

## Poly(butylene succinate) ionomer의 결정화 거동과 분해

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### Crystallization behaviour and Degradation of Poly(butylene succinate) ionomer

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#### 1. Introduction

An ionomer is defined as an ion-containing polymer with a small amount (usually up to 10-15 mol%) of ionic groups along the backbone chains or as pendant groups. Ionomers have been extensively studied because of the significant changes in their physical properties due to the formation of ionic aggregates, such as enhanced mechanical properties, high melt viscosity, and increased thermal properties.<sup>1-5</sup> Although there have been many studies of ionomers, the crystallization behaviour of degradable ionomers is still not understood. Only several studies have been carried out to explain the crystallization in PET/Surllyn blend.<sup>6</sup>

In this work, in order to extend the application fields of biodegradable polymer, we prepared and investigated semi-crystalline ionomer based on poly(butylene succinate) (PBS) which is one of the most promising biodegradable polymers to replace conventional plastics. We expected that introducing ionic groups into PBS main chains led to improved biodegradation rate and still acceptable mechanical properties. In addition, we investigated the effect of ionic aggregation on crystallization behaviour.

#### 2. Experimental

##### 2.1. Materials and Polymerization

PBS and PBSi were polymerized via two-step polycondensation. The monomer mixture was melted and stirred at 190 °C for 3 h. Evolved water and methanol were removed. Then, reaction temperature was gradually raised to 250 °C over a period of 30 min under a reduced pressure (<0.1 torr) and maintained for 5 h. The PBSi is denoted by the mole fractions of ionic groups determined from <sup>1</sup>H-NMR spectroscopy. For instance, PBSi-3 represents poly(butylene succinate)ionomer containing 3 mol% of dimethyl 5-sulfoisophthalate sodium salt (DMSI).

##### 2.2 Measurements

The thermal properties of PBSi were studied using a Perkin-Elmer DSC-7 with a heating and cooling rate of 10 °C/min. Dynamic mechanical analysis (TA-DMA 2980) was performed with a heating rate 3 °Cmin<sup>-1</sup>. The rheological behavior of PBSi was examined by the dynamic oscillatory viscometer (ARES, Rheometric Scientific Inc.), using a parallel-plate geometry which has a diameter of 20 mm and gap of 1.0 mm. The rheological properties were measured as function of the temperature (120 °C-280 °C) and the frequency (0.1-400 rad/s), with 10% of the

strain level. The size and morphology of ion clusters on PBSi were primarily investigated by TEM (JEOL 2000FX) at an operating voltage of 100 kV. The samples for the TEM observation were shadowed with Pt to increase contrast. The surface morphology of ionomer film was examined by non-contact mode AFM (XE-100, PISA) with a cantilever 125  $\mu\text{m}$  in length at resonance frequencies ranging from 265 to 400 kHz. The morphology of the interfacial surface was investigated using a scanning electron microscope (JEOL JSM-6340F). For scanning electron microscopy, the polymer films were fractured under liquid nitrogen and then dried in a vacuum oven at 40  $^{\circ}\text{C}$ . The samples were gold-coated by ion sputtering and examined by SEM. Morphology of spherulites was observed under a polarizing optical microscope (Nikon HFX-11A) equipped with video capture program. A small amount of the sample, sandwiched between slide glass and cover glass, was first melted on a hot plate at 150  $^{\circ}\text{C}$  for 2 min and then rapidly transferred to the hot stage (Mettler Toledo FP82HT) equilibrated at the desired isothermal crystallization temperature. With annealing for the required crystallization time, the spherulite morphology and the radius growth rate were measured. Small-angle X-ray scattering was performed using the synchrotron radiation of the Pohang Accelerator Laboratory (PAL) in Korea. The long period and the average lamellar thickness were calculated from the linear correlation function.

### 2.3. Degradation Study

Hydrolytic degradation of polyester was studied on compression molded film of 0.3 mm thickness in a basic aqueous solution of pH 7, 12 at 37  $^{\circ}\text{C}$ . The soil (pH 6.8, water content ca. 25%) burial test of PBS ionomer films was carried out using the thin PBS ionomer films (30 $\times$ 30 mm, 0.3 mm), which were buried in soil for 40 days.

## 3. Result and Discussion

PBS and PBSi were synthesized by a two-step process consisting of direct esterification and polycondensation. DMSI was restrictively incorporated up to 5 mol% because DMSI has poor solubility in the reaction mixture. The results of PBSis synthesis were summarized in Table 1. The molecular weight of PBSis consistently decreased with increasing ionic content. It is likely that inter and intra-chain interaction caused by ionic groups retarded polycondensation step. The melting point decreased with increasing ionic content but  $T_g$  is slightly increased with increasing ionic content.

