Effects of isothermal crystallization on fracture toughness and crack growth behavior of poly (lactic acid)

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Poly (lactic acid) (PLA) is a bioabsorbable and biocompatible thermoplastic, and therefore, has been used for bone fixation devices in orthopedic and oral surgeries [1–7]. Although the demand for such bioabsorbable devices is increasing in oral surgery, sudden fracture during service period prevents PLA devices from positive use in orthopedic surgery where the devices are subjected to higher stress. Therefore, it needs to understand the fracture behavior of PLA both qualitatively and quantitatively. Limited fracture properties of PLA thin films have already been studied [8–10]; however, few attempts have been made to investigate the fracture toughness and mechanism of PLA solids [11–13]. The microstructure of PLA is dramatically changed from amorphous to highly crystallized state as crystallization proceeds. Such structural change can be achieved by controlling molding [11] or annealing condition [13] during fabrication process, in which PLA plates are retained under conditions of fixed temperature and time.

The aim of this study is to characterize the effect of isothermal crystallization on the mode I fracture toughness of PLA solid. An amorphous and six crystallized PLA plates were prepared by quenching and annealing. Their crystalline structures were then characterized by polarizing optical microscopy (POM), and their thermal properties were measured by a differential scanning calorimetry (DSC). Mode I fracture toughness was estimated at a quasi-static loading rate, and then correlated with the crack growth behavior characterized by POM.

PLA plates 5 mm thick were fabricated from pellets (Lacty® #9030, Shimadzu Co. Ltd.) using a hot press attached with water cooling system. These pellets were melted at 180 °C and pressed at 30 MPa, and then quenched to room temperature for 10 min. The molded plates were then crystallized by annealing under different conditions: the temperatures were 70 and 100 °C, and the times were 3, 8 and 24 hr. Thin films placed on slide glasses were prepared from the middle-sections of the plates using petrographic thin sectioning technique, and their microstructures were observed using a polarizing optical microscope. For each of the crystallized samples, the average radius of spherulites was measured from a digital image of the microstructure. The crystallinity X_C were determined by DSC analysis and calculated using the following formula [8]:

$$X_C = \frac{100(dH_m + dH_C)}{93} \quad (1)$$

where dH_m and dH_C are the enthalpies of fusion and crystallization, respectively, and 93 (J/g of polymer) the enthalpy of fusion of PLA.

Single-edge-notched-bend (SENB) specimens were processed from the plates, and mode I fracture tests were performed at a quasi-static loading rate of 1 mm/min using a servohydraulic testing machine. The critical stress intensity factor K_{IC} was then calculated using the following formulae [14]:

$$K_{IC} = f(x)\frac{P_C}{BW^{1/2}},\ x = a/W$$
$$f(x) = \frac{6x^{1/2}}{(1+2x)(1-x)^{3/2}}[1.99 - x(1-x) \quad (2)$$
$$\times (2.15 - 3.93x + 2.7x^2)]$$

where P_C is the critical load. B and W are the specimen thickness and width, respectively. f is the geometrical correction factor expressed as a function of a/w, where a is the initial crack length. It is noted that the thickness B (5 mm) and the width W (15 mm) of the SENB specimens satisfy the condition $2B < W < 4B$ standardized for SENB specimens used in plane-strain fracture toughness test of plastics [14].

Crack growth behavior was characterized by POM. Double-edge-notched-bend (DENB) specimen was used to obtain an arrested crack for each sample [15]. Thin sections containing the arrested cracks were prepared using the petrographic thin section technique, and the samples were observed using the polarizing optical microscope.

Polarized micrographs of the microstructures of the PLA samples annealed at 70 and 100 °C are shown in Fig. 1. It is seen that the size and density of spherulites tend to increase with increase of annealing temperature and time. The averages of crystallinity and the radius of spherulites are presented in Table I. The crystallinity and radius increase with increase of annealing temperature and time, corresponding to the photographic results shown in Fig. 1.

