The Fracture Mechanism of Polylactic Acid Resin and the Improving Mechanism of Its Toughness by Addition of Acrylic Modifier

Masakazu Ito,[1] Satomi Abe,[2] Masaru Ishikawa[2]

[1]*Mitsubishi Rayon Co., Ltd., Corporate Research Laboratories, Miyuki-cho, Ootake, Hiroshima 739-0693, Japan*
[2]*Department of Polymer Science and Engineering, Faculty of Engineering, Yamagata University, Yonezawa, Yamagata 992-8510, Japan*

Received 19 October 2008; accepted 23 June 2009
DOI 10.1002/app.31292
Published online 7 October 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The fracture mechanism of polylactic acid (PLA) resin and the improving mechanism of its toughness by addition of an acrylic modifier were examined. Plane strain compression testing of PLA clearly showed strong softening after yielding. Because the stress for craze nucleation of PLA was close to the yield stress, brittle fractures resulted. The addition of an acrylic modifier to the PLA significantly lowered the yield stress and formed many voids. The release of the strain constraint because of the formation of many voids and the decrease of yield stress resulted in the relaxation of stress concentration, and the toughness was improved. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 1454–1460, 2010

Key words: biopolymers; brittle; compounding; crazing; toughness

INTRODUCTION

Polylactic acid (PLA) resin, which is derived from plants, is an environment-friendly material, which saves fossil fuel and helps control global warming.[1–3] However, because PLA is very brittle, it is difficult to use it as a general molding material.

When a load is applied to a polymer material, elastic deformation occurs followed by plastic deformation. In case of crystalline polymers, the plastic deformation starts with a slip of the C axis of the lamella crystal that constitutes the polymer[4]; in case of amorphous polymers, the plastic deformation starts with the generation of a local kink in the molecular chain when the pure shear stress reaches a threshold value.[5]

The heterogeneous shape of a molded material induces stress concentration, resulting in local plastic deformation. High dilatational stress arises from the plastic constraints at the tip of the local plastic zone—the value of the stress increases with the expansion of the local plastic zone.[6,7] When the dilatational stress reaches a threshold value, a void is formed. The density of the void increases with the increasing dilatational stress. The plastic strain concentration is generated with rapid expansions of the limitative void, when the plastic instability condition is satisfied at the void, which depends on the degree of the elastic modulus, the yield stress, and the dilatational stress.[8] This is called craze. Although there is limited understanding of the conditions that generate voids in polymer materials, they seems to be closely related to the mechanism of plastic deformation. It is believed that in crystalline polymer, the formation of a clear void is related to the breaking of the spherulite structure by plastic deformation of the lamella crystal of the C shaft, due to a slip, because an expansion of volume is confirmed after yielding.[9] On the other hand, in amorphous polymers, a kink in the molecular chain, which is a fundamental mechanism of plastic deformation, is believed to lower the local density—this seems to be a trigger for the formation of voids.[10] The unstable plastic expansion of voids is very sensitive to the yield condition. In certain polymer materials, true stress is reduced after the start of plastic deformation.[11] This decrease in yield stress is called softening. It is presumed that this softening promotes the unstable concentration of plastic strain. For example, shear bands, observed by compression tests of polystyrene (PS)[12] or by tensile tests of polycarbonate (PC),[13] are present in the propagation region where the concentrated plastic strain is formed by softening. Thus, we presume that this softening greatly affects craze formation from the void. For example, the formation of the craze of PS is known as surface craze—it starts from the sample surface.[14] Unstable

Correspondence to: M. Ito (itou_masaka@mrc.co.jp).

expansion of the void appears to be easily generated with low dilatational stress, because PS is a polymer material that shows strong softening.

To explain the mechanism of toughness improvement of polymer material by elastomer blending, the authors propose the release mechanism of the restraint of strain.[15,16] The toughness of the polymer material can be improved by a void formed from the elastomer, enabling Poisson contraction between voids, and relieving the stress concentration.

The part between voids deforms unstably when a stress is loaded to the polymer material that shows softening, and the craze is formed. This softening may influence the efficiency of the toughening improvement by a release of the restraint of the strain.

In this study, the softening of PLA resin was examined, and the effect of softening on the toughness of PLA blended with acrylic modifier was examined.

