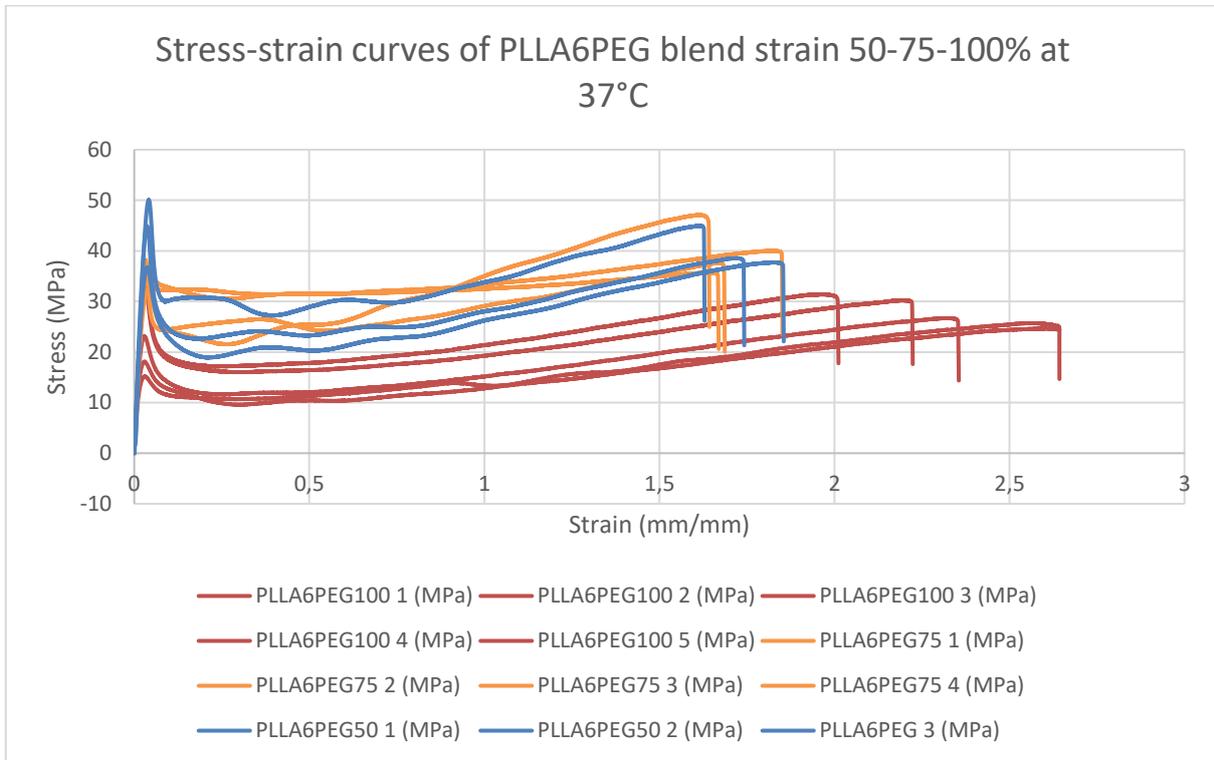
Figure 20 : Comparison of stress-strain curves for 50-75-100M PLLA6PEG at 37°C
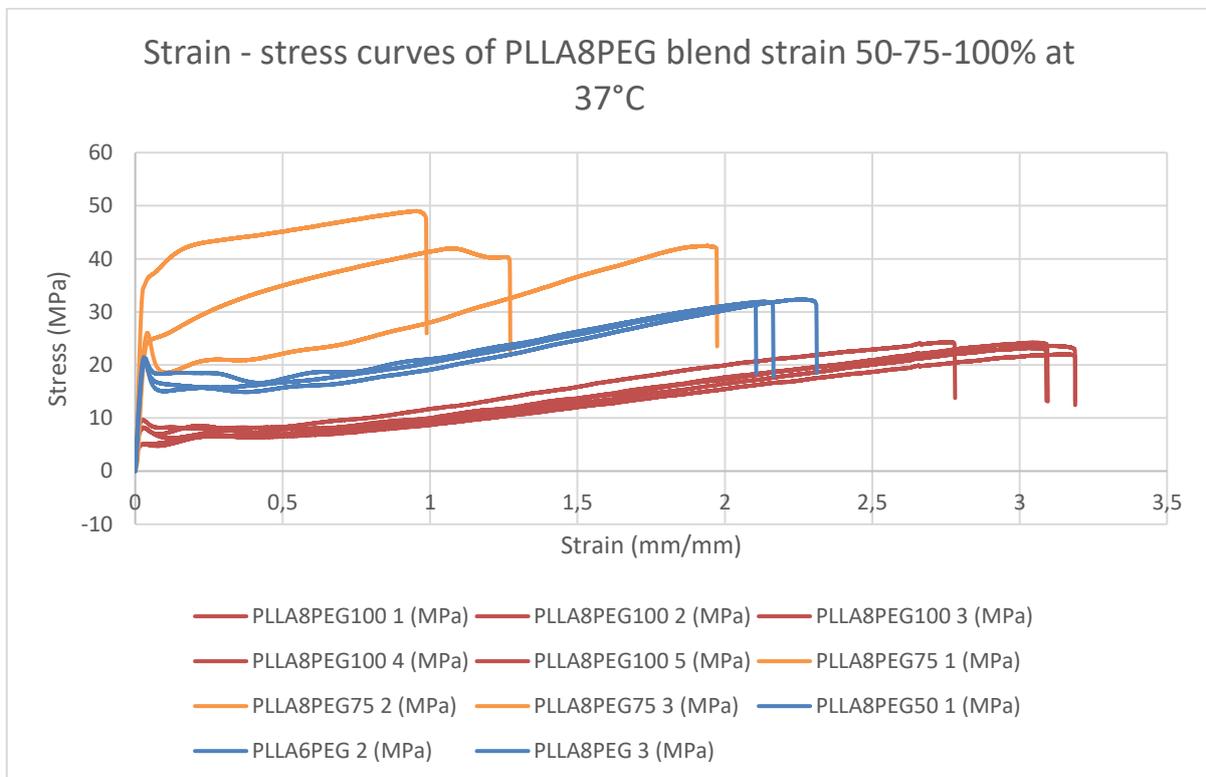
Figure 21 : Comparison of stress-strain curves for 50-75-100M PLLA8PEG at 37°C

