Structure and Properties of Segmented Block Copolyetheresters Based on PBT and PTMGT. 2. Mechanical and Dynamic Mechanical Properties

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1. INTRODUCTION

Segmented block copolyetheresters defined as copolymers having sequences of alternating polyester hard blocks and polyether soft blocks create labile physical cross-links upon crystallization of hard polyester blocks[1-3]. Since the nature of the physical interlocking is a crystallite formed exclusively from the crystallizable hard segment, the hard segment content (HSC) and hard segment length (HSL) will play an important role in determining the properties such as mechanical property and dynamic mechanical property.

In the previous study[4] we have synthesized the segmented block copolyetheresters based on poly(butylene terephthalate) and poly(tetramethylene ether glycol) (molecular weights: 650, 100, 2000) with various hard segment contents and investigated the effect of hard segment content and hard segment length on the thermal properties of the block copolyetheresters. The present study dealt with the structure-property relations in the copolyetheresters, especially for the mechanical and dynamic mechanical properties.

2. EXPERIMENTAL

The details of synthetic procedures and characterization methods were mentioned in the previous report[4,5]. The samples for the testing were prepared by the molding press. Copolyetherester chips were dried under vacuum at 120℃ for 3-4 hrs and then melt-pressed with 12-13 kg/cm^2 pressure at the temperature 20℃ above the sample melting temperatures. Samples for tensile testing had 0.1 mm thickness and those of dynamic mechanical analysis had 55 mm length, 12 mm width, and 2 mm thickness. The tensile properties were measured by Shimazu UTM 500-B Universal Testing Machine with a crosshead speed of 50 mm/min. The dynamic mechanical analyses were performed by Rheometrics Dynamic Spectrometer RDS-800 II with a heating rate of 5℃ and 1 Hz frequency. Rigaku D-Max 3B X-Ray Diffractometer was used for analyzing the crystal structure of tensile testing samples.

3. RESULTS AND DISCUSSION

3.1 Mechanical properties

Table 1 shows the identification of samples used in this study. Fig. 1 and 2 show the variation of elongation at break and ultimate stress with hard segment content (HSC). The elongation of PTMG 2000 samples decreases with increasing HSC, while those of PTMG 1000 and 650 show maxima at about 50 wt% HSC. The PTMG 2000 samples which show considerably high elongation, are thought to have relatively strong interlocking and carry out the load-bearing role, even when their hard segment lengths are short. On the other hand, in PTMG 1000 and 650 samples, short hard segment blocks could not form stable interlockings and consequently could not endure the external force. The stress increases with HSC for all the samples examined. The PTMG 2000 samples show relatively slow increasing tendency, which was thought to be due to the deformation of continuous soft segment matrix during deformation as confirmed by the X-ray diffraction experiments.

Table 1. Compositions and segment lengths of copolyetheresters

Sample	HSC (wt%)	HSC (mol%)	HSL	SSL	[η] (dl/g)
2000-H80	79.7	97.4	39.1	1.03	0.90
2000-H65	65.9	94.9	19.7	1.05	1.00
2000-H50	49.4	94.9	10.4	1.10	0.83
2000-H35	35.2	84.0	6.3	1.19	0.95
2000-H20	21.0	70.4	3.6	1.42	0.88
1000-H80	80.5	95.5	22.2	1.05	0.97
1000-H65	65.4	90.7	10.7	1.10	0.98
1000-H50	50.1	83.8	6.2	1.19	0.92
1000-H35	34.2	72.8	3.8	1.37	0.77
1000-H20	19.6	55.5	2.3	1.80	0.57
650-H80	0.803	0.935	15.2	1.07	0.69
650-H65	1.655	0.871	7.6	1.15	0.88
650-H50	0.489	0.772	4.5	1.30	0.83
650-H35	0.354	0.660	2.9	1.52	0.55
650-H20	0.206	0.479	1.9	2.09	0.66

3.2 Dynamic mechanical properties

Fig. 3-5 show the temperature dependence of G' for PTMG 2000, 1000, and 650 samples, respectively. As confirmed by these figures, the amorphous phase of the copolyetheresters is not always homogeneous. In case of PTMG 2000 there exist two amorphous phases: soft segment phase and hard/soft mixed phase when HSC is lower than 50 wt%, while in PTMG 1000 and 650 there exists nearly one amorphous phase which is composed of soft and hard segment for all the compositions examined. This results indicate that in PTMG 2000 long soft segment blocks gathered together and formed their own phases even though the major part of the amorphous phase was hard/soft mixed phase.

4. Conclusion

The elongation at break of PTMG 2000 samples decreased with increasing HSC, while those of PTMG 1000 and 650 showed maxima at about 50 wt% HSC. The PTMG 2000 samples are thought to have relatively strong interlocking and carry out the load-bearing role, even when their hard segment lengths were short, while, in PTMG 1000 and 650 samples, short hard segment blocks could not form stable interlockings and consequently could not endure the external force. The stress increased with HSC for all the samples examined. The PTMG 2000 samples showed relatively slow increasing tendency, which was thought to be due to the deformation of continuous soft segment matrix during deformation process as confirmed by the X-ray diffraction experiments.