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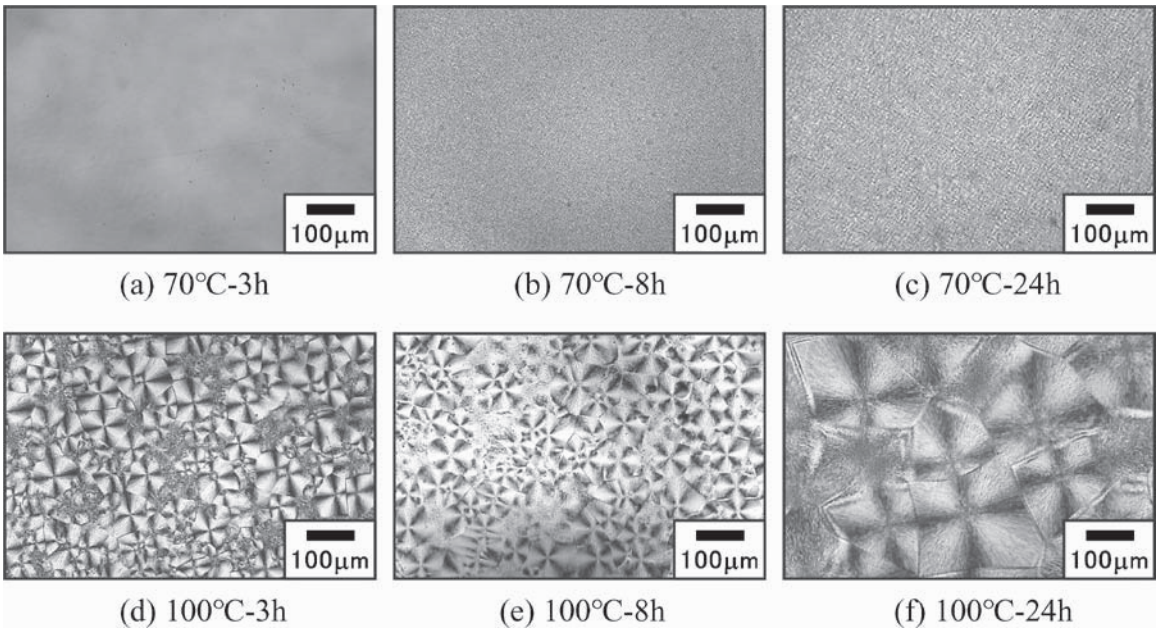


Figure 1 Polarizing microphotographs of microstructures of PLA. (a) 70 °C–3hr; (b) 70 °C–8 hr; (c) 70 °C–24 hr; (d) 100 °C–3 hr; (e) 100 °C–8 hr; (f) 100 °C–24 hr.

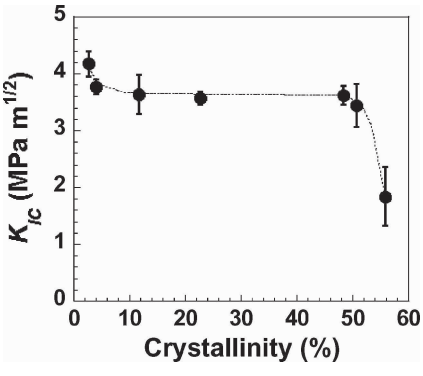


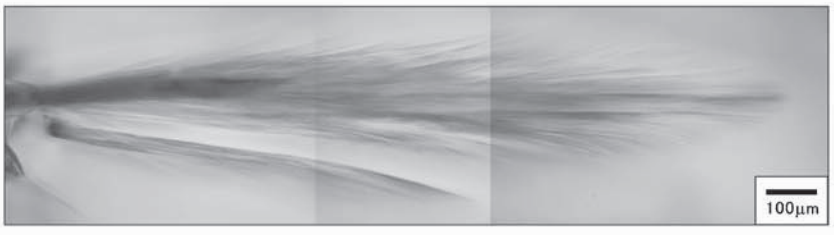
Figure 2 Effects of the crystallinity on fracture toughness of PLA.

Dependence of crystallinity on K_{IC} is shown in Fig. 2. As crystallinity increases, K_{IC} slightly decreases up to $X_c = 12\%$, and keeps constant up to $X_c = 50\%$. Above $X_c = 50\%$, K_{IC} rapidly decreases with increase of crystallinity. This dependence of crystallinity on K_{IC} is correlated with the POM results of crack growth behavior shown in Fig. 3. Extensive multiple crazes are generated around the crack-tip in the quenched specimen with low degree of crystallization ($X_c = 2.7\%$). This kind of multiple craze formation in a crack-tip region is generally observed in amorphous polymer [16]. The craze density appears to decrease with increase of crystallinity from $X_c = 2.7$ to 22.6%. As crazes initiate and grow in a crack-tip region with high-stress field, stress relaxation occurs and the local stress concentration factor K_I is reduced. Thus, the initiation of crack growth is delayed in the reduced stress field. Therefore, if craze density decreases with increase of crystallinity, stress concentration becomes severe and as a result, K_{IC} decreases. It is however interesting to see that K_{IC} almost keeps constant from $X_c = 11.6$ to 22.6%, although the craze density obviously decreases. It is presumed that the spherulites distributing in the crack-tip region may reduce the stress concentration due to local deformation and/or failure of the spherulites, and therefore increase K_{IC}. It is thus considered that decrease of crazes counterbalanced the increase of spherulites in terms of stress relaxation, resulting in the unchanged K_{IC}. The microstructure and crack growth behavior were dramatically changed for the specimens with crystallinity greater than 48.3%. In these crystallized specimens, it is observed that the main cracks without multiple craze formation propagate across the spherulites. It is noted that K_{IC} values of the PLA samples with $X_c = 48.3$ and 50.7% were almost the same as those of the samples with $X_c = 4$–22.6%. However, as X_c increases from 50.7 to 55.8% with the change of spherulite radius from 50 to 100 μm, K_{IC} dramatically decreases. It is considered that in the samples with $X_c = 48.3$ and 50.7%, fine short crazes generated in the amorphous region may reduce the stress concentration in the crack-tip region, though these crazes are not clearly observed in the POM micrographs. In the sample with $X_c = 55.8\%$, the spherulites are much larger than the other samples, and the coarse distribution of the spherulites prevents craze formation along the grain boundaries in the crack-tip region, resulting in brittle crack initiation without stress relaxation prior to the initiation. It is reported that for a crystalline polymer, K_{IC} decreases as spherulite diameter increases, corresponding to the present result [17].