**Table 1. Polymerization data and thermal properties of PBS and its ionomers**

Polymer Code	Composition		GPC result		Reaction time h	$\eta_{\text{inh}}^{\text{a}}$ gdL $^{-1}$	$T_g^{\text{c}}$ $^{\circ}\text{C}$	$T_m^{\text{f}}$ $^{\circ}\text{C}$	$T_c^{\text{g}}$ $^{\circ}\text{C}$	$T_m - T_c$ $^{\circ}\text{C}$	$\Delta H_f$ J/g
	Molar ratio in feed <sup>a</sup> (succinic acid/DMSI)	Molar ratio in real composition <sup>b</sup> (succinic acid/DMSI)	$M_n \times 10^{-4}$	$M_w/M_n^{\text{c}}$							
PBS	100/0	100/0	4.3	2.01	2+4	1.26	-10.7	114.5	80.1	34.4	79.7
PBSi-1	99/01	99/01	c	c	2+4	0.94	-9.2	113.6	71.2	42.4	77.2
PBSi-3	97/03	97/03	c	c	2+5	0.92	-6.8	112.0	64.3	47.7	73.4
PBSi-5	95/05	95/05	c	c	2+7	0.75	-3.0	110.7	55.8	54.9	63.5

<sup>a</sup> Molar ratio of DMSI to succinic acid in total diacid feed.

<sup>b</sup> Real composition was determined by  $^1\text{H-NMR}$ .

<sup>c</sup> GPC datas for ionomers were not measured because of adsorption on column by ionic groups.

<sup>d</sup> 0.5g/dL in phenol/1,1,2,2-tetrachloroethane (3/2) (v/v).

<sup>e</sup> Measured by DMA, 3  $^{\circ}\text{C}/\text{min}$ .

<sup>f,g</sup> Measured by DSC, 10  $^{\circ}\text{C}/\text{min}$ .

Figure 1 displays the melt viscosity curves. The parent PBS showed monotonous decrease in melt viscosity with increasing temperature, while PBSi-3 and PBSi-5 showed a falling inflection region. This result indicates that the chains close to ionic aggregates is relaxed with increasing temperature, mainly due to thermally unstable ionic aggregates at temperatures above 190 °C.  $\tan \delta$  curves in the melt are shown as a function of temperature in Fig. 2. Considering the multiplet-cluster model proposed by Eisenberg *et al.*, for ionomers the peak 2 or shoulder may be considered the evidence of the relaxation of chains in direct contact with the multiplets. On the other hand, the peak 1 at 220–240 °C may be attributed to the relaxation of relatively distant chains from multiplets. Figure 3 shows the temperature dependence of the long spacings calculated from the Correlation Function. In the region of 70 °C–80 °C, as the ion content increase, the interface amorphous region significantly increase compared to the crystalline thickness.

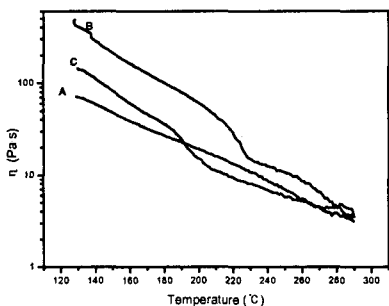


Figure 1. Melt viscosity versus temperature for PBS ionomers. A, PBS; B, PBSi-3; C, PBSi-5.

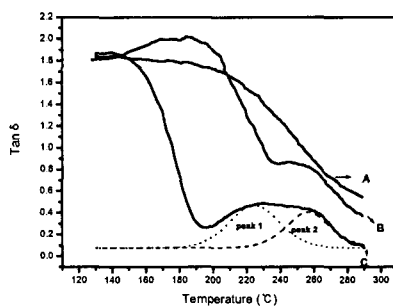


Figure 2.  $\tan \delta$  versus temperature for PBS ionomers. A, PBS; B, PBSi-3; C, PBSi-5.

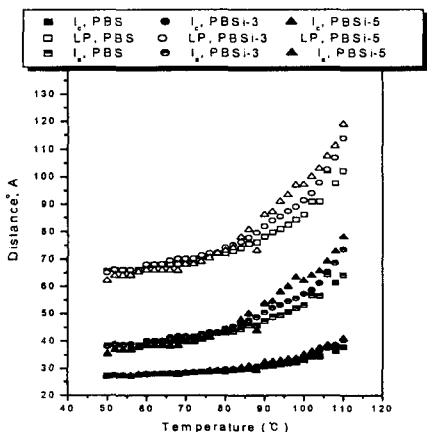
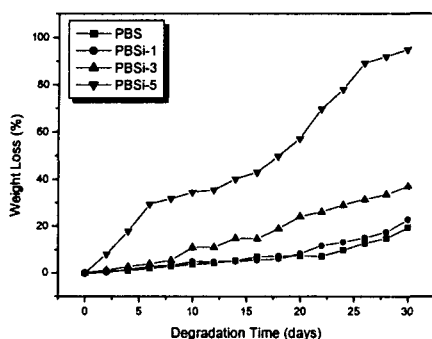


Figure 3. Variation of the microstructural parameters as a function of the temperature



Figure 4. TEM image of ioncluster in PBSi-3.



**Figure 5. Weight loss of PBSi films against degradation time in phosphate buffer solution of pH 12 at 37 °C**

As shown in Figure 4, TEM images provided the evidence for cluster formation with the size of 40–50 nm, demonstrating that clusters were aggregated each other. In contrast of the spherulitic texture of the PBS the morphology of PBSi appears as irregular lamellar growth disturbed by aggregated ionic clusters.(not shown here). Figure 5 displays the weight loss of PBS and PBSis. The hydrolytic degradation of the ionomers was dramatically accelerated compared with neat PBS, which seemed to be due to lowered crystallinity and enhanced hydrophilicity by introducing ionic groups into the main chain.

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