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Toughening of PLA stereocomplex by Impact modifiers

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충격보강제에 의한 PLA stereocomplex의 강인화 연구

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Abstract We tried to blend PLLA and PDLA at overall compositions to form PLA stereocomplexes (SC). The presence of the SC crystalline phase in the PLLA matrix was verified by differential scanning calorimetry (DSC). As a result, a various PDLA composition of the PLA SC blends can influence PLA SC formation. And the largest amount of PLA SC crystallites was formed when PLLA/PDLA ratio is 50/50. In addition, we have tried to do PLA SC toughening with two impact modifiers in 92/8, 85/15 ratio of PLLA/PDLA to enhance the mechanical properties such as impact strength. Thermal and mechanical properties of PLA SC were investigated by DSC, HDT, Izod impact tester and UTM. PLA SC formation decreased when 10-20 wt% of Strong120 (impact modifier) was added. On the other hand, there is no effect on PLA SC formation when 10-20% of Elvaloy (impact modifier) was added. HDT values dramatically increased over 100℃ with the addition of PDLA. However, HDT decreased as Strong120 and Elvaloy content increased. Finally, we could find well balanced composition of toughened PLA SC with 10wt% of impact modifier in flexural modulus and impact strength.

요 약 광학 이성질체인 PLLA와 PDLA를 전 조성에서 블렌드하여 PLA stereocomplex(SC)를 제조하였고 DSC를 통해 PLLA matrix안의 SC결정 형성 정도를 파악하였다. 결과적으로 PLA SC blend의 PDLA 함량이 SC 결정 생성 정도에 영향을 주며 PLLA/PDLA=50/50의 조성일 때 가장 많은 SC 결정이 생성되었다. 더 나아가 고유의 낮은 충격강도를 보강하기 위하여 PLLA/PDLA=92/8, 85/15 조성에서 충격보강제(Impact modifiers)를 도입하였다. 제조된 PLA SC/Impact modifiers의 열적기계적 성질은 DSC, HDT, Izod Impact tester, UTM을 통해 측정하였다. DSC 측정 결과 PLA SC 결정은 Strong120(Impact modifier)가 10-20wt% 도입되면 감소하는 경향을 보이나 반면에 Elvaloy가 도입될 때에는 아무런 영향을 주지 않는 것으로 관찰되었다. HDT의 값은 PDLA의 도입에 따라 급격하게 100℃이상으로 증가하였다. 하지만 Strong120과 Elvaloy가 도입됨에 따라 감소하는 경향을 보였다. 결국 Toughening된 PLA SC에서 10wt%의 Impact modifier를 blend하여 가장 최적의 충격강도와 굴곡탄성율을 갖는 물성을 발견할 수 있었다.

Key Words : Biodegradable, Stereocomplex, HDT, Impact Strength, Flexural Modulus

1. Introduction

Poly(lactic acid) (PLA), linear aliphatic biodegradable polyester derived from biomass through bioconversion and polymerization has become a potential candidate for various large-scale industrial applications in the areas of packaging, automotive, biomedical, etc[1,2].

However, inherent brittle characteristics of PLA and its low glass transition temperature around 60℃ has been the major limitation for its use in variety of application[3]. Polylactide can be synthesized using either L-lactide or D-lactide. Interestingly, in the 1980s, it was found that an

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equivalent mixture of PLLA and PDLA formed a stereocomplex[4,5]. The stereocomplex has a melting temperature (T_m=230℃) that is approximately 50℃ higher than the T_m of either PLLA or PDLA[6]. This significant increase in melting temperature is due to the strong van der Waals interactions in the stereocomplex crystalline structure [7-9]. Stereocomplexation enhances the mechanical properties, the thermal-resistance, and the hydrolysis-resistance of PLA based materials[10-12].

Several modifications such as copoly-merization, plasticization and blending with various biodegradable and non-biodegradable polymers have been suggested to improve the mechanical properties of the virgin matrix[13].

In this study, we could prepared PLLA composites with various amount of PDLA. Various PDLA volumes are blended with PLLA and stereocomplex crystallites were produced in the PLLA matrix. In addition, two kind of impact modifier (Grade name : Strong120, Elvaloy) was added to enhance mechanical property. Thermal and mechanical properties of stereocomplex were investigated by DSC, HDT, Izod impact tester, UTM.

2. Materials

Poly (L-lactide), (PLLA, 3001D) and Poly(D-lactide) (PDLA) resins were gained from Nature Works and SK Chemical company, respectively. The melt indices (MI) for the resins were 12 and 8 g/10min (190℃, 2.16 kg). Strong120(Ethylene copolymer) and Elvaloy (Ethylene/ N-Butyl Acrylate/Glycidyl Methacrylate Copolymer) samples were purchased from DuPont company. Melt index of Elvaloy and Strong120 was 12 g/10min (190℃, 2.16 kg).

