Effect of annealing on the fracture toughness of poly(lactic acid)

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Recent years, considerable attention has been paid to biodegradable polymers mainly due to increase of interest for preservation of environment and substitution of petrochemical polymers. Poly(lactic acid) (PLA) is one of typical of such polymers, and is being considered for use in a variety of industrial fields including car, computer and electric appliances. PLA is also utilized as an implant biomaterial in medical fields such as orthopedics and oral surgery [1, 2], and furthermore, PLA matrix biocomposites have recently been developed [3–5]. It is thus important to understand and characterize the mechanical behavior of PLA. Mechanical properties of PLA films have extensively been studied [6–8]; however, few attempts have been made to investigate the deformation and fracture behavior of bulk PLA [9, 10]. PLA is usually used in the forms of sheet, plate and rod, and therefore, mechanical behavior of these forms must be well understood. The aim of this study is to understand the fundamental effect of annealing on the fracture behavior of PLA. Amorphous state was obtained by quenching, and annealing was performed to the quenched plates to obtain highly crystallized solid structure. Thermal properties of the two different types were then measured by a differential scanning calorimetry (DSC). Mode I fracture toughness values, K_{IC} and G_{IC}, were evaluated under quasi-static and impact loadings. Fracture micromechanisms were also investigated by polarizing microscopy (POM) and scanning electron microscopy (SEM).

Plates of 5 mm thick were fabricated from PLA pellets (Lacty® #9030, Shimadzu Co. Ltd.) using a hot press with attached water cooling system. These pellets were melted at 180 °C, and then quenched to room temperature for 10 min. Some of the quenched plates were then annealed at 100 °C for three hours in an oven to crystallize them. Thermal properties such as the glass transition temperature, T_g, the melting temperature, T_m, and the crystallinity, X_C, were determined by DSC analysis. X_C was calculated using the following formula [6]:

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

where dH_m and dH_C are the enthalpies of fusion and crystallization, respectively, and 93 (J/g of polymer) is the enthalpy of fusion of PLA. Single-edge-notch-bend (SENB) specimens were prepared from the amorphous and crystallized plates, and then K_{IC} and G_{IC} were measured at a quasi-static rate of 1 mm/min using a servohydraulic testing machine and at an impact rate of 1 m/s using an instrumented drop weight testing system [11]. K_{IC} and G_{IC} were calculated using the following formulae [12]:

$$K_{IC} = f\frac{P_C}{BW^{1/2}} \quad \text{and} \quad G_{IC} = \frac{U_C}{BW\phi} \tag{2}$$

TABLE I Thermal properties of quenched and annealed PLA samples

	T_g (°C)	T_m (°C)	X_c (%)
Quenched	64.4	168	2.68
Annealed	66.3	169.5	48.34

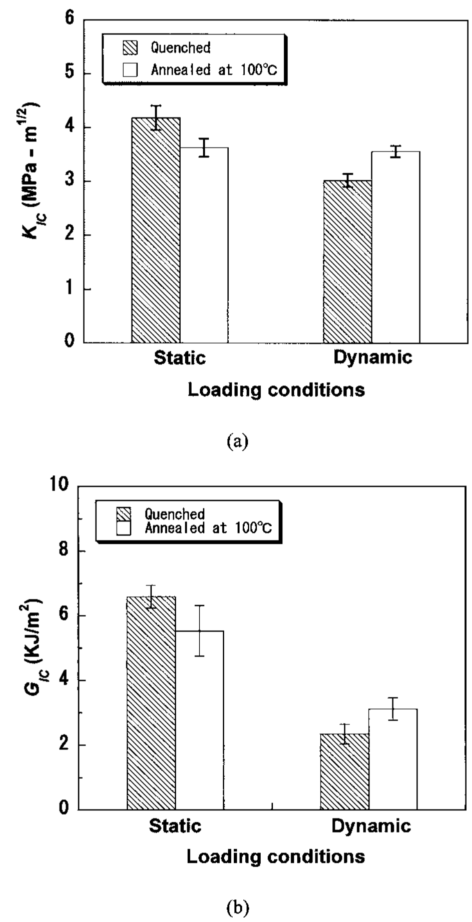

Figure 1 Effects of annealing and loading condition on K_{IC} or G_{IC}: (a) K_{IC} and (b) G_{IC}.

