Effect of Dialkyl Peroxide Blending on Tensile Properties of PLA/PBAT Polymer Alloys

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Poly(lactic acid) (PLA) and poly(butylene adipate/terephthalate) (PBAT) were used for polymer alloys, and the effects of the mixing ratio of PLA and PBAT and the addition of dialkyl peroxide (compatibilizing agent) were examined. The stress-strain curves of PLA/PBAT and PLA/PBAT/dialkyl peroxide specimens were measured using a tensile split Hopkinson bar (Kolsky Bar) method and a universal testing machine. The mixing ratio of PLA and PBAT and the dialkyl peroxide addition affected the shape of the stress-strain curve behavior. Regardless of the strain rate, the yield stress decreased and the elongation at break and strain energy increased with increasing PBAT content when the dialkyl peroxide was used. At high strain rate, the dialkyl peroxide addition increased the elongation at break and the strain energy, and changed the fracture surface to a whitened form that was markedly uneven. This result could explain the improvement in the Izod impact strength.

Key words: bioplastics, polymer alloys, strain rate effects, tensile split Hopkinson bar, fractography.

1. INTRODUCTION

The increasing use of plastic products worldwide is causing considerable damage to the environment; therefore, biodegradable plastics (plastics that can decompose in the natural environment) and bioplastics (plant-derived or recyclable-resource-based plastics) are being extensively investigated, and new biodegradable and bioplastics are continuously being developed.

Poly(lactic acid) (PLA) is a typical biodegradable bioplastic (plant-derived plastic). It has been recognized as a promising alternative material for petroleum-based plastics. In Japan, PLA is already being used to manufacture many indus-

trial products such as the interior parts of cars, parts of computer cases, and cell-phone cases. Many studies have been conducted to identify other industrial products that can be manufactured using PLA, but currently such applications are limited to machine parts that are subject to low loading. Polymer blends/alloys or natural fiber reinforcing have been required to overcome the low impact resistance and the brittleness of PLA. Because poly(butylene adipate/terephthalate) (PBAT) is a ductile and biodegradable polymer, polymer alloys of PLA and PBAT have great potential for high impact strength. For example, Fukuda, one of the authors, showed that the Izod impact strength of PLA and PBAT polymer alloys is increased when dialkyl peroxide is used [1]. Of particular note, when the mixing ratio of PLA : PBAT : dialkyl peroxide was 60 : 40 : 1, the Izod impact strength was 60 kJ/m^2, which is comparable to that of polycarbonate (PC).

Other than this, several attempts at the improvement of the low impact resistance and the brittleness have been conducted on PLA/PBAT blends. Jiang et al. investigated crystallization of the PLA component, phase morphology of the blend, mechanical properties and toughening mechanism of PLA/PBAT blends using dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), scanning electron microscopy (SEM) and an Izod impact test [2]. COLTELLI *et al.* examined the addition of acetyl tributyl citrate (ATBC) and PBAT to PLAT in order to improve tensile properties at low strain rate [3]. JIANG *et al.* studied the effects of addition of rigid nanoparticles on the tensile properties of PLA and PBAT blends [4]. YUAN *et al.* improved the compatibility of PLA with PBAT using maleic anhydride (MAH) and 2.5-dimethyl-2.5-di-(tert-butylperxy) hexane (L101) [5]. SIGNORI *et al.* studied the effect of processing at high temperature on the molecular weight distribution, the morphology and the thermo-mechanical properties of PLA and PBAT polymer alloys [6]. However, there has been less work reported on the basic mechanical properties of such plastics at high strain rates.

In the present study, the stress-strain curves of PLA and PBAT polymer alloys were measured at high strain rates (600–900 s^{-1}) using a tensile split Hopkinson bar (Kolsky bar), and at low strain rate (10^{-3} s^{-1}) using a universal testing machine (A&D Co., Ltd., RTM-500). The effects of the addition of dialkyl peroxide (compatibilizing agent) and the mixing ratio of PLA and PBAT on the Young's modulus, the yield stress, the elongation at break, and fracture morphology were also examined.

2. EXPERIMENTAL METHODS

2.1. Materials

PLA and PBAT alloys were prepared using PLA from Toyota Motor Corporation (Eco-plastic S-17) and PBAT from BASF SE (Ecoflex). The mixing

ratios (weight fraction) of PLA and PBAT were 80 : 20, 70 : 30, and 60 : 40. In order to examine the effect of a compatibilizing agent, dialkyl peroxide (NOF Corporation, PERHEXA 25B) was used at a weight ratio of one. The chemical structural formulas of PLA, PBSL and dialkyl peroxide are shown in Fig. 1. The polymer alloys were prepared using a twin-screw extruder (TECHNOVEL CORPORATION) at 180°C. The screw speed was 400 rpm, and the feed rate was 100 g/min. After melt mixing, the strands prepared by the twin-screw extruder were cooled rapidly, pelletized, and then dried. Next, 5-mm-thick plates were prepared using a conventional hot press at 190°C and 5 MPa for 30 min.
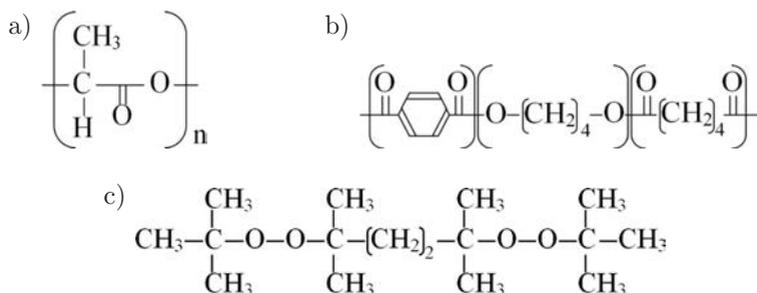

FIG. 1. Chemical structural formula of: a) PLA, b) PBAT and c) dialkyl peroxide (PERHEXA 25B).

