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Temperature dependence of shape recovery of HMW and VHMW poly-(L-lactide)

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Abstract: Within this work, the influence of recovery temperature on thermal induced shape recovery behaviour of injection molded biodegradable poly-(L-lactide) (PLLA) was investigated. Shape retention, shape recovery and shape recovery rate were determined for high molecular weight (HMW) PLLA (320 kDa) and very high molecular weight (VHMW) PLLA (700 kDa) at recovery temperatures of 50, 60, 70, 80 and 90 °C, respectively, using DMA experiments. It was found that for both polymers, shape recovery reached a plateau of around ~70% at 80 °C, which could not be increased at higher temperatures. However, shape recovery rate did show to be affected by higher temperatures. Moreover, it was found that the polymer with the higher molecular mass exhibited a higher shape recovery rate.

Keywords: PLLA, DMA, Shape Memory Polymer

1 Introduction

4D biomaterials, in particular shape memory polymers (SMP), are of high interest in biomedical engineering.[1–3] External stimuli such as temperature, light, humidity or pH may be used to trigger the shape memory effect. In this context, some polymers show temperature-dependent changes in their physiochemical properties, e.g. the glass transition temperature T_g can be used as shape transition temperature.

SMP basically consist of a hard and a soft segment. The hard segment serves as cross-linking point, which physically stores the permanent form. Moveable chain segments connect the network points, which is referred to as the reversible phase or soft segment. This segment is responsible for the process of shape recovery by temporarily deforming and realigning the molecular chains as a result of the thermal stimulus.[4]

Thermal programming is achieved by heating the soft segment material above T_g. The heating acts like a molecular switch by softening the amorphous phase. At the same time, a mechanical force is exerted, causing the material to deform. The force is maintained until complete fixing. During this process, elastic energy is stored in the polymer, enabling the polymer to recover the original shape, e.g. by reheating the material above T_g.

In a biomedical context, shape memory (SM) behaviour of biodegradable poly-(L-lactide) (PLLA) is particularly interesting, as PLLA is a well-known, established and long-term clinically proven material for the manufacture of a broad range of medical devices, e.g. grafts, meshes, stents or suture material. PLLA is a semi-crystalline polymer and can be processed by either solvent-based or thermal methods. Although blending is a common approach to improve mechanical performance and enhance SM behaviour of PLLA [5], PLLA itself shows distinct SM properties due to its semi-crystalline nature [2]. As the thermal induced shape recovery effect requires temperatures above T_g, it may be unsuitable to be exploited after implantation. However, the use of SM effect has the potential to be highly beneficial for the manufacturing of biomedical devices. Within this work, influence of temperature on shape recovery for high molecular weight (HMW) and very high molecular weight (VHMW) PLLA was investigated using dynamic-mechanical analysis (DMA).

2 Materials and Methods

2.1 Sample preparation

HMW PLLA (Resomer L210) (M_W = 320,000 g/mol, inherent viscosity η = 3.3 - 4.3 dL/g)) was purchased from Evonik Industries (Essen, Germany). VHMW PLLA (Resomer L214) (M_W = 700,000 g/mol, inherent viscosity η = 5.9 dL/g) was purchased from Boehringer Ingelheim Pharma (Ingelheim, Germany). To avoid thermal degradation during injection

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molding, the polymer granules were dried in a vacuum drying chamber at 40 °C/40 mbar overnight prior to processing.

Samples for DMA testing were fabricated by injection molding using a Haake MiniJet II (Thermo Fisher Scientific, Karlsruhe, Germany) equipped with a 60×10×1 mm stainless steel mold. After injection molding, samples were thermally annealed using a standard lab heating plate equipped with a thermally equilibrated (70 °C) aluminium block with a drilled hole for the temperature sensor.