3. Experimental

3.1 Preparation of blends

PLLA and PDLA pellets were dried in a vacuum oven for 24h at 60℃. The PLLA/PDLA blends with weight ratios of 100/0, 92/8, 85/15, 75/25, 50/50, 25/75, 0/100 were prepared in a Twin screw extruder [BA-19(L/D=42, 19Φ, Co-rotating), BauTek, Korea]. The temperature profile along the extruder barrel was 180-190℃, and the temperature at the die was 190℃. The screw speed was 200 rpm.

In case of PLLA/PDLA = 92/8, 85/15 blends, impact modifiers were incorporated at 10-20 wt% for toughening of PLA Stereocomplex. Toughened PLA SC composites were prepared using twin screw extruder (BA-19) in a one step. The recipes of composites are shown in Table 1.

[Table 1] Compounding recipes of PLLA/PDLA blends with impact modifiers

Grade	PLLA (wt%)	PDLA (wt%)	Strong120 (wt%)	Elvaloy (wt%)
PLLA100	100	0		
PL92D8	92	8		
PL85D15	85	15		
PL75D25	75	25		
PL50D50	50	50		
PL25D75	25	75		
PDLA100	0	100		
PL92D8_Str10	92	8	10	
PL92D8_str20	92	8	20	
PL92D8_ev10	92	8		10
PL92D8_ev20	92	8		20
PL85D15_str10	85	15	10	
PL85D15_str20	85	15	20	
PL85D15_ev10	85	15		10
PL85D15_ev20	85	15		20

3.2 Characterization

Thermal properties were analyzed with Perkin-Elmer Pyris Diamond differential scanning calorimeter (DSC) calibrated with indium as standard. The specimens were heated from 0 to 250℃ at a rate of 10℃/min, followed by an isothermal at 250℃ for 2min, and a subsequent cooling scan to 0℃ at a rate of 5℃/min. And then the specimens were reheated to 250℃ at 10℃/min. Glass transition temperature (T_g), melting temperature(T_m) and the enthalpy of melting($\triangle H_m$) were measured. The thermal properties of stereocomplexes and homopolymers were presented in Table 2.

Tinius Olsen 3-station heat distortion temperature test machine (Model303 HDTM) was used to measure the HDT values. The dimensions of the specimens were 130mm x 3.2mm x 13mm. They were arefully molded by a compression molding machine. HDT test was carried out according to ASTM D648. A load (0.455MPa) was applied directly to the mid-point of the test sample. The entire "station" was then submerged into a thermally controlled oil bath. The temperature of bath was increased at a rate of 2℃/min. Both applied load and elevated temperature would combinedly cause the test sample to deflect downward and the temperature at which it gave a deflection of 0.25 mm was subsequently taken as the HDT value.

Flexural and impact tests were carried out according to ASTM D790 and ASTM D256 (notched, 3.2mm). Tests for flexural modulus and flexural strength were performed using UTM (Tinius Olsen, H5KT). Span length was 100mm and the crosshead speed was set at 1.3mm/min. The impact strength test was analyzed by Izod impact strength tester (Sejin, SJTM-131) in room temperature.

The phase structure of the blends was observed by field-emission scanning electron microscopy (FE-SEM). A JEOL Ltd. JSM-7500F scanning electron microscope was used for measurements at an acceleration voltage of 5 kV. All of the samples were fractured by immersion in liquid nitrogen for about 10 min. The fractured surface was then coated with a thin layer of gold before the observation.

4. Results and Discussion

Table 2 shows the DSC results from the thermogram of the PLLA/PDLA blends at the first heating step. Also, Table 2 shows that a various PDLA composition of the PLLA/ PDLA blends can affect their stereocomplex formation. It was highly reproducible through investigating of pellet type product.

In the literature, the enthalpy of melting ($\triangle H_m$) of stereocomplex crystallites gives a maximum at mixing PDLA ratio 50wt%[14]. This reflects that equimolar mixing is favored for stereocomplexation. Although continuous mixing such as our preparation method does not give a sufficient time to accomplish a thermodynamically stable morphology, we have obtained same results with some literatures.

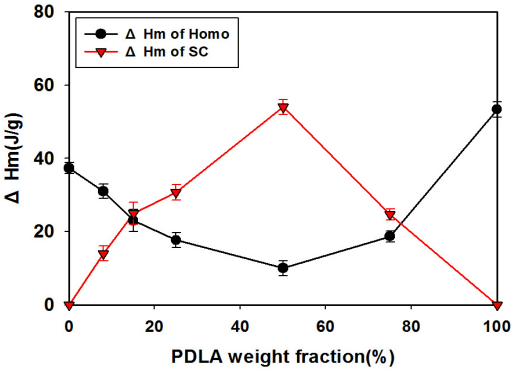
In table 2, the PLA SC formation increased until 50/50 composition as PDLA increases. And it was maximized in equimolar composition. Therefore, equimolar composition shows maximum PLA SC content as seen in Figure 1. However, it was hard for us to make a 100% PLA SC formation due to the limit of our method.