Figure 2 shows photographs of the cryo-fractured surfaces of the specimens. These were taken using a scanning electron microscope (SEM, Hitachi

80 : 20   70 : 30   60 : 40
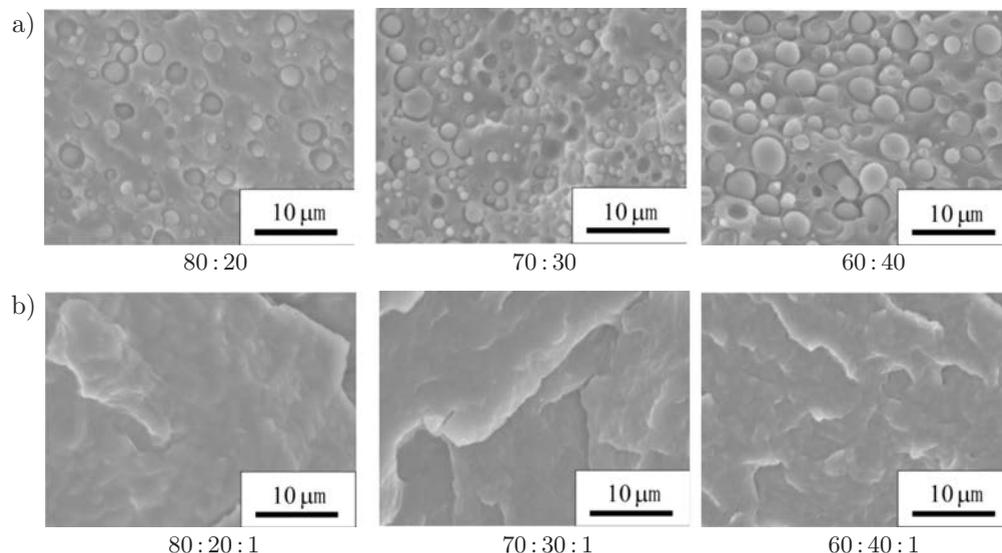
80 : 20 : 1   70 : 30 : 1   60 : 40 : 1

FIG. 2. Photographs of cryo-fractured surfaces taken using a scanning electron microscope for: a) PLA : PBAT, b) PLA : PBAT : dialkyl peroxide.

S-3000NA). In the case of specimens without a compatibilizing agent, a two-phase structure consisting of the PLA matrix and PBAT particles of the same size (domain) can be observed. PBAT spherical particles of 1–3 µm diameter for PLA : PBAT = 80 : 20, 1–4 µm for 70 : 30 and 2–5 µm for 60 : 40 were dispersed in the PLA matrix. When the compatibilizing agent was used, PBAT particles and phase separation were not observed.

2.2. Tensile test specimens and experimental setup

Tensile test specimens were produced from the 5-mm-thick plates using a milling machine. In the case of static tests, a gage mark area of approximately 5 mm × 5 mm and a gage length of 10 mm as shown in Fig. 3a were used. Dynamic tensile test specimens with a gage mark area of approximately 2 mm × 2 mm and a gage length of 4 mm as shown in Fig. 3b were used. The quasi-static tests were conducted with a strain rate of 10^{-3} s^{-1} using a universal testing machine (A&D Company, Ltd., RTM-500). At high strain rates of 600 to 900 s^{-1}, the dynamic properties of the specimens were examined by the tensile split Hopkinson (Kolsky) bar test [7], as shown in Fig. 4. The input and output bars were made of stainless steel (SUS304), and their diameters and lengths were 12 mm and 2000 mm. Strain gages were applied to both sides of the input and output bars at distances of 1750 mm and 350 mm from the specimen, respectively. Because the stress histories were almost the same on both ends of the specimens, the strain and stress on the specimens were calculated
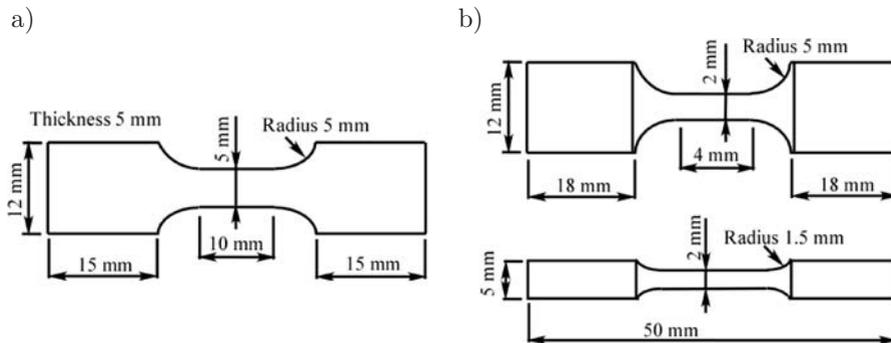

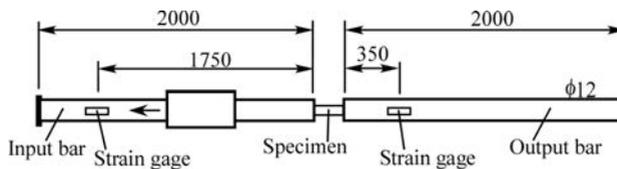FIG. 3. Specimen shape of tensile tests: a) static tests, b) dynamic tests.

