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# To characterize the properties of PLLA (Poly L- lactide) tube by wide angle X-ray scattering (WAXS) and X-ray differactograms (XD) methods

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**Abstract**
The main purpose of the microstructural/morphology study of PLLA (poly L-lactide) tube is to evaluate the changes in morphology at various stages of manufacturing polymer scaffold which influences mechanical properties of the PLLA material. This study is applicable in improving the polymer scaffold's fracture toughness. In this study, we investigated deformation mediated superstructures and cavitation of poly (L-lactide) (PLLA) as well as their dependence on stretching temperature by wide angle x-ray scattering (WAXS) and crystallization analysis coupled with mechanical testing. It is found that the crystalline deformation are strongly influenced by stretching stress during deformation, which significantly depends on the stretching temperature. Crystalline shear accompanied by crystalline deformation at higher stretching temperatures promotes the formation of cavities oriented along the stretching axis. Based on the findings, it is possible to modify the mechanical properties of polymer materials by regulating their superstructure during deformation.

**Keywords:** PLLA tube, deformation, crystallization, WAXS and XD

## Introduction

Deformation processing of semi-crystalline polymers is generally used to modulate their mechanical properties for fabricating final products, which directly depends on the formation of superstructures. During the stretching, deformation of semi-crystalline polymers, the superstructure evolution involves the variation of crystalline and amorphous phases, including orientation-induced crystallization, crystal transition, chain orientation, fibril formation, and cavitation, etc. It is a great importance to investigate the superstructure transition and their correlations with stress strain curves of semi-crystalline polymers under stretching. Poly (L-lactide) (PLLA) is a biodegradable and biocompatible polymer, which can be used in biomedical fields. Its proper mechanical properties and environmental friendliness makes it a promising material. Since PLLA is a semi-crystalline polymer, its mechanical properties depend very much on its crystallinity, crystal and amorphous orientation as well as morphology during preparation. The superstructure formation and mechanical behavior of PLLA under different stress and temperature have brought a great attention.

The main structure variation of amorphous PLLA under stretching is the strain induced crystallization and orientation. The crystallinity, orientation as well as cavitation of deformed PLLA tube increase with the increase of strain rates. The aim of this work is to investigate the deformation mechanism of crystallized PLLA, and explore their dependence on stretching temperature by WAXS/WAXD, and crystallization analysis. For this purpose, the initiation and development of cavities as well as the evolution of lamellar structure with stretching strains have been systematically studied. Based on those results, the deformation mechanism of crystallized PLLA at different stretching temperature is discussed. The radial expansion/axial elongation process results in the modification of the crystalline morphology of the polymer precursor. Deformation processing of semi-crystalline polymer is generally used to modify their mechanical properties for fabricating its desired application, which directly depends on the formation of microstructures. Different stretching condition and temperature play crucial role in determining mechanical behavior of semi-crystalline polymers. Molecular orientation refers to the relative orientation of polymer chains along a longitudinal or covalent axis of the polymer chain. The fracture strength of a semi-crystalline polymer material depends on or is influenced by the morphology since a semi-crystalline polymer includes crystalline regions separated or surrounded by amorphous regions. To improve the fracture toughness by reducing size of the polymer crystals and increasing the density of the nuclei from which the crystals grow. Smaller crystals lead to more tie chains between crystals that are polymer chains that are part of the both crystals. Many small crystalline regions are preferable to fewer larger crystalline regions. Crystal size and density, as well as the total crystallinity, are a result of the temperature and processing history of the polymer. Careful control of the processing and temperature conditions of the polymer allow one to obtain a polymer with the desired morphology, that is the desired crystal size, density, and orientation, to maximize both strength and toughness.

## Material and Methods

For conducting the study, the instruments used like, wide and small angle x-ray scattering, tube forming machine, and polarized light microscope. The materials/ chemicals are such as deformed tube, annealed, and sterilized scaffold, aluminum pouch, and mandrel etc. The different processing stage mentioned in below table 1.