2.2 DMA experiments

Shape memory behaviour of HMW and VHMW PLLA was investigated in line with the method previously reported [6], using a DMA 850 test bench (TA Instruments Inc., USA). Experiments were carried out in single cantilever mode, with a sample size of 17.5 mm × 10 mm × 1 mm. In a first step, the test chamber was heated to load temperature T_s = 70 °C and the samples were equilibrated for 30 min before a force of 8.0 N was applied at a rate of 0.8 N/min in a second step. The samples were held at 8.0 N for 30 min before temperature was lowered to the fixing temperature T_f = 15 °C at 5 K/min. Samples were kept at T_f for 30 min. Afterwards, the force was released and held at 0 N (force control) for 5 min at 15 °C before the temperature was increased to T_R = 50, 60, 70, 80, and 90 °C, respectively, at 5 K/min with F set to 0 N. Lastly, samples were kept at the set temperature at F = 0 N for 90 min (Fig. 1).[6]

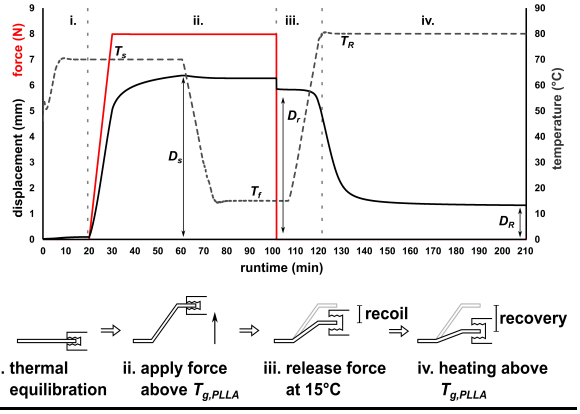

Figure 1: Representative diagram of displacement, force and temperature as function of time for HMW PLLA with T_R = 80 °C for SM characterization and schematic [6] of the mechanical load on the sample. Characteristic values D_s, D_r and D_R are indicated.

From displacement, force, and temperature each as function of time, displacement at load values D_s were extracted at highest deformation at strain temperature T_s. Recoil displacement values D_r were extracted as first value after the force was released at fixing temperature T_f, and recovery displacement values D_R were extracted as last value at the end of the procedure.

Shape retention S_r was calculated using $S_r = D_r \times 100/D_s$ and shape recovery S_R was calculated using $S_R = (D_r\text{-}D_R) \times 100/D_s$.[1,6] Shape recovery rate $K_R = \mathrm{d}D/\mathrm{d}t$ was determined as slope from time/displacement plots in the linear region of the recovery region (iii and iv, Fig. 1) of the plot. Linear fits with manual set borders were performed using Origins Linear Fit MiniTool (OriginPro 2018b, OriginLab, Northampton, USA).

2.3 DSC experiments

Thermal properties investigation was performed under nitrogen atmosphere at ambient pressure using a DSC 1 star system (Mettler Toledo, Zurich, Switzerland). Sample weights were in the range of 4 - 7.5 mg. Conventional calibration was performed using highly pure indium and zinc. Thermograms were analyzed with respect to glass transition (T_g), melting temperature (T_m), and degree of crystallinity (χ). For the latter, heats of fusion was quantitatively evaluated by determining the endothermic peak areas, which were compared with the melting peak area of totally crystalline PLLA (χ_{100} = 93.7 J/g).[7]

3 Results and Discussion

As revealed by DSC experiments, HMW and VHMW PLLA showed thermal properties in a comparable range after thermal annealing (Table 1). Overall, M_w did not show to have a strong influence on T_g and χ.

Table 1: Thermal parameters T_g, T_m and χ of HMW and VHMW PLLA specimens prepared by injection molding after thermal annealing as obtained from DSC experiments (n = 5).

	HMW PLLA (L210)	VHMW PLLA (L214)
T_g (°C)	62.55 ± 0.67	64.54 ± 0.34
T_m (°C)	179.84 ± 0.55	178.55 ± 0.20
χ (%)	55.96 ± 1.25	53.91 ± 4.78

DMA experiments were carried out to evaluate the influence of recovery temperature (T_R) and M_w on shape recovery behaviour. As both materials, HMW and VHMW

PLLA, are very brittle and show nearly no plastic deformation, samples were heated above T_g before displacement (Fig. 1). As the first two steps (i and ii, Fig. 1) were the same for all testing conditions, the data were averaged over all samples, n = 10. In summary, D_s, D_r and S_r data were in a comparable range for HMW and VHMW PLLA and appeared to be independent from M_W. Both polymers exhibited very good S_r above 90% when displaced above T_g and fixed at T_f = 15 °C (Table 1).

