

## **Study on effective parameters on phase separation in Segmented polyurethanes**

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### **Abstract**

Phase separation in segmented polyurethanes is an important phenomenon, which affects on characteristic properties of polyurethanes. Morphology, formation and distribution of microdomains (hard segments and soft segments) are effective parameters on adhesion and interfacial interaction of polyurethane system. In this work segmented polyurethanes based on 4,4 -diphenylmethane diisocyanate (MDI) and 1,4-butanediol (BDO) were synthesized and the effect of hard segment content as well as type of polyol on phase separation of synthesized polyurethanes has been studied and also correlation between microstructural factors on final properties of polymer well defined.

Keywords: pharmaceutical synthesis, green chemistry, green engineering, solvent selection

### **Introduction**

Segmented polyurethanes that consist of alternating soft and hard segments offer unique possibilities of tailor-made polymers by varying block length and composition [1]. Thermodynamic immiscibility between hard and soft segments induces phase separation and generates a two-phase morphology in these segmented block copolymers. There are some reports on evaluation of structure-properties in these segmented polyurethanes [2-4].

In the present study the effect of hard segment content and type of polyol on the thermo-mechanical properties as well as size of soft and hard domains and micro phase separation of synthesized polyurethane networks have been studied.

### **Experimental**

The polybutadiene polyol was prepared locally [5] with low vinyl microstructures and Mn being about 2500 gr/mol. Polybutadiene polyol was degassed at 50 °C for 24 hr before use. MDI (4,4-diphenylmethane diisocyanate), BDO (1,4-butane diol ) from Merck were used after drying at 50 °C and 800 mm-Hg vacuum for 8 hr.

### Synthesize method

All the polyurethanes synthesized using one-shot method. The procedure was as follows: Polyol, MDI and BD were mixed vigorously for a few minutes. The above mixture was poured in a rectangular mould. The mould was preheated and coated with silicon before use. The mould was in an 85°C oven for 3 days. All of tests were carried out on the specimens that maintained in a desiccator for 7 days. Final cross-linked products (networks) were insoluble in common solvents. Polyurethanes were synthesized in various molar ratios and hard segment contents of 25 %, 40% and 55%.

### Analytical techniques

A VPO Knauer apparatus was used to determine Mn of polyols. Toluene as solvent at 90°C and benzyl was used for calibration. DMTA analysis was carried out through heating rate of 4 C/min from -100°C to 250° C. A Polymer-Lab DSC was used. The DSC runs were performed under nitrogen using a heating rate of 10°C/min with sample weight of 10 mg. AFM (Atomic Force Microscopy) was used to study of two phases in network. Surfaces for AFM analysis prepared from fractural area of samples broken in liquid Nitrogen. The static mechanical properties were carried out by MTS tensile machine with a separation speed of 500 mm/min. FTIR(Bruker) spectroscopy was used to study of hydrogen bonding and phase separation of networks.

### Results and discussion

FTIR results are shown in Figure 1. polyurethane N-H groups consist of, hydrogen bonded ( $3330\text{ cm}^{-1}$ ) and non-hydrogen bonded groups ( $3400\text{ cm}^{-1}$ ). More than 95% of hydrogen bonds in HTPB polyurethanes occur between N-H hydrogen bonded groups in hard segment phase [4]. If phase separation develops via annealing, there is an increased population of hydrogen bonded N-H groups in hard segment phase. Furthermore C=C bond ( $1640\text{ cm}^{-1}$ ) is chosen as reference peak. It is also mentioned in the literature that there is no interference of peaks in HTPB based polyurethanes [5]. Therefore one can choose the relative intensity of N-H hydrogen bonded peak to C=C bond peak in HTPB as a proof for qualitative detection of phase separation evolution through annealing. Experiments showed that as the hard segment content of polyurethanes as well as type of polyol affect on thermo mechanical properties as well as phase separation of polyurethanes. AFM results show that one can recognized relationship between hard segment content of and domain sizes in polyurethanes.

The results (Table 2) show that as already expected, increased population of N-H hydrogen bonded groups and degree of phase separation is obtained for Type A samples. Moreover, DSC thermographs (Figure 2) manifest that Type A samples begin with low glass transition temperature at -32°C caused by soft phase ( Figure 2a ,TypeA) followed by a small crystallization exotherm and larger melting endotherm (Figure 2b,Type A) which are due to crystallization and destructive melting of HTPB soft phase during DSC. There is also a clear glass transition related to hard phase at 72°C (Figure 2a, Type A). On the other hand type B samples start with a low glass

transition at -30°C followed by a crystallization exotherm and melting endotherm with relatively similar magnitude and there is no observable upper  $T_{gh}$ . DMA results (Figure 3) show that annealing at 110°C gives a sharper damping peak for hard segment phase. Therefore, results manifest that Type A samples consist of much more ordered microdomains that give rise to a detectable  $T_{gh}$  for hard phase, on the other hand type B samples have hard segment micro-domains with disordered structure and no detectable hard phase glass transition. In other words the incompatibility of soft segments and hard segment units are enough to produce thermodynamic driving force for phase separation at 65°C, however the thermal energy at this temperature is not sufficient to provide appropriately mobile hard segments to improve fineness of these phase separated microdomains through order-disorder transitions [2].

