

Micro-Phase Separation Structure of Nonionic Polyether-Polyester Polyurethane Based On MDI

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Abstract—Segmented polyether-polyester polyurethanes with an amorphous hydrophilic soft segment phase were prepared from 4,4'-diphenylmethane diisocyanate (MDI), polybutylene adipate glycol 2000 (PBA2000) and polyethylene glycol 1000 (PEG1000) with 1,4-butanediol (BDO) as the chain extender. Furthermore, the micro phase separation structure of the polyurethanes was studied. The studies show, the micro-structure of nonionic polyurethane has been remarkable influenced by the structure, molecule and concentration of its soft segments.

Keywords-polyurethane; micro-structure, polyether; polyester

I. INTRODUCTION

Polyurethanes usually have frozen hard domains and reversible soft domains (microphase structure) due to the incompatibility of the constituent segments[1], and almost all of the application properties of polyurethane materials have consanguineous correlativity with its microstructure[2,3].

Generally, the polyurethane with different microphase separation structure will show an obvious difference on their macroscopical properties even if they had a same chemical structure. The microstructure of polyurethane macromolecule is strongly dependent on the chemical structure, components, relative content, molecular weight, crystallinity of polymeric monomers and the cross-linking degree of soft and hard segment phases etc [4].

II. EXPERIMENTAL

A. Materials and Preparation of Polyurethane

Both PBA2000 and PEG1000 are employed as the mixed soft segment of polyurethanes and MDI as the hard segment, BDO is used as chain extender, dimethyl formamide (DMF) as solvent.

The two-step procedure is followed to synthesize polyurethanes, which gives less random and more block polymer [5].

B. Preparation of Specimens and Analytical Methods

Polyurethanes are casted onto a glass plate. After dried at 80oC, these polyurethanes are further heat treated for 10min at 150oC. Finally, these polyurethanes were broken to pieces for thermal analysis.

Phase inversion temperature (PIT) of these polyurethanes is detected with modulated differential scanning calorimeter, DSC (Du Pont DSC-2000). The specimens (about 10mg) are heated from -50oC to 150oC at the heating rate of 20oC/min. Wide angle X-ray diffractometer is adopted to investigate the crystallinity (D/max-3C, Japan) of samples at the conditions of $2\theta=0-50^\circ$, 3o/min, Cu K α , 40KV, 30mA and room temperature.

III. THE STRUCTURE OF POLYURETHANE AND ITS PIT

TABLE I. POLYESTER-POLYETHER POLYURETHANES MATERIAL AND THEIR PROPERTIES.

Item / Serial number	Group A					Group B					Group C				
	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
Hard segment con. %	15.8	19.8	23.5	26.8	30.9	17.5	21.9	25.8	29.4	33.6	19.6	24.4	28.6	32.4	36.9
Hard segment mol. wt	319	420	522	622	760	318	420	521	624	759	316	419	520	623	760
Ether bond content %	5.5	5.1	4.9	4.7	4.4	10.0	9.5	9.0	8.6	8.0	15.7	14.8	14.0	13.2	12.4
Soft segment mol. wt			1700					1500					1300		
Soft charge ratio ^①			3:7					1:1					7:3		
PIT °C	23.0	23.0	30.0	37.0	45.0	28.0	28.0	32.0	39.0	39.0	36.0	35.0	38.0	44.0	44.0

Notes: Soft charge ratio means PEG1000:PBA2000.

IV. THE MICROSTRUCTURE OF SAMPLES

With regard to the glass transition range (Figure 1), all the endothermic peaks of samples are neither a typical glass transition graph of amorphous soft segments nor a typical watery fusion graph of crystalline soft segment; they have both features of amorphous and crystalline polymer simultaneously.

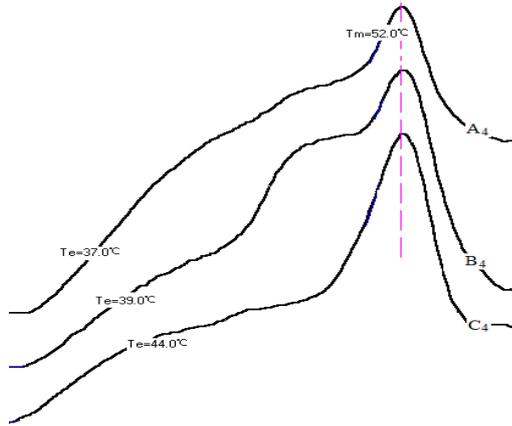


FIGURE I. THE DSC SPECTRUMS OF A4/B4/C4.

In fact, the phenyl existed in hard monomer MDI and the polar ester groups existed in soft monomer PBA2000, which can form steady hydrogen bonding with carbamate groups (hard segment), which results in a poor micro phase separation degree of samples. Also, the crystallization ability of soft segments of polyester-polyether polyurethanes has been impaired markedly because the soft monomer

PEG1000 has a shorter chain segment and a interchain attraction between PEG and PBA[4].

