블록 코폴리에테르에스테르 블렌드의 융점 강하

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Melting Depression for Blends of Two Multiblock Copolyetheresters

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1. Introduction

Blending is cheap and leads to new thermoplastics, many properties which can be predicted from those of the components. Due to the incompatibility of their components , most blends feature coarse phase morphologies with weak interfaces between the phases. Consequently the blends are brittle.

Thermoplastic elastomers which have two kinds of segments in the chain have flexible(soft) and rigid(hard) segments and exhibit a unique combination of strength, flexibility, and processibility. These kinds of multiblock copolymers and blendings were investigated about the correlation between physical properties and phase structures.[1] Two multiblock copolymer blending that soft segments are same can be miscible and will show each property such as melting points, phase separations because of the different segments.

Copolyetheresters have been studied about blending with various homopolymers and copolymers[2,3]. Some of them can be cocrystallized and may occur intermolecular interactions and interchange reactions. Interchange reactions of condensation polymers on blending take place whenever the conditions(appropriate temperatures, time, and chemical compositions) are ready.

During blending of two homopolymers, interchange reactions result in the complete randomised copolymers consisted of homopolymer sequences. It cause the melting of crystallizable homopolymer to depress and copolymer will be amorphous[4]. But few polymers such as PBT(poly(butylene terephthalate)) and PBN(poly(butylenenaphthalene-2,6-dicarboxylate)) are able to be crystalized with forming iso-dimorphic co-crystals.

In present paper, Blends of copolyetheresters which have two different hard

segments and the same soft segments were examined with the melting depression represented by interchange reactions.

2. Experimental

2.1. Material

Copolyetheresters with PBT, PBN hard segment and PTMG(poly(tetramethylene oxide) glycol, Mw 2000) soft segment were synthesized by the conventional two step condensation reaction. Each hard segment of copolyetheresters has 80, 65, 50, 35wt% content.

All samples dissolved in the cosolvent (phenol/1,1,2,2-tetrachloroethane 1:1 wt/wt) and the solutions have 10wt% solid content. Solution blending with copolyetheresters of the same hard segment contents between different hard segments copolymers were performed by weight ratio 1:1 and precipitated in sufficient ethanol. Samples were washed for 5 hours at least and dried at room temperature.

2.2. Characterization

The studies of melting behaviors of copolyetherester blends were performed by using DSC 2910(TA Instrument Inc.) Cell was purged by dry nitrogen and heating, cooling rate were fixed 20°C/min. After heating to 260°C, melt blending was performed in DSC cell for various time(30, 60, 120, 300min.).

3. Results and Discussion

After precipitation, all samples were scanned by DSC and showed two melting peaks which were similar to the each hard segment melting from copolyetheresters. Melting temperatures of solution blend samples were little decreased than those of pure copolyetheresters. It is possible for one hard segment to have difficulty in crystalizing on its precipitating because of the other hard segments. PBN crystal melting($T_{m,PBN}$), higher melting peak originated from PBN hard segment copolyetherester, more decreased than PBT one($T_{m,PBT}$) at higher hard segment content copolymers.

In the case of ester-ester interchange reactions at high temperatures, usually above T_m, randomisation is driven from the transition of the block copolymer into a random one. This results in the amorphous copolymer which wasn't able to be crystallized. But blendings of two multiblock copolyetheresters consisted of PBN and PBT hard segment may form iso-dimorphic cocrystals as blending of homopolymer was done. Then, Induced heterogeneous chain sequences in spite of

interchange reaction, copolyetherester melting from different hard segment is alive with melting depression to some extent. Figure 1 shows melting depression phenomena with blending time. Higher melting peaks are from PBN rich sequences hampered their crystallization by alternate sequences. It took time to accomplish the complete randomisation of each hard segments.

All melting behavior data of samples were summarized in Table 1.

5. Reference

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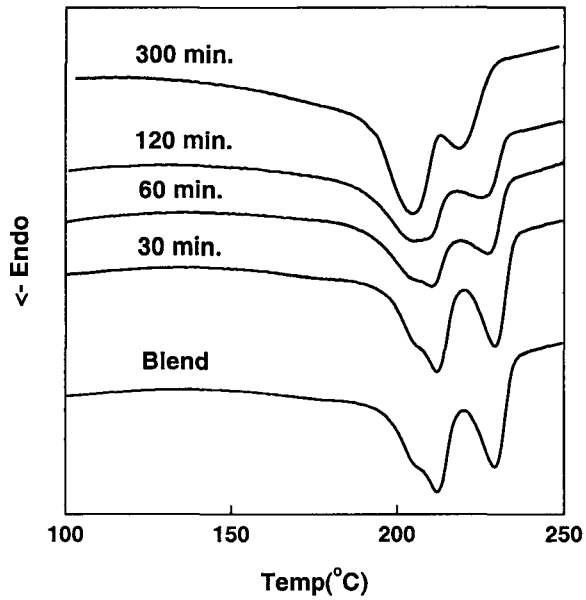

Fig. 1 Thermograms of different blend time (4GN-4GT 2000 H80).

Table 1. Melting data of copolyetheresters blending.

Composition	Time(min.)	$T_{m,PBT}$(°C)	$T_{m,PBN}$(°C)	$\Delta H_{m,PBT}$(J/g)	$\Delta H_{m,PBN}$(J/g)
H80	Homo	219.97	240.17	39.06	32.87
	Blend	219.17	236.92	46.15	
	30	212.03	229.38	36.93	
	60	210.34	226.61	32.23	
	120	207.2	225.35	34.3	
	300	204.82	218.36	43.79	
H65	Homo	216.6	237.65	32.62	25.91
	Blend	216.21	235.85	44.86	
	30	212.01	232.51	34.49	
	60	208.71	230.2	33.89	
	120	205.56	226.09	29.13	
	300	196.2		25.02	
H50	Homo	210.7	231.73	26.18	18.06
	Blend	210.16	229.55	39.04	
	30	205.94	228.25	26.66	
	60	199.34	225.59	22.07	
	120	195.94	214.04	18.65	
	300	186.56		16.77	
H35	Homo	194.62	228.08	20.45	13.5
	Blend	189.32	227.01	22.94	
	30	187.9	226.9	18.68	
	60	183.36	225.98	17.82	
	120	178.45	218.72	11.26	
	300	174.52		13.96	