### **Conclusion**

Hard segments microdomains are kinetically frozen and thermodynamically imbalanced and appropriate annealing results in a finely ordered phase separated structure with different thermomechanical properties. We have shown that through appropriate annealing, very well ordered polyurethanes could be obtained.

### **References**

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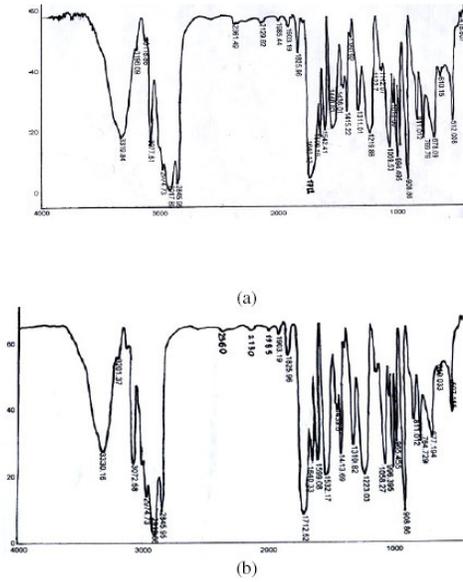


Figure 1: FTIR of annealed samples, Type A, (a) & Type B (b)

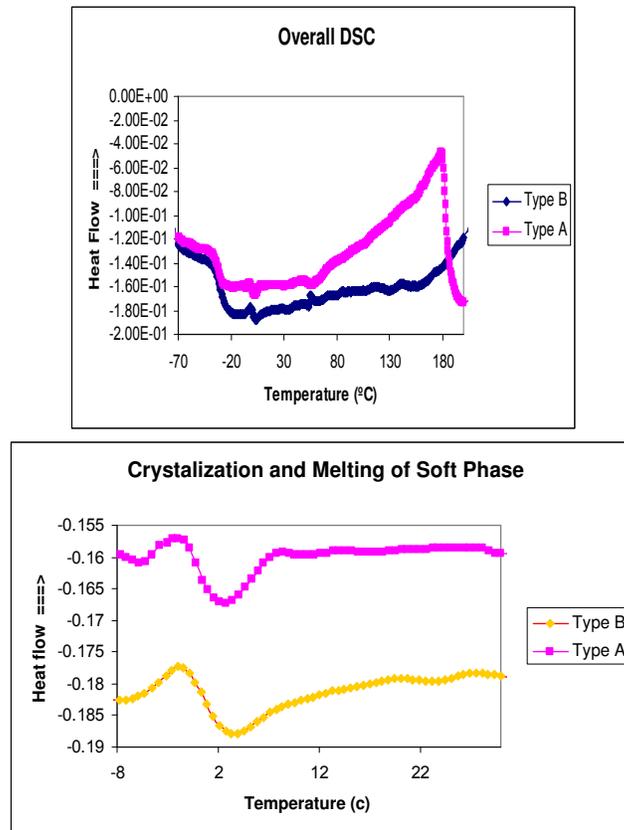


Figure 2: DSC of annealed samples, overall DSC (a) and crystallization and melting of soft phase (b).

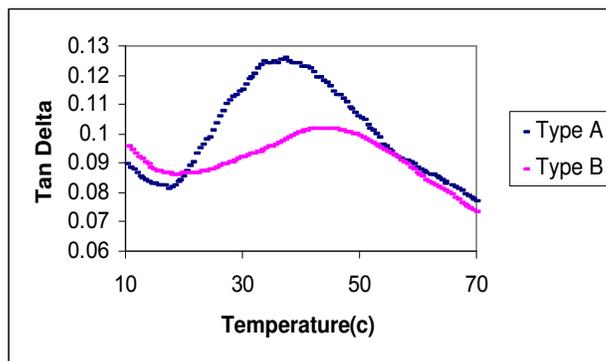


Figure 3: Tan  $\delta$  of annealed samples

Table 2: Relative intensity of transmittance peaks in Type A and B samples

N-H hydrogen bonded group divided by C=C Transmittance intensity	
Type A	0.99
Type B	0.92