Preparation of Poly(lactic acid) Fiber by Dry–Jet–Wet Spinning. II. Effect of Process Parameters on Fiber Properties

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ABSTRACT: The dry–jet–wet spinning process was employed to spin poly(lactic acid)(PLA) fiber by the phase inversion technique using chloroform and methanol as solvent and nonsolvent, respectively, for PLA. The as spun fiber was subjected to two-stage hot drawing to study the effect of various process parameters, such as take-up speed, drawing temperature, and heat-setting temperature on the fiber structural properties. The take-up speed had a pronounced influence on the maximum draw ratio of the fiber. The optimum drawing temperature was observed to be 90°C to get a fiber with the tenacity of 0.6 GPa for the draw ratio of 8. The heat-setting temperature had a pronounced effect on fiber properties. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3774–3780, 2006

Key words: poly (lactic acid); dry-jet-wet spinning; biodegradable fiber; fiber spinning

INTRODUCTION

Poly(lactic acid) (PLA) fiber has been one of the most innovative textile materials for a number of bio and medical applications. PLA may be spun into filament by melt-spinning and solution-spinning techniques. Investigations in the 1970s led to the production of PLA fibers, but a precise spinning process could not be developed.[1] Schneider[2] reported the melt spinning of PLA for the first time to get the fiber with moderate physical properties. Afterward, various researchers reported PLA fiber spinning and the factors affecting its properties.[3–12] The Penning et al.[4] study showed that draw ratio plays an important role in the development of the fiber with required mechanical properties and morphology of the fiber. Similar observations were reported by Eling et al.[5] It was observed that the tensile strength is strongly dependent on the drawing temperature, which may be associated with the occurrence of two crystal modifications. It has also been observed that take-up speed has a pronounced effect on mechanical properties and molecular orientation of the fiber.[3,6] Cicero et al.[7] explored a large range of processing conditions for textile grade melt-spun PLA fiber, and investigated its effect on the thermal, mechanical, and morphological properties.

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The solvent composition and molecular weight of PLA are the important factors that also contribute towards the resultant properties of the fiber.[13,14] In case of fibers prepared by using different nonsolvent, chloroform spinning solution, it was observed that the tensile strength, structure, and degradability of the fibers were predominantly governed by the nonsolvent volatility.[15] It has been shown that with the use of highly volatile nonsolvent, the fiber exhibited better tensile strength and faster degradation rate. Postema et al.[12] carried out the drawing by low deformation rates/entrance velocities at high temperature in the liquid state of PLA leading to uniform alignment of molecular chains to develop the fiber with tensile strength of 2.3 GPa.

The spinning of PLA fiber by a dry–wet phase inversion process was investigated by Eenink et al.[16] but the postspinning operations were not performed, and the fiber was used for a drug delivery system. Tsuji et al.[17] performed the wet spinning of complex fibers from a mixed solution of poly(D-lactic acid) and poly(L-lactic acid). The tensile strength of the wet-spun complex fiber was very low, and could not be drawn at high temperatures. Wet spinning of PLLA and PLGA was also carried out by Nelson et al.[18] It was reported that solvent systems, polymer blends, and winding rates alter mechanical and morphological properties of the fibers. From the literature it was observed that no extensive study was carried out for the dry–jet–wet spun PLA fiber. In a previous article of this series, it was shown that PLA fiber could be

produced by the dry–jet–wet spinning technique and subsequent hot drawing leading to a tensile strength of 0.6 GPa.[19] It was observed that the properties of the PLA fiber are dependent on the draw ratio. The aim of the present study was to investigate the effect of additional process parameters on PLA fiber by the dry–jet–wet spinning technique. The main advantages of producing the PLA fiber by this technique are that the minimum polymer degradation occurs during the spinning process and leads to better molecular chain orientation, which ultimately results in the development of the high tenacity fiber.

EXPERIMENTAL

Materials

PLA was received from Polymer Laboratory, University of Uppsala, Sweden, and was stored under vacuum at ambient conditions. Chloroform and methanol were supplied from Merck India. Chloroform was dried over P_2O_5 prior to the polymer dissolution. The intrinsic viscosity of the dried PLA was 3.32 dL/g.