For PLLA8PEG, the results obtained with PLLA/PEG programmed at 75% are surprising. From the other tensile tests, it can be deduced that these samples are probably wrong.
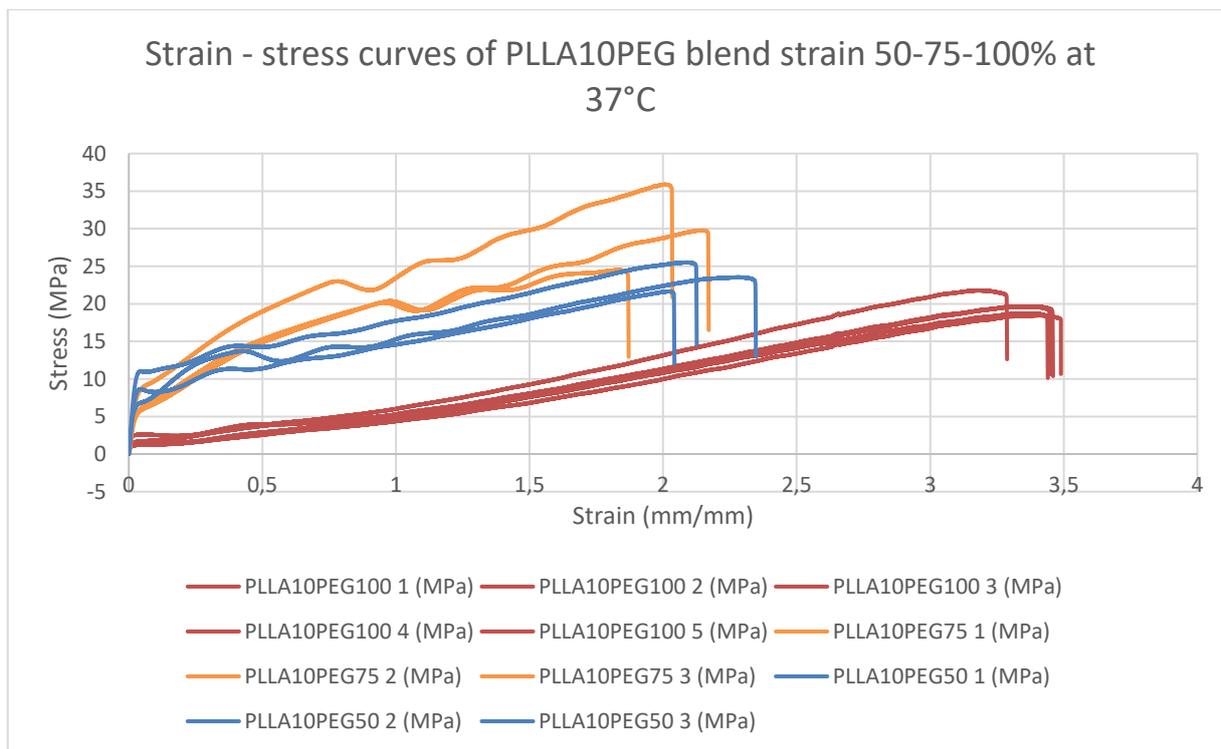
Figure 22 : Comparison of stress-strain curves for 50-75-100M PLLA8PEG at 37°C

