

Effect of Laser Surface Modification on the Crystallinity of Poly(L-Lactic Acid)

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Crystallinity of semicrystalline polymers such as aliphatic homopolymer poly(L-lactic acid) (PLLA) affects their degradation and physical properties. In this paper, the effects of laser irradiation using the third harmonic of a Nd:YAG laser on the crystallinity, long-range order, and short-range conformations at the surface of PLLA films are investigated. The factors affecting the transformation are also studied. Detailed characterization of the effect of laser treatment is accomplished using microscopy, X-ray diffraction, and infrared spectroscopy. The cooling rates in the process and the spatial and temporal temperature profiles are numerically examined. The simulation results in conjunction with melting and crystallization kinetics of PLLA are used to understand the effect on sample crystallinity. The effects of laser fluence and annealing conditions on the crystallinity of the processed films are examined. Since degradation profiles depend on crystallinity, laser processing can potentially be used to achieve a modified spatially controlled polymer surface with promising applications such as controlled drug delivery.
[DOI: 10.1115/1.3039519]

1 Introduction

Biodegradable polymers have generated considerable interest due to wide-ranging applications. Poly(α -hydroxy acid) family of polymers, especially poly(lactic acid) (PLA), and its copolymers with poly(glycolic acid) (PGA) are particularly attractive since they are approved by the United States Food and Drug Administration (USFDA) and demonstrate high strength and high modulus. They degrade, primarily hydrolytically, in physiological and other environments to produce bioabsorbable products. These have been used extensively in drug delivery devices, fixation plates and pins, and tissue engineering scaffolds with promising uses in packaging and agriculture. While publications on biodegradable polymers are numerous, good reviews on PLA can be found in Refs [1,2] discussing the structure, properties, and crystallization behavior of PLA.

In drug delivery and packaging applications, it is imperative to control the properties of the polymer. Lee and Gardella [3] studied the surface structure-property relationships in poly(α -hydroxy acid)s and their degradation process. Since the degradation (over six months to three years) and mechanical properties of PLA are strongly influenced by the sample crystallinity, there is a need for surface modification techniques to create interfaces with suitable properties to meet specific biomedical applications. Tsuji and Ikada [4] studied the hydrolysis of PLA with varying crystallinity and concluded that PLA chain hydrolysis initiates in the amorphous regions within and between the spherulites.

Properties of PLA can be altered with either bulk or surface modifications. Bulk processes have the potential to affect only overall properties, so while overall degradation rate may be affected, degradation profiles are difficult to control. While surface treatment methods such as coating, chemical modifications, and plasma treatment have been shown to affect cell affinity, no surface structural modifications have been attempted as these methods are inherently difficult to control spatially [5]. More recently, laser processing of biodegradable polymers has generated interest. However, the main focus of several authors has been micro- and

nanoscale fabrication or study of surface properties such as wettability [6,7]. Laser treatment as a means of surface modification is attractive due to its flexibility, ease of use, and spatial control.

Aguilar et al. [8] studied the effects of laser patterning on the degradation and chemical modification of PGA. X-ray photoelectron spectroscopy (XPS) studies suggest chemical changes and tests in phosphate buffer solution (PBS) indicate slightly increased degradation during initial stages without affecting overall degradation time. However, the authors did not study the reasons for variation in degradation profiles between the processed and unprocessed samples. Lazare and Benet [9] used single excimer pulse irradiation to induce periodic roughness on the surface of PET (Mylar) films. They used ellipsometric measurements to indicate the presence of a thin surface layer with variant optical properties although the changes in crystallinity were not investigated. Dunn and Ouderkirk [10] studied the excimer laser texturing of crystalline PET and observed an increase in refractive index of the treated polymer to suggest that anisotropy of a newly formed amorphous layer causes texturing. The authors also used IR reflection absorption spectroscopy to compare the spectra of amorphous and laser treated samples to deduce formation of a possibly quasisamorphous layer of the order of 90 nm. However, they did not study the effect on the long-range order or crystallinity in the material and possible causes.

The primary subject of this work is to utilize laser irradiation to reduce the crystallinity at the surface of PLA films, which can allow for more control over the degradation profile especially with increased contribution toward initial surface erosion from amorphous regions. Microscopy wide angle X-ray diffraction (WAXD) and Fourier transform infrared (FTIR) spectroscopy are used to study the morphology, crystallinity, and short and long-range conformation changes. Furthermore, a simple 2D axisymmetric heat transfer model is used to understand the temperature gradients in the process and their effect on crystallinity evolution in the material during processing. The effects of annealing temperatures and laser fluence have been considered.

2 Background

High molecular weight PLA is a colorless, stiff, thermoplastic polymer with a glass transition of $\sim 60^\circ\text{C}$ and melting tempera-

Contributed by the Manufacturing Engineering Division of ASME for publication in the JOURNAL OF MANUFACTURING SCIENCE AND ENGINEERING. Manuscript received October 11, 2007; final manuscript received October 3, 2008; published online September 4, 2009. Review conducted by Shaochen Chen.

ture of the order of 170–210°C, which is higher than most low-melting polymers, making it suitable for thermal processing. PLA can exist as isomers poly-L-lactide (PLLA), poly-D-lactide (PDLA), or poly-DL-lactide (PDLLA), of which PLLA is semicrystalline due to its tacticity while PDLA is amorphous. PLLA can be crystallized by slow cooling from melt, annealing at various temperatures above glass transition and under strain. Semicrystalline polymers such as PLLA are known to crystallize by chain folding, forming lamellae perpendicular to the chain axis and thickness of the order of 10–30 nm. To consider the effect of laser processing on PLLA, it is important to understand the structure, melting, and crystallization of polymers, in general, and PLLA, in particular. During nanosecond laser irradiation, short laser pulses can cause rapid heating and melting with cooling rates significantly higher (10^8 – 10^9 K/s) than traditional thermal processes. The total amount of the structural change in the material is a function of inception of nucleation and propagation (growth), which are a strong function of the undercooling and hence cooling rates. Nonisothermal crystallization studies of PLLA have shown that the kinetics of melt crystallization of PLLA are relatively slow as compared with other semicrystalline polymers and hence the potential to affect its crystallinity using laser processing [11].

2.1 Crystallization and Melting. While thermodynamics of melting are relatively well understood, its kinetics are still under deliberation. In polymers, the melting transition occurs over a temperature range, with the equilibrium melting temperature defined in terms of the energy of the free surface using the *Gibbs–Thompson equation* and varies with the thickness distribution of the lamellae in the material. Laser heating is rapid in comparison with traditional processes and while reversible melting is expected for quasi-isothermal processes, nonisothermal conditions with superheating such as laser irradiation allow for irreversible melting. With rapid melting, chains undergo a sudden increase in entropy and radius of gyration, while the melting rate is an increasing function of temperature. In general, melting is a fast process that is completed with low superheating as compared with crystallization, which is a relatively slower process that needs a high supercooling [12,13].