EXPERIMENTAL

Materials

The materials used in this study were PLA (Mitsui Chemical Co., LACEA H-100; $M_w = 125{,}000$, injection molding grade), PC (Mitsubishi Engineering Plastics Co., Iupilon S2000F; $M_v = 24{,}000$, injection molding grade), and an acrylic modifier.

The acrylic modifier was a core-shell type modifier, which was composed of a poly(methyl methacrylate) and a crosslinked alkyl acrylate rubber. A mixture of alkyl acrylate and allyl methacrylate was copolymerized by conventional emulsion polymerization to obtain acrylic rubber latex, and methyl methacrylate was copolymerized in the rubber latex to obtain the core-shell type modifier. The rubber particle was observed by a transmission electron microscope, to determine the rubber particle size. The particle size range was 100–300 nm, and the number average particle diameter was 170 nm. The glass temperature of the acrylic rubber by the dynamic mechanical analysis was 240–250 K. Mitsubishi Rayon Co., supplies this type of acrylic modifier as Metablen W-450A.

The PLA compounds were composed of PLA and acrylic modifier without a stabilizer. The concentration of acrylic modifier in the PLA compounds was 0, 5, 10, 20, 30, and 50 wt %. The PC compounds were composed of PC and acrylic modifier without any stabilizer. The concentration of acrylic modifier in the PC compounds was 0 and 10 wt %.

A 30-mmφ twin screw extruder (Werner & Pfleiderer, ZSK30 M9.2) was used for melt blending these materials. The screw rotational frequency was 250 rpm, and the barrel temperature was 493 K for PLA compounds and 543 K for PC compounds. The quantity of delivery was 2 kg/10 min. Before blending, PLA and PC were dried using a hot air oven at a temperature of 343 K for 12 h.

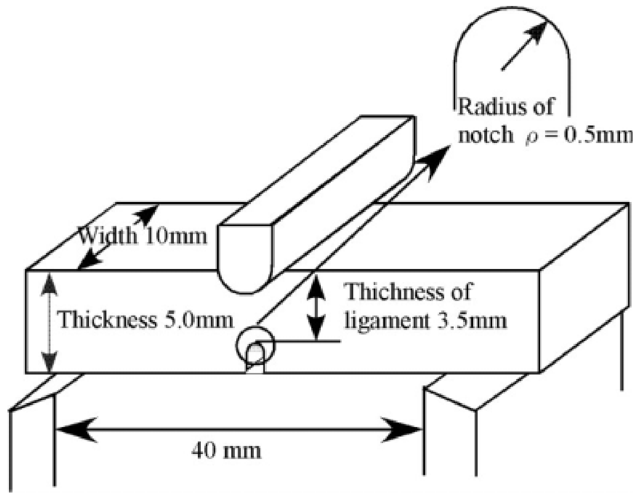

Figure 1 Evaluation of toughness by three-point bending test of a specimen with a U-shaped notch.

Specimens were prepared by injection molding (Meiki, Nadem 1200-JS) at an injection temperature of 503 K for PLA blends and 553 K for PC blends. The mold temperatures were 313 K for PLA blends and 343 K for PC blends. Drying of blends before the injection molding was carried out by a vacuum oven at 333 K for 24 h.

Mechanical analysis

To evaluate the stress-strain curves, dumbbell-shaped specimens were used. The parallel part was 60 mm long, 10 mm wide, and 2 mm thick.

To evaluate the toughness, rectangular bars with a round notch (U-notch) were used. The specimen was 50 mm long, 10 mm wide, and 5 mm thick. The radius of notch tip was 0.5 mm, and the ligament thickness was 3.5 mm, as shown in Figure 1.

The toughness was evaluated with a three-point bending test of the specimen with the U-notch. The test temperature was 296 K, and the bending speed was 2 mm/min. The nominal stress-strain curve was measured by a uniaxial tension test of the strain rate 0.2/min. An instron type testing equipment (Autograph AG5kNE, Shimadzu Co.) was used.

