Bulk modification of poly (lactic acid) by CO_2 laser radiations

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Abstract. Poly(lactic acid) (PLA) is a bioresorbable aliphatic polyester. It has varying rates of degradation influenced by factors including its percentage of crystallinity (χ) and glass transition temperature (T_g). In order to improve its bioresorbability for medical applications modification of the polymer is required. Many approaches are considered in the literature including bulk modification. The aim of the present study is to assess the efficacy of CO_2 laser modification by characterising PLA material before and after laser treatment.

Extruded PLA sheets were used for laser trials. A Design of Experiments (DoE) methodology was used to set various combinations of levels for laser power and scanning speed.

It was found that CO_2 laser processing of PLA induces bulk property changes. The increase in laser interaction with the polymer led to a decrease in the percentage crystallinity (χ). This trend was observed from the first heat scan of Differential Scanning Calorimetry (DSC). For both the first and second heat scan, ANOVA revealed that there was a statistical significance of scanning speed on the crystallisation temperature (T_c) and χ. There were some permanent changes in the polymer matrix due to laser treatment. XRD analysis evidinced similar behaviour. By controlling χ, one can control the bioresorption of the polymer. The percentage contribution of surface layers of the polymer to bulk property modification needs further investigation.

Keywords. bioresorbable, CO_2 laser, design of experiment, scanning speed, percentage crystallinity

1. Introduction

PLA is one of the most widely researched and utilised biodegradable thermoplastics. This aliphatic polyester has various medical applications such as vascular stents[1], drug delivery systems[2], orthopaedic implants, and scaffolds. For applications such as drug delivery, bioresorption is required in which there is bulk degradation and total removal of the by-products through natural pathways. The resorption time can be controlled by various factors like polymer crystallinity, water diffusion rate into the polymer, molecular weight, molecular weight distribution and the stereoisomeric content [3].

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Laser modification is considered a simple and easily controlled process. Grabow et al.[4] studied the effect of CO_2 laser sterilisation and cutting on Poly-L-Lactide (PLLA). The sterilisation procedure of the material influenced mechanical properties. Physicochemical properties of biodegradable PLLA were studied after treatment with KrF laser and CO_2 laser by Stepak et al. [5,6]. In the previous research, the effect of laser parameters at different levels upon degradation rate is not explored fully. Also, the persistence of laser interaction effect after the first heat scan in DSC analysis is questionable. This paper aims to develop a sound knowledge-base in this area.

The focus here is on the bulk modification of PLA for drug delivery applications using CO_2 laser radiations. The polymer-laser interaction depends upon various factors such as laser power, scanning speed, spot-size, wavelength, the process environment, etc. These parameters may lead to various properties modifications of the polymer due to thermal effects which may influence the rate of degradation.

2. Experimental Work

2.1. Material

General purpose extrusion grade of PLA Ingeo™ Biopolymer 2003D (density 1.24 g/cm^3, MFI 6 g/10min at 210°C and 2.16 Kg load) was obtained from NatureWorks LLC (USA). PLA films (thickness: 1mm) were obtained by using a Prism twin screw extruder (TSE) of L/D ratio 25:1.

2.2. Laser-Irradiation

Irradiation was carried out using a CO_2 laser (Synrad: J48) which provides a continuous laser beam of wavelength 10.6 μm. Coupons of material were exposed to the unfocussed laser beam (beam diameter 5mm). The coupons were mounted on a linear servo motor actuated set of X-Y-Z stages (Intelligent Actuator). The laser beam was switched on and the samples scanned through from edge to edge to avoid "hot spots". All irradiation was at normal incidence. The power of the laser beam and speed of translation of the coupon were varied in a Designed Experiment as is described below.

2.3. Design of Experiments

Statistical design of experiments (DOE) was applied for planning the trial to collect appropriate data and analyse by the analytical method, resulting in valid and objective conclusions. In this experiment, two controllable input parameters were taken: laser power and scanning speed. PLA films were irradiated at three levels of laser power and scanning speed (Table 1). The levels chosen gave a visible effect on the samples without causing damage as determined by trial and error. Nine different sets of laser trials were carried out. Replicates of the experiments were made to give a total of 18 experiments.

Table 1. Factor levels for laser power and scanning speed

Parameters	Notations	Units	Levels		
			Low	Mid	High
Laser power	P	W	4.5	5.0	5.5
Scanning speed	S	mm/s	3.0	4.0	5.0

2.4. Characterisation

2.4.1. Differential Scanning Calorimetry (DSC)

DSC analysis was carried out on 19 samples with a mass of around 5 mg each. The tests were carried out using a Perkin-Elmer DSC 4000 (Temperature performance: accuracy ±0.1°C and precision ±0.02 °C). Tests were carried out in a N_2 atmosphere for a temperature range of -20 to 200°C (two heat scan: 10°C/min). For the reliability of the data, heat flow and temperature were calibrated with a standard material (indium).

