

전단이 조성이 다른 poly(butylenes succinate-co-butylene 2-ethyl-2-methyl succinate) 공중합체의 결정화거동에 미치는 영향

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Effect of shearing on the crystallization behavior of poly(butylenes succinate-co-butylene 2-ethyl-2-methyl succinate) copolymers with different copolymer composition

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1. Introduction

Recently, the use of synthetic polymers as plastic materials keeps on increase, raising serious environmental problems mainly due to their low degradability in nature. Consequently, biodegradable polymers are attracting much attention from material researchers. Among the various biodegradable polymers aliphatic polyesters are recognized as one of the most promising biodegradable materials because they are readily susceptible to biological attack[1]. Thus, many investigations are currently being carried out to enhance the biodegradability of the polyesters by simply modifying their physical properties. Copolymerization of various monomers is among the best of suitable approaches towards achieving improved biodegradability in different applications.

Shear induced crystallization of semi-crystalline polymers is a matter of great importance in controlling the final morphologies and properties. Thus, the importance of shear-induced structural changes in polymeric materials is much raised recently in the field of polymer processing.

2. Experimental

2.1. Materials

poly(butylene succinate) (PBS) and poly(butylene succinate-co-butylene 2-ethyl-2-methyl succinate) (PBSEMS) copolymers were synthesized from succinic acid (SA), 2-ethyl-2-methyl succinic acid (EMSA), and 1, 4 butanediol by a two step reaction of esterification and polycondensation. Esterification was carried out with various compositions of SA and EMSA at atmospheric pressure under nitrogen

purging. A mixture of acid/diol in a 1.0 : 1.0 molar ratio was reacted with stirring at 200°C for 120-150 min until evolution of water was complete. The water formed during the esterification was distilled off. After premixing with a catalyst, titanium isopropoxide (TIP) (0.5 wt% of diacid), at 100°C, polycondensation was carried out at 230°C under reduced pressures for 180-240 min. Three copolymers with different copolymer composition were prepared as summarized in Table 1.

2.2. Measurement of physical properties

Advanced Rheometric Expansion System (ARES) (Rheometric Scientific, Inc.) was employed to measure the dynamic rheological properties. The parallel plates of diameter 25 mm were used, whose gap was 1 mm. The specimen was melted at 140°C and then quenched to the desired crystallization temperature of 80°C for a time sweep measurement. The experiment was carried out at the three different frequencies 0.5, 1, and 5 rad/sec with a 5% strain till the value of storage modulus (G') leveled off. The molten disk-shaped specimen was then taken off the plates and further used for measuring other properties such as thermal and morphological properties.

Wide angle x-ray diffraction (WAXD) experiments were carried out on MX18 diffractometer (Mac Science Co.) with nickel filtered $\text{CuK}\alpha$ radiation of 40 kv and 200 mA. Scanning was carried out on the equator in the 2θ range from 5° to 60° at the scan speed 5° /min.

DSC 2010 (TA Instruments, Dupont) differential scanning calorimeter was used to evaluate thermal properties of PBS and PBS copolymers. About 5 mg samples were heated from 10 to 140°C at a rate of 10°C/min in a nitrogen atmosphere to obtain heating scan thermogram.

3. Results and discussion

Figures 1 (a)-(d) show the variation of storage modulus (G') with time at 80°C for PBS, PBSEMS9505, PBSEMS9010, PBSEMS8020, respectively. At the early stage of experiment, G' increases slowly indicating an induction time for crystallization. Subsequently, an abrupt increase of G' takes place in a minute. This phenomenon can be ascribed to the formation of crystallites probably due to the shear induced crystallization. As the crystallites grow to larger sized spherulites within the system through nucleation and growth, the homogeneous melt system changes to the heterogeneous system. Thus the G' increase with the crystallization time[2]. Long induction time and slow crystallization rate are observed with increasing comonomer unit containing ethyl-methyl side groups. The introduction of comonomer unit serves to decelerate crystallization behaviors as compared with neat PBS. Especially, PBSEMS8020 shows dramatically slow crystallization behavior compared with the others. However, the ceiling value of G' is almost same irrespective of copolymer composition.

WAXD profiles of PBS and PBSEMS9505 crystallized under shear are shown in Figure 2(a) and (b), respectively. Neat PBS displays same WAXD patterns, independent of applied frequency. Three diffraction peaks appear at about $2\theta = 19.38^\circ$, 21.62° , and 22.46° , representing (020), (021), and (110) planes, respectively. In the case of copolymer, a little different diffraction pattern was observed depending

on the applied frequency. PBSEMS9505 crystallized without shear shows almost same peak shape as neat PBS but a little shift of peak position to higher scattering angle. Contrastively, that crystallized with shear shows different peak shape but no peak shift compared with neat PBS. According to Wunderlich[3], the introduction of a methyl group as a side-chain to polyethylene resulted in isomorphism and the lattice parameter of the α -axis increased with methyl content.