In the uniaxial tensile test, the true stress-strain curve after the beginning of the plastic deformation was not obtained, because the PLA test piece was brittle. Therefore, the true stress-strain curve was measured by a plane strain compression test, using a die. The test piece was 10 mm wide and 2 mm thick, and the die was 6 mm wide and 10 mm long. The compressive strain speed was 0.5 mm/min. An instron type testing equipment (Autograph AG-

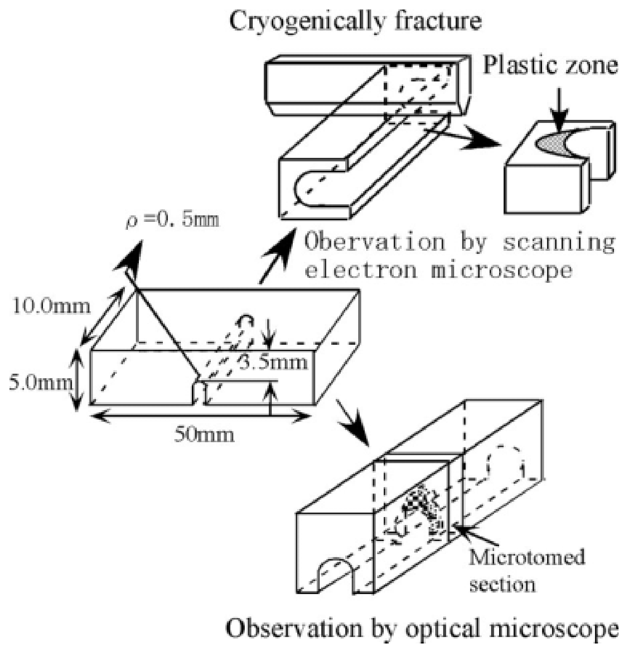

Figure 2 Dimensions of the U-notched sample and cutting direction for observation of deformation.

100KNE, Shimadzu Co.) was used in this mechanical test.

Morphological analysis

To discuss the deformation processes of U-notched bars in three-point bending tests under plane strain, thin sections of about 25 μm were cut normal to the plane of the notch using a microtome[17] (Fig. 2). The morphologies of the plastic deformation zone developing from the tip of the notch tip were studied with an optical microscope for the microtomed sections. The microstructure of the plastic deformation zone was observed with a scanning electron microscope for the surfaces of the cryogenically fractured samples (Fig. 2). Samples subjected to the bending test were unloaded, and then cast in epoxy resin to fix the form of the deformation zone. The resin consisted of 100 parts per hundred (phr) of Epon828 (diglycidyl ether of bisphenol A, Shell Chemical Co.) and 60 phr of Ankamide506 (Polyamide-amine, BTI Japan). The appropriate form was cut, and the cast sample was immersed in a liquid-nitrogen bath for 5 min, and then immediately broken normal to the plane of the notch.

The morphology of the plastic zone of PC blended with an acrylic modifier of 10 wt % was also observed to examine the effect of softening on the deformation behavior of the plastic zone, in comparison with that of PLA.

RESULTS

Deformation and fracture of PLA resin

The stress-strain curves of PLA evaluated by the uniaxial tension test are shown in Figure 3. Although a few test pieces showed necking without large strain, many test pieces yielded and broke right after yield without necking.

Figure 4 shows the true stress-strain curve of PLA evaluated by the plane strain compression test, compared with PC. The true stress was significantly reduced—sharply after yield in comparison with PC. This phenomenon is called softening. In other words, PLA demonstrated strong softening.

An optical microscope photograph of the part with the yielding fracture is shown in Figure 5. On the uniaxial tensile deformation, both the shearing deformation and the formation of surface craze

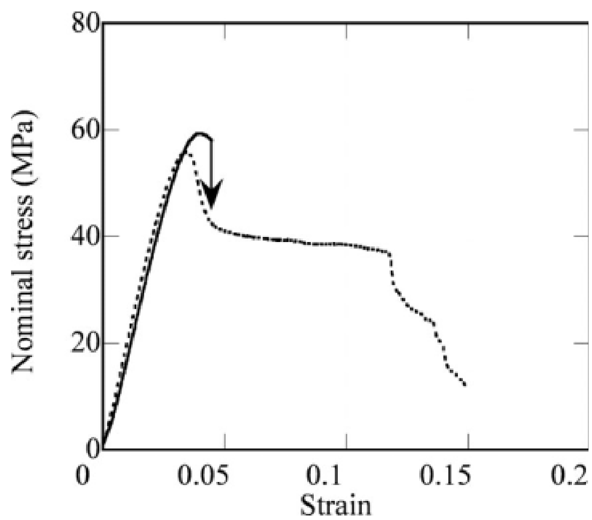

Figure 3 The stress-strain curve of the PLA evaluated by the uniaxial tension test.