Crystallization of polymers from the melt can be described in terms of primary nucleation and crystal growth and the *Lauritzen–Hoffman theory* is widely accepted for modeling the variable dependence of growth. While detailed treatment can be found elsewhere [12], nucleation rate can be seen very simply as a function of the free energy of nucleation barrier ($\Delta G \propto (T_m)^2/(\Delta T)^2$) and the free energy of activation ($\Delta G\eta$) and is given by [14]

$$i = \left(\frac{NkT}{h} \right) \exp \left(- \frac{\Delta G + \Delta G\eta}{kT} \right) \quad (1)$$

where h is the Planck constant, k is the Boltzmann constant, N is the number of uncrystallized elements in the nucleation process, T_m is the equilibrium melting temperature, and $\Delta T = T_m - T_c$ is the undercooling (T_c is the crystallization temperature). Hence, nucleation is controlled by undercooling and follows a bell shaped curve that reaches a maximum at $T_c = T_c^*$, which is of the order of 105–110°C in PLLA. During laser processing, large deviations from T_m occur and hence the final development of crystallinity is expected not to be limited by the nucleation barrier but growth kinetics. Growth is primarily seen to proceed by sequential deposition on new strands on a flat molecular surface and the growth rate G of the crystal (of thickness l) can be simplified as [15]

$$G = G_0 \exp \left(- \frac{U^*}{R(T_c - T_\infty)} \right) \exp \left(- \frac{K_g}{T_c \Delta T f} \right) \quad (2)$$

where K_g is the nucleation constant, $f = 2T/(T_m + T)$ is a factor accounting for heat of fusion change due to deviation from T_m , U^* is the activation energy of segment transport, R is the gas constant, T_∞ is the temperature at which no motion is seen, and G_0 is

the front factor (relatively independent of temperature). In case of PLLA, primarily regime II growth (high nucleation rate with low growth velocity) is seen during isothermal crystallization with peak growth rates of the order of 2–5 $\mu\text{m}/\text{min}$ [11].

2.2 Overall Crystallization Kinetics and Nonisothermal Crystallization. Overall crystallization hence proceeds through simultaneous nucleation and growth and the time dependent overall degree of transformation is described by the Avrami equation of the form

$$\phi(t) = 1 - \exp(-kt^m) \quad (3)$$

where $k = \pi n v^3/3$ and depends on the shape of the growing crystallites and type and number of nuclei formed with n the number of nuclei formed per second and v the growth velocity of nuclei, both being temperature dependent. m is the Avrami exponent, which depends on nucleation type and growth geometry but not rate. However, in laser processing it is important to consider nonisothermal crystallization kinetics. Considering the approach used by Nakamura et al. [16], the heat balance in unit mass can be described by $d\phi(t)/dt = (R(T - T_s)/\Delta H_f) + (C_p/\Delta H_f)(dT/dt)$, where Φ is the mass fraction of the transformed polymer, R is the heat transfer coefficient to surroundings at temperature T_s , ΔH_f is the heat of crystallization per unit mass of the transformed polymer, and C_p is the mean specific heat of the polymer. The equation can be solved to obtain $T(\tau)$, the temperature as a function of time during cooling. In our analysis, a numerical model as described later in the study will be used to obtain the cooling profile. The transformed fraction as a function of time can be simplified to Avrami form as

$$\phi(t) = 1 - \exp \left[- \left(\int_0^t K(T(\tau)) d\tau \right)^m \right] \quad (4)$$

where $K(T) = k(T)^{1/m}$ and $k(T)$ is the isothermal crystallization rate constant depending on the polymer properties.

3 Materials and Methods

3.1 Sample Preparation. PLLA powder samples with less than 0.01% residual solvent and less than 0.01% residual monomer were obtained from PURAC[®] America. The inherent viscosity (η) in chloroform at 20°C was 1.61 dl/g. Mark–Howink equation [17] with $\eta = 5.45 \times 10^{-4} M_v^{0.73}$ was used to calculate the viscosity average molecular weight as $M_v = 56,756$. Films of nominal thickness of 20 μm ($\pm 10 \mu\text{m}$) were prepared by solvent casting and similar thickness specimens were selected for each experiment. PLA granules were dissolved in methylene chloride (0.1 g/3 ml, Sigma Aldrich[®]), stirred constantly for 3 h using a magnetic stirrer, cast in a glass dish, and left to settle for 10 h at -20°C . The film was cut into $15 \times 15 \text{ mm}^2$, dried for 24 h prior to use [18], and subsequently annealed at temperatures of 110°C and 135°C for 3 h. Amorphous samples were prepared by melting films at 200°C (3 min) between cover slips and subsequent quenching by placing in dry ice. While both hot-pressing and solution casting can be used to prepare films of PLLA, the former provides thicker films (100–200 μm) that have to be melt annealed. We prefer the latter method as it yields thinner films allowing study of crystal structure change utilizing optical transmission and bulk X-ray diffraction (XRD) techniques. It also eliminates any induced structural orientation due to pressures applied at elevated temperatures and thermal effects on the material prior to surface modification.

3.2 Experimental Setup. The experimental setup (Fig. 1) consists of a 0.5 W Q-switched Nd:YAG (neodymium-doped yttrium aluminum garnet) laser operating at 355 nm in TEM₀₀ mode utilized as the light source with a 50 ns pulse duration and a 1 kHz repetition rate. The laser scan velocity is governed by synchronized motion stages and optimized at 0.3 cm/s. 28 μm diameter beam was used with fluence varying from 30 J/cm² to 50 J/cm².

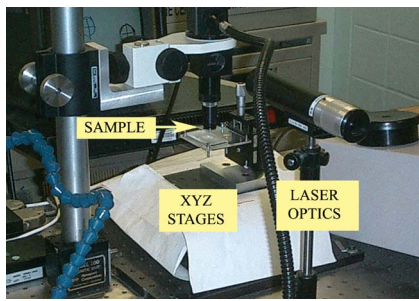


Fig. 1 Experimental setup

To study the effects of laser repetition rate, the frequency was increased to 1.5 kHz with a corresponding increase in the relative beam travel velocity to 0.45 cm/s while maintaining pulse overlap. The sample was placed in a holder on computer-controlled XY stages and a $0.9 \times 0.5 \text{ cm}^2$ area treated in open air. Ultraviolet (UV) laser at 355 nm was selected as irradiation at longer UV wavelengths allows for primarily thermal effects (as the photon energy is below the bond breaking energy of the C–C and C–H bonds) as opposed to photochemical bond breakage at shorter wavelengths and allows for greater affected depth due to the absorption coefficient dependence on wavelength [7]. This would be beneficial in this scenario, as we do not intend to alter chemical functionality at the surface and a thermal contribution to laser material interaction is important for inducing structural changes.

3.3 Characterization. The morphology of PLLA films was observed in transmission mode using a high resolution optical microscope (Nikon Eclipse). The microstructure of the microtomed sample cross section was also observed with the aid of a scanning electron microscope (SEM) (JEOL JSM-5600 LV) at voltages of 3–5 kV after gold coating (4–6 min). The coating time is optimized to obtain good imaging and at the same time prevent surface charge. For SEM observation 300 μm thickness samples were used for ease of microtoming. WAXD measurements were carried out using an Inel X-ray diffractometer. Film specimens were exposed to monochromatic Cu K α radiation ($\lambda = 1.542 \text{ \AA}$) at 30 kV and 30 mA and the scattered intensity was measured in the Bragg angle range (2θ) from 10 deg to 90 deg. Mass absorption coefficient calculated for PLLA indicates that X-rays penetrate through the bulk of the film.

A Thermo-Nicolet FTIR spectrophotometer with attenuated total reflectance (ATR) attachment using a ZnSe crystal at a fixed angle of 45 deg was used for measuring the IR spectrum of the samples; the data were recorded with a 4 cm^{-1} resolution (averaging over 128 scans) and were analyzed by OMNIC software. ATR technique of IR spectroscopy was utilized for measurement of sample spectra, since it is unaffected by the sample thickness and the evanescent field generated to probe the surface is nontransverse and hence has vector components that can interact with dipoles in all directions allowing more information to be probed. Care was taken to ensure that reproducible pressure was maintained between the sample and the crystal for a set of experiments and each measurement was repeated at least twice. It is important to note that the depth of penetration of the beam can be estimated using the equation [19] $d_p = \lambda / 2\pi n_1 \sqrt{(\sin^2 \theta - n_{21}^2)}$, where λ is the radiation wavelength in air, n_1 is the ATR crystal refractive index (ZnSe: 2.4), θ is the incident angle (fixed at 45 deg), and n_{21} is the ratio of the sample to crystal refractive indices (0.6083 based on n_2 of 1.46). d_p as calculated for our setup ($\theta = 45 \text{ deg}$) varies from 0.98 μm to 2.8 μm in the wave number range from 2000 cm^{-1} to 650 cm^{-1} . ATR correction was applied to all spectra to normalize the effect of wavelength dependence.