Table 2: Displacement at load (D_s), recoil displacement (D_r) and shape retention ($S_r = D_r \times 100/D_s$) for HMW and VHMW PLLA as obtained by DMA experiments. Values are averaged over n = 10 and given with ± SD.

	HMW PLLA (L210)	VHMW PLLA (L214)
D_S (mm)	6.39 ± 0.42	6.72 ± 0.38
D_r (mm)	5.84 ± 0.38	6.21 ± 0.34
S_r (%)	91.45 ± 0.46	92.32 ± 0.66

After fixation at T_f = 15 °C, shape recovery was investigated at different temperatures (50, 60, 70, 80 and 90 °C) with n = 2 each. Table 3 shows the data for recovery displacement (D_R). Interestingly, even when heated just to T_R = 50 °C and T_R = 60 °C, which is below T_g of PLLA (Table 1), both polymers exhibited slight shape recovery. Between T_R = 80 °C and T_R = 90 °C, no distinct difference in D_R could be observed, indicating that a maximum in D_R was reached.

Table 3: Recovery displacement (D_R) at different temperatures T_R for HMW and VHMW PLLA as obtained by DMA experiments. Values are averaged over n = 2 and given with ± SD.

	HMW PLLA (L210)	VHMW PLLA (L214)
$D_{R,50°}$(mm)	5.6 ± 0.4	5.7 ± 0.1
$D_{R,60°}$(mm)	4.8 ± 0.2	5.0 ± 0.2
$D_{R,70°}$(mm)	2.1 ± 0.1	2.4 ± 0.1
$D_{R,80°}$(mm)	1.2 ± 0.1	1.6 ± 0.2
$D_{R,90°}$(mm)	1.3 ± 0.2	1.4 ± 0.1

Following to this, shape recovery (S_R) was calculated (Table 4). S_R reached a plateau of ~70% at T_R = 80 °C. Heating to T_R = 90°C did not lead to a higher S_R. Both polymers showed similar S_R and M_W did not seem to have a pronounced influence. From the data, it can be seen that even at temperatures below T_g, a certain amount of shape recovery occurred. This can be explained when expanding thermal analysis beyond DSC experiments and considering results from DMA, in particular storage modulus E' and loss modulus E'', which revealed that the materials mechanics are already affected by temperatures above 50 °C.[8]

Table 4: Shape recovery ($S_R = (D_r-D_R)\times 100/D_s$) at different temperatures T_R for HMW and VHMW PLLA as obtained by DMA experiments. Values are averaged over n = 2 and given with ± SD.

	HMW PLLA (L210)	VHMW PLLA (L214)
$S_{R,50°}$(%)	6.9 ± 0.3	6.8 ± 0.3
$S_{R,60°}$(%)	17.2 ± 0.9	17.5 ± 0.4
$S_{R,70°}$(%)	57.2 ± 1.0	57.3 ± 0.6
$S_{R,80°}$(%)	71.9 ± 0.7	69.0 ± 2.1
$S_{R,90°}$(%)	71.4 ± 0.9	71.1 ± 0.1

The comparable values for SR for HMW PLLA and VHMW PLLA indicate a negligible influence of the difference in M_W on the shape memory behavior. In both cases, strain-induced crystallization leads to changes in crystalline structure from lamellar to a fibrillary morphology, resulting in a relatively low SR below 90% [9]. To further investigate the influence of M_W and temperature, shape recovery rate $K_R = dD/dt$ was determined for HMW PLLA (L210) and VHMW PLLA (L214) and each recovery temperature (Fig. 2). K_R values are given in Table 5. From these data, it can be seen that with increasing temperature the rate of recovery increased. Contrary to D_R and S_R, where no difference between T_R = 80 °C and T_R = 90 °C could be found, heating to T_R = 90 °C led to an increase in K_R. Moreover, VHMW PLLA (L214) showed an overall faster shape recovery compared to HMW PLLA (L210).

Table 5: Shape recovery rate $K_R = dD/dt$ obtained from slopes of linear fits (Fig. 2) for HMW and VHMW PLLA at different temperatures T_R as obtained by DMA experiments. Values are averaged over n = 2 and given with ± SD.

