Effect of Ultrasound on the Properties of Biodegradable Polymer Blends of Poly(lactic acid) with Poly(butylene adipate-*co*-terephthalate)

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Abstract: This study investigated the effect of ultrasound irradiation on the blend of poly(lactic acid) (PLA) and poly(butylene adipate-*co*-terephthalate) (PBAT). The blends of PLA/PBAT(50/50) (PBAT50) were prepared in a melt mixer with an ultrasonic device attached. Thermal, rheological, and mechanical properties, morphology, and biodegradability of the sonicated blends were analysed. The viscosity of the sonicated blends was increased by the ultrasound irradiation owing to the strong interaction. The morphology of the sonicated blends was significantly dependent on the duration of the ultrasound irradiation. For PBAT50, the phase size reduction was maximized when the blends were ultrasonically irradiated for 30 sec. At longer duration of ultrasound irradiation, the PBAT phase underwent flocculation. Measurement of the tensile properties showed an increased breakage tensile stress and an enhanced Young's modulus when the blends were properly irradiated. This improvement was ascribed to better adhesion between the PLA matrix and the PBAT domain and to better dispersion of the PBAT phase. However, the tensile properties were maximized after excessive energy irradiation, which was ascribed to an emulsifying effect leading to coalescence of the PBAT phase. Impact strength was increased to reach a peak with the ultrasound irradiation, and was higher than the untreated sample for all sonicated samples due to the difference of failure mechanism between the tensile test and the impact test.

Keywords: poly(lactic acid), poly(butylene adipate-*co*-terephthalate), biodegradable, blend, ultrasound.

Introduction

In recent years, much concern has increased on the deterioration of our environment due to solid waste pollution. One way to solve that problem is replacing commodity synthetic polymers with biodegradable polymers. Among them, aliphatic polyester is one of the most promising biodegradable materials because they are readily susceptible to biological attack.[1-4]

Poly(lactic acid) (PLA), a biodegradable aliphatic polyester, produced from renewable resources has received much attention in the research of alternative biodegradable polymers.[5,6] Lactides and lactic acid monomers are obtained from the fermentation of crop like corn and sugar feed stocks.[7] Polymerization of lactic acid into PLA produces biodegradable thermoplastic polyester with good biocompatibility and physical properties, such as high mechanical strength, thermoplasticity and fabricability.[8] PLA has mostly been used for biomedical applications such as drug delivery systems[9] and controlled release matrices for fertilizers, pesticides and herbicides.

Poly(butylene adipate-*co*-terephthalate) (PBAT) is a commercially available aliphatic-*co*-aromatic co-polyester with high flexibility, excellent impact strength, melt processibility, and melting point of 120 °C, which is lower than that of PLA. Many studies on PBAT, in the form of films and molded objects, have exhibited significant biodegradation within one year in soil, water with activated sludge, and sea water.[10-13]

Despite the good properties of PLA, the applications are limited due to its low flexibility and low impact strength. To improve the flexibility and the impact strength of PLA, blending,[14-18] copolymerization and reactive extrusion techniques were used. Some of these blends were found to be immiscible, resulting in poor mechanical properties. Recently, as a new technique, ultrasound irradiation was applied to solve various problems that were encountered in many fields.[19,20]

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Thus, our research focused on the analysis of the effect of ultrasonic irradiation on the immiscible blends system. We have examined PLA/PBAT blends by DSC and selected the blend of PBAT content 50 wt% that has shown the least compatibility. With sonication time, the change of thermal, rheological, mechanical properties, morphology, and biodegradability were investigated.

Experimental

Materials. Fiber grade PLA (Nature work 6200D, M_w= 147 k) produced by Cargil-Dow Co. were used and a biodegradable co-polyester, PBAT (SG400, M_w=60 k), supplied from SK Chemicals Co. The chemical structures of PLA and PBAT are shown in Scheme I.