FIG. 4. Experimental set up for dynamic tensile tests.

from the strain of the bars, as measured by the strain gages, using the following equations [8, 9]:

$$(2.1) \qquad \varepsilon(t) = \frac{2c_3}{L} \int_0^t [\varepsilon_I(t) - \varepsilon_T(t)]dt,$$

$$(2.2) \qquad \sigma(t) = \frac{AE}{A_S} \varepsilon_T(t).$$

Here ε_I and ε_T are the axial strains induced in the input bar by the incident wave, and in the output bar by the transmitted wave, respectively. E and c_3 are Young's modulus and elastic wave velocity, respectively, of both the input and the output bars. L is the gage length. A and A_S are the cross-sectional areas of the input/output bars and specimens, respectively. Because the strain rate changed slightly during tensile loadings, it was determined using the averaged value of the strain rate-strain curve [10]. The material constants of the stainless steel (SUS304) bars used in the calculations are listed in Table 1. The specimens were preserved in a desiccator at a humidity of 30–40% until just before use in order to prevent them being affected by moisture absorption. The specimens were maintained at a temperature of 23±2°C.

Table 1. Material constants of input and output bars.

Density	8.0×10^3 kg/m^3
Velocity of bar wave, c_3	4970 m/s
Young's modulus, E	200 GPa

3. Results and discussion

3.1. Static tests

Figures 5a and b show the effects of PBAT content on the nominal stress-nominal strain curves at a strain rate of 10^{-3} s^{-1} using the universal testing machine. After tensile loading, the stress increased linearly with increasing strain. After showing the maximum stress, the stress decreased gradually. Cracks were observed and finally the specimens broke at the fracture point. Regardless of dialkyl peroxide addition, the maximum stress and Young's modulus decreased and the elongation at break increased with increasing PBAT content. It seems that PBAT improved the brittleness and fracture toughness of PLA. When PLA : PBAT : dialkyl peroxide $= 60 : 40 : 1$, the stress remained steady at approximately 25 MPa in a strain range of 0.04 to 0.11. After that, it decreased gradually.
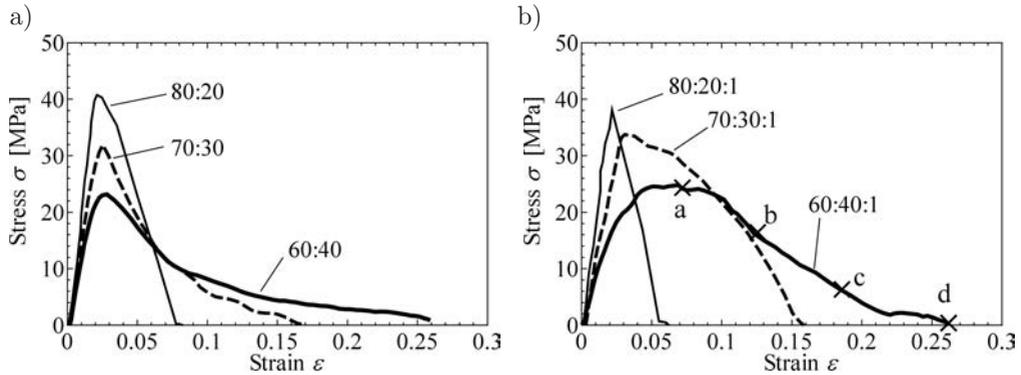
a)

b)

FIG. 5. Effect of PBAT content on stress-strain curve at a strain rate of 10^{-3} s^{-1}: a) without dialkyl peroxide, b) dialkyl peroxide addition.

Figure 6 shows photographs taking during deformation of the specimen when PLA : PBAT : dialkyl peroxide $= 60 : 40 : 1$ in Fig. 5b. The specimens of the dialkylperoxide addition continued to deform uniformly below a strain of 0.10 as shown in Fig. 6a. Necking started at a strain of 0.125, and a clear crack was observed at a strain of 0.185. After that, the specimens broke. It is a little difficult to see from this photograph, but whitened regions were observed near the cracks.
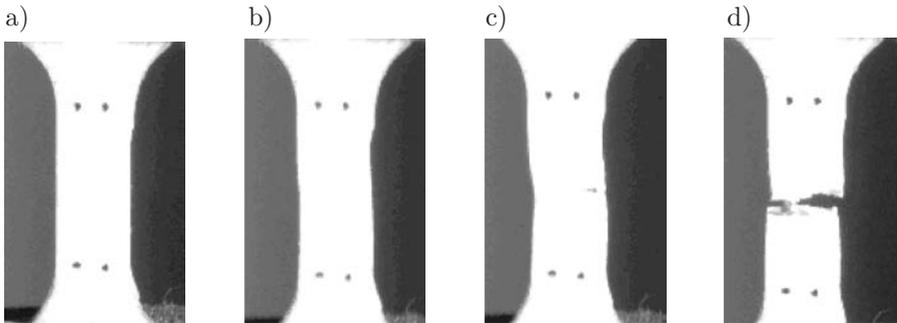
a)   b)   c)   d)

