

MDSC를 이용한 폴리에스테르와 코폴리에테르에스테르의 가역적 용해거동 분석

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Reversible Melting Behaviors of Polyesters and Copolyetheresters studied by MDSC

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1. Introduction

Melting and crystallization are not reversible because supercooling is always needed for crystal growth. But, recently reversible melting and crystallization phenomena in semi-crystalline polymers, based on modulated differential scanning calorimetry(MDSC) with quasi-isothermal experiment mode were observed in the melting range and continuously proved by others¹. These reversible process often displays an additional reversing heat capacity² and occurs at the fold surface. Androsch and Wundlich saw two possible locations for such reversible process in their ethylene copolymer. The first was found in chain segments that melted only partially because of their attachment to other, higher melting(lamellar) crystals, whereas the second one was found in secondary, fringed-micellar crystals, grown with the network of larger crystals³.

In this paper, quasi-isothermal MDSC measurement for polyesters and copolyetheresters with different compositions was performed.

2. Experimental

2.1. Samples

PBT, PBN, PTT homopolymer were synthesized by traditional two step polycondensation reaction. Copolyetheresters comprised with PBN hard segment and PTMGN soft segment were copolymerized with different molecular weights(Mn; 1000, 2000, 2900) and different hard segment contents(80, 65, 50, 35wt%).

2.2. Quasi-Isothermal Measurement

A commercial thermal analyzer 2910 MDSC system of TA Instruments Inc. was used for the measurements. For the calibration of the heat-flow amplitude, sapphire was used. In quasi-isothermal MDSC measurement, the sample was first heated to melting temperature above 20°C. After 5min, it was cooled around the onset temperature of melting. The amplitude was set to 1.0 K, coupled to periods of 60s. Separate experiments for 20 min were carried out every 2.0 K over the whole temperature range. After MDSC 2nd heating, reversing heat capacity was measured.

3. Results and Discussion

For the quasi-isothermal experiment, approach to steady state and accomplished steady state were certified by the perfection of Lissajous figures. The heat capacities of a quasi-isothermal analysis in the melting range appeared reversible melting and crystallization. MDSC reversing heat capacity and the additional reversing heat capacity of quasi-isothermal experiment were shown in Figure 1. The integral of the amplitude of the quasi-isothermal experiment with a normal baseline during melting were calculated and summarized in Table 1. comparing with the heat of fusion of MDSC measurement. Among the homopolymers PTT has the smallest additional reversing heat capacity. Additional reversing heat capacity of copolyetheresters were converted into that of the same hard segment contents and shown in Figure 2. The amount of reversible melting and crystallization seems to be similar irrespective both of the hard segment content and of the PTMG molecular weight for the copolyetheresters.

4. Conclusion

By the quasi-isothermal MDSC, the various structure polyesters and copolyetheresters with different comonomers and comonomer contents were investigated about reversible melting and crystallization in the melting range by quasi-isothermal mode. PTT has more little reversible part. Additional reversing heat capacity of copolyetherester has been little influenced by the hard segment contents and the PTMG molecular weight.

5. 참고문헌

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Table 1. Additional reversing heat capacity and heat capacity of samples.

	Quasi-area	C_p -area	Quasi/ C_p (%)	HSC	qu/HSC
PBN	5.86	74.43	7.87	-	-
PBT	5.15	83.13	6.20	-	-
PTT	3.22	93.43	3.45	-	-
PBN	5.86	74.43	7.87	1	5.86
4GN2900 H80	4.4	45.4	9.69	0.8	5.50
4GN2900 H65	3.88	38.84	9.99	0.65	5.97
4GN2900 H50	3.1	27.1	11.44	0.5	6.20
4GN2900 H35	1.5	12.04	12.46	0.35	4.29
4GN2900 H80	4.4	45.4	9.69	0.8	5.50
4GN2000 H80	3.8	48.58	7.82	0.8	4.75
4GN1000 H80	5.13	47.44	10.81	0.8	6.41
4GN2900 H80	4.4	45.4	9.69	0.8	5.50
4GT2900 H80	3.96	30.2	13.11	0.8	4.95
3GT2900 H80	2.1	61.7	3.40	0.8	2.63

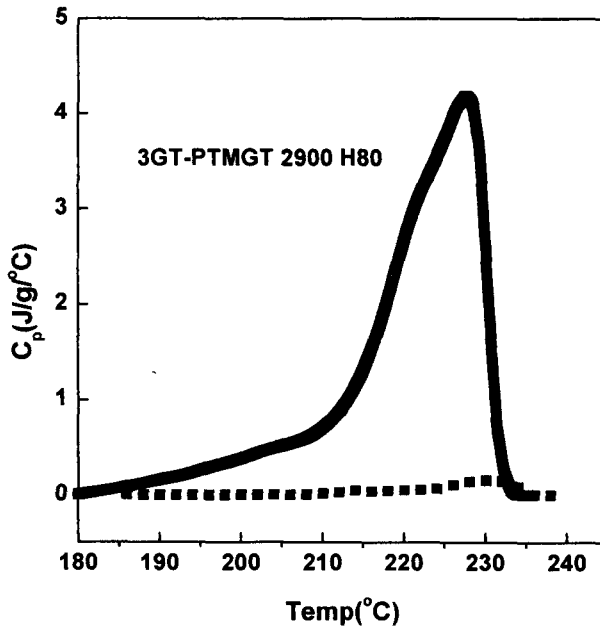


Figure 1. Heat capacity by MDSC(thick line) and additional reversing heat capacity by quasi-isothermal MDSC(dotted line) in the melting range.

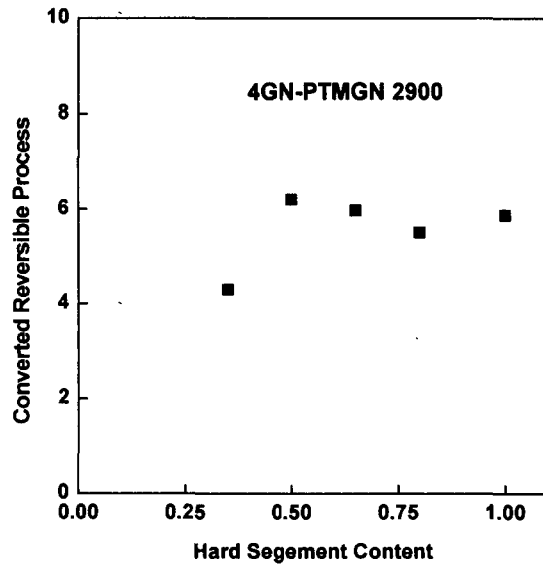


Figure 2. Amount of converted reversible process of copolyetherester.