Blend Preparation. PLA and PBAT were dried in a vacuum oven at 50 °C for at least 12 hrs before use. The composition ratios of PLA/PBAT system were 0, 25, 50, 75, and 100 wt%. Dried pellets of PLA and PBAT were mixed in a container and blended in a melt mixer (Haake Reocord 9000) attached ultrasonic device (1500W, Sonics Korea) at a fixed temperature of 180 °C and rotation speed of 60 rpm, respectively. The pulse on/off ratio of sonication was 7:3 and the sonication time was from 10 sec to 5 min. Specimens of blended samples were obtained by compression molding after drying at 50 °C for at least 12 hrs under vacuum.

Thermal Properties. Differential scanning calorimetric studies for the thermal property characterization were performed on a modulated DSC (TA Instrument Model 2910) at a heating rate of 10 °C/min. To investigate the effect of ultrasound on the compatibility of the blends, dynamic mechanical analysis (TA instrument Model Q800) was examined in single cantilever clamp under conditions of amplitude 10 and frequency 1 Hz at a heating rate of 5 °C/min.

Rheological Properties. Rheological properties of the blends and pure resins were measured using a ARES (ARES, TA Instrument) on which a 25 mm diameter parallel plate was mounted. The frequency range was set at 0.1~500 rad/sec and the applied strain was 10%. The plate gap was set at 1.2 mm.

Mechanical Properties. Testing of the mechanical prop-

erties of the blends was done using Universal Testing Machine (Lloyd Instruments, LR5K plus). A gauge length of 25.4 mm and a crosshead speed of 50 mm/min were used. Impact testing was done using a pneumatic driving instrumented impact tester (Ceast Model 6545) in Izod mode with a notch of 2.54 mm according to ASTM D256. All the reported results are also averages of at least ten measurements for each blending system.

Morphology. Scanning electron microscopy (SEM) observations of the blended samples were performed on Hitachi model S-2200C. The samples, fractured during impact test, were coated with gold to make them electrically conducting. The average particle diameter was obtained from eyeview analyzer of the SEM micrographs. The surface roughness was measured with a three dimensional atomic forced microscopy (AFM, PSIA). A scanning type was contact mode with the rate of 1~2 Hz, and the serve gain was 24.164×10^{-6} (nm/step).

Biodegradability. As a biodegradation study, biological oxygen demand was measured by respirometer (Compute-OX AV4R) controlled at 20 °C. The extent of biodegradation was quantified as the pressure drop and was converted to the oxygen consumption during the experiment. The activated sludge from an industrial wastewater treatment plant was aerated for 24 hrs before use.

Results and Discussion

Thermal Properties. The results of DSC scan of the PLA/PBAT blends were summarized in Table I. They showed two glass transition temperatures (T_g) for the second scan. A direct proof of polymer miscibility in blend can be obtained by observing the behavior of the T_g with the blend composition. Increasing PBAT contents in the blends resulted in two different behaviors. The higher T_g decreased from 62 °C for pure PLA to 58 °C for blend containing 75 wt% PBAT due to active interaction between PLA and PBAT chains. On the other hand, the lower T_g of the blends slightly increased with increasing PLA content. Despite the slight shift of two T_gs, the blend system was considered immiscible because the shift was not enough to be classified as a miscible blend system. The difference of two T_gs seemed to be the largest at PBAT content 50 wt%, which indicated the least compatible composition. In this study, PBAT50 having the least com-

Scheme I
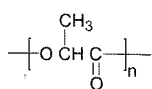
PLA (6200D)
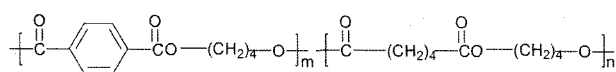
PBAT (SG400)

Table I. Glass Transition Temperatures of PLA/PBAT Blends

Code	PBAT (wt%)	T_g (°C) of PBAT	T_g (°C) of PLA
PLA	0	-	62
PBAT25	25	-34	59
PBAT50	50	-35	59
PBAT75	75	-35	58
PBAT	100	-36	-

patibility was chosen to investigate the effect of ultrasound effect because the most improvement of the properties was expected.