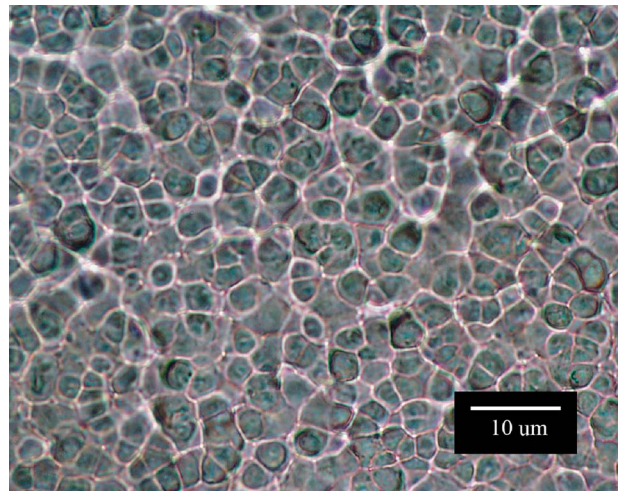


Fig. 2 Optical transmission micrograph of sample PLLA film annealed at 110°C

4 Results and Discussion

The morphology of the solution cast and annealed polylactide films observed under the optical microscope is shown in Fig. 2. The micrographs indicate crystalline films with formation of spherulitic crystallites with polygonal interfaces. The crystallite size is $\sim 3 \mu\text{m}$ for 110°C annealed specimens. The film cross section under the microscope suggests that these are likely 3D structures, stacked through the thickness. Similar morphology was observed under SEM.

4.1 Effects on Long-Range Order. The crystal structure of PLLA has been well studied and three different crystal modifications are seen, viz., the α -form, the β -form, and the γ -form depending on processing conditions. The α -form is the most commonly observed polymorph seen both for solution cast and melt processed samples with an orthorhombic unit cell with 2 10_3 (3 monomeric units per 10 $\text{\AA}$ rise) polymeric helices [20,21]. The unit cell dimensions indicated by Marega et al. [21] are $a = 10.7 \text{ \AA}$, $b = 6.126 \text{ \AA}$, and $c = 28.939 \text{ \AA}$. The structure of PLA as proposed by Kobayashi et al. [20] is shown in Fig. 3. The X-ray diffraction profile of PLLA annealed at 110°C along with the treated sample (40 J/cm^2), amorphous sample, and background scatter are shown in Fig. 4. The crystallinity of the samples was determined based on simplifications of the *Ruland method* as discussed by Alexander and Campbell [22,23]. The background scattering was separated and the amorphous fraction was fitted using a Gaussian profile, as shown in Fig. 4. The fitted amorphous profile was scaled accordingly to fit the baseline of the measured diffraction patterns at different laser fluences. Mass fraction of the crystalline phase (X_c) was obtained by dividing the total intensities of the crystalline reflection with the total intensity between $2\theta = 14 \text{ deg}$ and 22 deg . The disorder factor due to lattice defects and thermal disorder was not considered in the calculations. The most prominent peak is seen at 16.7 deg, which represents the (110) and (200) reflections and smaller peaks are seen at 14.7 deg and 19.1 deg representing planes with Miller indices of (010) and (203), respectively. This agrees with the α -form of PLLA in line with other observations in literature for solution grown crystals. Crystallite thickness can be measured using the *Scherrer equation* [23], $t_{hkl} = k\lambda / B_{hkl} \cos \theta$, where t_{hkl} is the crystallite size perpendicular to the plane (hkl), K is the crystallite shape factor (0.9), λ is the wavelength, B_{hkl} is the width at half-maximum, and θ is the Bragg angle. For samples annealed at 110°C, the crystallite thickness was measured to be in the range of 15–20 nm using the (110/200) reflection, as seen in Fig. 13.

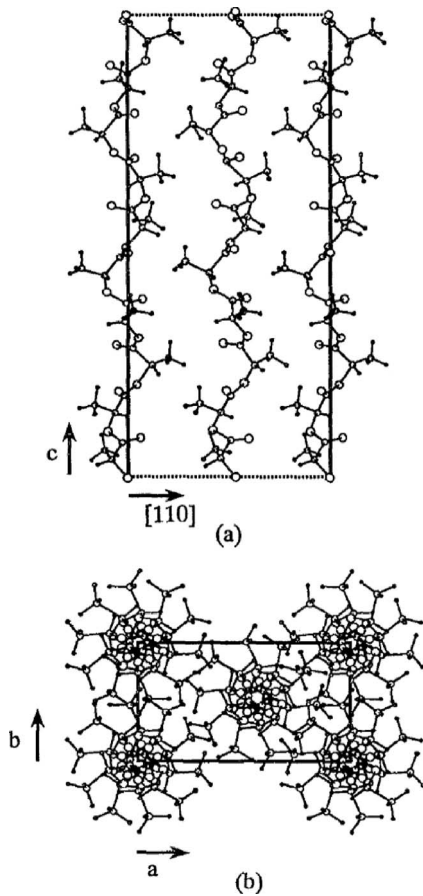


Fig. 3 α -form structure of PLLA indicating the a , b , and c directions of the orthorhombic 10_3 unit cell [20]

Effects of laser fluence ($30\text{--}50\text{ J/cm}^2$) have been studied to allow for processing control by simply changing the laser power. The WAXD profiles of the crystalline fraction of untreated sample and sample irradiated at various laser fluences are shown in Fig. 5. There is a reduction in the intensity of both (110/200) and (203) peaks. The (110/200) peaks show increasingly reduced intensity

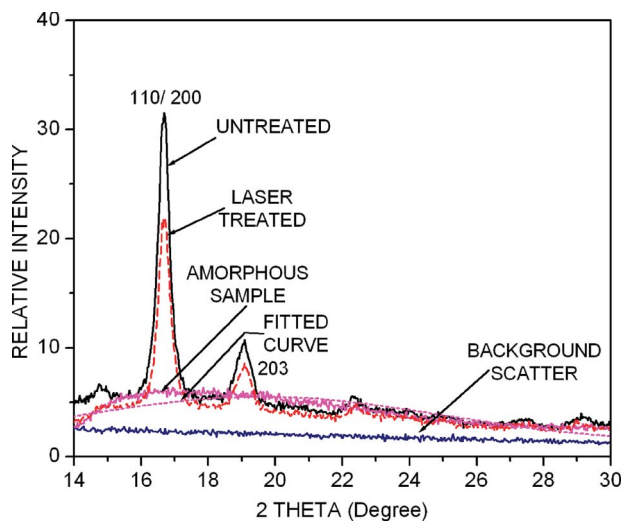


Fig. 4 WAXD profiles of untreated sample annealed at 110°C , laser treated (40 J/cm^2), amorphous sample, and background scatter. Note reduction in 110/200 and 203 peaks.