**Table 1:** Sample Requirement for testing

| Sr. No. | Testing | Process Stage |
|---|---|---|
| 1. | Wide Angle x-ray Scattering (WAXS) | 1. Deformed Tube |
| | | 2. Annealed Scaffold |
| | | 3. Sterilized Scaffold |
| 2. | Mechanical Testing | 1. Deformed Tube |
| | | 2. Sterilized Scaffold |

### 1. Wide Angle X-ray Scattering test (WAXs and WAXD)

The wide angle x-ray scattering (WAXD or WAXS) study was conducted for show the effect of deformation parameters such as pressure, temperature, axial and radial expansion percentage ratio. After annealing, crimping and development state for analyze tube/scaffold morphology i.e., morphology remains same or changes due to temperature effects. Depending upon the process of conditions i.e., temperature and strain, PLLA can exist in four different crystalline forms. Effect of stretching was increases the deformation of tube. Wide angle x-ray scattering (WAXS) is used to characterize nano scale arrangement of crystallites and polarized light microscopy (PLM) is used to determine the distribution of crystallite orientation with in deformed tube and scaffold wall. The study was conducted to analyze present deformed tube whether it is isotropic and anisotropic in nature.

The wide angle x-ray scattering (WAXD/WAXS) testing should be carried out for determine the strength and biodegradation of semi-crystalline morphology. It determines the crystals structure and size in expanded tube, degree of crystallinity, orientation distribution of crystallites and orientation angle. The testing carried out for observed that fracture toughness is increased by having large numbers of small crystals domain in polymer surrounded by amorphous domain. It used to characterize on nano scale arrangement of crystallites. The WAXS provide information about crystallinity and nano scale arrangement at a specific position. The polarized light microscopy (PLM) testing carried out for to observe that fracture toughness affected by overall degree of crystallinity and number/size of crystals domains in semi-crystalline polymers. It determines a distribution of crystallite orientation within an expanded tube and scaffold wall.

### 2. Crystallinity

The polymer grading is based on their molecular weight, glass transition temperature (Tg), crystallinity (Xc), and stereoisomeric characteristics. Here, glass transition tempearture (Tg), and melting temperature (Tm) are important thermal properties. Processing of a polymer at elevated temperatures results in the change in morphology of a polymer and influences its crystallinity (Xc). Xc defines as the degree of crystallinity of a polymer in percentile value. Crystallinity is the degree of long range order in a material, and strongly affects its properties. A totally amorphous polymer has Xc value of 0 % and a fully crystalline polymer has Xc value of 100 %. The glass transition temperature is the temperature range where the polymer substrate changes from a rigid glassy material to a soft (not melted) material. The melting point of a substance is the temperature at which the substance changes from solid to a liquid. For a pure substance, melting occurs at a single temperature. In order to get desired properties from extruded tubes, correct polymer grade must be set. The XRD test is performed to know the crystalline size, degree of orientation angle at 2θ ($^o$) and crystallite index. To characterize microstructure analysis of PLLA system during each stage of manufacturing process to obtain desired/optimum morphology which enhance fracture toughness until deployment state. To check the effect of deformation process parameters on the morphology of the polymer tube and mechanical properties can be studied. X-ray scattering techniques are a family of non-destructive analytical techniques which reveal information about the crystal structure, chemical composition, and physical properties of materials and thin films. Wide angle x-ray scattering is the same technique as small angle x-ray scattering (SAXS): only the distance from sample to the detector is shorter and thus diffraction maximal at larger angles are observed.

**Result and Discussion**

One of the main reasons for using WAXD for polymer analysis is that crystalline polymers are frequently presented in the form of fibers with preferential crystal orientation with respect to the fiber axis; the crystallographic PLLA is perpendicular to the fiber axis that is along a vertical direction. The WAX analysis can readily reveal the preferential orientation of polymer crystals for a diffraction pattern recorded on the film. The diffraction spots on the equatorial PLLA represent the diffraction of PLLA. The term “wide angle x-ray scattering” and “wide angle x-ray diffraction” are often used without clear distinction because there is little difference in their instrumentation. The ‘scattering’ is a more general term than ‘diffraction’ that refers to constructive interference of scattered rays from crystallographic PLLA. Wide angle x-ray scattering (WAXS) is considered to be an appropriate technique for examining both crystalline and non-crystalline materials. WAXS is particularly useful for polymers because a non-crystalline (amorphous) structure is the common characteristic of polymers, even for crystalline polymers because they are not totally crystalline.

The study performed well at slower deformation rate which facilitates the development of an oriented molecular structure with reduced internal stresses. Toughness is the strength with which the material opposes rupture. The strength and toughness of the crystallite regions can be further increased by inducing orientation in the amorphous regions. The stress may also induce orientation in amorphous region. The greater the number of smaller crystalline domain which enhance the fracture toughness. Based on the analysis and morphology, one can optimized stretch blow molding ratio and parameters. The study performance based on various deformation parameters with the wide angle x-ray scattering. The crystal structure being/ mostly alpha’ morphology in crimped and deployment state. The PLLA initially results in higher crystallinity and preffered orientation in the circumferential direction. The PLM is capable of distinguishing between isotropic and anisotropic substance. The inner radial section of the tube exhibits birefringence and an outer radial section is optically isotropic when viewed with polarized light. The degradation rate decrease with increasing crystallinity.