[Table 2] Thermal properties of PLLA/PDLA blends

1st Scan	T_g(℃)	T_m(℃)	$\triangle H_m$,H (J/g)[a]	$\triangle H_m$,SC (J/g)[b]	$\triangle H_m$,SC/ $\triangle H_m$Total (J/g)
PLLA100	62	168	37	-	-
PL92D8	58	167/231	31	14	0.31
PL85D15	58	167/237	23	25	0.52
PL75D25	59	166/231	17	30	0.63
PL50D50	61	174/231	10	54	0.84
PL25D75	61	174/230	19	25	0.56
PDLA100	63	177	54	-	-

[a] Experimental heat of fusion of homopolymers
[b] Experimental heat of fusion of stereocomplex

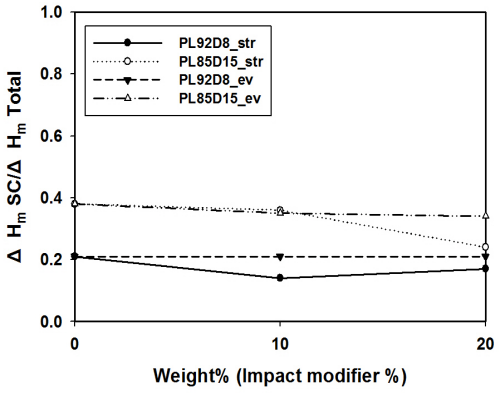
On the other hand, PLA SC formation decreased at 25/75 owing to nonequimolar composition.



[Fig. 1] PLA SC formation amount with PLLA/PDLA compositions

While crystallinity of PLA has been larger according to the formation stereocomplex, PLA SC could not improve the impact strength, which is its own weakness point[10]. Therefore, two kinds of impact modifier (Strong120, Elvaloy) was added into the PLLA/PDLA blends to improve the impact strength.

Table 3 and Figure 2 presents thermal properties and formation percentages of PLA SC with impact modifiers. PLA SC formation decreased when Strong120 as impact modifier was added. However, there is no impact on PLA SC formation when Elvaloy was added.



[Fig. 2] PLA SC formation percentages of PLLA/PDLA blends with impact modifiers

Moreover, toughened PLA SC contained 15 wt% PDLA had higher PLA SC formation than 8wt% contained PDLA. It is expected that more PLA SC was formed as PDLA amount in PLLA/PDLA blends increase.

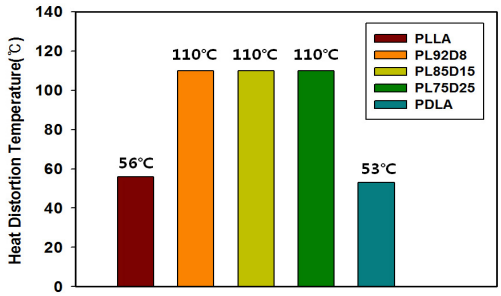
Figure 3 presents heat distortion temperatures (HDT) of PLA stereocomplex. With the addition of PDLA until 25wt%, HDT dramatically increased over 100℃. According to some literatures, storage modulus of PLA SC is higher than pure PLLA at high temperature [15]. That means thermal stability and HDT increased by forming stereocomplex.

[Table 3] Thermal properties of PLLA/PDLA blends with impact modifiers

1st Scan	T_g(℃)	T_m(℃)	$\triangle H_{m,H}$ (J/g)[a]	$\triangle H_{m,SC}$ (J/g)[b]	$\triangle H_{m,SC}$/ $\triangle H_m$ Total (J/g)
PL92D8	58	167/218	30	8	0.21
PL85D15	56	167/219	28	17	0.38
PL92D8_str10	60	167/218	31	5	0.14
PL92D8_str20	59	166/218	29	6	0.17
PL85D15_str10	58	167/219	27	15	0.36
PL85D15_str20	61	168/219	31	10	0.24
PL92D8_ev10	59	175/220	30	8	0.21
PL92D8_ev20	58	167/219	26	7	0.21
PL85D15_ev10	58	166/218	24	13	0.35
PL85D15_ev20	58	167/219	23	12	0.34