Spinning and drawing

The process of spinning PLA was reported in an earlier article.[19] PLA was dried at 110°C under vacuum for 24 h prior to the spinning. The polymer was dissolved in chloroform using a moisture free glass assembly under constant stirring at ambient conditions for 24 h. The polymer solution was subsequently spun on a spinning machine fabricated by Bradford University Research limited. The polymer solution was extruded through the spinneret of 0.5 mm into the coagulation bath containing methanol. The air gap between the spinneret and coagulation bath was kept as 25 mm. The polymer solution throughput rate was 0.4 g/min. The fiber was collected on bobbins, and was subjected to a drawing and heat-setting process in the second step.

X-ray diffraction

X-ray diffraction (XRD) patterns of the PLA filaments were recorded in the 2θ range of 10 to 35° on a Phillips X-ray diffractometer equipped with a scintillation counter. CuKα radiation (wavelength, 1.54 Å) was used for X-ray diffraction experiments. The amorphous PLA sample was prepared by quenching of the molten polymer in liquid nitrogen.

Differential scanning calorimetry (DSC)

DSC studies on sutures were carried out on a Perkin-Elmer DSC-7 system. Vacuum-dried samples were loaded and the thermograms were run in the temperature range of 50–200°C under nitrogen atmosphere at a heating rate of 10°C/min. The heat of fusion (ΔH_f) values were obtained from the area under the melting thermograms. The crystallinity was obtained by the following expression:

$$\text{Crystallinity (\%)} = \frac{\Delta H_f}{\Delta H_{f(\text{crys})}} \times 100 \qquad (3)$$

where ΔH_f is the heat of fusion of the sample and $\Delta H_{f(crys)}$ is the heat of fusion of 100% crystalline PLA and was taken as 93.7 J/g.[20]

Mechanical properties

The tensile properties of PLA fibers were measured using an Instron tensile tester. All the experiments were carried out using a gauge length of 50 mm and a rate of testing of 50 mm/min.

Sonic modulus

Sonic modulus of fibers was measured on a pulse propagation meter (PPM 5R). The single filament was mounted between two transducers containing a piezoelectric ceramic crystal with a natural frequency of 5 kHz. The velocity of the longitudinal wave in the material was measured by having the fiber between two transducers. The sound velocity was measured by taking length and time measurements from the recorder as per the following equation.

$$C = \frac{\Delta l}{\Delta t}$$

where Δl is the distance in mm, Δt is the transit time in μs, is the velocity of sound in km/s. The Young's modulus was determined as per the equation.

$$E = \rho C^2$$

where, ρ is the density (g/cc^3).

The modulus in gram per denier (gpd) would therefore be obtained by the following equation.

$$E(\text{gpd}) = (E/\rho) = C^2K$$

where, K is the conversion factor of 11.3.

Scanning electron microscope

The surface characteristics of fibers were studied using a STEREOSCAN 360 (Cambridge Scientific Industries Ltd.), scanning electron microscope, after coating them with silver.

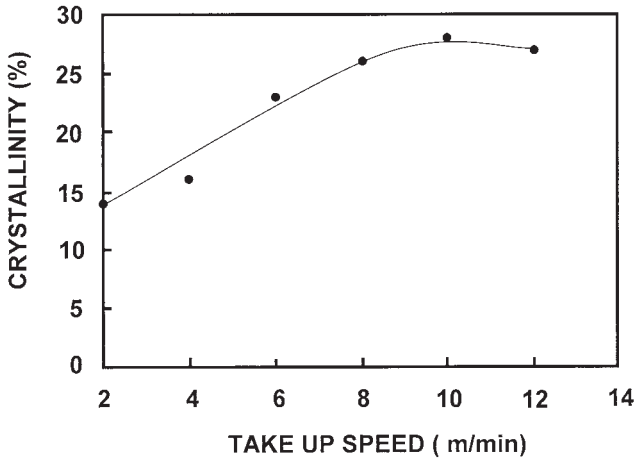

Figure 1 Effect of the take-up speed on the crystallinity of as-spun fiber.