DMA of the sonicated and the untreated PBAT50 were compared first to see the ultrasonic effect. Generally, the peak of tangent delta curve in DMA has been considered as a glass transition temperature. Figure 1 showed the plot of glass transition temperatures obtained from DMA against sonication time. The upper curve was T_g of PLA phase and the lower one was that of PBAT. Interestingly, as sonication time increased, the difference between two T_gs became narrower, showed the narrowest at around the sonication time of 11 sec and became wider again. It means there is an optimum energy input by ultrasound to increase the compatibility of the blend system. Thus, in this study, we investigated many properties of PBAT50 on this short period of ultrasonic irradiation and attempted to figure out the reason of existence of an optimum point.

Rheological Properties. The viscosity curves at 180 °C for the sonicated and the untreated PBAT50 were shown in Figure 2. All the melts in the shear rate range studied exhibited non-Newtonian flow behavior. The viscosity of the blends was increased as sonication time increased. The higher the frequency, the lower the viscosity. The viscosity was increased remarkably when longer than sonication of 10 sec was applied. Generally, the addition of a low-molecular-weight component to immiscible blends results in decreasing viscosity due to plasticizing action by the added component.[21] However, interaction by the ultrasound in this blend system increased the viscosity. This might be due to the strong interaction such as transesterification reaction as shown later. The increased interaction at the phase boundary reduced the free volume and the chain mobility; hence it induced the increased viscosity.

Mechanical Properties. Figure 3 showed the tensile stress to break and Young's modulus versus sonication time. The
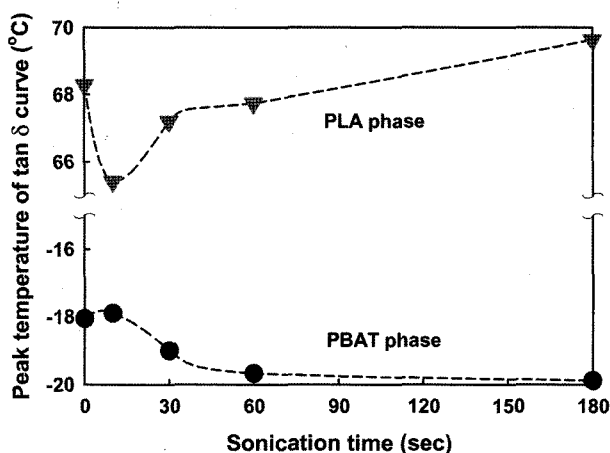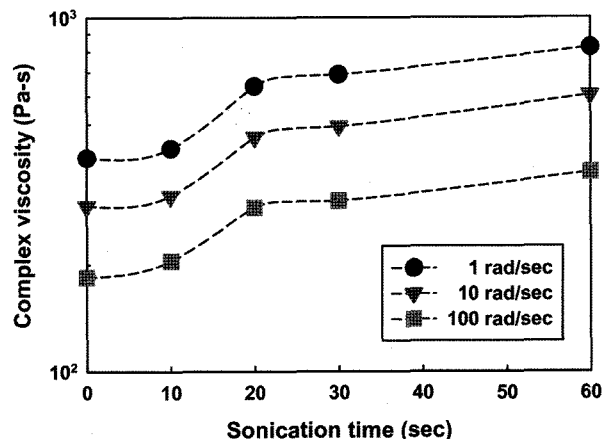

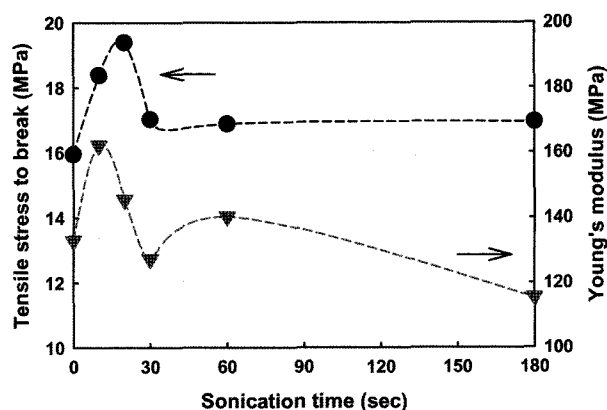**Figure 2.** Complex viscosity versus sonication time for PBAT50 with various frequency rates.