FIG. 6. Photographs of specimens when PLA : PBAT : dialkyl peroxide $= 60 : 40 : 1$ at a strain rate of 10^{-3} s^{-1}: a) $\varepsilon = 0.07$, b) $\varepsilon = 0.125$, c) $\varepsilon = 0.185$, d) $\varepsilon = 0.26$.

Figure 7 shows the effect of the dialkyl peroxide addition on the stress-strain curves at low strain rate. When PLA : PBAT $= 70 : 30$ and $60 : 40$, the dialkyl peroxide addition affected the shape of the stress-strain curve, and after the maximum stress, the stress did not decrease rapidly, whereas when PLA : PBAT $= 80 : 20$, the dialkyl peroxide addition did not affect the shape of the stress-strain curve. In all cases, the dialkyl peroxide addition did not affect the Young's modulus, maximum stress or the elongation at break.
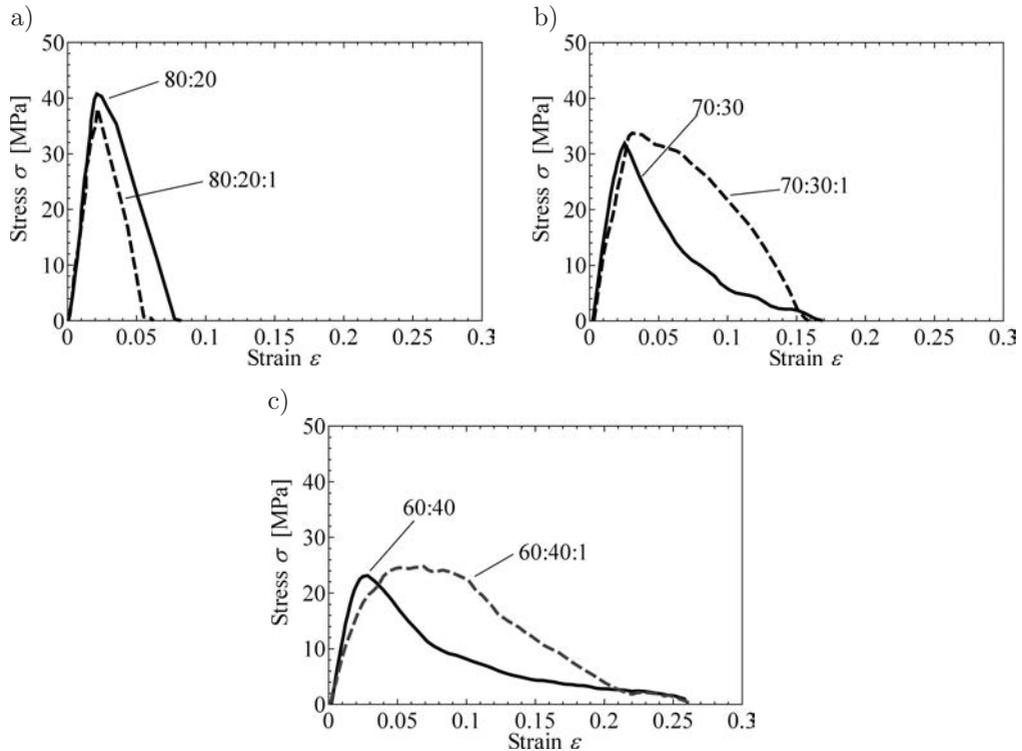
a)

b)

c)

FIG. 7. Effect of dialkyl peroxide addition on stress-strain curve at low strain rate:
a) $80:20$ and $80:20:1$, b) $70:30$ and $70:30:1$, c) $60:40$ and 60:40:1.

3.2. Dynamic tests

Figure 8 shows the effects of PBAT content on the stress-strain curves of polymer alloy specimens obtained from the strain history and stress history using Eqs. (2.1), (2.2). When dialkyl peroxide addition was not used, the maximum
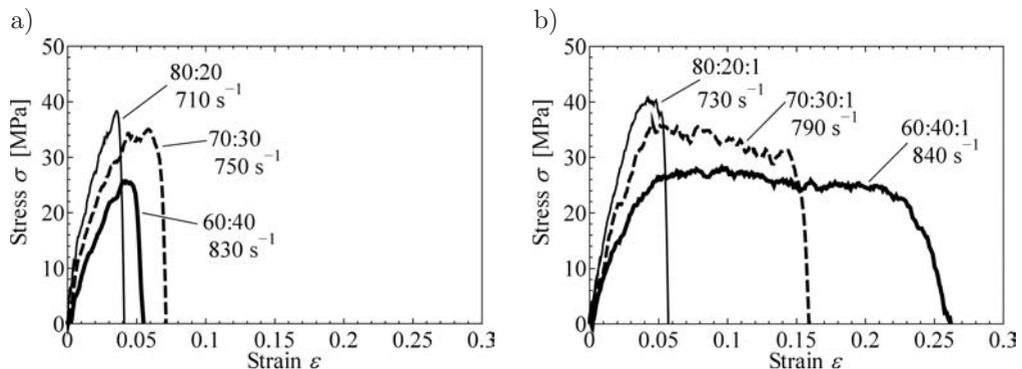
a)

b)