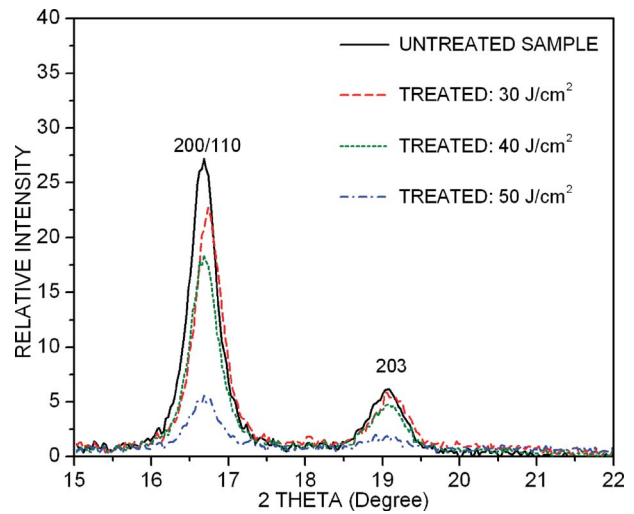


Fig. 5 WAXD profiles indicating effects of laser fluence on the long-range order of PLLA sample. Profiles represent the crystalline fraction in the material. The variation in crystallinity with fluence can be seen in Fig. 13.

with increasing fluence, which indicates that the laser treatment primarily resulted in reduced order perpendicular to the helical chain direction c (see Fig. 3) and hence sample crystallinity. Figure 13 indicates the effect of laser treatment at different fluences on the measured mean crystallinity and crystallite thickness of the sample (the bar indicates standard error). The crystallinity of the sample was reduced by 7–8% for lower intensities to almost half the original value at higher fluences. Since WAXD provides integral intensity data from the complete depth of the sample film (see Sec. 3.3), this can be attributed both to increased energy input causing melting of crystallites at progressively increasing depths in the sample films and more complete melting at higher temperatures in the surface regions. The crystallite thickness is not observed to change considerably. However, as seen in Fig. 13, mean crystallite thickness reduces at higher fluences, which indicates that disruption of structure might stem from partial melting at lower fluence regimes and more complete melting of high melting crystals at higher fluence, causing random displacements. This would explain why no significant broadening occurs in the XRD profiles and the main effect seen on irradiation is a reduction in the measured intensity.

Figure 6 shows the SEM images of the untreated $300\text{ }\mu\text{m}$ sample and those treated at 30 J/cm^2 and 50 J/cm^2 , respectively. While no direct melting regions can be distinguished, it is apparent that the affected depth increases with increased fluence. Crazing in 3D in thick parts has been widely observed in semicrystalline polymers and it has been suggested [24] that the crazes are initiated between the amorphous regions zones between the crystal lamellae, which is in accordance with our observations.

4.2 Effects on Short Range Order Using Infrared Spectroscopy. FTIR spectroscopy provides considerable information regarding short-range order in semicrystalline polymers including chain conformations, crystallinity, and phase transformations. In PLLA, the polymer backbone bond stretching and skeletal bending modes are sensitive to changes in chain conformation apart from changes owing to index of refraction and density transitions. New absorption bands appear due to lower molecular symmetry in a crystal field contributing to active vibrations or splitting of bands due to intramolecular interactions. The chemical structure of PLLA is shown below:

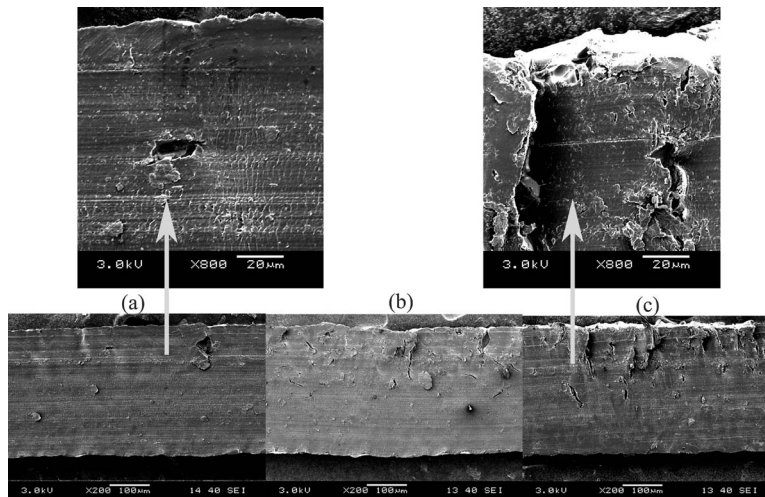
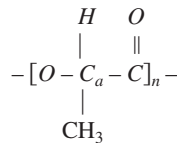


Fig. 6 SEM images of 300 μm (a) untreated sample and samples treated at (b) 30 J/cm^2 and (c) 50 J/cm^2 , indicating microtome induced crazing in treated samples, which is indicative of increase in the amorphous fraction in the polymer due to laser irradiation. Also, the affected depth increases with increase in fluence.



ATR-FTIR spectrum of untreated, laser treated (30 J/cm^2), and amorphous PLLA films are shown in Fig. 7. It can be seen that the carbonyl (C=O) stretching region, CH_3 and CH bending region, and skeletal stretching (C–O–C) regions of original crystalline PLLA show sharper peaks with band splitting in carbonyl and C–O–C stretching regions and a band at 920 cm^{-1} in accordance

with observations in literature [25]. The PLLA monomer has three skeletal bonds C–O (ester), O–C $_{\alpha}$, and C $_{\alpha}$ –C, with the ester bond assumed to be *trans* due to the electron delocalization. Minimum energy calculations by Brant et al. [26] indicate four feasible rotational isomeric states: *t't*, *t'g*, *g't*, and *g'g* corresponding to *trans* angles of -160° and 160° (*t'* and *t*) and *gauche* angles of -73° and -48° (*g'* and *g*), respectively. Henceforth, only *g* and *t* have been used in the text and should be self-explanatory. The *gt* conformers have the lowest energy and correspond to a 10_3 helix with the C=O groups perpendicular to the helix (*E* mode). While the simulated spectrum shows 55% *gt*,

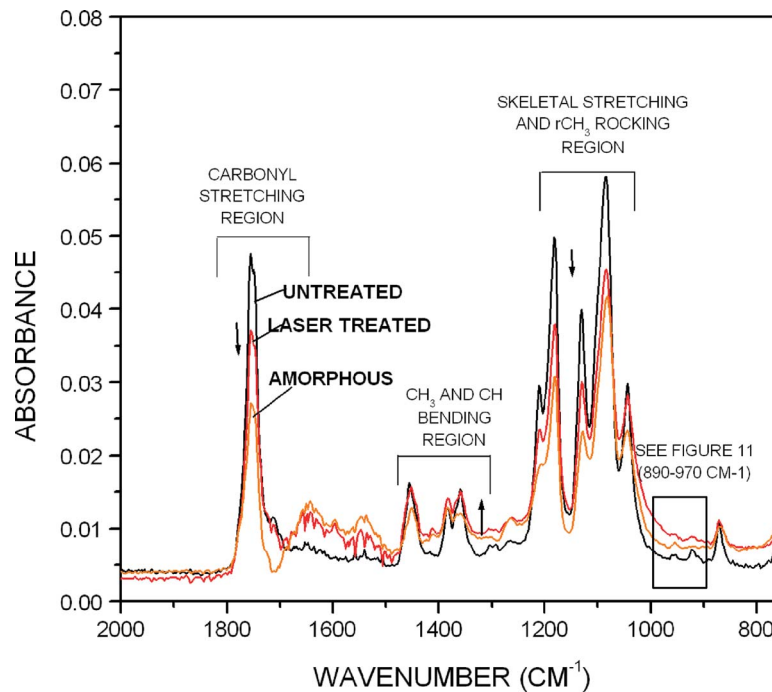


Fig. 7 FTIR spectra of untreated specimen annealed at 110°C , laser treated (30 J/cm^2), and amorphous specimens from 2000 cm^{-1} to 700 cm^{-1} , indicating the important bending, stretching, and rocking modes of PLLA