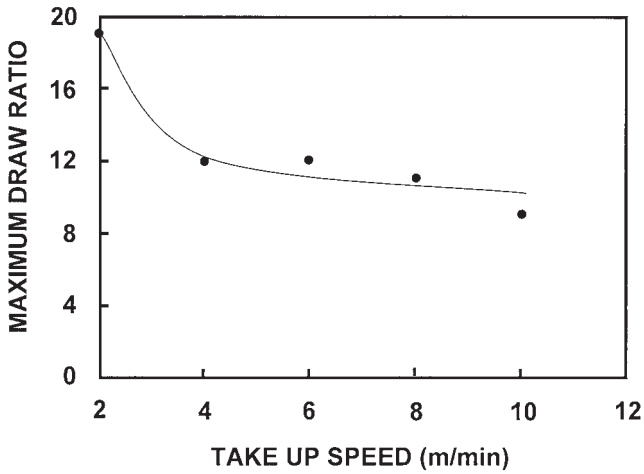

Figure 2 Effect of take-up speed on maximum draw ratio of the fibers drawn at drawing temperature of 90°C and heat-setting temperature of 120°C.

RESULTS AND DISCUSSION

Our efforts have been to produce PLA fiber with good mechanical properties. This is where the influence of processing parameters on the physical structure has been investigated. The effect of draw ratio on PLA fiber spun by the dry–jet–wet technique has already been reported in a previous study.[19] This investigation deals with the influence of the take-up velocity (the velocity at which the PLA filament was collected by take-up rollers during the spinning process), draw ratio, drawing temperature, and heat-setting temperature on the physical structure of the fiber.

Effect of take-up speed

The take-up speed for spinning was varied in the range of 2 to 12 m/min. It is observed that as the take-up speed increased, the crystallinity of the as-spun fiber also increased (Fig. 1). For a take-up speed of 2 m/min, the crystallinity of the as-spun fiber was 14%, which goes on gradually increasing with the increase in the take-up speed up to 10 m/min and then tends to level off. A maximum crystallinity of 28% was achieved for a take-up speed of 12 m/min, leading to the enhanced crystallization. This may be because of the fact that as the take-up speed increases, wet stretch also increases proportionally, which results into improved molecular chain orientation. The as-spun fibers were drawn to the extent of maximum draw ratio (MDR) at a drawing temperature of 90°C and a heat-setting temperature of 120°C. The MDR tends to lower gradually as the take-up speed increases. For the take-up speed 2 m/min, the maximum draw ratio was achieved up to 19, which gradually decreased to 9 with an increase in the take-up speed to 10 m/min (Fig. 2). Because the spinning process follows the stretching of the extruded filament during coagulation, the orientation of molecular chains sets in. As the take-up speed increases, this enhances the molecular orientation within the as-spun fiber. As a result, the maxima in attainable draw ratio is reduced.

The Differential Scanning Calorimetry (DSC) analysis and X-ray analysis of the drawn fibers were carried out for determination of crystallinity (Fig. 3). It was observed that the crystallinity of resultant fibers was increased for the fibers spun at a take-up speed of 2 to 10 m/min, respectively. There is significant difference in the crystallinity observed by X- ray and DSC analysis.

The mechanical properties of drawn fibers spun at different take-up speeds are shown in Figure 4. The tensile strength of the fiber increases initially and tends to stabilize. The elongation, on the other hand, decreases with the take-up speed, confirming that the

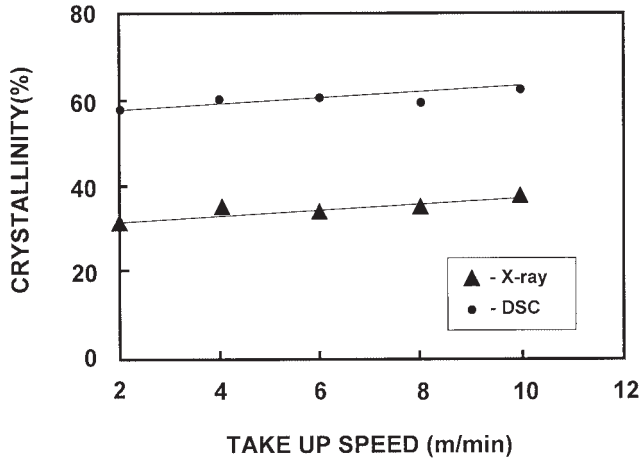

Figure 3 Effect of take-up speed on the crystallinity of drawn fibers. Experimental conditions as in Figure 2.