We consider that the most of soft segment existed as amorphous structure, but quite a number of soft segment also existed as crystalline particle and crystalline orientation. These crystalline particles have different crystalline modification, crystal perfection and crystalline dimension. The consecutive change of the slope of DSC spectrums implies that the crystalline particles have different melt temperature.

Actually, as the amount of PEG is increased, a co-continuous PEG and PBA morphology forms in the soft matrix. Absorption of water vapor by PEG segments will further enhance the phase separation in the soft matrix since the polarity difference will be greater between PEG and PBA phases. In the absence of water, PEG and PBA show partial miscibility when mixed. This also suggests that in copolymers containing low levels of PEG, it will be dissolved / distributed within continuous PBA matrix. In contrast, as PEG content is increased above a critical level and the system is brought in contact with water vapor, permeability of moisture will be improved markedly. This will dramatically change the polarity of PEG domains and force them to phase separate from PBA, resulting in a co-continuous PEG / PBA soft matrix.

The foregoing analysis for the supramolecular structure of samples can be strongly verified by their wide angle X diffraction (WAXD) datum (Table 2)

TABLE II. THE WAXD IMAGE DATUM OF POLYESTER-POLYETHER POLYURETHANES MATERIAL A4, B4 AND C4.

PU	Items	1	2	3	4	5	6	7	8	9	10
A4	2θ	10.10	13.78	22.68	23.54	26.32	31.26	37.74	40.60	41.78	43.76
	d value	8.75	6.42	3.92	3.78	3.38	2.86	2.38	2.22	2.16	2.07
	Count	031	031	036	036	033	033	025	024	024	023
	Relative intensity	86	86	99	98	90	90	68	66	65	64
B4	Half-high width	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
	Integra intensity	33	33	38	38	35	35	26	25	25	25
	2θ	10.38	15.38	17.72	21.74	24.24	28.64	37.00	44.36	—	—
	d value	8.52	5.76	5.00	4.08	3.67	3.11	2.43	2.04	—	—
C4	Count	028	025	031	032	034	032	025	026	—	—
	Relative intensity	83	73	91	94	99	94	73	75	—	—
	Half-high width	0.02	0.02	3.32	11.16	16.12	24.96	0.02	0.02	—	—
	Integra intensity	30	27	5502	19080	29106	42834	27	27	—	—
C4	2θ	7.68	8.76	21.30	21.94	24.98	29.26	31.42	34.06	36.00	41.68
	d value	11.50	10.09	4.17	4.05	3.56	3.05	2.84	2.63	2.49	2.16
	Count	023	027	031	032	033	033	031	028	029	029
	Relative intensity	71	80	94	96	98	99	94	84	88	86
C4	Half-high width	0.02	0.02	0.02	0.02	0.02	45.60	0.02	0.02	0.02	0.02
	Integra intensity	25	28	33	34	35	79717	33	30	31	30

Several wider diffraction peaks of samples imply that there are a mass of crystalline particle whose crystal perfection is very poor existing in polyurethanes.

The datum of relative intensity and integra intensity show that there are a large deal of amorphous macromolecule and a small quantity of crystallized macromolecule existing in samples simultaneously. Further more, the distribution of half-high width of WAXD spectrums becomes wider and wider (0.020 ~ 0.020, 0.020 ~ 24.960 and 0.020 ~ 45.600 respectively) with the decline of soft segment average molecular weight (from A4 to C4) of polyurethanes. This implies that the crystallization ability of mixed soft segment has been impaired from Group A to C, and the reason has been analyzed in the foregoing discussion. However, from Group A to C, the crystallinity of PEG1000 in soft phase has been improved notwithstanding the average molecular weight of soft segments is decreasing (Figure1 and Table 2). Just as we analyzed, it is because that the microphase separation of PEG in soft domain from PBA has been improved with the increment of PEG in the mixed soft phase.

According to Table 2, all the WAXD spectrums have 8~10 bragg diffraction peaks with different half-high width, every diffraction peaks is the reflection of many crystalline particles with uniform crystallization modality. Without doubt, there are some of crystallized macromolecules with different crystallization structure existing in samples.

V. CONCLUSIONS

For the mixed soft segments of PEG1000 and PBA2000, the crystallinity of PEG1000 in soft phase has been improved with the increasing dosage of PEG1000 in the mixed soft monomers even if the average molecular weight of soft segments is decreasing.

Within a group, the phase inversion temperature of polyurethanes moves to higher temperature with the increase of their hard segment content. It is because of the worse micro phase separation.

The incensement of the soft segment molecular weight results in a decrease of the soft phase PIT. However, when the hard segment content is higher, this tendency becomes not so much clear anymore because of a higher compatibility of the two phases.

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