2.4.2. X-Ray Diffraction (XRD)

XRD was carried out to analyse the crystalline nature of the PLA films. The diffractograms were obtained in the range of 10°-80° using Cu Kα radiation with the wavelength of 0.15418 nm in a Siemens D500 X-ray powder diffractometer (operating at 40 kV and 30 mA). Three samples were cut from the film to carry out the trials for the confirmatory test.

3. Results and Discussion

Table 2. Thermal characterisation of laser treated and non-treated samples of PLA

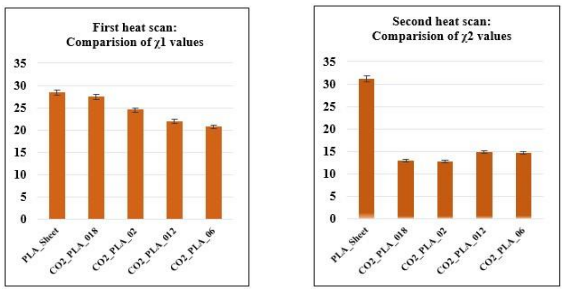
Sample ID	P	S	First DSC heat scan data			Second DSC heat scan data		
			T_c1 (°C)	ΔH_m1 (J/g)	$\chi1$ (%)	T_c2 (°C)	ΔH_m2 (J/g)	$\chi2$ (%)
CO_2_PLA_01	Low	Mid	95.90	25.53	27.45	125.02	14.66	15.76
CO_2_PLA_02	Low	High	104.38	22.75	24.46	126.03	11.81	12.70
CO_2_PLA_03	Mid	Low	118.06	22.08	23.75	125.04	13.45	14.46
CO_2_PLA_04	Mid	High	99.98	24.04	25.85	126.03	12.36	13.29
CO_2_PLA_05	High	Mid	99.89	24.44	26.28	125.53	11.87	12.76
CO_2_PLA_06	High	Low	121.32	19.22	20.67	125.37	13.61	14.64
CO_2_PLA_07	Mid	Mid	93.45	25.56	27.49	124.53	14.79	15.91
CO_2_PLA_08	High	High	109.40	22.46	24.15	125.37	12.96	13.93
CO_2_PLA_09	Low	Low	100.29	23.73	25.51	126.04	12.87	13.83
CO_2_PLA_010	High	Mid	107.59	24.76	26.62	124.87	14.81	15.92
CO_2_PLA_011	Low	Mid	98.75	24.54	26.39	124.33	14.95	16.07
CO_2_PLA_012	High	Low	120.81	20.40	21.93	125.70	13.82	14.86
CO_2_PLA_013	High	High	110.83	23.73	25.52	125.20	14.01	15.07
CO_2_PLA_014	Mid	Mid	114.23	21.54	23.17	125.19	15.24	16.38
CO_2_PLA_015	Mid	Low	108.39	23.43	25.20	125.70	12.79	13.75
CO_2_PLA_016	Low	Low	108.24	20.31	21.84	126.71	13.87	14.92
CO_2_PLA_017	Mid	High	120.26	20.12	21.64	126.04	13.65	14.67
CO_2_PLA_018	Low	High	94.06	25.54	27.47	125.69	12.00	12.90
PLA_Sheet	Untreated		111.39	26.39	28.37	118.05	28.95	31.13

3.1. Thermal Characterisation

Thermal properties of the laser-treated and non-treated PLA sheets were obtained using DSC through the first and second heating scan. Table 2 summarises the results for glass transition (T_g), crystallisation temperature (T_c) and melting temperature (T_m), enthalpy of crystallisation (ΔH_c) and enthalpy of melting (ΔH_m). The combinations of various levels of P and S are also given in the table. The percentages of crystallinity (χ) were calculated ($\chi 1$: first scan and $\chi 2$: second scan) by considering ΔH_m: 93 J/g for 100% crystalline PLA [7,8].

As there were no significant changes in T_g, T_m and ΔH_c, only χ and T_c were considered for further analysis. The value of χ for PLA sheet without any laser treatment was observed to be around 28.37% and 31.13% from the first and second heat scan of DSC respectively.

The laser interaction is at its minimum for low P and high S, while it is maximised for high P and low S. It was observed that $\chi 1$ (from DSC scan 1) decreased with an increasing laser interaction as shown in the bar graph (Figure 1(a)). However, the same trend was not observed in the second heat scan (Figure 1(b)).