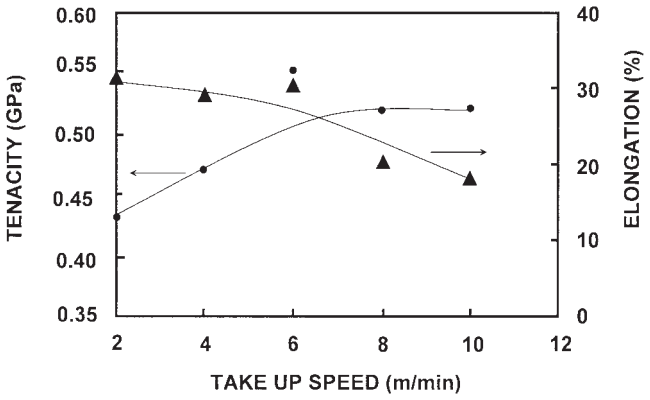

Figure 4 Effect of the take-up speed on mechanical properties of drawn fiber. Experimental conditions as in Figure 2.

structure developed at a high take-up speed is more orientated with least molecular chain entanglements.

The molecular chain orientation of drawn fiber was observed to be directly visualized from the sonic modulus study. Figure 5 represents the sonic modulus plotted against the take-up speed of the as-spun fiber, which is the function of the molecular chain orientation. The value of the sonic modulus increased from 7.18 to 9.69 GPa for the fibers, which were spun at a take-up speed of 2 to 10 m/min. The drawing prior to coagulation process causes better molecular orientation, which is reflected in the resultant orientation of drawn fibers. A similar trend of molecular orientation in terms of birefringence was reported in case of PLA fibers produced by high-speed melt spinning and spin drawing.[6]

The cross-sectional morphology of the as-spun fibers (prior to drawing) was studied by using Scanning Electron Microscopy. It is observed that the cross section of as-spun fibers observed in trilobal even though the spinneret hole is circular in shape [Fig. 6(a–c)].

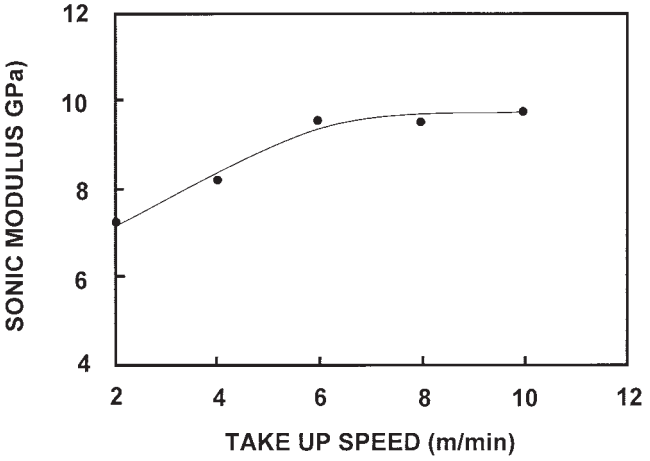

Figure 5 Effect of take-up speed on sonic modulus. Experimental conditions as in Figure 2.

Figure 6 (a–c) SEM of fibers cross sections collected at different take-up speeds, (a) 2 m/min; (b), 6 m/min; (c), 10 m/min.

This may be due to the difference in the rate of exchange of solvent and nonsolvent in the coagulation bath at the time of coagulation. The as-spun fibers showed cross-sectional porosity in all within. Also, the porosity of the as-spun fibers was observed to be dependent on the take-up speed. For the fiber spun at 2 m/min, the residence time in the coagulation bath is highest, which causes more porous structure due to complete precipitation [Fig. 7(a–c)]. As the take-up speed increases, the least coagulation leads to the fiber with less porous structure.