	HMW PLLA (L210)	VHMW PLLA (L214)
$K_{R,50°}$(mm/min)	0.007 ± 0.002	0.010 ± 0.012
$K_{R,60°}$(mm/min)	0.025 ± 0.003	0.029 ± 0.002
$K_{R,70°}$(mm/min)	0.104 ± 0.021	0.140 ± 0.019
$K_{R,80°}$(mm/min)	0.297 ± 0.052	0.407 ± 0.016
$K_{R,90°}$(mm/min)	0.480 ± 0.051	0.543 ± 0.011

At T_R = 70 °C and T_R = 80 °C, K_R was 34.6% and 37.1% higher for VHMW PLLA compared to HMW PLLA, respectively (Table 5). This decreased to K_R being only 13.1 % higher for VHMW PLLA at T_R = 90 °C, still L214 showed a considerable higher shape recovery rate as L210.

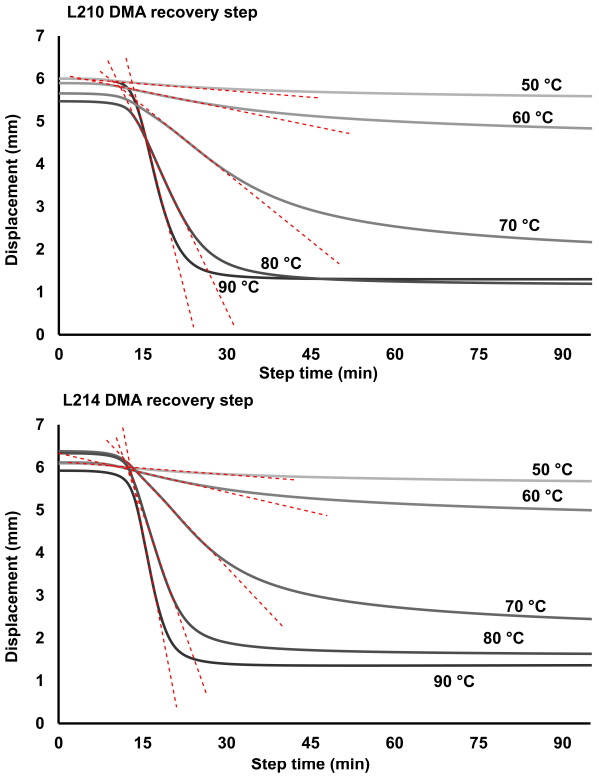

Figure 2: Progression of temperature induced shape recovery of HMW and VHMW PLLA at T_R = 50, 60, 70, 80 and 90°C, respectively. Shown are sections iii and iv (see Fig. 1) for each displacement vs. time plot. Curves are averaged (n = 2). Red lines indicate slopes of the linear regions for determination of K_R. The offset in displacement at the start of the segment is due to material inhomogeneities.

The differences in K_R may be of particular interest, as both materials exhibited comparable values for χ (Table 1), indicating that the increase in molecular chain length and amount of lactic acid $n_{lactic\ acid}$ as repeating unit ($n_{lactic\ acid,HMW}$ = 4,444 versus $n_{lactic\ acid,VHMW}$ = 9,722 as calculated from n = $M_W/M_{lactic\ acid}$ using M_W for HMW and VHMW PLLA and $M_{lactic\ acid}$ = 72 g/mol) enables to store a higher amount of elastic energy, which can be released upon heating. This is of interest, as a higher molecular weight of PLLA directly influences the biocompatibility, as inflammation reaction is reduced with increasing M_W.[10]

4 Conclusion

Temperature induced shape recovery of polymers is a promising tool to generate 4D materials and to enhance the processing of the materials. Within this work, it was shown, that for HMW PLLA (L210) and VHMW PLLA (L214) shape recovery reaches a temperature plateau, which is relevant regarding the thermal susceptibility of PLLA towards degradation. Heating above T_R = 80 °C did not show to have any beneficial effect on S_R. However, heating above this temperature did lead to an increase in shape recovery rate, making the shape recovery process faster.

In terms of the influence of molecular weight, both, HMW PLLA and VHMW PLLA variants used did not show any differences in D_S, D_R, S_r, or S_R. However, the shape recovery rate was overall considerably higher for VHMW PLLA (L214) compared to HMW PLLA (L210), indicating a pronounced influence of polymer chain length.

Author Statement

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