Figure 3. Tensile stress to break and Young's modulus versus sonication time for PBAT50.

tensile stress to break was improved at short irradiation time of ultrasound but soon reached a peak and decreased. When sonication time was 20 sec, a tensile stress to break of 19.4 MPa was obtained, which was 22% higher than that of untreated PBAT50. The trend of Young's modulus was similar to that of tensile stress to break even though its maximum was not as same as that of tensile stress to break. As shown later, this was attributed to a more uniform distribution and finer domain formation using ultrasound.

Figure 4 showed the impact strength of PBAT50 as a function of sonication time. An interesting fact was that the impact strength also showed a maximum when ultrasound irradiated for 30 sec. This behavior was similar to the tensile properties. Coalescence of the PBAT droplets and reduced surface area with an excess energy of ultrasound was believed to be the reasons for the reduction in impact strength. However, sonicated systems still had much higher impact strength than untreated systems, which were different from
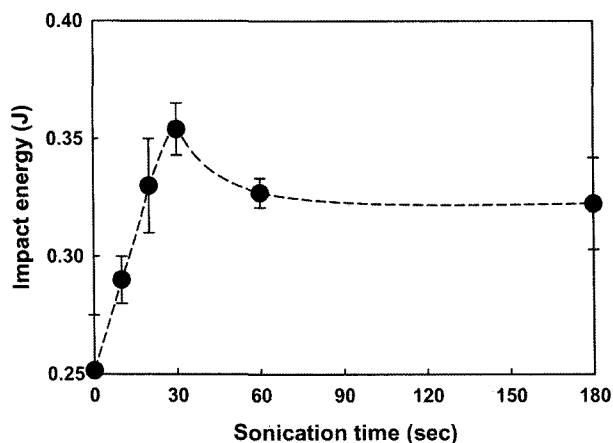

Figure 1. Effect of ultrasound irradiation on the compatibility of PBAT50.

Figure 4. Impact energy versus sonication time for PBAT50.

the case for the tensile properties (see Figure 3). This could be surmised from the difference of failure modes between tensile test and impact strength test. The compatibilizer produced during mixing with ultrasonic irradiation was included in the coalesced PBAT phase that decreased the tensile properties of the PBAT phase. Under tensile stress, breakage could happen at the contacting surface area of the PBAT particles, which was occupied by the compatibilizer. Also, as shown later, excess energy brought poor dispersion of the PBAT phase. Hence the excessively sonicated system always had lower tensile properties than the untreated system. On the other hand, in impact strength tests, a propagating stress was transmitted to the PBAT phase through the compatibilized phase, which deformed the PBAT phase. Excess energy was consumed by plastic deformation of the PBAT particles. In a untreated system, a propagating stress passed around the PBAT phase since they were immiscible and the phases were separated. Hence, good adhesion enabled the sonicated system always to have higher impact strength.