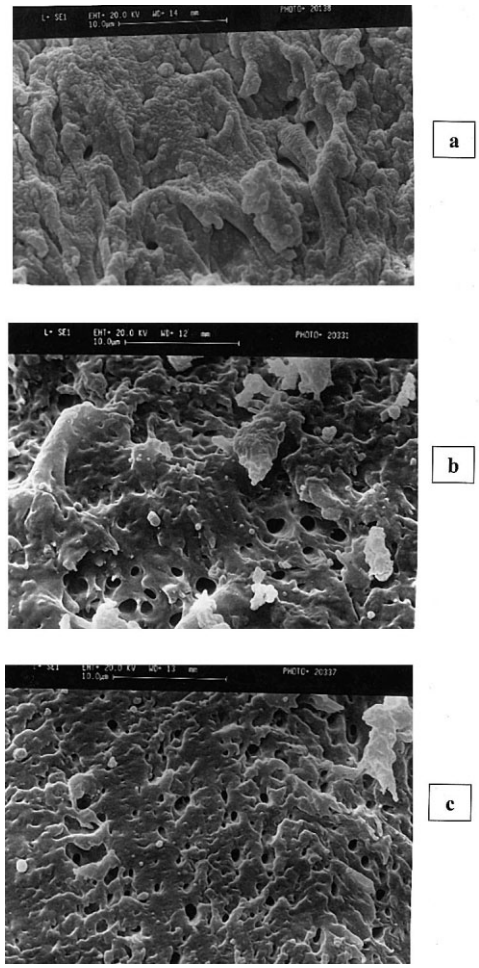

Figure 7 (a–c) SEM of fibers cross sections collected at different take-up speeds. (a) 2 m/min; (b), 6 m/min; (c), 10 m/min.

Effect of drawing temperature

The as-spun fiber produced at a take-up speed 10 m/min was drawn at various temperatures in the range from 70 to 110°C, and subsequent heat setting was carried out at 120°C for a total draw ratio of 8. It was observed that there is no significant effect on crystallinity of the fibers drawn at this temperature range. The values obtained from both the analytical techniques, that is, DSC and X-ray diffraction, were almost identical, as shown in the Figure 8. Cicero et al.[7] studied the drawing temperature range from 50 to 110°C for melt-spun PLA fibers drawn at the draw ratios of 5, 6, and 7. It was observed that drawing temperature has an effect on the crystallinity, and a drop of around 6 to 7% in the crystallinity was observed. The molecular orientation was observed to be dependent on drawing temperature. It may be noted here that the the T_g of PLA is 65°C, and this drawing is carried out well above the T_g. As the drawing temperature increased, the mobility of the molecular chains also increases, easily yielding higher molecular

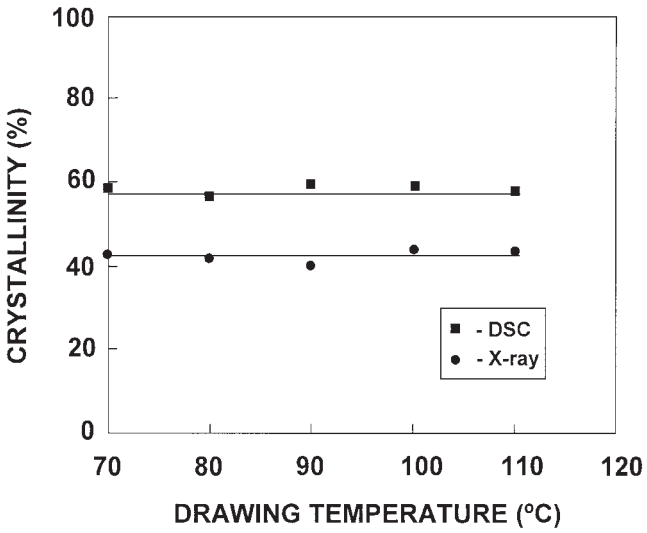

Figure 8 Variation of the percent crystallinity with the drawing temperature as measured from DSC and X-ray diffraction. The as-spun fiber collected at 10 m/min, total draw ratio was 8, and heat-setting temperature 120°C.

orientation. The trend in sonic modulus against drawing temperature is presented in Figure 9. The modulus increases as the drawing temperature increases, and tends to stabilize beyond 110°C.