Figures 3(a) and (b) show DSC thermograms in the heating process for neat PBS and PBSEMS9505, respectively, which are crystallized under shear at 80°C. The PBSEMS9505 shows new endotherm peak at about 99°C neat PBS doesn't display, associated with comonomer unit. The comonomer unit disturbs the crystallization of PBS unit resulting in a few degrees lower melting temperature. Additionally, there is no melting peak associated with co-crystallization. Melting behaviors of neat PBS and its copolymer seem to be independent of the shear applied during crystallization.

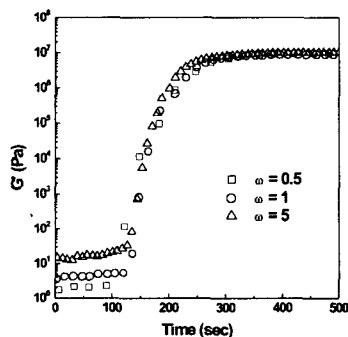
4. References

- [1] S. J. Huang, *Encycl Polym Sci Eng*, vol. 2: Biodegradable polymers, New York, Wiley-Interscience, 1985.
- [2] W. J. Yoon, H. S. Myung, B. C. Kim, and S. S. Im, *Polymer*, **41**, 4933-4942 (2000).
- [3] B. Wunderlich, *Macromolecular physics*, vol 1, Academic Press, 1973.

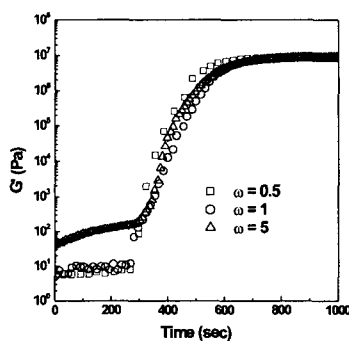
Table 1 Copolymer compositions of the samples used

Sample	Composition (mol%)	
	Feed Ratio [SA]/[EMSA]	Polymer Ratio ^a [SA]/[EMSA]
PBS	100/0	100/0
PBSEMS9505	95/05	94.0/6.0
PBSEMS9010	90/10	89.4/10.6
PBSEMS8020	80/20	77.3/22.7

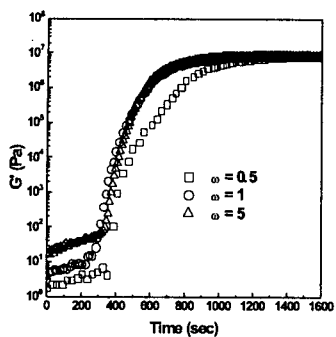
^a Composition measured by ¹H-NMR



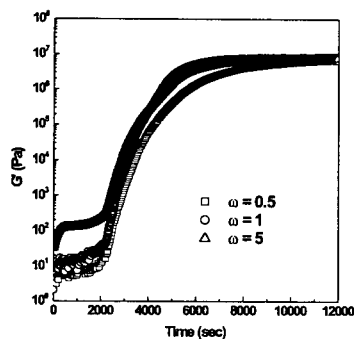
(a)



(b)

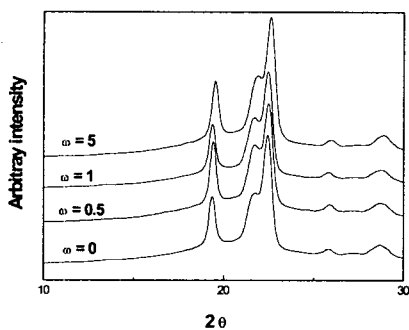


(c)

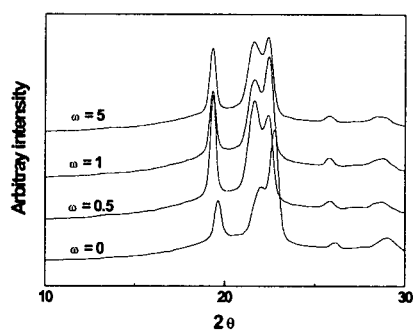


(d)

Figure 1. Variation of storage modulus (G') with time at 80°C for (a) PBS, (b) PBSEMS9505, (c) PBSEMS9010, and (d) PBSEMS8020

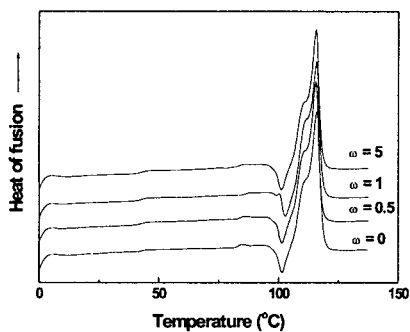


(a)

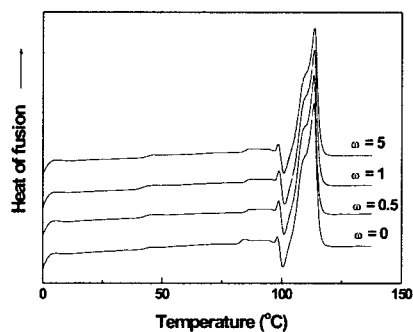


(b)

Figure 2. Effect of shearing level on WAXD patterns of (a) PBS and (b) PBSEMS9505.



(a)



(b)

Figure 3. DSC heating scan thermograms of (a) PBS and (b) PBSEMS9505