Morphologies. SEM micrographs of fractured surfaces prepared at impact test showed the morphology of PBAT50 and the domain size with sonication time as given in Figure 5 and plotted in Figure 6, respectively. For untreated PBAT50, Figure 5(a) showed typical immiscible sea (PLA) and island (PBAT) morphology with the average domain size of about 8.8 μm. The domain size decreased as sonication time increased until sonication time of 30 sec (the domain size of about 4.7 μm) as shown in Figures 5(b)~(d). After 30 sec, the domain size became larger again (Figures 5(e)~(f)). From the plot of domain size against sonication time as presented in Figure 6, the minimum size was seen at sonication time of 30 sec. It might be due to that ultrasound supplied enough energy to PBAT50 system to proceed a reaction such as transesterification, to improve adhesion between the two phases, and to result in reduction of the interfacial tension between two phases. For blends longer than sonication of 30 sec, however, PBAT domains were poorly distributed
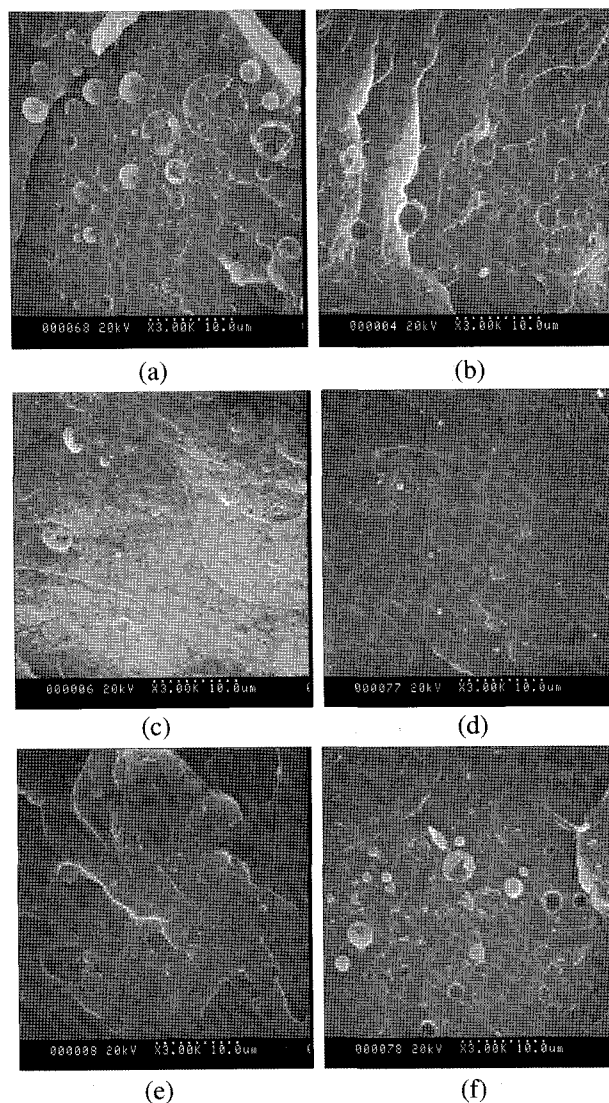

Figure 5. SEM photographs of fractured surface of PBAT50 ($\times$ 3,000). The sonication time is; (a) 0 sec, (b) 10 sec, (c) 20 sec, (d) 30 sec, (e) 60 sec, and (f) 180 sec.
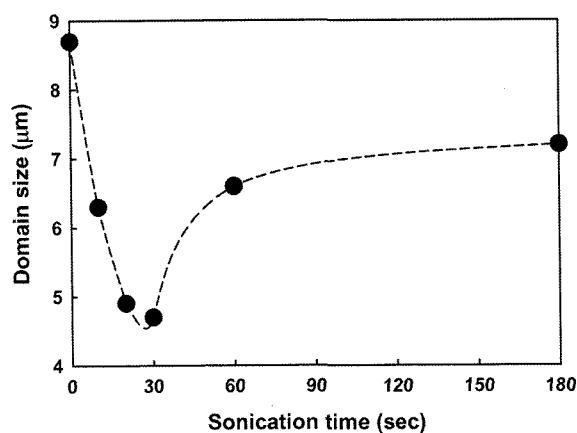

Figure 6. Domain size versus sonication time for PBAT50.

and larger than those at sonication of 30 sec. It was believed the excess energy led to flocculation of the domains. This trend was similar to the behavior of a surfactant in an emulsion system.[22]

From emulsion studies, flocculation of the dispersed phase is known to occur because of strong interparticle interactions. The quantity of surfactant required to cover an interface fully is related to many variables. The optimum sonication time beyond which significant size reduction of the dispersed droplet no longer occurs was 30 sec. Instead of size reduction, excess energy tended to coalesce the dispersed PBAT phase. Plochocki *et al.*[23] similarly observed a minimum of dispersed phase size with compatibilizer amount in a blending system of low-density polyethylene/polystyrene. The flocculation and coalescence of the PBAT phase caused poor dispersion of the PBAT and the interfacial area between two phases was reduced. This might be the reason why the optimum existed in thermal and mechanical test.