The mechanical properties of the fiber were adversely affected by the drawing temperature. Figure 10 shows the mechanical behavior of the fiber drawn at various temperatures. It is observed that tenacity decreased sharply at very high temperature. Elongation was also dropped as the drawing temperature increased. This may be due to the overall contribution of the molecular chains toward the orientation reaching to its limiting values. Penning et al.[4] performed the drawing of melt-spun PLA fiber to determine the op-

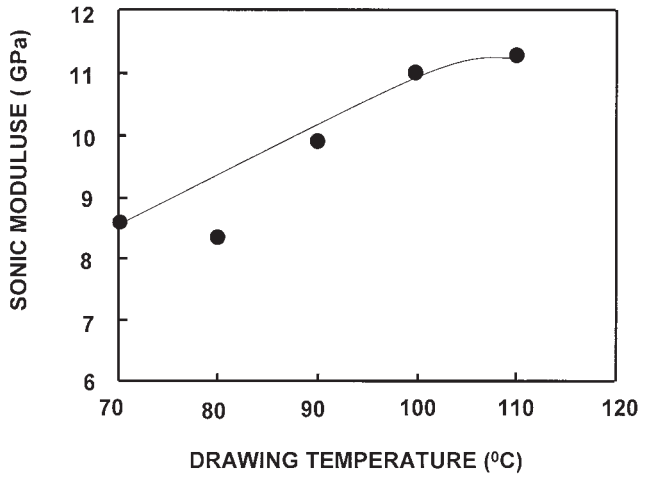

Figure 9 Effect of the drawing temperature on sonic modulus. Experimental conditions as in Figure 8.

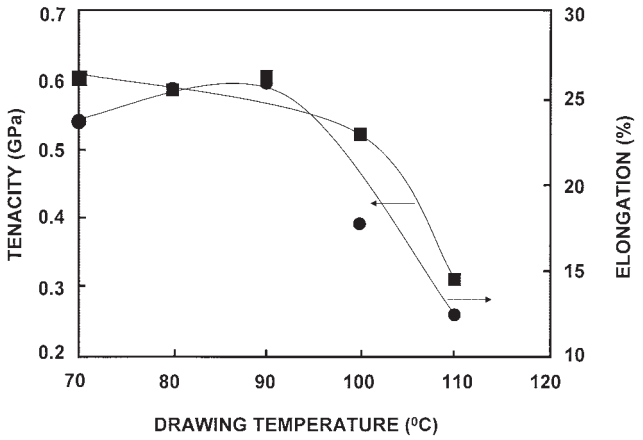

Figure 10 Effect of drawing temperature on the mechanical properties of drawn fiber. Experimental conditions as in Figure 8.

timum drawing temperature at which the fibers with the highest strengths are obtained. It is observed that optimum drawing temperature appears to be some 40–50°C above the T_g. In a tube-drawing experiment of solution-spun PLA fiber, Eling et al.[5] reported the four zones of drawing temperatures. The mechanical properties of PLA fibers drawn at temperatures in the range of T_g to T_m, dependence results from the cold drawing of the crystals formed in the fiber upon solution extrusion.

Effect of the heat-setting temperature

The as-spun fiber spun at 10 m/min was drawn at 90°C for a draw ratio 8 and the heat setting was