Both the cross linking and crystallinity can increase the glass transition temperature (Tg). It is very easy to explain why cross linking increases Tg since the presence of covalent bonding between chains and reduces molecular freedom and thus the free volume. Similarly, the presence of crystalline regions in an semi-crystalline material restricts the mobility of the disordered amorphous regions; thus the glass transition temperature increases which is totally depends on the percentage of crystallinity. A polymer can be considered partly as crystalline and partly as amorphous. The crystalline domains act as a reinforcing grid, like the

iron framework in concrete, and it improves the performance over a wide range of temperature. However, too much crystallinity causes brittleness. The crystallinity parts give sharp narrow diffraction peaks and the amorphous component gives a very broad peak. The ratio between these intensities can be used to calculate the amount of crystallinity in the material. As mentioned above, mechanical properties of the polymer also depend on its crystallinity. Crystallinity increases the mechanical strength of the polymer. Crystallinity also influences the degradation rate of the polymer. Increase in crystallinity decreases the degradation rate. Polymer grading is based on their molecular weight, glass transition temperature (Tg), crystallinity (Xc), and stereoisomeric characteristics. Here, Glass transition temperature (Tg), and melting temperature (Tm) are important thermal properties. Processing of a polymer at elevated temperatures results in the change in morphology of a polymer and influences its crystallinity Xc. Any of the parameters changes within expected range as per requirement without effecting final product when it exposed to different process parameters - such as temperature and time according to manufacturing process. Xc defines the degree of crystallinity of a polymer in percentile value. As a polymer crystallizes, it becomes more mechanically strong. Polymers can also be more resilient when crystallized. The degradation rate decreases with increasing crystallinity. The melting point of a substance is the temperature at which the substance changes from a solid to a liquid. For a pure substance, melting occurs at a single temperature. The desired properties from extruded tubes received through selection of correct polymer grade and the extrusion process set. The visual inspection of deformed tube surface should be clear and transparent.

The WAXS test result concluded that the smaller size of the crystalline regions or domains, the greater the fracture toughness of the polymer which is positively correlated with a high density of small crystallites. The deforming polymer induces a preferred orientation along the axis of the deformed polymer which increases the strength. If the satisfactory results not found then, the testing should be conducted along with additional improvement in WAXS test conducted at deformation process.

## 1. XRD Analysis of Deformed tube

The XRD analysis of deformed tube and sterilized scaffold were carried out in the method of x-rays copper K-alpha. The generator was in a range between 40-45 KV and 30-32 mA. The sample was scanned in transmission range between 10-35º. The crystallinity of deformed PLLA tube was found in range from 29-33 %, the crystallinity size of the deformed tube was found in range from 31-37ºA and the degree of orientation angle was found in range from 09-13 degree (2θ value).

**Table 2:** XRD Analysis of Deformed tube

| Sample No. | Crystallinity (%) | Crystallite Size (ºA) | Orientation at 2θ (º) |
|---|---|---|---|
| 1 | 29.96 | 31.20 | 9.50 |
| 2 | 32.55 | 36.25 | 12.75 |