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where P_C and U_C are the critical load and energy, respectively. Maximum load and the corresponding energy were chosen as P_C and U_C, respectively. B and W are the specimen thickness and width, respectively, and f and ϕ are the correction factors which are given by functions of a/W where a is the crack length. Crack growth behaviors were studied by POM with use of the petrographic thin section technique. At the impact rate of loading, double-notch-4-point-bend (DNB) specimens were used to obtain arrested cracks for POM [13]. Fracture surface morphology was also characterized by SEM.

Table I shows the thermal properties of PLA obtained by DSC analysis. T_g and T_m slightly increased due to annealing as a result of crystallization. The quenched PLA had low crystallinity of 2.7%, and the present annealing formed a crystallized state with moderate crystallinity of 48.3%.

Results of the toughness measurement are shown in Fig. 1. At quasi-static loading rate, K_{IC} and G_{IC} of the quenched PLA are higher than those of the annealed, while at impact loading rate, the relationship was reversed. In general, progress of crystallization in a semi-crystalline polymer results in embrittlement of

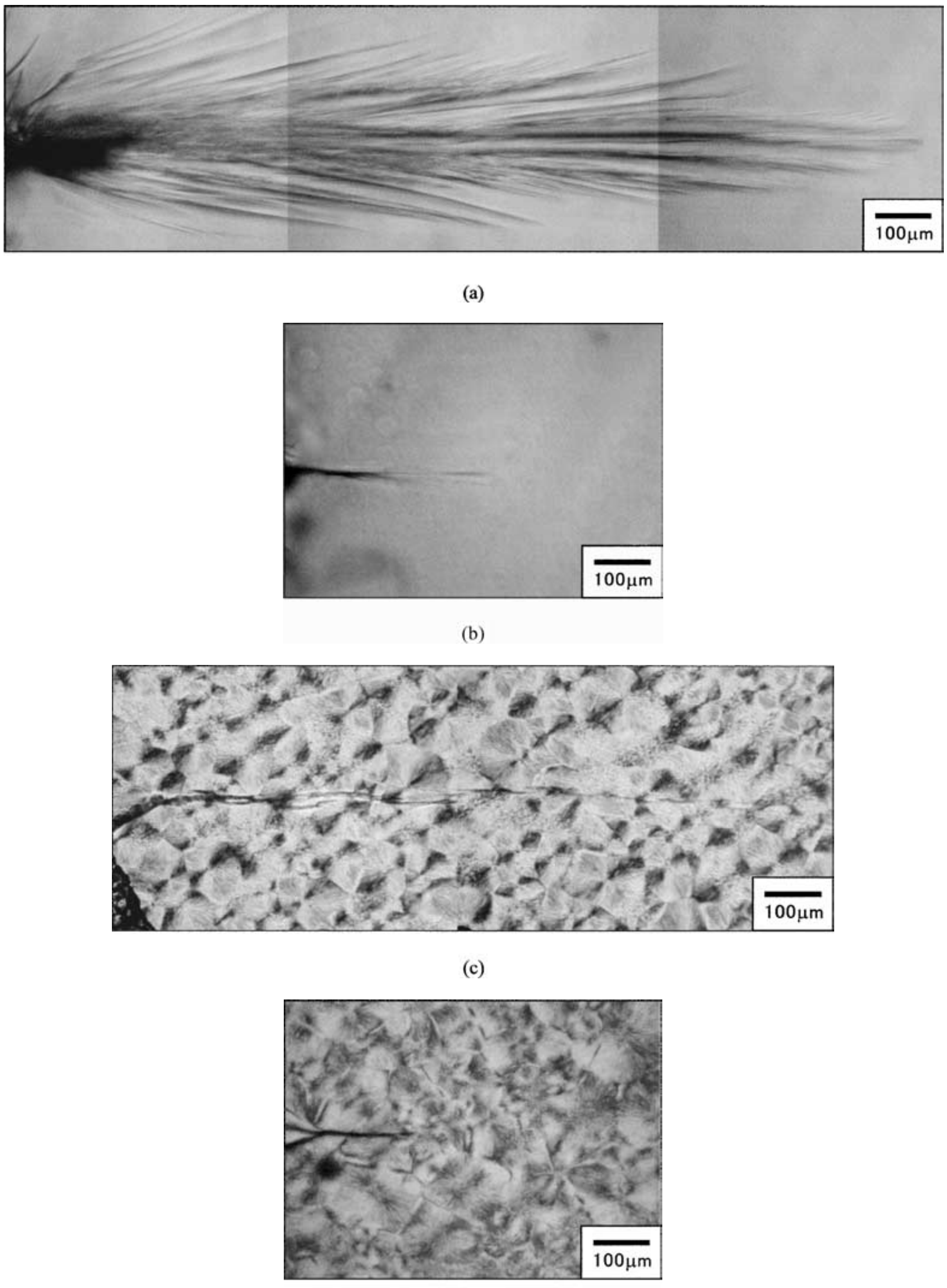
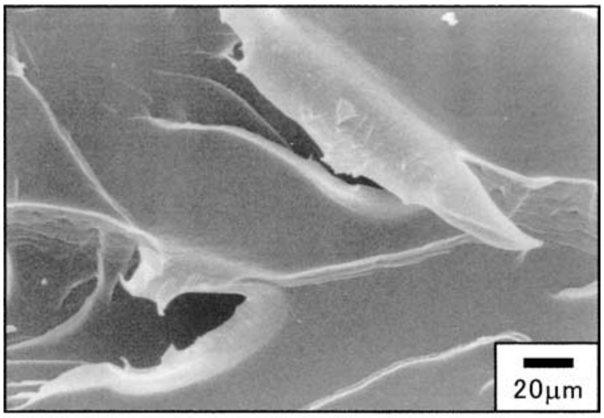
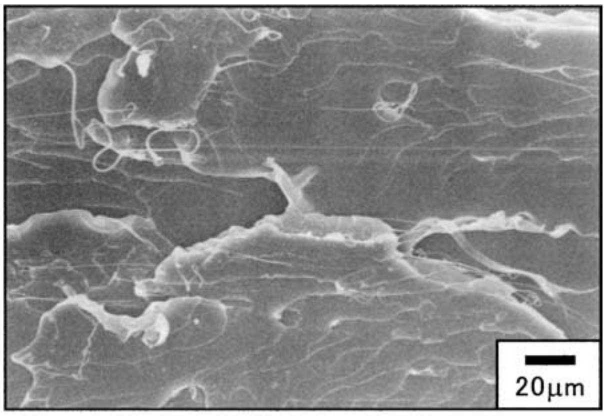


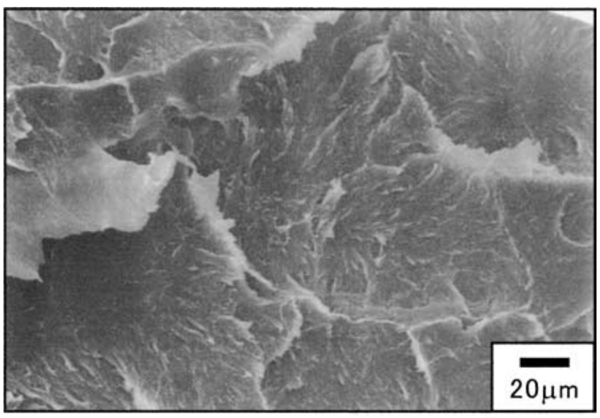
Figure 2 Polarizing microphotographs of crack behaviors of PLA: (a) quenched-static, (b) quenched-impact, (c) annealed-static, and (d) annealed-impact.