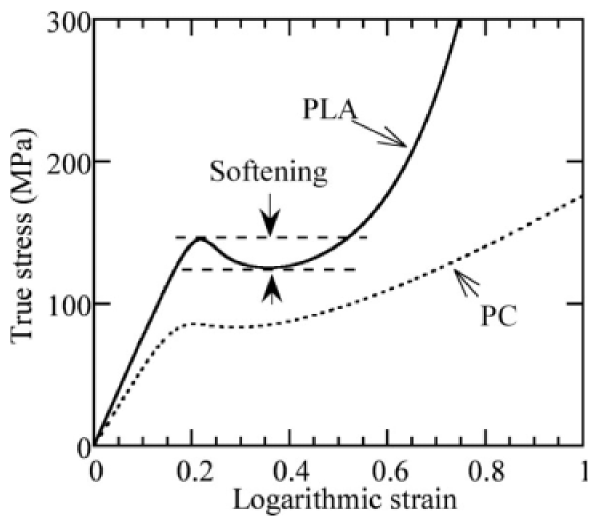

Figure 4 True stress-strain curve of the PLA, evaluated by plane strain compression, compared with PC.

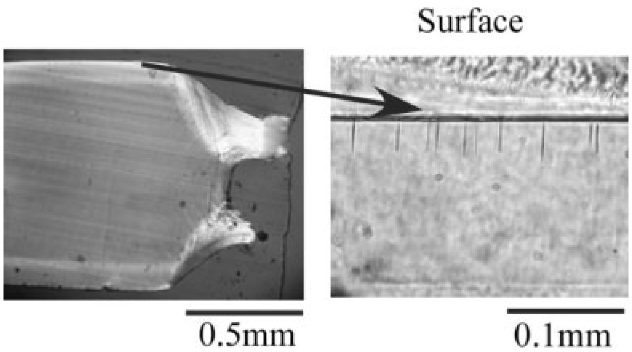

Figure 5 Optical microscope photograph of the part with the yielding fracture.

occurred with plastic deformation. Figure 6 shows an optical microscope photograph (left) of a slice of the plastically deformed region of the U-notched specimen and a scanning electron microscope photograph (right) of the surface prepared by fracturing at liquid nitrogen temperatures. In the optical microscope observation of the slice, the surface craze appeared at the tip of the notch, and the scanning electron microscope photograph of the fracture surface showed the formation of craze in the interior, remote from the notch tip.

The plastic deformation and fracture of PLA blended with an acrylic modifier

Nominal stress-strain curves in the uniaxial tensile test of the PLA blended with an acrylic modifier are shown in Figure 7—the two graphs in the figure are the same except for the strain scale. The uniaxial tensile yield stress of the blend drastically decreased with the addition of the modifier, and large plastic deformation accompanying the necking was possible. The yield fracture was suppressed. The addition of the modifier reduced the decrease in stress after

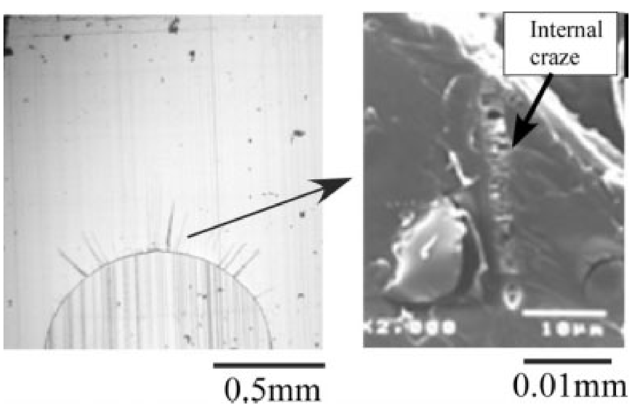

Figure 6 Optical microscopic photograph of the slice of the plastically deformed region of the specimen with U-shaped notch and an electron scanning photograph of the fracture surface, prepared by fracturing at liquid nitrogen temperatures.

the yield, arising from softening. The effect of the addition of the modifier on the bending moment-displacement curve of the U-notched specimen is shown in Figure 8. The brittle fracture was suppressed by the addition of the modifier, and a considerable improvement of toughness was accomplished by general yielding. General yield bending moment decreased drastically with increasing amount of modifier.