FIG. 8. Effect of PBAT content on stress-strain curve at a strain rate of 710–840 s^{-1}:
a) without compatibilizing agent, b) compatibilizing agent addition.

stress and Young's modulus decreased with increasing PBAT content. However, a clear tendency for the elongation at break to occur was not observed. When dialkyl peroxide was added, the maximum stress and Young's modulus decreased and the elongation at break clearly increased with increasing PBAT content. It seems that PBAT improved the brittleness and fracture toughness of PLA only when dialkyl peroxide addition was used.

In Fig. 9, the effect of the dialkyl peroxide addition on the stress-strain curves were examined at high strain rate. When PLA : PBAT = 80 : 20, the dialkyl peroxide addition did not significantly affect the shape of the stress-strain curve behavior. The Young's modulus, maximum stress and elongation at break of PLA : PBAT = 80 : 20, were almost the same as that of PLA : PBAT : dialkyl peroxide = 80 : 20 : 1, as shown in Fig. 9a. When PLA : PBAT = 70 : 30, the dialkyl peroxide addition slightly increased the elongation at break. When PLA : PBAT = 60 : 40 as shown in Fig. 9c, the dialkyl peroxide addition significantly affected the elongation at break. As a result, when PLA : PBAT = 70 : 30 and 60 : 40, the dialkyl peroxide addition increased the strain energy, i.e. the areas under stress-strain curve before the breaking point.
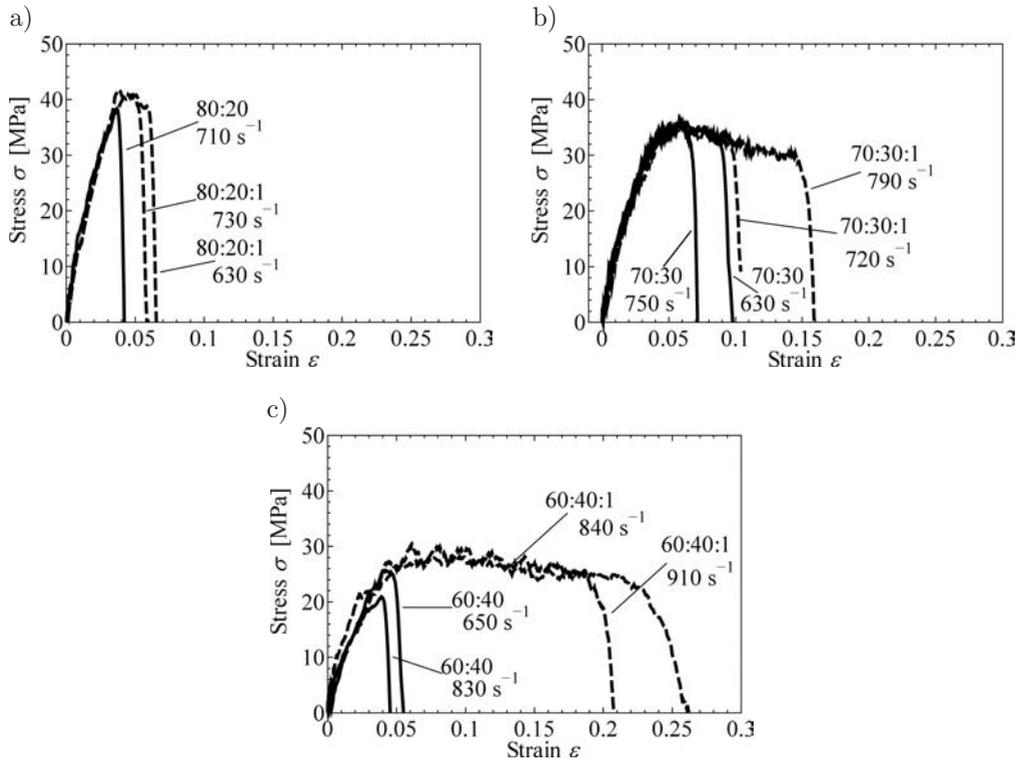

FIG. 9. Effect of dialkyl peroxide addition on stress-strain curve at high strain rate: a) 80 : 20 and 80 : 20 : 1, b) 70 : 30 and 70 : 30 : 1, c) 60 : 40 and 60 : 40 : 1.