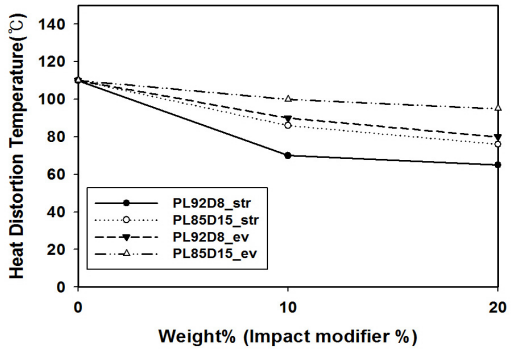
[a] Experimental heat of fusion of homopolymers

[b] Experimental heat of fusion of stereocomplex



[Fig. 3] Heat distortion temperatures of PLA SC blends

Figure 4 shows that HDT decreased as impact modifiers(Strong120 and Elvaloy) content increase. Also, the incorporation of impact modifier into the PLA SC blends decrease stiffness of specimens, gradually. Because the specimen loaded with 0.455 MPa softened more and more, downward speed was getting faster to reach 0.25mm[12]. Consequently, HDT was measured at lower temperature. This effect reducing HDT by Strong120 was greater than that by Elvaloy as shown in Figure 4.



[Fig. 4] Heat distortion temperatures of PLA SC blends with impact modifiers

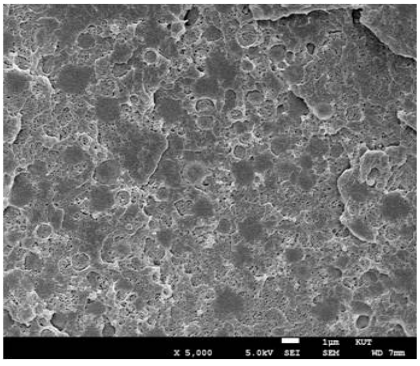
Table 4 shows that the impact strength of PLA series such as pure PLA, their PLA SC and PLA SC with impact modifier. Firstly, the impact strength of pure PLA are better than that of PLA stereocomplex. And PLA SC contained 8wt% and 15wt% PDLA units have a similar value of impact strength. Secondly, impact strength of PLA SC with impact modifiers significantly increased with the increase of impact modifiers (10-20wt%).

Figure 5a-5b shows SEM micrographs of PLA SC blends with impact modifiers. Two phase(domain and matrix) microstructure were not observed with an explicit interface between the two phases. Interfacial interaction between domain and matrix was enough to have a good adhesion. SEM observations shows that PLA SC/Impact modifiers blends exhibit compatible features because the domain size ranges from 1 to 4㎛.

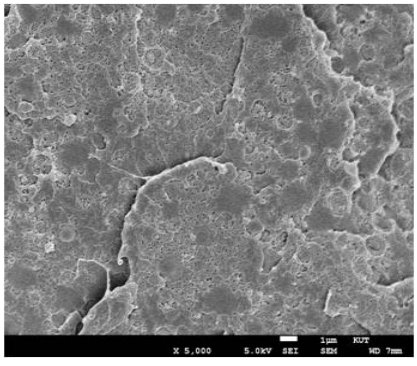
[Table 4] Mechanical properties of PLLA/PDLA blends with impact modifiers

Grade	IS (J/m)	FM (MPa)
PLLA	18	3700
PDLA	16	3650
PL92D8	10	3500
PL85D15	11	3950
PL92D8_str10	34	3000
PL92D8_str20	38	2400
PL85D15_str10	34	3200
PL85D15_str20	38	2500
PL92D8_ev10	30	3050
PL92D8_ev20	45	2350
PL85D15_ev10	40	3100
PL85D15_ev20	50	2450

* IS : Notched Izod Impact Strength
* FM : Flexural Modulus



(a)



(b)

[Fig. 5] FE-SEM images of PLA SC blends with impact modifiers (a) PL92D8_str10 (b) PL92D8_ev10

5. Conclusion

In this study, we blended PLLA and PDLA with 10-20wt% impact modifier to enhance mechanical property and thermal property with overall compositions. DSC data illustrate that diversity of PDLA composition in the PLA SC blends can affect PLA SC formation. In the case of equimolar composition in PLLA/PDLA blend, the most PLA SC crystallites could be formed. And that composition has a reasonable heat of fusion level. In melt blending such as our preparation method, the perfect formation of the stereocomplex could not have a sufficient time. Therefore, 100% SC formation was hard to make it with a conventional melt compounding. PLA SC formation decreased when Strong120 was added. However, there is no change of PLA SC formation with adding Elvaloy.

Due to the incorporation of PDLA, HDT dramatically increased over 100℃. Stiffness of blends decreased as impact modifier content increase. Therefore, HDT declined when Strong120 and Elvaloy 10-20wt% were added. Impact strength was improved considerably with the incorporation of impact modifiers (10-20wt%). Finally, we could find well balanced composition of toughened PLA SC with 10wt% of impact modifier in flexural modulus and impact strength.

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