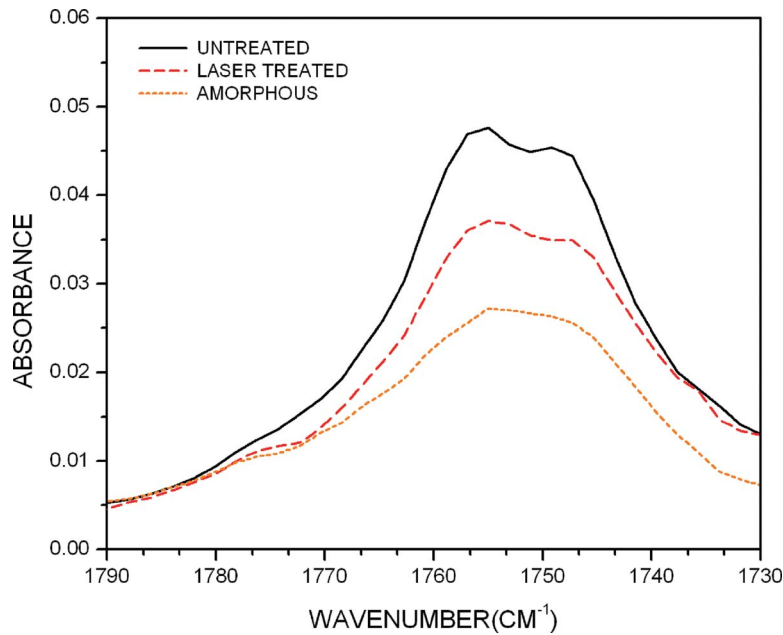


Fig. 8 Carbonyl C=O stretching region of PLLA samples: untreated, laser treated (30 J/cm²) and amorphous indicating factor group splitting; the primary conformations in the original sample being *gt* and *tt*, respectively. Amorphous sample does not show any splitting while the laser treated sample shows reduction in *gt* conformers.

37% *gg* conformers (straight conformers), and 4% each of other bent conformations [27], experimentally *gg* conformers are seen to be much lower and with more *tt* conformers, which give extended chains and do not challenge the stiffness shown in the PLLA chains. Following this analysis, Meaurio et al. [28] observed that the carbonyl region of PLLA splits into four peaks during crystallizations at 1776 cm⁻¹, 1767 cm⁻¹, 1759 cm⁻¹, and 1749 cm⁻¹ corresponding to *gg*, *tg*, *gt*, and *tt* conformations, respectively, primarily due to intramolecular coupling. The details of the C=O stretching region (1790–1730 cm⁻¹) of the spectrum and the corresponding second derivatives are shown in Figs. 8 and 9, respectively. Pronounced splitting is seen in the original sample with broad peak in the amorphous sample and the treated

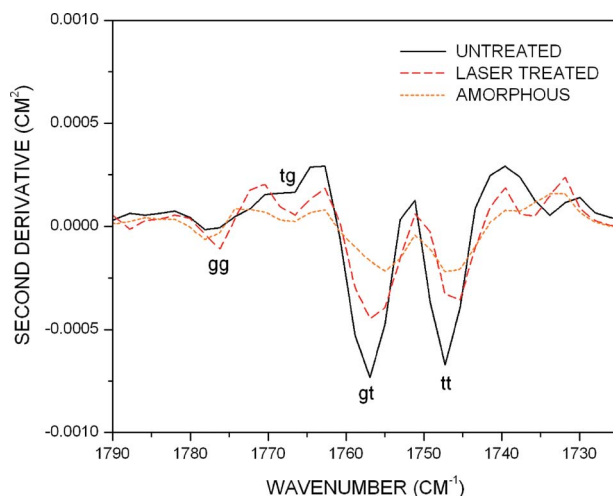


Fig. 9 Derivative spectrum of the carbonyl stretching region indicating the distribution of conformers. The primary conformation consists of *gt* conformers at 1757 cm⁻¹ followed by *tt* conformers at 1747 cm⁻¹.

sample showing reduced splitting. Analysis of the second derivative spectrum (Fig. 9) indicates peaks at 1776.2 cm⁻¹, 1766.7 cm⁻¹, 1757 cm⁻¹, and 1747 cm⁻¹, which are consistent with literature with the latter two peaks slightly shifted with respect to the transmission spectra peaks. As can be noted, negligible *gg* conformers are seen, which correspond to a 4₁ helix, *gg* being the only conformation with C=O groups parallel to the helix (*A* mode). The CH₃ and CH bending regions in Fig. 7 (1250–1400 cm⁻¹) also indicates broader peaks due to laser irradiation. The skeletal stretching region of PLLA (1050–1260 cm⁻¹) and its derivative spectrum are shown in Fig. 10, consisting of asymmetric C–O–C stretching vibrations 1180 cm⁻¹ and 1210 cm⁻¹, respectively, parallel and perpendicular to the helix for the amorphous specimen. These modes split into 1180 cm⁻¹/1192 cm⁻¹ (*A* modes) and 1212 cm⁻¹/1222 cm⁻¹ (*E*₁ modes) for the cold crystallized samples while reduced factor group splitting is seen in the laser processed samples suggesting reduced crystal perfection [29]. As shown in Fig. 11 (970–850 cm⁻¹ region), the band at 920 cm⁻¹ reduces while the peak at 955 cm⁻¹ increases slightly upon laser processing with significant increase seen at higher fluences. The 920 cm⁻¹ band was assigned [25] to coupling of the ν C–C backbone stretch with CH₃ rocking mode in the 10₃ helical conformation of PLLA.

As observed earlier, XRD indicates a 10₃ helical structure based on the α -form of PLLA and from the IR spectra the *gt* conformers represent the crystalline conformers. Hence, peaks corresponding to *gt* conformation can be used to understand the effect of laser processing. Spectral curve fitting was used (Fig. 12(a) untreated and Fig. 12(b) treated at 40 J/cm²) to obtain the heights of the peaks at 1747 cm⁻¹ and 1757 cm⁻¹ corresponding to primary conformers seen, *tt* and *gt*, respectively. Using a similar approach, the effect of laser fluence is demonstrated by comparing the reduction in peak heights of *gt* conformers as a function of the fluence as seen in Fig. 13, which follows the same trend as seen in WAXD. While this band is due to the added contributions from the *gt* conformers in the crystal lamellae and the interphase re-

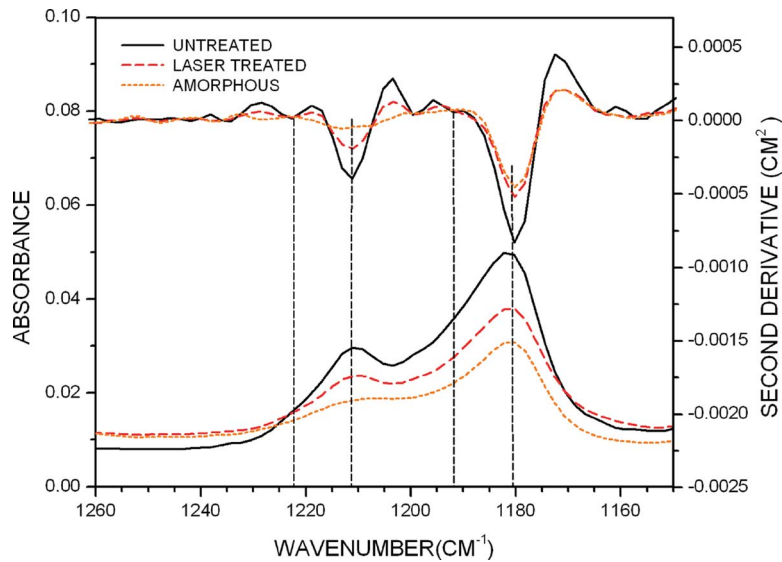


Fig. 10 Lower crystalline perfection is seen in the samples represented by broader bands. The mean factor group splitting is seen at 1222 cm^{-1} .

gions, the reduction has to be attributed to conformation changes happening in the crystal domains of the polymer. The reduction is less drastic as compared with the WAXD peaks due to smaller d_p associated with IR spectrum in the carbonyl region. However, the reduction in conjunction with reduced lamellar thickness may imply transition from partial to complete melting at higher fluences in the layer at the surface probed by the ATR crystal.