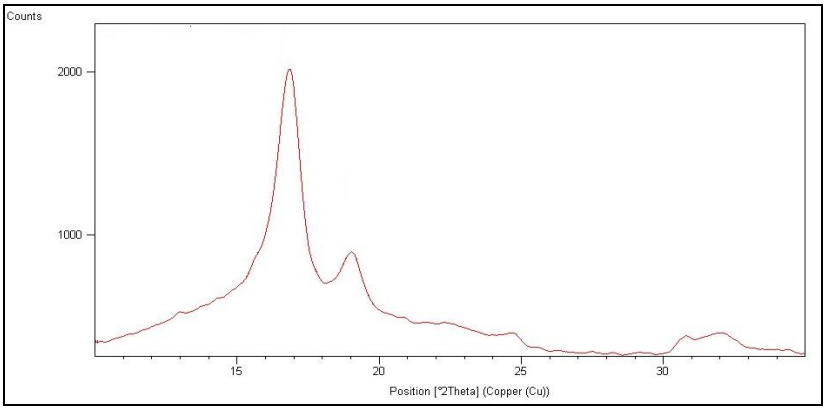


**Fig 1:** XRD analysis of deformed tube

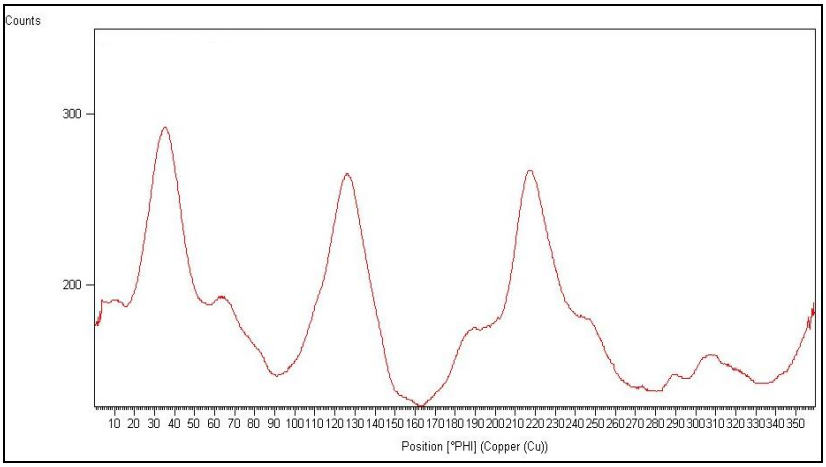


**Fig 2:** XRD analysis of deformed tube

## 2. XRD Analysis of Sterilized Scaffold

The crystallinity of sterilized scaffold was found in range from 34-39% and the crystallite size was in range from 40-45 °A.

**Table 3:** XRD Analysis of Sterilized Scaffold

| Sample No. | Crystallinity (%) | Crystallite Size (°A) |
|---|---|---|
| 1 | 34.75 | 45.45 |
| 2 | 39.50 | 40.85 |