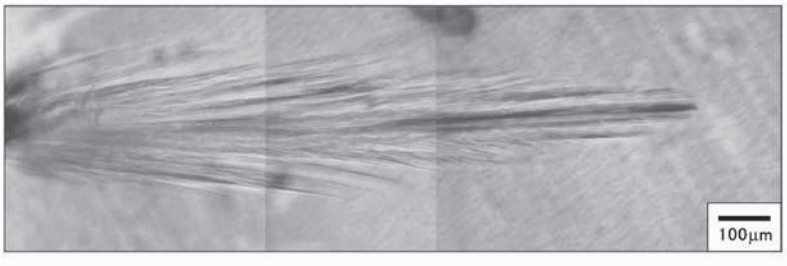
TABLE I The crystallinity and average radius of spherulites of PLA

Annealing condition	X_c (%)	Spherulite radius (μm)
Quenched	2.7	–
70 °C–3 hr	4	–
70 °C–8 hr	11.6	5
70 °C–24 hr	22.6	10
100 °C–3 hr	48.3	30
100 °C–8 hr	50.7	50
100 °C–24 hr	55.8	100

(a) X_c=2.7%

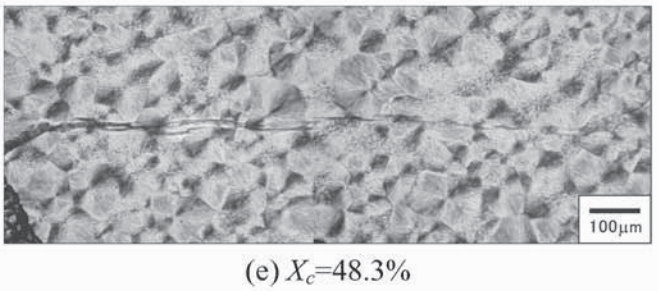


(b) X_c=4%

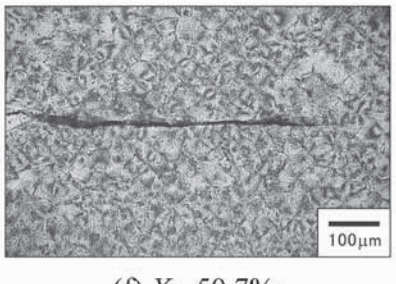


(c) X_c=11.6%

(d) X_c=22.6%



(e) X_c=48.3%



(f) X_c=50.7%;

Figure 3 Polarizing microphotographs of crack behaviors of PLA. (a) $X_c = 2.7\%$; (b) $X_c = 4\%$; (c) $X_c = 11.6\%$; (d) $X_c = 22.6\%$; (e) $X_c = 48.3\%$; (f) $X_c = 50.7\%$; (g) $X_c = 55.8\%$.

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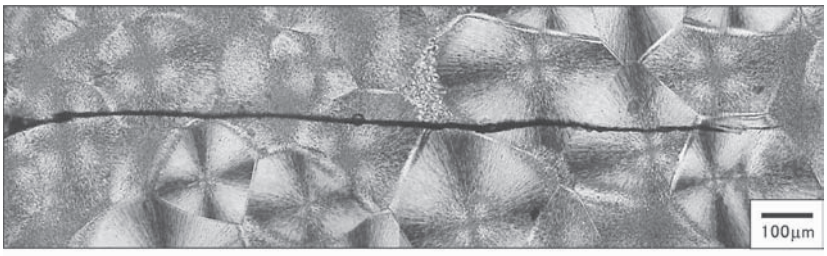

(g) X_c=55.8%

Figure 3 (*Continued*.)

In summary, the effects of isothermal crystallization on the fracture toughness, K_{IC}, and crack growth behavior of PLA were investigated. A unique dependence of crystallinity on K_{IC} was found, and the change of K_{IC} was closely related to the changes of microstructure and crack growth behavior. It is concluded that in practical use of PLA, one must be very careful for microstructural change which may cause severe change of fracture toughness. Further study is required to elucidate the detail of the relationship between the microstructure, i.e., the size and density of spherulites, and crack growth behavior.

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