4.3 Further Discussion. The interaction of lasers with polymers is in its entirety a complex process and our intent here is to utilize a simplified 2D axisymmetric heat conduction model to understand the rapid heating of the material surface and the temperature distribution and cooling rate under nanosecond pulse irradiation. The cross section considered for analysis was 30

$\times 150 \mu\text{m}^2$ with convective boundary conditions at all boundaries except insulating conditions at the bottom. Melting was not modeled separately but latent heat of melting was considered [1] with density variations on melting not considered. Temperature dependent thermal conductivity and specific heat were used from literature [30]. The laser heat source was considered to be a Gaussian with exponential decay along the thickness using laser intensity as [31] $Q(r,y) = Q_0 \exp(-ar^2) \exp(-by)$, where the constants are $a = 3/r_0^2$, $b = 3/y_0$, and $Q_0 = 9\alpha P / \pi r_0^2 y_0$; r_0 and y_0 are the radius and the depth, respectively, where intensity falls to 5% of the peak value; α is the absorptivity of the material to laser irradiation taken as 14% [2]; and P is the laser power. Standard commercial finite element program ABAQUS was used to implement

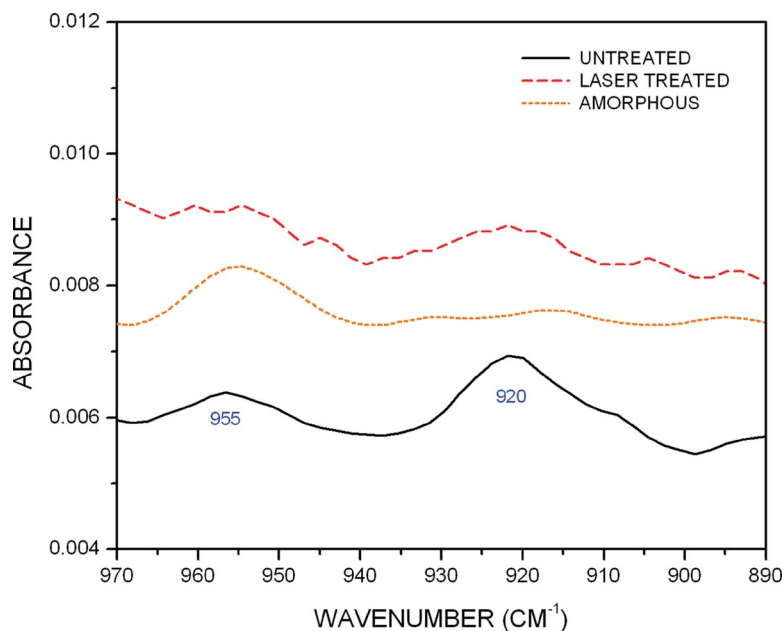


Fig. 11 970–890 cm^{-1} region of FTIR spectrum indicating reduction in the band at 920 cm^{-1} (corresponding to coupling of the $\nu\text{C}-\text{C}$ backbone stretch with CH_3 rocking mode in 10_3 helical conformation of PLLA) with laser treatment

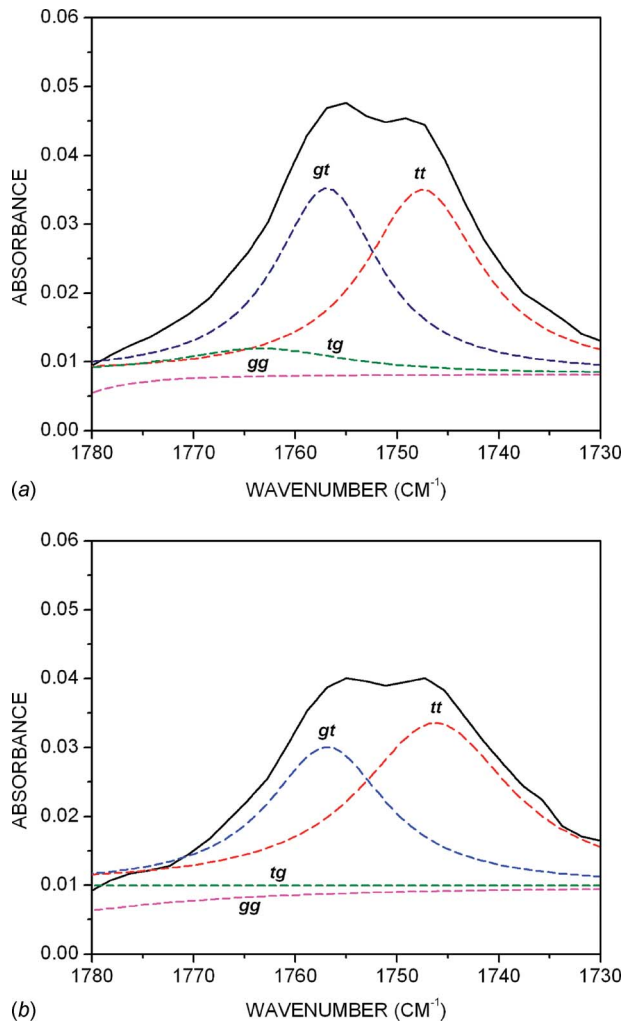


Fig. 12 Curve fitting for various conformers in the carbonyl region of PLLA films for (a) untreated sample and (b) sample treated at 50 J/cm²

the numerical simulation. While the actual pulse is a moving heat source with a spacing of 3 μm , multiple pulses were used at a single point to simplify the analysis. A four-node axisymmetric quadrilateral element was used along with a user subroutine (DFLUX) developed in FORTRAN to model the volumetric flux and multiple pulses.

4.3.1 Temperature Profiles and Cooling Rates. The temperature distribution in the sample cross section (30/cm²) during irradiation due to a single pulse is shown in Fig. 14(a) at the end of the 50 ns during which heat flux is supplied by the pulse and in Fig. 14(b) at the end of the laser pulse at 1 msec. The temperature time history at the center of the laser beam is shown in Fig. 15. From differential scanning calorimetry (DSC), the melting temperature of our material was found to be in the range of 451 K. Crystal reorganization is seen at 381 K and 436 K due to a low heating rate of 4.7 K/s (10°C/min), indicating the presence of low-melting crystals in line with observations in literature from cold crystallized solvent-cast films. However, in our process, the heating rates are of the order of 10⁹ K/s, so this reorganization is not expected and hence the equilibrium melting temperature is expected to be lower. The top surface of the material experiences melting temperatures to a depth of the order of 2–4 μm . An increase in the affected depths (including complete surface and partially melted subsurface regions) would be expected with an increase in fluence due to higher temperatures away from the surface, which would explain the variation in crystallinity with fluence seen in WAXD and SEM. Also, there exists a critical temperature close to and below the melting point above which conformational disorder can increase. This along with the presence of low-melting crystals would contribute to an increase in tie chain molecules and interlamellar material, while the crystallite core may still exist, leading to partial melting at depths higher than those seen by considering melting temperatures alone. As seen in Fig. 17, the reduction in relative intensity of the *gt* conformer peak to the *tt* peaks in FTIR spectrum is more pronounced at higher fluences and considering that the probed depth is of the order of 2 μm , this may indicate that more complete melting is seen at higher fluences in the surface regions. Also, while the degradation temperature of PLLA is of the order of 295°C, FTIR results do not indicate any new bands indicating the absence of degradation possibly due to the rapid kinetics of heating versus degradation and small superheating in the material at higher flu-