AFM micrographs of PBAT50 and their average roughness were shown in Figure 7 and Figure 8, respectively. The surface of the sonicated PBAT50 indicated smoother than that of the untreated one. Similar to SEM results, the plot of roughness against sonication time showed minimum point at around sonication time of 20 sec.

Biodegradability. PBAT50 were biodegraded with activated sludge by a respirometer as shown in Figure 9. The degradation progressed as time went by and it did much slower for the blend treated by ultrasound. The results without sonication were found AOU(Accumulated oxygen uptake) value of 25,000 ppm while those with sonication of 30 sec was only 2,000 ppm after 5 days at 20 °C. It means that though the sonication time was short even several tenths of seconds, the effect on the biodegradation rate would be large.

Degradation behavior of polymer could be affected by molecular weight, chain configuration, hydrophilicity, crystallinity, and so on.[24] In this case, the faster degradation of the untreated blends than sonicated ones might be due to more space in the immiscible blends so that microorganisms more easily began to degrade blends and more oxygen consumption was obtained. Although it was not the best result to intend, it might be explained not only the simply domain size reduction in blends, but also the interaction between PLA phase and PBAT phase.

Conclusions

The miscibility between PLA and PBAT was determined by measuring the T_g by DSC. Among the blend systems, PBAT50 (the blend of PBAT content 50%) was selected for the study of ultrasound effect because of its poor compatibility. The ultrasound was applied to PBAT50 during melt mixing and it resulted in a dramatic reduction of the dispersed PBAT size. The sonicated system showed good adhesion at the interface. From SEM micrographs of fractured surfaces,
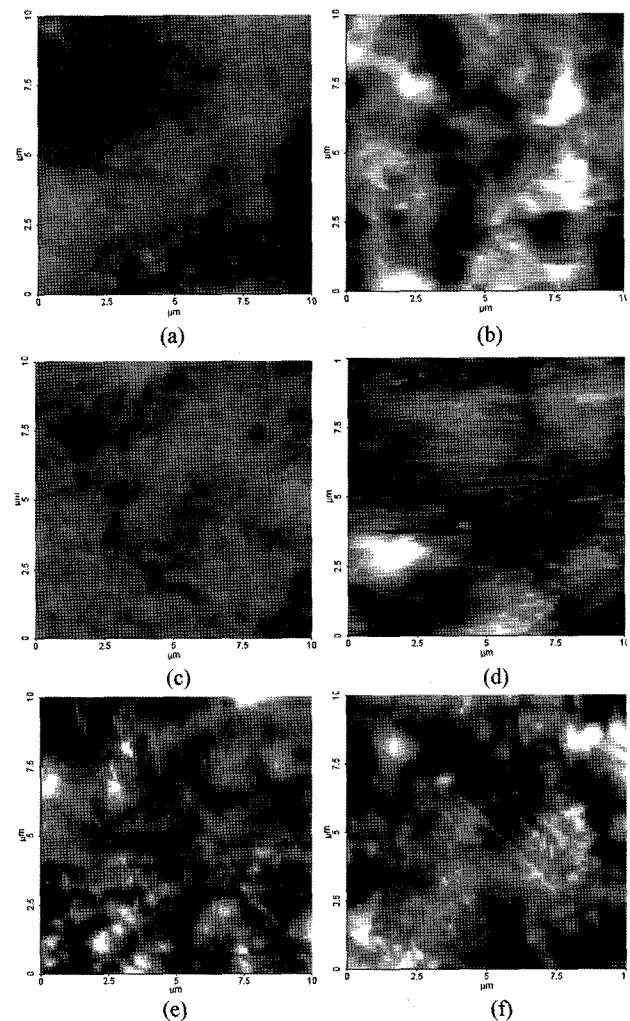