Changes in the general yield, in the plastic zone formed at the notch tip by addition of varying amounts of acrylic modifier are shown in Figure 9. It was clearly found that the plastic deformation region, consisting of craze, spread over a wide range compared with unmodified PLA alone. Given the same bending displacement, the width increased and the length decreased as the amount of acrylic modifier was increased.

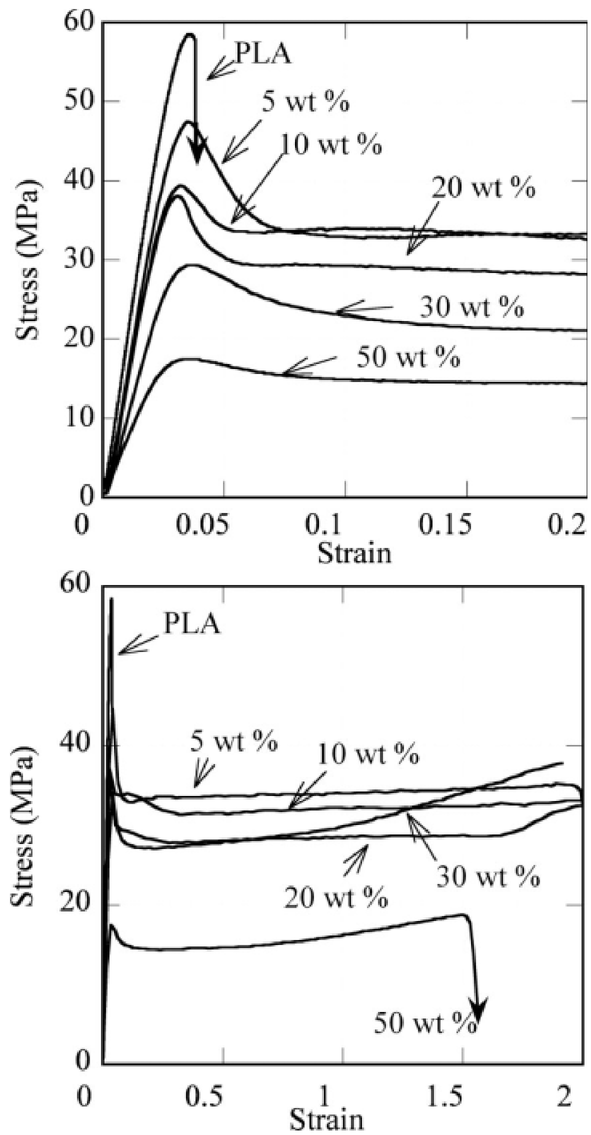

Figure 7 Stress-strain curves in the uniaxial tensile test of the PLA blended with an acrylic modifier.

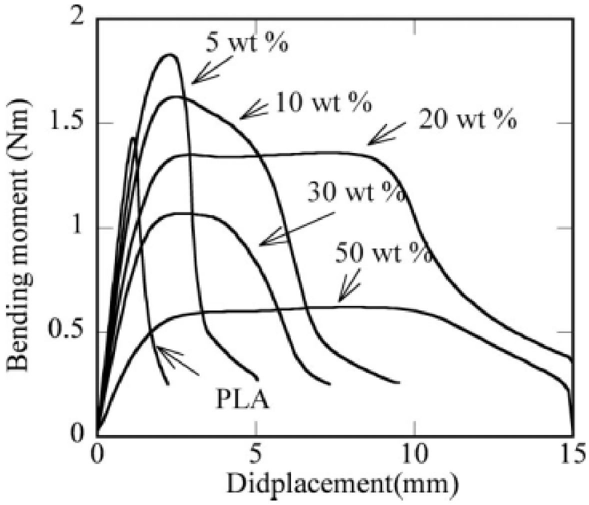

Figure 8 The effect of adding a modifier on the bending moment-displacement curve of the U-notched specimen.

Figure 10 shows a scanning electron microscope photograph of craze and the plastic zone formed at this notch tip for the PLA blended with 30 wt % acrylic modifier. This confirmed that the craze consists of line up of voids. There was no indication that the void greatly deformed plastically in the maximum principal stress direction.