A second test performed with the tensile machine is constant strain recovery. This method measures the stress exerted by the material to recover its original shape. Again, we compare the different PEG contents with 100% deformation to see if the plasticiser also affects this parameter.
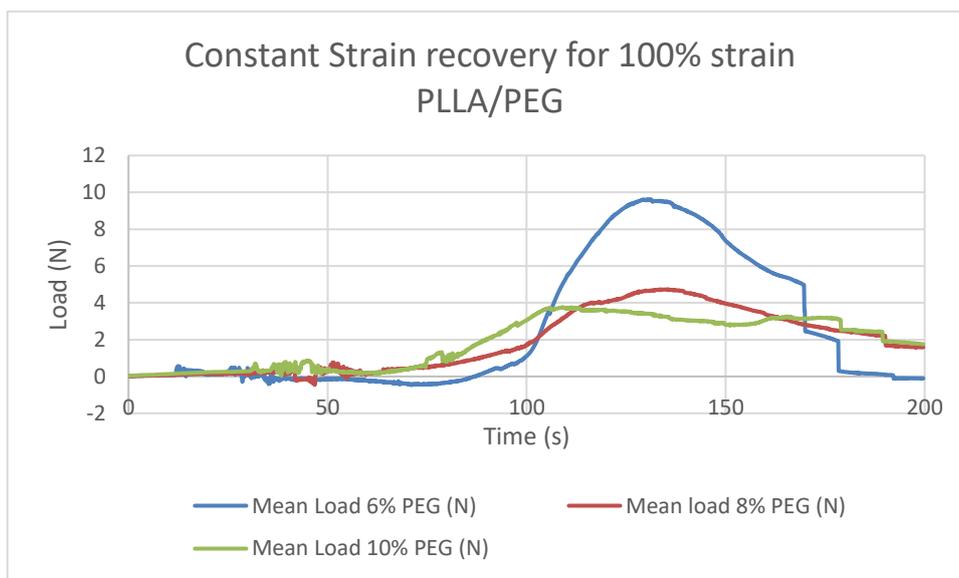
Figure 23 : Comparison of recovered 100% strained PLLA/PEG under constant strain

It is observed that the load exerted by the polymer decreases when PEG is added to the PLLA/PEG blend. As the material becomes more ductile with higher PEG content, it will exert less force to return to its original shape.

Figure 24 : Comparison of recovered 50-75-100% strained PLLA6PEG under constant strain

Figure 25 : Comparison of recovered 50-75-100% strained PLLA6PEG under constant strain

Figure 26 : Comparison of recovered 50-75-100% strained PLLA6PEG under constant strain