The averaged values of all results at high strain rate are shown in Fig. 10 using bar charts. The dialkyl peroxide addition did not affect the maximum stress. The dialkyl peroxide addition increased the elongation at break for each mixing ratio as discussed in the previous paragraph. The dialkyl peroxide addition increased the strain energy. The above results could explain the improvement in the Izod impact strength as shown in Fig. 11 [11]. For comparison with the re-
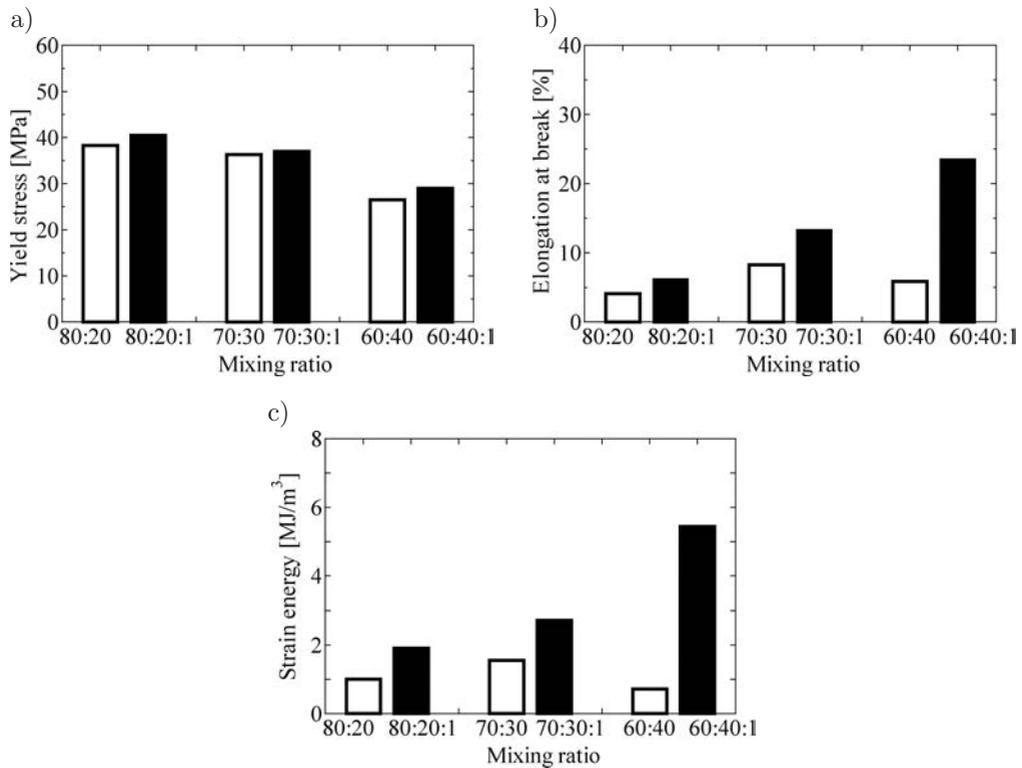
a)

b)

c)

FIG. 10. Effect of PBAT content on yield stress, elongation at break and strain energy at high strain rate: a) yield stress, b) elongation at break, c) strain energy.
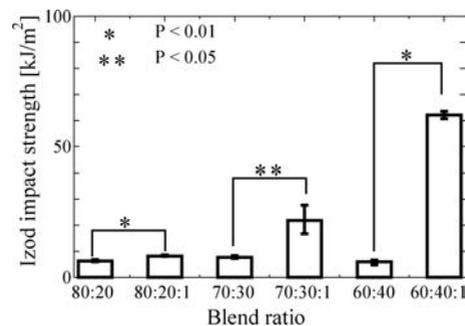
FIG. 11. Izod impact strength of PLA/PBAT alloys [11].

sults at high strain rate, the results of low strain rate are shown in Fig. 12 using bar charts. At low strain rate, the dialkyl peroxide addition did not affect the yield stress or the elongation at break. The dialkyl peroxide addition certainly increased the strain energy when $PLA : PBAT = 70 : 30$. However, the increased amount at low strain rate was not smaller than that at high strain rate. From these results, it was found that the dialkyl peroxide addition was effective in increasing the Izod impact strength.
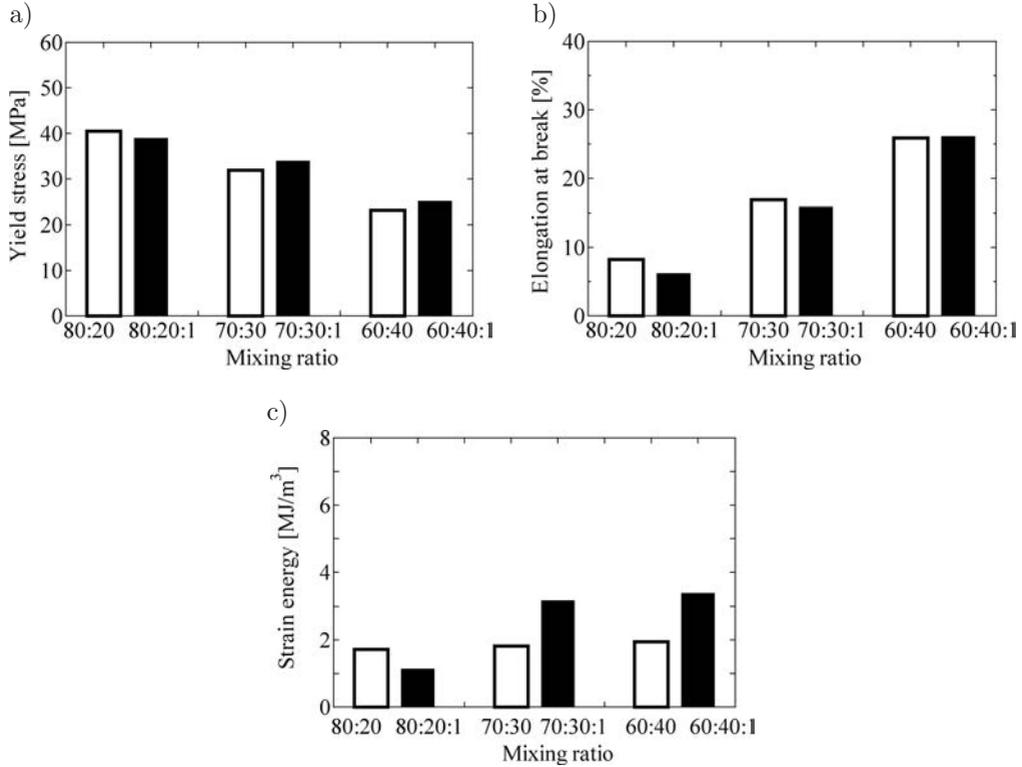
a)