Figure 11 shows an optical microscope photograph of the deformation zones of PLA and PC, both of which were blended with acrylic modifier of 10 wt % to examine how softening and orientation hardening influence the morphology of the plastic zone with the void. Compared with the plastic zone of PLA with an acrylic modifier of 10 wt % consisting of craze, which propagated strongly in the notch direction, the local plastic zone of PC with an acrylic modifier of 10 wt % expanded widely from the notch.

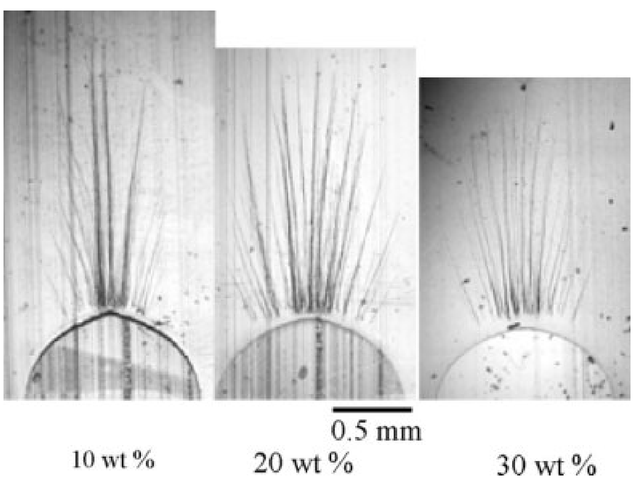

Figure 9 Changes in the plastic zone formed at the notch tip caused by addition of varying amounts of acrylic modifier.

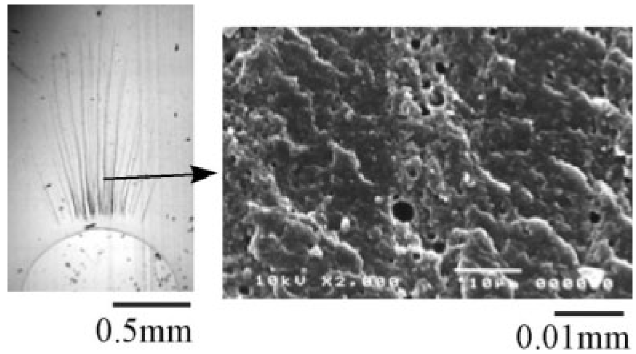

Figure 10 Scanning electron microscope photograph of craze and the plastic zone formed at this notch tip.

Figure 12 shows the bending moment-displacement curve of PLA blended with an acrylic modifier of 10 wt %, compared with that of PC.

DISCUSSION

Deformation and fracture of PLA resin

Uniaxial tensile deformation, shown in Figures 3 and 6, indicated that both shearing deformation and the formation of surface craze occurred simultaneously with plastic deformation. Strong softening led to a concentration of plastic strain, and resulted in necking fractures immediately after yielding.

The bending deformation of the U-notched bar showed that the brittle fracture began with surface craze at the tip of notch, without the development of a clear shear plastic zone.

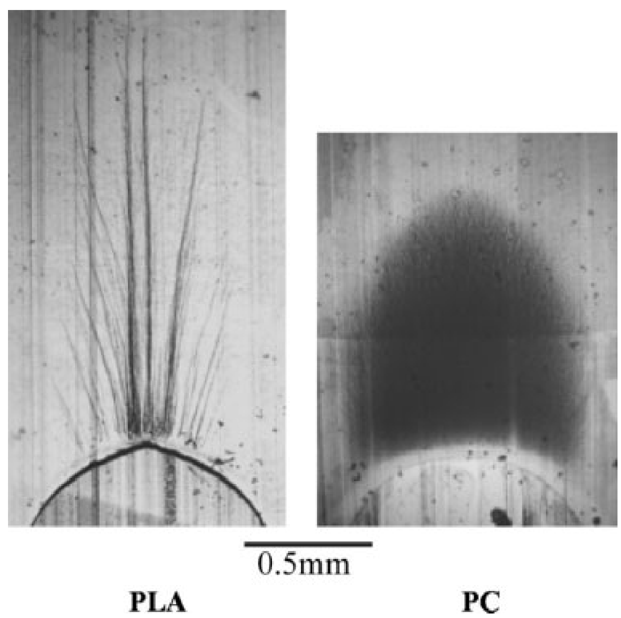

Figure 11 Optical microscopic photograph of the stable plastic zone developed from the notch tip on PC blended with an acrylic modifier of 10 wt %, compared with PLA.