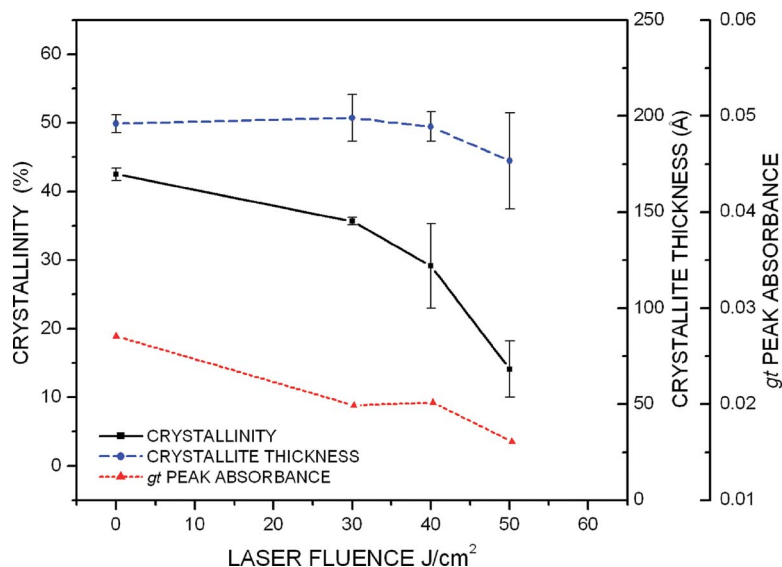


Fig. 13 Effect of laser fluence on the crystallinity and crystallite thickness of PLLA film samples obtained from WAXD and *gt* peak absorbance values from curve fitting of carbonyl region of FTIR spectra

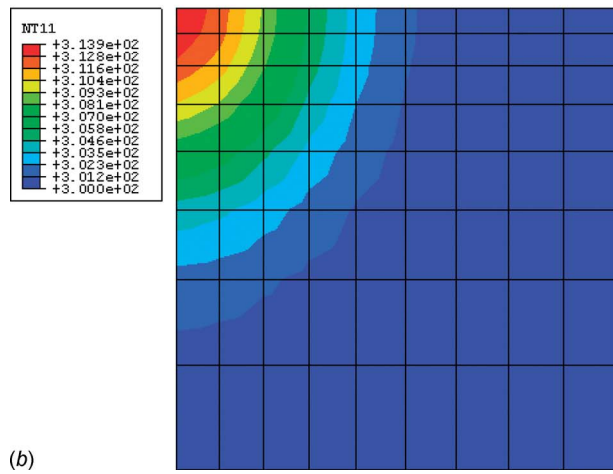
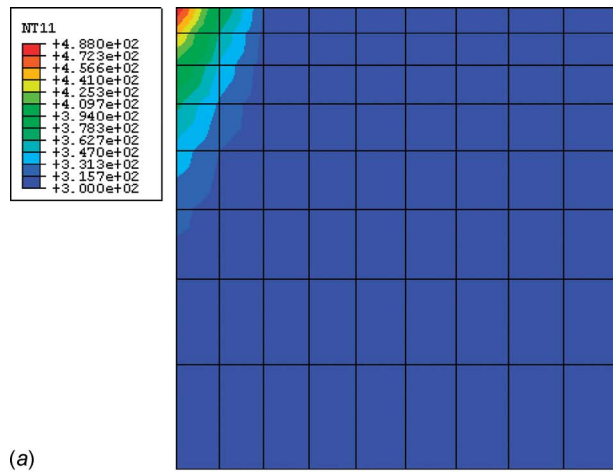


Fig. 14 Temperature distribution in the film cross section ($30 \times 30 \mu\text{m}^2$) at (a) 50 ns during which heat flux is supplied and (b) 1 ms after single pulse laser irradiation at 30 J/cm^2 as obtained from the numerical analysis

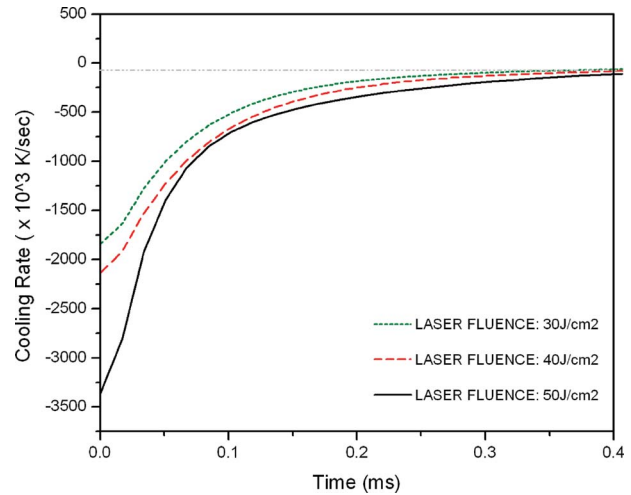


Fig. 16 Comparison of peak cooling rates in the material on laser irradiation at different laser fluences as obtained from the numerical analysis

ences. Furthermore, at 355 nm, the photon energy $E = 1245/\lambda = 3.5 \text{ eV}$ is not enough for direct bond breaking [7] and hence photochemical effects can be assumed to be negligible.

The cooling rates as a function of time during the laser pulse are shown in Fig. 16 and are of the order of 10^6 K/s . Since there is considerable rapid undercooling during the pulse duration and considering the dependence of nucleation on undercooling ΔT (Sec. 2.1), nucleation may be considered nonlimiting in the overall crystallinity developed and growth will primarily govern the overall crystallinity evolution. However, Vasanthkumari and Penning [11] showed that growth in PLLA follows regime II kinetics based on the K_g values in Eq. (2). Maximum spherulite growth rates are seen around 130°C ($5 \mu\text{m/min}$) and reduces with increasing molecular weights. In this light, the overall development of crystallinity can be estimated. Innace and Nicolais [32] obtained the Avrami parameters as a function of temperature with

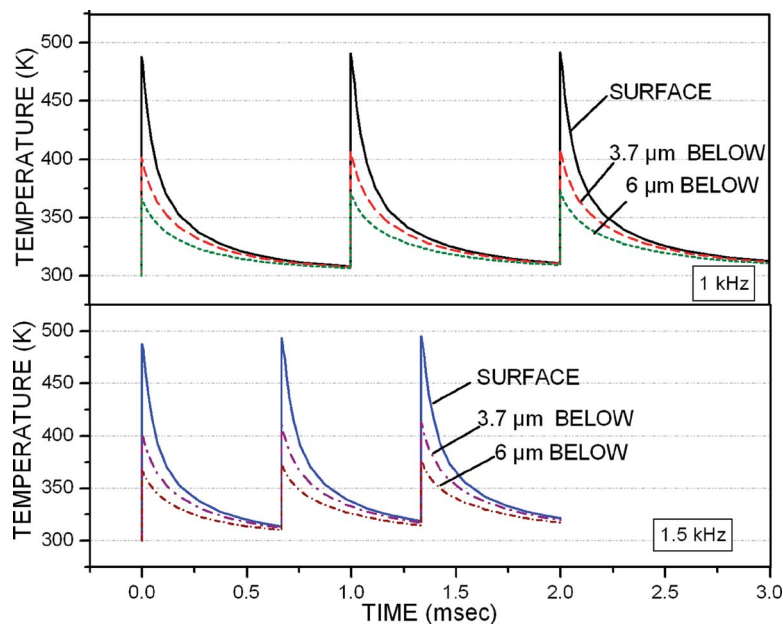


Fig. 15 Numerically obtained time history of temperature at the center of the laser beam (as seen in Fig. 14) at various distances from the surface at laser repetition rates of 1 kHz and 1.5 kHz, respectively

