생분해성 수지인 Poly(lactic acid) 와 Poly(butylene adipate terephthalate) 블렌드의 초음파를 이용한 기계적 물성 강화.

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Increasing of properties that biodegradable polymer blends of poly(lactic acid) with poly(butylene adipate terephthalate) by using sonication.

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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 as biodegradable polymers. Among them, aliphatic polyester is one of the most promising biodegradable materials because they are readily susceptible to biological attack.

The Representative example of biodegradable polymer is poly (lactic acid), [PLA] which one's properties are intergrades of polyamide, [PA] and poly (ethylene terephtalate), [PET]. PLA is linear aliphatic polyester produced by poly-condensation of naturally produced lactic acid or by the catalytic ring opening of the lactide group. The ester linkages in PLA are sensitive to both chemical hydrolysisand enzymatic chain cleavage.

Despite its good properties, the applications and even blends are limited due to its low flexibility and low impact strength. To improve the flexibility and the impact strength of PLA, blending copolymerization with other biodegradable polymers. Some of these blends were found to be immiscible, resulting in poor mechanical properties in order to sudden decrease of molecular weight when melting process. Research to improve PLA's shortcoming is tried variously and blended with Poly (Butylene adipate telephtalate), [PBAT] that a degradable rate is superior and molecular backbone structure is soft comparatively.

PBAT is one among series aliphatic/aromatic copolyester that also decompose towater and carbon dioxide by microorganisms. After Blend, we expect that supplement PLA's shortcoming, impact property and price rises quantity, processing that is increases transparency sacrifice and the biodegradable rate increases In this study, we have prepared PLA-PBAT blends to obtain biodegradable polymers with good impact resistance and investigated various aspects of the thermal, rheological, and mechanical properties in the blend system. As we use ultrasound waves in order thing to pick up chemical and physical changes that purpose of an experiment.

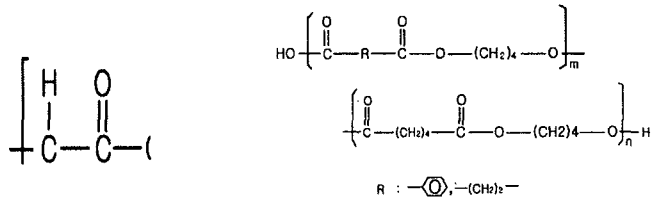
Experimental

PLA (Cargill-Dow Co., 2002D) and PBAT (SK Chemicals Co., SG400) are biodegradable co-polyester. The chemical structures of PLA and PBAT are shown in Figure 1.

Differential scanning calorimetric (DSC) studies for the thermal properties characterization

were performed on a Modulated DSC (TA Instrument, MDSC2910). The heating rate was 10℃/min.

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



(a)PLA (b) PBAT

Fig. 1 The molecular formation of PLA and PBAT

Testing of the mechanical properties of the blends was done using Universal Testing Machine (Lloyd Instruments, LR5K plus). Impact testing was done using a pneumatic driving instrumented impact tester (Ceast, Model 6465) in Izod mode according to ASTM D256. Dynamic mechanical analysis (TA instruments, DMA Q800) is used in single cantilever clamp under conditions of amplitude 10um, frequency 1MHz. Scanning electron microscopy (SEM) observations of the blended samples were performed on Hitachi model 2950A.

Results and discussion

The glass transition temperatures (Tg) of the PLA-PBAT without sonic are a direct proof of polymer miscibility in blend. It can be obtained by observing the behavior of the Tg with the blend composition. However, in the case of treating blends with ultrasound waves, these appear some miscibility. This can confirm through thermograph of DSC.

PLA:PBAT	Without sonic		With sonic	
	Tg of PLA(K)	Tg of PBAT(K)	Tg of PLA(K)	Tg of PBAT(K)
0:100	.	236.83	.	236.83
25:75	333.79	236.69	330.43	237.22
50:50	333.11	235.34	328.14	239.46
75:25	333.37	237.69	333.73	239.67
100:0	334.70	.	334.70	.

Table 1. Tg of PLA / PBAT blends

Fig.2 shows complex viscosity versus angular frequency at 180°C for PLA-PBAT blends of differential sonication time. The general behavior of the blends follows that of typical thermoplastic polymers, i.e. near Newtonian behavior at low shear rate and shear-thinning at high shear rate. As increase of sonication time, its complex viscosity is generally increased than without sonication blend. This is due to the changes of domain size because breakdown of ultrasound. On the other hand, storage modulus tends to increase according as increase of sonication time. Two factors from the view of a rheological point should be taken into consideration to obtain a polymer blend with good mechanical properties as increasing of sonication times. The first fact is that the viscosity ratio of the dispersed phase to the matrix phase should be less than 1 for stable morphology. The second factor is that it should be

close to 1 for good dispersion.

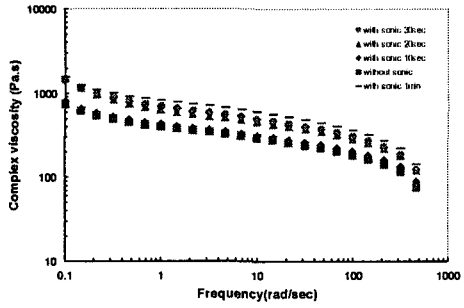


Fig.2 Complex viscosity vs. frequency for PLA and PBAT blends

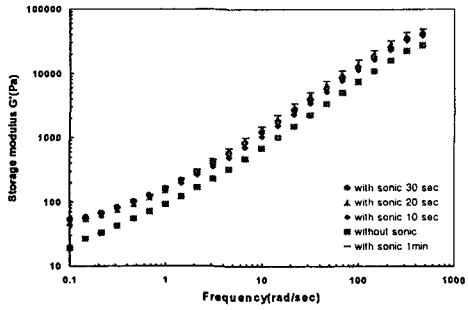


Fig.3 Storage modulus vs. frequency for PLA and PBAT blends

Fig.4 shows the tensile strength according to sonication time. The tensile strength increase at up to 30 seconds and when over 30 seconds, the tensile strength is decrease. The reason optimum at 30 second, domain size of breakdown using ultrasound and sonochemistry is aspect to interaction. In the same aspect, Fig. 5 shows the result of impact energy.