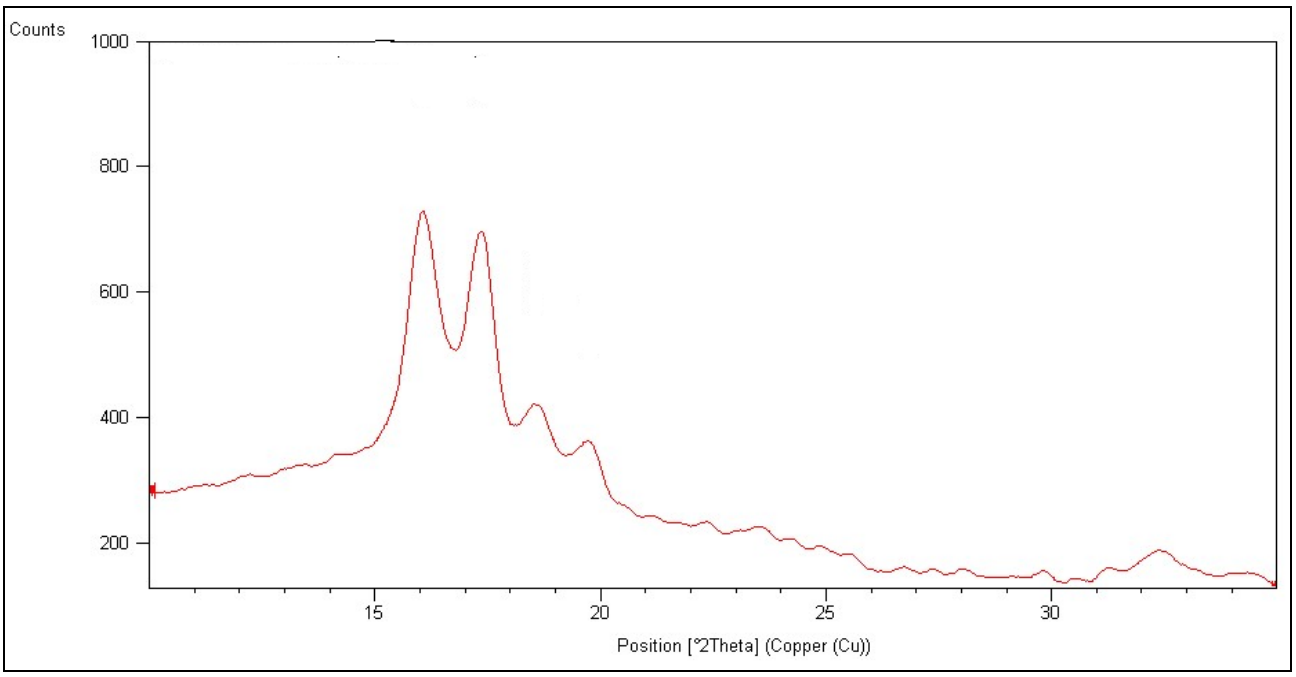


**Fig 3:** XRD analysis of sterilized scaffold

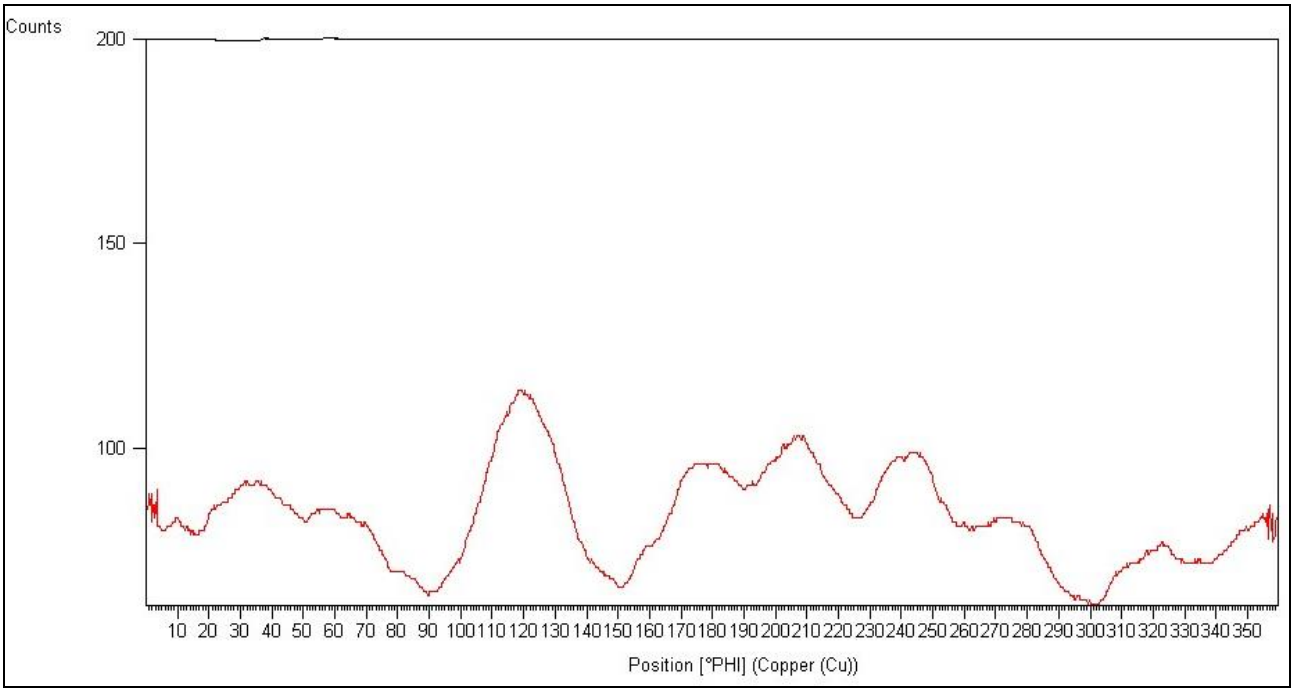


**Fig 4:** XRD analysis of sterilized scaffold

The mechanical characteristics of the deformed tube were described below;

**Table 4:** Mechanical characteristics of the deformed tube

| Sr. No. | Tube Diameter (mm) | Strain at break (%) | Y-Moduls ($N/mm^2$) | Tensile Strength ($(N/mm^2)$) |
|---|---|---|---|---|
| 1 | 2.50 | 68-70 | 2200-2300 | 65-67 |
| 2 | 3.00 | 100 | | |
| 3 | 4.00 | 85-90 | 1400-1500 | |

## Conclusion

Based on the results of the study, smaller the crystallinity or domains, greater the polymer's fracture toughness, which is correlated positively with a dense crystallite distribution. It was observed that the morphology of the material was optimized during each process step of PLLA tube which enhance the fracture toughness during each step. Molecular orientation is enhanced with a slower deformation rate of the tube/scaffold, which helps reduce internal stress and facilitates the development of a molecular structure with

reduced orientation. If there are any major changes in observation, they should be investigated further.

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