The lack of data and therefore repeatability on these tests does not allow us to draw any definite conclusions, but it appears that samples programmed at different deformations exert similar loads when returning to th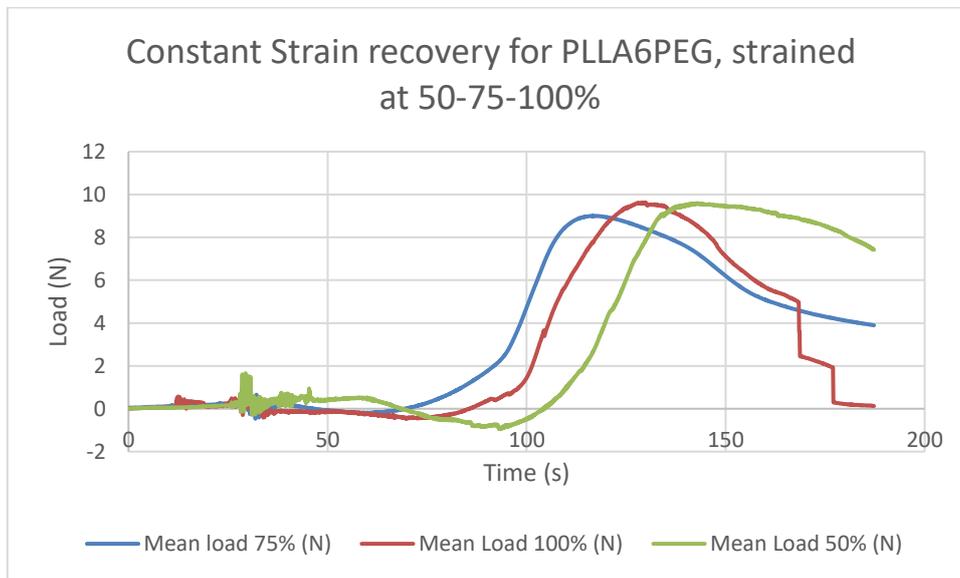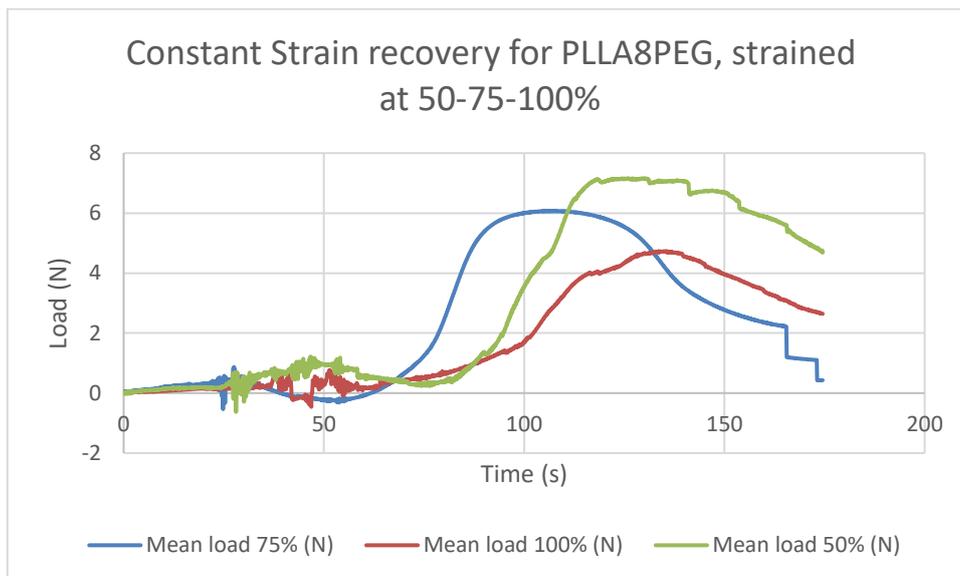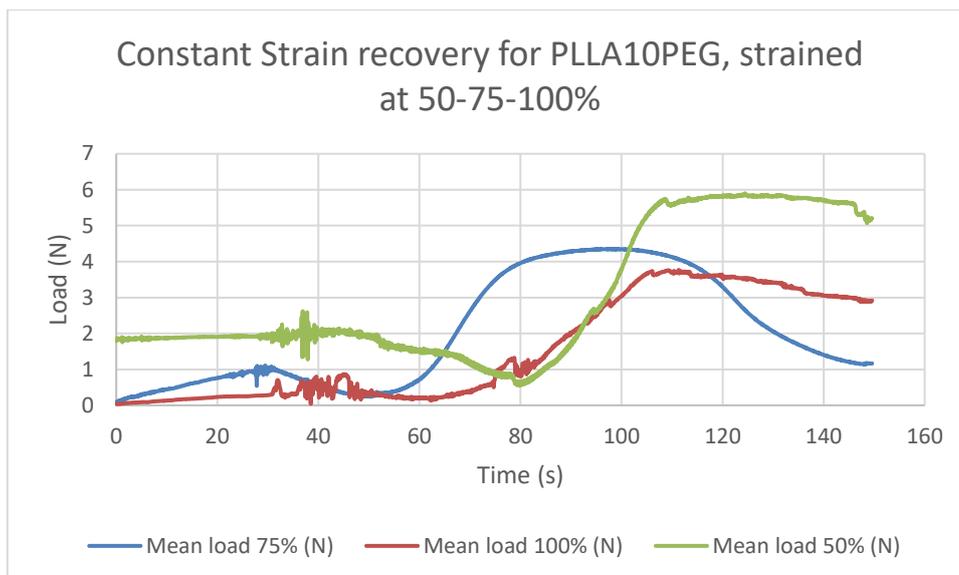eir initial shape. According to this observation, the 50% samples should have a better shape memory than the 75% and 100% samples since their deformation is lower, and the load applied to recover the initial shape is approximately the same or higher.