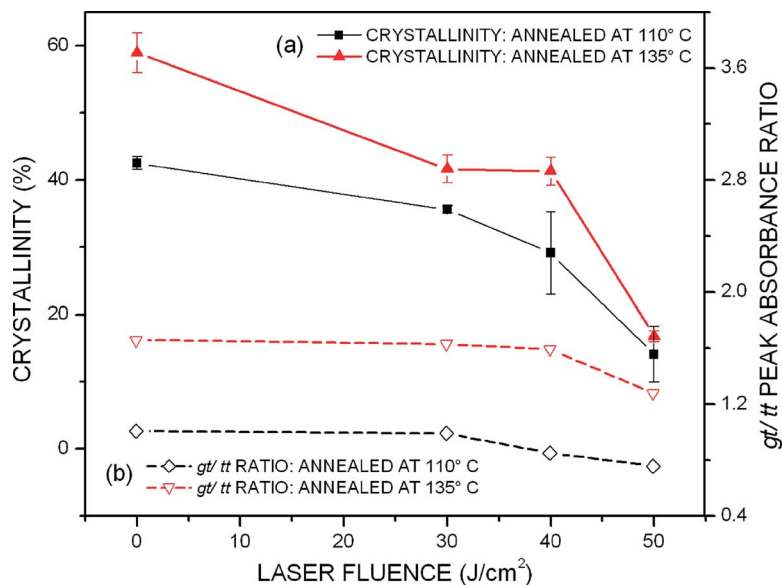


Fig. 17 (a) Comparison of sample crystallinity versus laser fluence at annealing conditions of 110°C and 135°C. (b) Comparison of absorbance of the *gt* to *tt* conformer peaks in the carbonyl (C=O) stretching region versus laser fluence at annealing conditions of 110°C and 135°C.

Avrami exponent m in the order of 3 and k values in the range of 5×10^{-8} – 8×10^{-10} . From the laser quench rate $T(t)$ as obtained in Fig. 15, the values of $K(T(t))$ in nonisothermal Avrami equation (4) were obtained. Considering a single pulse at 0.1 ms, the value of the integral crystallization rate constant was calculated as $\int_0^{0.1} K(T(\tau)) d\tau = 2.95 \times 10^{-4}$. Hence, the value of degree of transformation Φ (0.1 ms) is expected to be almost zero and the material is expected to be amorphous. While it is observed from Fig. 16 that the cooling rate reduces with reduced fluence, that variation is not expected to be important as long as it above a certain threshold. The effect of multiple pulses can be seen from Fig. 15, which shows the temperature evolution $T(t)$ during three pulses. Slight overheating is observed as compared with a single pulse though this may be lower for the moving laser source in the actual case and potentially each molecule goes through a few thermal cycles. It has been seen that repeated rapid heating cooling cycles may cause lower melting temperatures in the material and hence subsequent to first pulse, lower melting may be seen. It was observed that further increasing the fluence does not reduce the crystallinity further. This is due to limited depth of laser affected zone and the fact that further increasing the laser fluence leads to structural damage to the film due to increased thermal effects.

In addition to above observations, molecular dynamics studies of interaction of infrared lasers with polymer crystal indicate rapid energy distribution and vibrational excitations from the laser pulse can lead to significant coiling and structure change in the crystal [33] and this may be an additional contributing factor toward amorphization, which has not been studied here.

4.4 Effect of Annealing Conditions. The effect of annealing temperatures is an important aspect, which has been evaluated. In addition to the crystallization at 110 deg as described earlier, samples were cold crystallized at a higher annealing temperature of 135°C and laser fluence effects were studied. Annealing was observed to increase the intensity of the peaks at 16.7 deg and 19.1 deg, indicating that crystallite growth during annealing occurs in the (110) or (200) direction or along the a -axis and b -axis perpendicular to the helical PLLA chain direction (c -axis). Figure 17 shows the sample crystallinity as a function of the laser fluence at annealing conditions of 110°C and 135°C, respectively. As seen in the figure, the initial sample crystallinity at annealing con-

dition of 135°C is observed to be higher. It was seen earlier that at a particular fluence, the contribution to the crystallinity reduction is due to a more complete melting in the surface regions, which see higher temperatures closer to the melting point of the crystals and additional contribution from partial melting below this region. Additionally, it has been seen in literature that as-cast films crystallized at higher annealing temperatures show higher melting points [34]. For treatment at the same fluence, samples annealed at 110°C show slightly lower crystallinity. This is likely due to more complete melting of crystals formed at 110°C as compared with 135°C, which do not melt completely owing to higher required melting temperature. However, at higher fluence of 50 J/cm² the difference between the different annealed specimens is reduced considerably. This is most likely due to higher temperatures at this fluence, which cause more complete melting of the higher melting crystals at 135°C. Figure 17 also shows the *gt/tt* conformer ratio for both annealing temperatures. There is a reduction in the *gt/tt* ratio for both annealed samples, which confirms that the α -form or the 10_3 helix seen in XRD is preferred by the *gt* conformation irrespective of annealing conditions. Also, the conformational data are obtained from FTIR-ATR and hence primarily from the surface regions. At lower fluences, the *gt/tt* ratio does not change much since there is a reduction in both *gt* and *tt* conformers due to melting in the top region. At higher fluence, we see a similar reduction in the *gt/tt* ratio for both annealing conditions, which may also indicate that more complete melting is seen at higher fluences in the surface regions probed by FTIR.

5 Conclusions

It has been shown that UV nanosecond laser irradiation at 355 nm can be used to reduce the crystallinity of aliphatic homopolymer L-PLA, by primarily affecting a layer at the surface of the sample. Laser processing affects both long- and short-range orders in the polymer. WAXD results show the reduction in intensities perpendicular to the helical PLLA axis with reduced overall crystallinity. The FTIR spectra exhibit broadening reduced intramolecular interactions characteristic of crystal structure and reduction in *gt* conformers due to laser irradiation, which also confirms that these conformers primarily crystallize in the α -form. Rapid melting at the surface quench rates in the process, which are de-

terminated to be of the order of 10^6 K/s, multiple thermal cycles, superheating and heat accumulation due to pulsed nature of the process, and primarily regime II kinetics of PLLA contribute to an overall reduction in crystallinity in the material, and partial melting may be an important contributory factor. Final crystallinity is a function of the laser fluence while the annealing temperature does not seem to have a considerable effect especially as fluence increases. Hence, laser surface treatment would allow for a controllable practically applicable and automated process that can spatially control the surface morphology and hence degradation and other properties associated with a different crystallinity at the surface.

Acknowledgment

Financial support from Columbia University is acknowledged. Contribution of PLLA sample material by PURAC America is also acknowledged. Professor J. Koberstein's advice and invaluable discussions are sincerely appreciated. Assistance from Professor Helen Lu's group for sample preparation and Dr. Louis Avila for FTIR equipment is highly appreciated. Assistance from Andrew J. Birnbaum with the numerical modeling is appreciated. This work used equipment at the Columbia University MRSEC supported by NSF DMR-0213574.

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