(a) (b)

Figure 1. Comparison of percentage of crystallinity from the first and second heat scan of DSC

3.2. Analysis of Variance (ANOVA)

ANOVA technique was applied to determine whether the factors P or S, or a combination of P and S, have a statistically significant effect on any of responses from the DSC characterisation of the samples.

It is normally assumed that the first scan removes the thermal history of the polymer sample. However, it was found S and the quadratic term for S (S*S) had a statistically significant effect on T_c and χ for both the first and second heat DSC scans (Table 3).

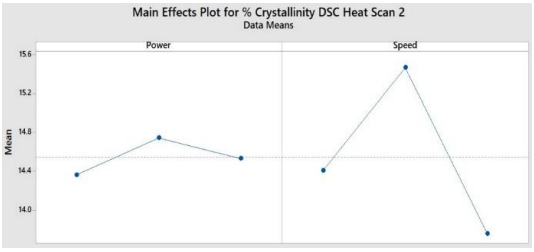


Figure 2. Main effects plot for the factors power and scanning speed

Figure 2 is a main effects plot that shows the effect of changing the factors P and S on the response variable χ_2. The quadratic term for S has an effect that is evident when viewing Table 3. The quadratic term for S had statistical significance with a p-value of 0.024. This analysis indicates that the S had a significant effect on the responses T_c and χ. There were no cases where it was found that P or the interaction of P and S were statistically significant.

Table 3. Statistically significant factors, the response variables and the associated p-values

Response	**T_c1**	**χ_1**	**T_c2**		**χ_2**
Factor	S*S	S*S	S*S	S	S*S
P-value	0.048	0.039	0.006	0.018	0.024

3.3 Confirmatory Test using XRD

The crystallinity and crystalline structures were further investigated using XRD. Samples with the maximum interaction (CO_2_PLA_06), minimum interaction (CO_2_PLA_02) and a non-irradiated sample (PLA sheet) were selected for XRD analysis. The results are shown in Figure 3.

Non-irradiated extruded PLA Sheet shows a crystalline peak at 16.4°. The intensity of this diffraction peak decreases with the increase in the CO_2 laser radiations indicating that the crystallinity of PLA decreases, as was observed in the first heat scan of DSC. Figure 3 also shows the formation of new crystalline structures with a peak at 22.4° in the laser treated samples. In general, PLA crystallises in α-form (and/or ά-form) which is described as orthorhombic, or pseudo-orthorhombic with the diffraction peaks at 14.9, 16.4, 19.1 and 22.4 corresponding to (010), (110), (203) and (015) crystallographic planes, respectively [9,10]. The α-modification of PLA is believed to grow under normal conditions like melt, cold or solution crystallisation.

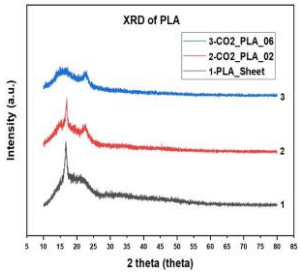


Figure 3. Comparison of XRD profiles of maximum laser interaction CO_2_PLA_06 and minimum laser interaction CO_2_PLA_02 with non-irradiated PLA samples (PLA_Sheet)

4. Conclusions and future work

A change in the polymer crystallinity was observed as the laser interaction with the polymer increased. The change was observed for both the first and second heat scan of the DSC. ANOVA results indicates that for both heat scans the scanning speed of the laser was a statistically significant factor relating to changes in crystallisation temperature and percentage crystallinity for the CO_2 laser treated samples. There was no statistical significance of power during the ANOVA analysis, which may be due in part to the narrow range of powers used.

The samples were further investigated through XRD. It was found that apart from the decrease in the percentage of crystallinity with an increase in laser interactions, there was also a formation of new crystalline structures. Since a decrease in polymer crystallinity increases the bioresorption rates of the polymer, it may be possible to adjust this parameter through CO_2 laser processing [11]. This could be confirmed by way of degradation analysis of laser treated materials.

It is likely that the laser may have affected surface layers of the polymer that contributes to the change in crystallinity. Contact angle measurements and hardness testing may facilitate a better understanding of the changes occurring due to irradiation. In the context that the heat affected zone from the laser extends a limited distance into the coupons, further analysis may reveal a more dramatic response of the PLA to laser irradiation than the current bulk analysis shows.

The overall study shows that the first heat scan of DSC does not obliterate the laser treatment effect. Laser treatment may have lead to some permanent changes like the reorganisation of the conformational structure, thermo-degradation, crosslinking, etc. in the bulk matrix of the polymer. Further investigations concerning the biodegradation studies and chemical modification of PLA due to CO_2 laser irradiations will be conducted in future work.

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