In order to visualise the shape memory effect and to put our samples in the desired application conditions, we placed them in ovens at 37°C and 40°C. After 24 hours, we removed them and measured them to determine the optimal configuration, see Table 3, 4, 5 and 6 in Annex I.

There is a clear difference in shape memory between the samples deformed at different percentages as expected. As mentioned above, the 100% deformed samples show very little shape memory, which was more marked on the PLLA6PEG.

With the 50 and 75% samples, we note that all show signs of shape memory, whether in the 37°C or 40°C oven. This is a surprising first result compared to the assumptions made earlier. Indeed, according to the results obtained with DSC and DMTA, we should only have recovery for the PLLA10PEG samples at 40°C and mainly for those that were placed in the 37°C oven.

A second surprising point is the behaviour of the samples that underwent a 75% deformation. When these were placed in the 37°C oven, their behaviour followed the logic stated since the beginning of this report, i.e. the higher the PEG content in the PLLA/PEG mixture, the greater its shape memory, see Table 3 in Annex I. For the samples placed in the 40°C oven, the phenomenon was reversed, with the PLLA6PEG samples recovering the most, see Table 4 in Annex I. This behaviour had already been observed with the 100% deformed samples. At 40°C, as we approach the glass transition temperature of PLLA6PEG, some of the chains start to move, so it is possible that the higher recovery strength of the PLLA6PEG samples compared to the other two types of samples may result in higher recovery, even though the Tg is higher for the PLLA6PEG. At 37°C, the temperature is too far from the Tg of PLLA6PEG for the same phenomenon to occur.

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For the 50% deformed samples, recoveries were even greater than for the 75%, as expected. The PLLA6PEG samples showed a shape memory effect but to a much lesser extent than the PLLA8PEG and PLLA10PEG. In many cases, the latter were able to return to their original size or to come very close to it. Surprisingly the PLLA8PEG samples had a similar shape memory effect to PLLA10PEG and came back to their original shape, see Table 5 and 6 in Annex I.

In order to verify the observed results in more detail they would need to be repeated in order to have optimal repeatability and to be certain of the results obtained. There are many factors involved in the process that could impact the quality of the samples and therefore the results analysed later. Firstly, the human factor is important given the method used to manufacture the samples. An error in the quantities of PEG added can lead to inconsistencies in the results. As the process of making and programming the samples was time consuming, it was not possible to carry out enough tests to have optimal repeatability to draw conclusions. Secondly, aging has a significant impact on the properties of shape memory polymers and in particular Tg. This may explain the differences between the results assumed after analysis of the DSC tests and the results obtained after recovery of the samples heated to 37 and 40°C. Thirdly, the glass transition phenomenon is not fixed at a specific temperature. As we have seen from the DSC analyses, it is more like a slope than a peak like the melting temperature. This is why the samples were able to partially react even though the oven temperature was below their Tg. Fourthly, the physical structure can vary between samples, which can also have an impact on the shape memory of the samples.

7 Conclusion

In conclusion, we have demonstrated, through DSC, TGA and DMTA tests, that the addition of low molecular weight PEG has an impact on the thermal characteristics of PLLA. The plasticizer influences the Tg, Tcc, Tm but also the crystallinity rate of the polymer. These thermal parameters will also vary proportionally with the amount of PEG injected. The higher the PEG content in the PLLA polymer, the lower its Tg, Tcc and Tm. Conversely, the crystallinity rate will increase.