b)

c)

FIG. 12. Effect of PBAT content on yield stress, elongation at break and strain energy at low strain rate: a) yield stress, b) elongation at break, c) strain energy.

3.3. Observation of fracture surfaces

Because the effect of dialkyl peroxide addition on the dynamic properties of polymer blends was pronounced when $PLA : PBAT = 60 : 40$, the fracture surfaces of specimens were observed when $PLA : PBAT = 60 : 40$ and $PLA : PBAT : dialkyl peroxide = 60 : 40 : 1$. Figure 13 shows photographs of the fracture surface after dynamic tensile tests. When $PLA : PBAT = 60 : 40$, the fracture surface was flat and smooth, and was perpendicular to the applied stress. It appeared that a brittle fracture had occurred. When $PLA : PBAT : dialkyl peroxide = 60 : 40 : 1$,

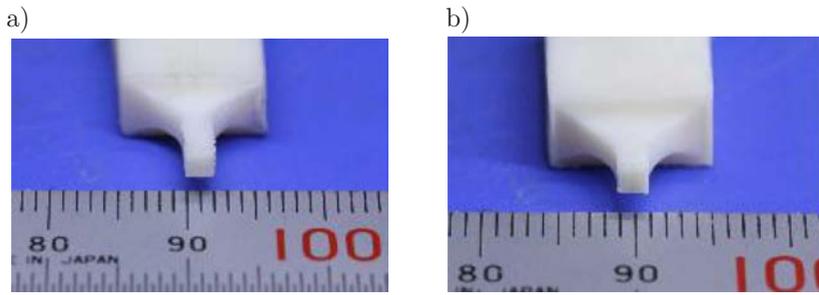a)   b)

FIG. 13. Fracture surface after dynamic tensile test: a) PLA : PBAT = 60 : 40,
b) PLA : PBAT : dialkyl peroxide = 60 : 40 : 1.

a slightly whitened and markedly uneven fracture surface was observed. The
dialkyl peroxide addition caused a ductile fracture surface.

Figure 14 shows magnified images of the fracture surfaces in Fig. 13. Many
holes of several hundred micrometers in diameter could be observed on the frac-
ture surface of the specimens without the dialkyl peroxide. When the dialkyl
peroxide was used, such holes were not observed. The formation mechanism for
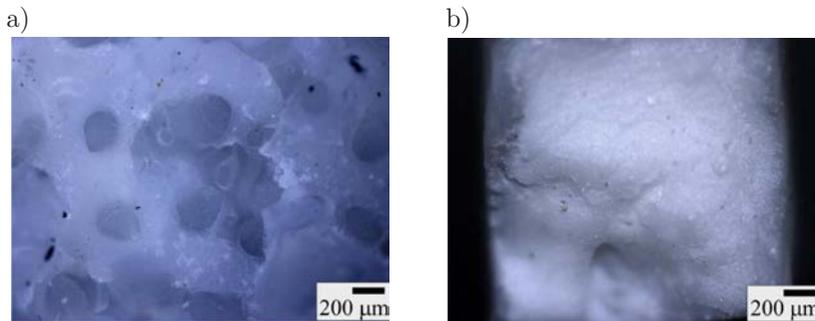these holes is still unclear, and more detailed investigation is required. Figure 15

a)   b)

FIG. 14. Enlarged images of Fig. 13: a) PLA : PBAT = 60 : 40,
b) PLA : PBAT : dialkyl peroxide = 60 : 40 : 1.
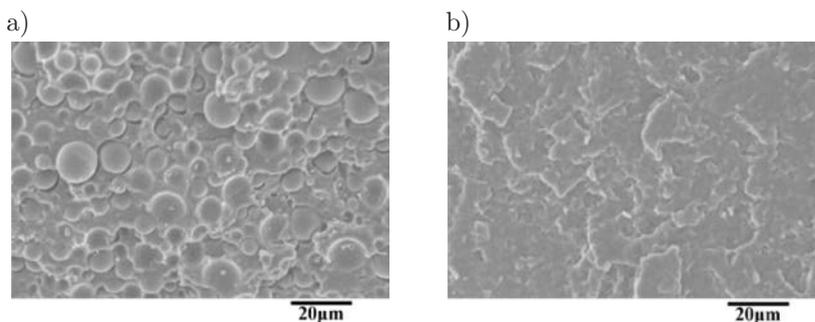
a)   b)

FIG. 15. Fracture surfaces captured by SEM: a) PLA : PBAT = 60 : 40,
b) PLA : PBAT : dialkyl peroxide = 60 : 40 : 1.

shows photographs of the fracture surfaces captured by the SEM. The tensile fracture surfaces at high strain rates were almost the same as the fracture surfaces after cooling using liquid nitrogen, as seen in Fig. 2. On this level, the fracture surfaces had no distinctive features. Distinctive fracture surfaces could be observed at the optical microscope level.