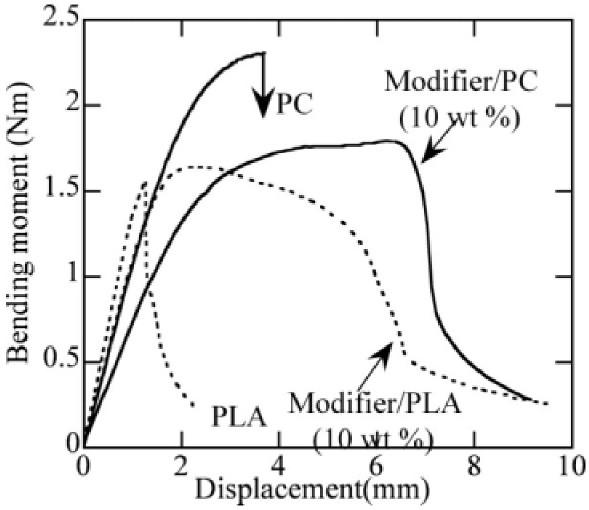

Figure 12 The bending moment-displacement curve of PC blended with acrylic modifier of 10 wt %, compared with that of PLA.

The craze is formed when the plastic instability condition in expanding the void generated by dilatational stress is satisfied. In an amorphous glassy polymer, it is thought that the stress for the nucleation of craze increases in proportion to the molecular weight. On the other hand, the shear yield stress required to induce a local kink in the molecular chain is independent of the molecular weight.[18] Therefore, in a low-molecular-weight polymer, the craze is able to form prior to the macroscopic shear plastic deformation. A similar tendency has been confirmed in crystalline polymers for the molecular weight dependence of the yield and craze formation stresses.[19]

Transfer of the relative position between molecular chains by slip is necessary for the expansion of the void, unlike the case of shear plastic deformation.[18] The resistance to slip between relative molecular chains seems to be dependent on the cohesion between molecular chains. Although there are few studies on the relationship between the stress of the slip and the molecular structure, we suppose that the cohesion of the polymer, in which stereo regularity and packing density are low, is small.

The formation condition of the craze of PLA is similar to that of PS or acrylonitrile–styrene copolymer. Because both the shear plastic deformation and the surface craze occur simultaneously in the uniaxial tensile test, it is presumed that the cohesion of PLA is close to its yield stress. Figure 6 indicates that the void in PLA is formed by low dilatational stress because of the small expansion of the plastic zone. The unstable plastic expansion of voids seems to occur due to strong softening of PLA and the void changes to surface craze by propagation.

The plastic deformation and fracture of PLA with acrylic modifier

The addition of acrylic modifier led to necking deformation in the uniaxial tensile test and general yielding in the bending test of the U-notched specimen. It was confirmed that the addition of acrylic modifier to PLA resulted in an improvement of toughness.

It is well known that the addition of elastomer to the matrix resin decreases its yield stress and makes it deform stably. This results in an improvement of toughness.

To explain the mechanism of toughness improvement of polymer material by elastomer blending, the authors propose the release mechanism of the restraint of strain.[15,16] When a load is applied to the blend polymer, a void is formed from the elastomer, which has less strength than the matrix. The many voids formed from the elastmers lead to the release