Regarding mechanical properties, the increase in PEG content will increase the ductility and decrease the tensile strength of the material. These changes in the properties of PLLA will have the effect of promoting the shape memory behaviour of the material. The higher the amount of PEG, the more ductile the PLLA will be and the lower its Tg, so the shape memory effect can be activated at lower temperatures. On the other hand, its mechanical strength properties are greatly diminished, which may close doors for certain fields of application. In this case, it is important to know how to gauge and find the optimum combination for the desired application.

In our study, we are interested in a medical application. Our constraints are to have a material with a certain plasticity and, above all, an activation temperature of the shape memory phenomenon below 40°C. In view of the thermal and mechanical analyses, we can eliminate the use of a PLLA/PEG mixture containing 6% or less plasticizer. Similarly, it is not possible to deform the polymers beyond 50%, at the risk of them not regaining their desired initial shape. Theoretical analyses would lead us to a blending solution with 10% injected PEG. However, based on the results of free recovery in the ovens, we note that the samples containing 8% PEG show similar or even better shape memory characteristics than those containing 10%. Based on the tensile tests performed at 37°C, we should favour the PLLA8PEG samples, as their mechanical strength properties are better than those of the 10% PEG samples. However, they are still lower than what would be desired to replace part of a bone. This weakness of the PLLA/PEG mixture would need to be reinforced with other particles. This could be a new topic for TFM.

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9 Annex I

Table 1 : Tg of PLLA/PEG blend strained at 100%

Programming (100% strain)	6% PEG	8% PEG	10% PEG
Non recovered	49,25°C	43,61°C	37,5°C
	42,06°C	39,39°C	37,96°C
Free recovery 37°C	52,87°C	44,05°C	37,82°C
Free recovery 40°C	51,09°C	42,88°C	36,34°C
CS recovery	50,36°C	45,89°C	38,94°C

Table 2 : Tg of differents PLLA/PEG samples strained at 100%

Programming (100% strain)	6% PEG	8% PEG	10% PEG
File ?	7,78%	10,32%	12,55%
	8,84%	10,54%	14,28%
Free recovery 37°C	4,11%	9,66%	13,26%
Free recovery 40°C	5,23%	7,34%	14,98%
CS recovery	6,33%	11,49%	15,05%

Table 3 : Recovery lenght of PLLA/PEG blends 75% strained and recovered at 37°C

Recovery temperature of 37°C	Recovery lenght (cm)	Mean recovery lenght (cm)	Programmed lenght (cm)	Inital lenght (cm)
6%	10,6	10,47		
	10,5			
	10,3			
	10,5			
	10,4			
	10,5			
8%	9,8	9,7	10,7	7,5
	9,6			
	9,4			
	9,9			
	9,8			
	9,7			
10%	8,9	9,12		
	9,3			
	9,1			
	9			
	9,3			
	9,1			

Table 4 : Recovery length for PLLA/PEG blends 75% strained and recovered at 40°C

Recovery temperature of 40°C	Recovery lenght (cm)	Mean recovery lenght (cm)	Programed enght (cm)	Initial lenght (cm)
6%	8,1	7,97	10,70	7,5
	8,7			
	8,4			
	7,3			
	7,55			
	7,75			
8%	9,2	9,15		
	9,2			
	9,3			
	9			
	9,1			
	9,1			
10%	9	9,62		
	9,9			
	9,75			
	9,65			
	9,8			
	9,6			

Table 5 : Recovery lenght of PLLA/PEG blends 50% strained and recovered at 37°C

Recovery temperature of 37°C	Recovery lenght (cm)	Mean recovery lenght (cm)	Programmed lenght (cm)	Initial lenght (cm)
PLLA6PEG	9,2	9,14	9,7	7,5
	8,85			
	9,5			
	8,7			
	9,4			
	9,2			
PLLA8PEG	7,9	8,01		
	7,75			
	8,3			
	8,1			
	8			
PLLA10PEG	7,95	7,96		
	8,2			
	7,9			
	7,8			
	7,9			
	8			

Table 6 : Recovery lenght of PLLA/PEG blends 50% strained and recovered at 40°C

Recovery temperature of 40°C	Recovery lenght (cm)	Mean recovery lenght (cm)	Programmed lenght (cm)	Inital lenght (cm)
6%	9	8,8	9,7	7,5
	8,6			
8%	7,6	7,5		
	7,4			
10%	7,8	7,825		
	7,9			
	7,7			
	7,9			