Figure 16 shows the fracture surface of specimens after the Izod impact tests shown in Fig. 11 [11]. Figures 16(a-1) and (b-1) show that the fracture surface
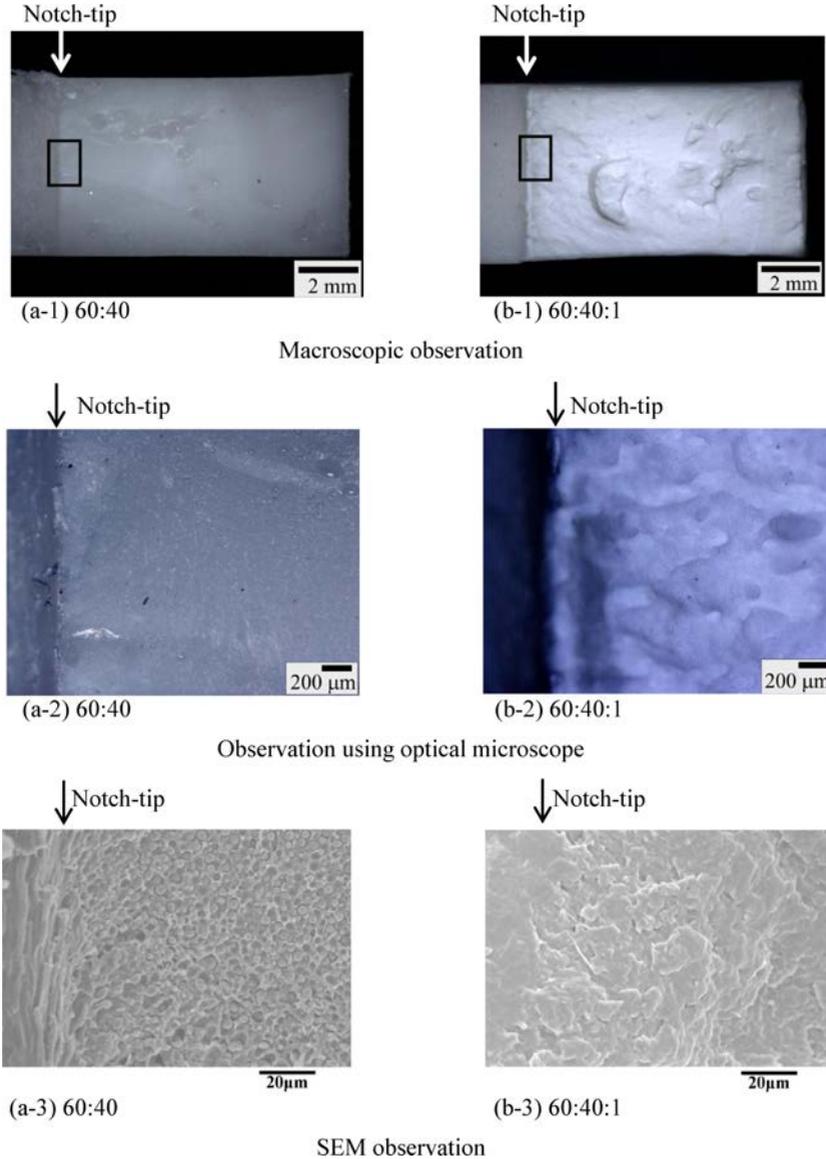

Fɪɢ. 16. Fracture surfaces after Izod impact test.

was flat and smooth when PLA : PBAT = 60 : 40, whereas a slightly whitened and markedly uneven fracture surface was observed when PLA : PBAT : dialkyl peroxide = 60 : 40 : 1. Optical microscope photographs in Fig. 16(a-2) and (b-2) show that there are no holes even when PLA : PBAT = 60 : 40, unlike the fracture surface of the dynamic tensile test sample, which has many holes. SEM photographs show that the fracture surfaces were almost the same as the fracture surfaces after cooling using liquid nitrogen as seen in Fig. 2, similar to the results of the tensile fracture surfaces at high strain rate.

4. Conclusions

The stress-strain curves of PLA/PBAT and PLA/PBAT/dialkyl peroxide specimens were measured using a tensile split Hopkinson bar method and a universal testing machine. Only in the dynamic tensile test did the dialkyl peroxide addition increase the elongation at break and change the fracture surface to a whitened form that was markedly uneven. When dialkyl peroxide was added, the elongation at break increased with increasing PBAT content. When PLA : PBAT = 70 : 30 and 60 : 40, the dialkyl peroxide increased the areas under stress-strain curve before the breaking point. It seems that the dialkyl peroxide addition caused a ductile fracture surface. This result could explain the improvement in the Izod impact strength. In order to clarify the main reason for this the degree of cross-linking should be measured.

Acknowledgment

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