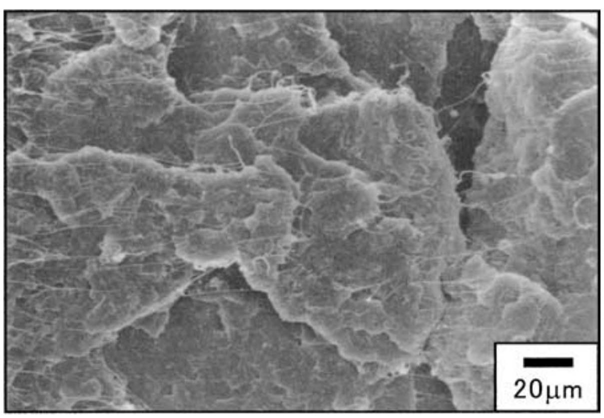
(a)



(b)



(c)



(d)

Figure 3 SEM microphotographs of fracture surfaces: (a) quenched-static, (b) quenched-impact, (c) annealed-static, and (d) annealed-impact.

the polymer and hence decrease of fracture toughness [14]. This matched with the present result obtained at quasi-static loading rate; however, at impact loading rate, advanced crystallization caused increase of fracture toughness.

Different types of crack growth behavior observed by POM are shown in Fig. 2. For the quenched-static sample, multiple craze formation was observed in the vicinity of the crack tip. This type of crack-tip crazing is usually observed in amorphous polymers [15]. At impact rate, the number of crazes was dramatically reduced as shown in Fig. 2b. Multiple crazes result in the relaxation of stress concentration and additional energy dissipation in the crack-tip region, and therefore, suppression of craze formation at impact rate caused the decrease of K_{IC} and G_{IC} as shown in Fig. 1. For the annealed sample, on the other hand, crack propagated through spherulites and along spherulite boundaries with few or no crazes formed around the main crack. It appears that crack branching occured at quasi-static rate, whereas only single crack was observed at impact rate.

SEM microphotographs of fracture surfaces are shown in Fig. 3. The fracture surface of the quenched-static sample exhibited deep concavities due to multiple craze formation shown in Fig. 2a. These were not observed in the quenched-impact. The annealed-impact showed the formation of crevices not observed in the annealed-static, suggesting microcracking along the interfaces of spherulites. This microcracking might enlarge the fracture toughness of the annealed at impact loading rate. For both the impact samples, fibril structures are observed (see Fig. 4), suggesting that heat generated due to high strain rate at the crack tip and as a result, the crack-tip temperature rose above T_g [16, 17].

In summary, the effects of annealing and loading rate on the fracture behaviour of poly (lactic acid) were investigated. Annealing lowered K_{IC} and G_{IC} under quasi-static loading; in contrast annealing increased the toughness under impact loading. Multiple craze formation resulted in the high K_{IC} and G_{IC} of the quenched-static, and the suppression of the crazing lowered the toughness at impact loading rate. For the annealed condition, microcracking at the spherulite interfaces might

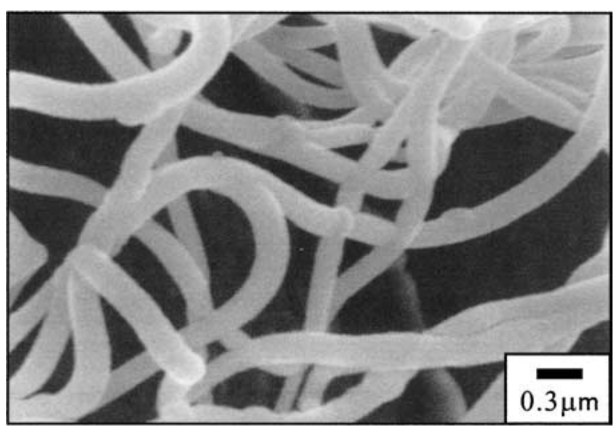


Figure 4 Fibril structure appeared on the fracture surface of annealed sample under impact loading.

have been responsible for the increase in the toughness. Further study is required to elucidate the detail of the toughening mechanism.

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