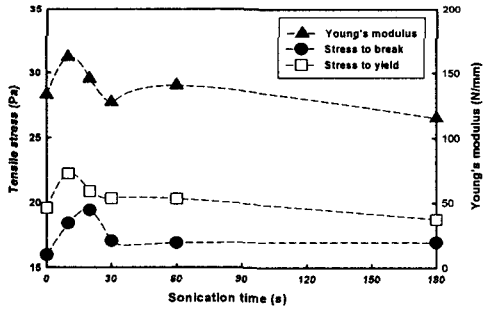


Fig.4 Tensile stress vs. sonication time for PLA and PBAT blends

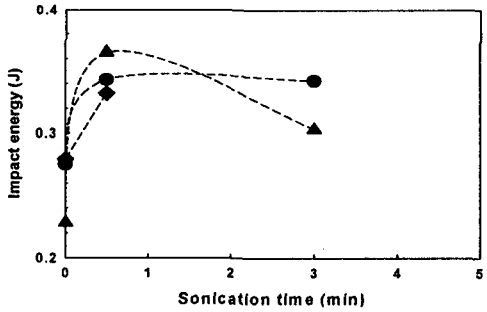
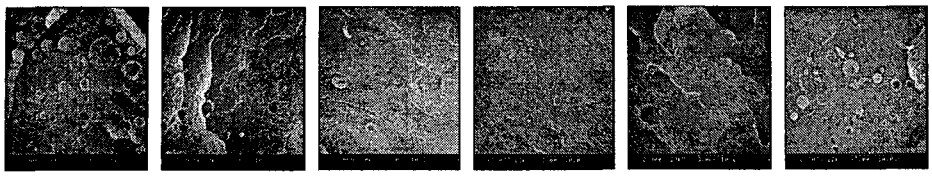


Fig.5 Impact energy vs. sonication time for PLA and PBAT blends

SEM micrographs given in Fig.6 show the morphology of binary blends of PLA and PBAT. In Fig.6, from (a) to (f) is noticed sonication times as from without sonic to 3min sonic. It is immiscible material to PLA and PBAT each other. But there is influence in the miscibility according of sonication time. As Fig.6, the miscibility of binary material, domain size is good in Fig.6 (c) and (d), 20 seconds and 30 seconds.By observing the changes in the domain sizes after the annealing, we can confirm the desired effect since significant coalescence is typically optimized in immiscible polymer blends through the sonication during 30 seconds.

This data shows best experimental results to equal with impact test in this experiment. Clearly, it shows that domain size in 30 seconds decreased certainly and that polymer's domain size that become sonication more than without sonic blends.

AFM was used to evaluate the effect of ultrasonic treatment on the interface morphology. That result the graph of average roughness is Fig.7. It shows, respectively, similar domain size's patterns of SEM micrographs. That is, relation of two results is that domain's cavitation effect which happened to surface by sonication in PLA-PBAT blend.



(a) (b) (c) (d) (e) (f)

Fig.6 SEM micrographs of PLA/PBAT blend

(a) Simple mixing (without sonic) (b) Ultrasonic mixing (10 sec.) (c) Ultrasonic mixing (20 sec.)
(d) Ultrasonic mixing(30 sec.) (e) Ultrasonic mixing (1 min.) (f) Ultrasonic mixing (3min.)

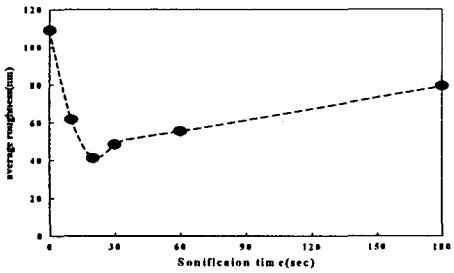


Fig.7 the average roughness of PLA/PBAT blend's AFM

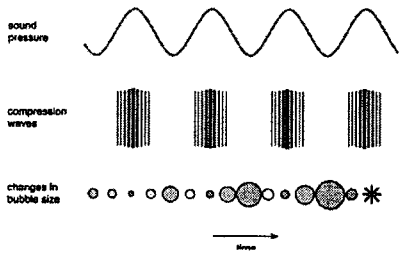


Fig.8 The cavitation by sonication and change in bubble size

Conclusions

This experiment was the study which blends of PLA with PBAT. The blends were mixed using mixer and their molded properties were examined. Since these two polymers are incompatible, their behaviors, in general, follow those of incompatible polymer blends. So using ultrasound, we tried to increase compatibility and derive improvement of properties. The study of thermal properties revealed that the Tg of PLA in the blends was slightly decreased with increasing PBAT content, and stability of the blends at high temperature was lower than that of pure PLA and PBAT. The tensile strength and tensile modulus of the blends were slightly increased with sonification PBAT content, the impact strength increased much higher than pure PLA a can be seen in a toughening system.

The PLA and PBAT used in this study are immiscible. Partial miscibility of the dispersed phase with the matrix can bring about many property changes, including tensile properties. We feel that this should be examined further to improve the mechanical properties of the PLA and PBAT system.

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