Figure 7. AFM micrographs of molded surface for PBAT50. The sonication time is; (a) 0 sec, (b) 10 sec, (c) 20 sec, (d) 30 sec, (e) 60 sec, and (f) 180 sec.
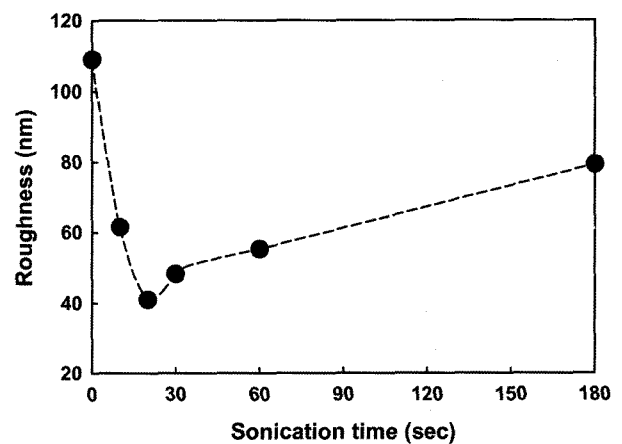

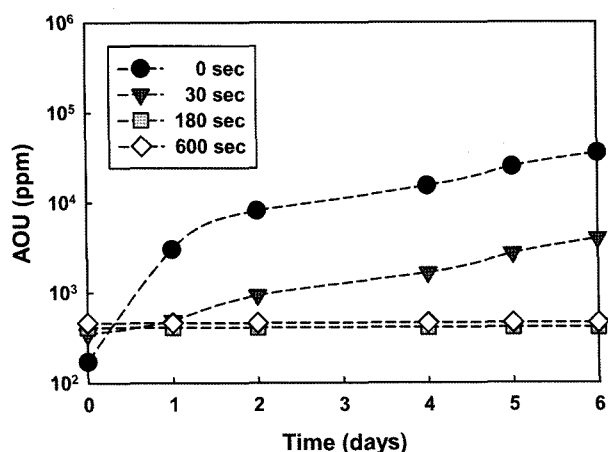**Figure 8.** Roughness of molded surface versus sonication time for PBAT50.

Figure 9. AOU versus elapsed time for PBAT50 with various sonication time.

the treatment by ultrasound to PBAT50 was found to increase the adhesion between the matrix and the dispersed phase. The sonicated blends displayed a much finer dispersion of the minor phase in the matrix polymer. The emulsifying ability of ultrasound also induced a reduction in the particle size. A chemical reaction was believed to occur between PLA and PBAT to produce a block or graft copolymer that provided a strong interaction at the interface. However, optimum energy input by ultrasound for the best mechanical properties and dispersion of the PBAT phase were observed. Excess energy input coalesced the PBAT particles. Tensile properties were enhanced with an optimum ultrasonic energy while impact strengths were always higher for sonicated system than for untreated ones. This was ascribed to the difference of the failure mechanisms between these two tests. Also, the difference of the optimum sonication time for each test could be explained by similar reason. The effect of the ultrasound was almost the same as that of the emulsifier. The property changes of PBAT50 after sonication of 30 sec were summarized in Table II. After optimum sonication time, as the domain size were increased, T_g difference, complex viscosity, and surface roughness were increased. On the other hand, tensile stress and impact energy were decreased. Generally, larger the domain size polymer blends has, lower the mechanical properties and viscosity because of poor miscibility. In this case, however, the complex viscosity was increased. This might be considered due to the improvement of the interface adhesion between domain and matrix in

spite of their low miscibility. We feel that the mechanism of compatibilization by ultrasound should be examined further and this study is under way and will be reported in the near future. Despite ambiguity of its mechanism, with the goal of applying ultrasound to an incompatible polymer blends, it is envisioned that this study would seem to stimulate more interest in the development of the compatibilization by ultrasound.

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Table II. Properties of PBAT50 after Sonication of 30 Sec

Sonication Time (sec)	Domain Size (μm)	T_g Difference (°C)	Complex Viscosity at 100 rad/sec (Pa·s)	Tensile Stress to Break (MPa)	Impact Energy (J)	Surface Roughness (nm)
30	4.7	86.2	303	17.0	0.35	48.3
60	6.6	87.4	366	16.9	0.33	55.3
180	7.2	89.5	-	16.9	0.32	79.3

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