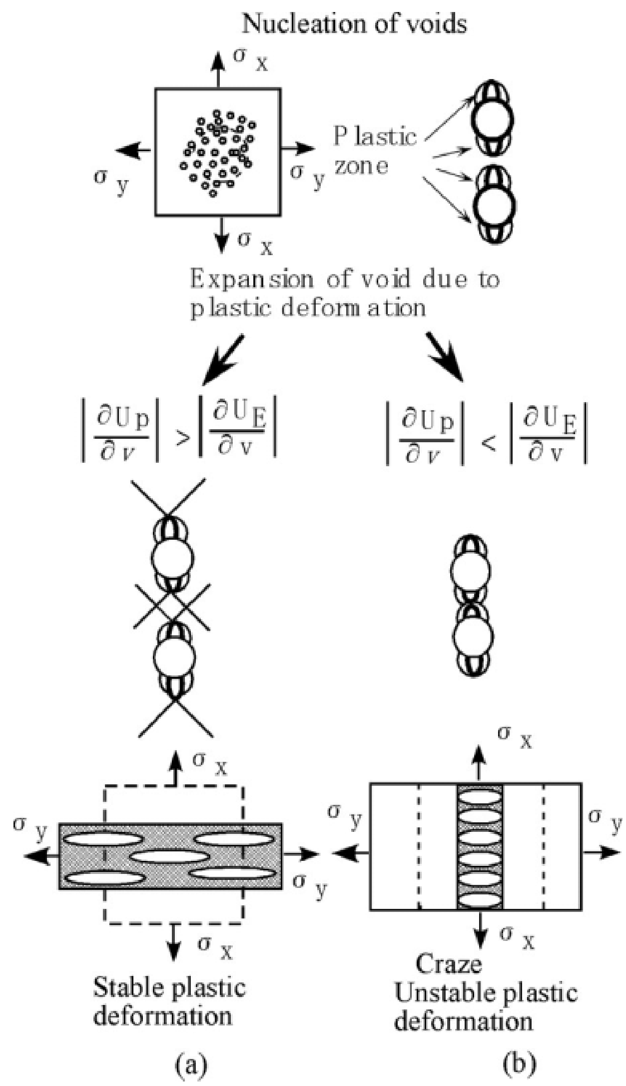

Figure 13 Illustration of plastic instability for void expansion.

of the restraint of strain and permit Poisson contraction between voids. As a result, the stress concentration around the U-notch is relaxed, and the toughness of the polymer material is improved. Examples illustrating this improvement of toughness by the release of restraint of strain include the PC, polyamide, and iso-PP blended with elastomer.

In this section, we discuss the relationship between the stability of the expansion of voids and the toughness.

When a polymer blended with an elastomer takes a load, and the dilatational stress reaches a critical level, a void is formed. The formed void is expanded by plastic deformation. By the expansion of void volume (V), the energy (U_P) expended by plastic deformation is $\partial U_P/\partial v$, and the decreased level of elastic strain energy (U_E) is $\partial U_E/\partial v$.

$$\frac{\partial U_P}{\partial V} > \frac{\partial U_E}{\partial V} \quad (1)$$

In case of eq. (1), the load from the outside must be increased for expansion of the void, because the energy (U_P) expended in plastic deformation of the void is larger than the decreasing elastic energy (U_E).[8] Therefore, deformation progresses steadily, as shown in Figure 13(a). It is already known that in notched PC, the brittle fracture begins at the tip of the local plastic zone developed from the notch, because the maximum stress appears at the tip of the local plastic zone due to plastic constraints. The addition of an elastomer to PC leads to an increase in the size of local plastic zone developed from the notch, and general yielding, as shown in Figure 12. The local plastic zone shows a homogeneous distribution of plastic strain at the general yield, as shown in Figure 11. The orientation hardening of PC has a positive slope over a wide strain range, although a slight drop of yield stress was observed immediately after the initial yield. As a result, the condition of eq. (1) is satisfied, and stable plastic deformation of the void occurs.

In the meantime, when the relaxation quantity of elastic energy (U_E) from the expansion of the void surpasses the resistance (U_P) by plastic expansion of void, as expressed in eq. (2), the void expands spontaneously and unstably, as shown in Figure 13(b). This unstable void expansion occurs when the condition of plastic instability, which depends on the stress around the void and volume percentage of the void, are satisfied.[8]

$$\frac{\partial U_P}{\partial V} < \frac{\partial U_E}{\partial V} \quad (2)$$

The distribution of plastic strain in the local plastic zone of PLA blended with a modifier was nonhomogeneous. Strong softening, immediately following the initial yield, is observed in PLA, as shown in Figure 4. This leads to concentrated unstable plastic expansion of the void, as shown in Figure 13(b), because the condition of eq. (2) is satisfied.

In toughening of PLA by addition of a modifier, the decrease of yield stress and the formation of many voids contributed to the relaxation of stress concentration, and the toughness was improved moderately.

CONCLUSION

It was proven that very strong softening occurs after yielding in PLA. Because the stress for craze nucleation of PLA was close to that of the yield stress, a brittle fracture resulted. The addition of an acrylic modifier to the PLA significantly lowered the yield stress and formed many voids. The release of the strain constraint due to the formation of many voids and the decrease of yield stress resulted in the relaxation of stress concentration, and the toughness was improved moderately.

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