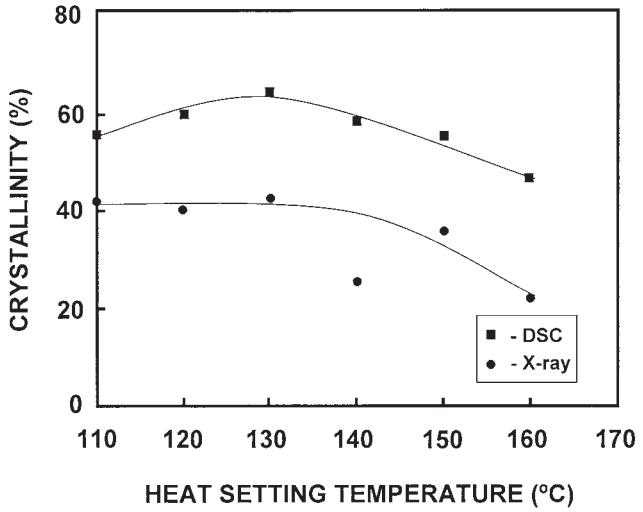

Figure 11 Variation of the percent crystallinity with the heat-setting temperature as measured from DSC and X-ray diffraction. The as-spun fiber collected at 10 m/min, total draw ratio was 8, and drawing temperature 90°C.

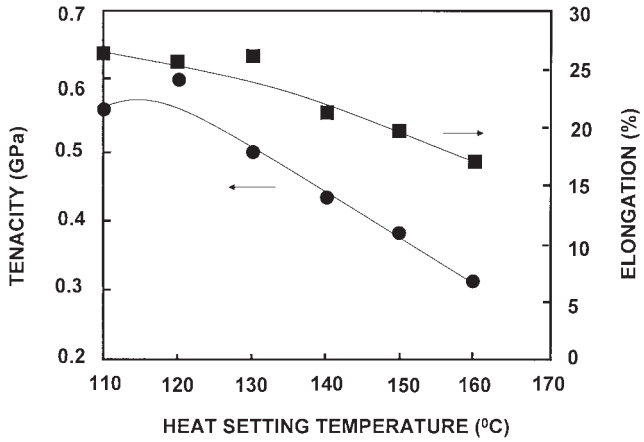

Figure 12 Effect of the heat-setting temperature on the sonic modulus. Experimental conditions as in Figure 11.

carried out at various temperatures under tout condition. The crystallinity and mechanical properties observed to be deteriorated with the increase in the heat-setting temperature (Figs. 11 and 12). This may be due the damage in the crystalline region, which indirectly affects the mechanical properties. Again, the molecular orientation after the initial rise dropped with the increase in the heat-setting temperature (Fig. 13). This may be due to the recoiling of molecular chains at a very high temperature. During the heat setting, both crystallization and relaxation of chains takes place simultaneously. During the heat setting the distribution of free chain segment lengths between points of intermolecular attraction may have been broadened, resulting in poorer tensile properties.

CONCLUSION

The important parameters affecting properties of dry–jet–wet spun PLA fiber are the take-up speed, draw

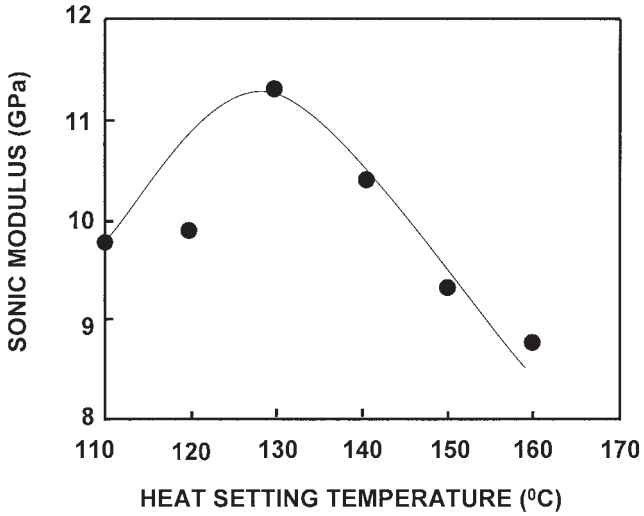

Figure 13 Effect of the heat-setting temperature on the mechanical properties of drawn fiber. Experimental conditions as in Figure 11.

ratio, drawing temperature, and heat-setting temperature. It was observed that as the take-up speed increased the wet stretch increased, which led to better orientation of the as-spun fiber and resulted improvement in the mechanical properties. The as-spun fiber showed porous morphology. Both the drawing temperature and heat-setting temperature had significant effect on the structure and properties of the fiber. The strength the fiber decreased beyond a drawing temperature of 90°C. The optimum drawing temperature and heat-setting temperature were observed 90 and 120°C, respectively, for our set of the experiment.

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