The dynamic mechanical analysis revealed that the amorphous phase of the copolyetheresters was not always homogeneous. In case of PTMG 2000 there existed two amorphous phases: soft segment phase and hard/soft mixed phase when HSC was lower than 50 wt%, while in PTMG 1000 and 650 there existed nearly one amorphous phase which was composed of soft and hard segment for all the compositions examined. This results indicated that in PTMG 2000 long soft segment blocks could form their own phases even though the major part of the amorphous phase was hard/soft mixed phase.

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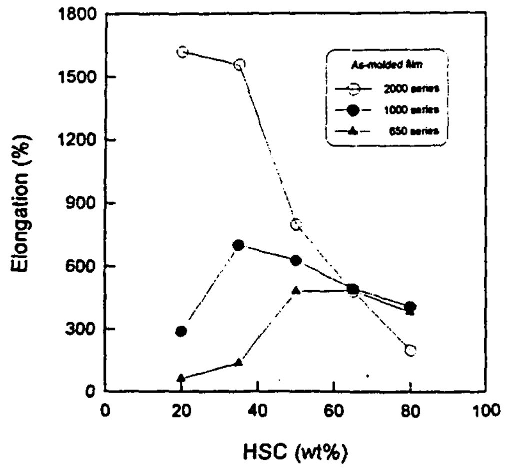

Fig. 1. Variation of elongation of the copolyetherester as-molded films with different hard segment content (HSC).

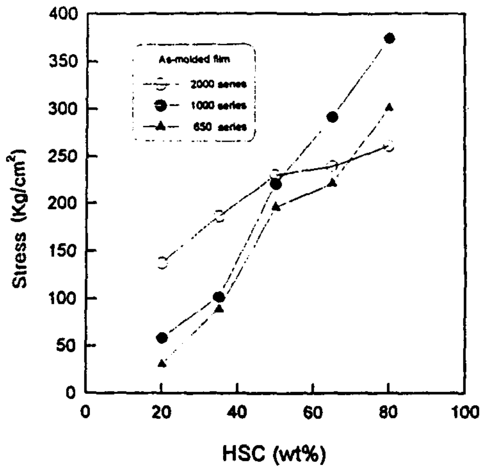

Fig. 2. Variation of stress of the copolyetherester as-molded films with different hard segment content (HSC).

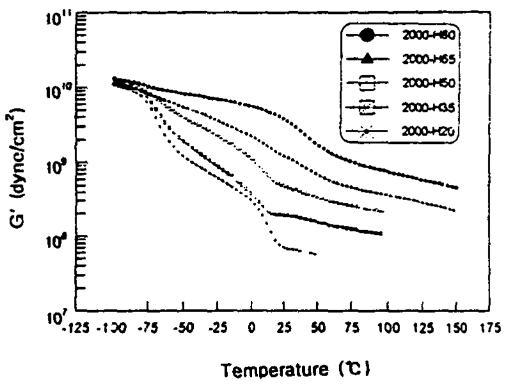

Fig. 3. Dependence of G′ on the temperature for 2000 series.

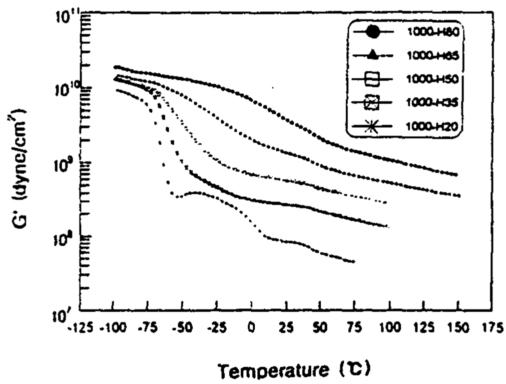

Fig. 4. Dependence of G′ on the temperature for 1000 series.

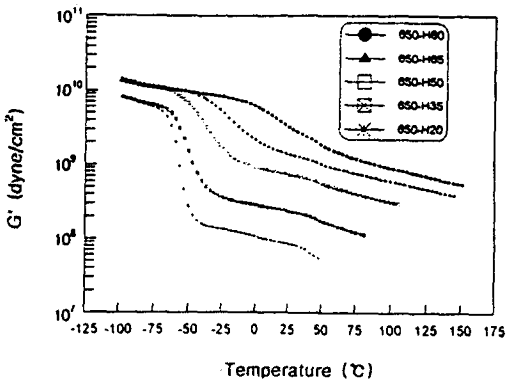

Fig. 5. Dependence of G′ on the temperature for 650 series.