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Thermal and Mechanical Properties of Polyurethanes based on Novel Chain Extender

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1. INTRODUCTION

Most segmented polyurethanes are prepared from a two-step method where the polyol is end-capped with an excess of diisocyanate, followed by chain extension with stoichiometric amount of chain extender. In the final polymer the hard and soft segments tend to segregate, due to thermodynamic immiscibility and the differences in chemical structure between hard and soft segments, and produce a phase separated morphology of hard segment-rich and soft segment-rich phase. Phase separation is of primary importance, since it strongly affects the properties and gives rise to the interesting and useful properties of these materials. It is desirable there is always a chance of partial phase separation, but at the phase boundaries there is always a chance of partial phase mixing.

The phenomenon of phase mixing is quite complex, and much theoretical work has been done in order to predict the behavior of the components in the mixture. One simple method of predicting phase compatibility is based on the composition of solubility parameters δ of both phases and the calculation of interaction parameter χ. DSC is a most attractive method, since it is accurate and the measurements are relatively easy. It was proposed that the degree of phase separation could be measured by the magnitude of heat capacity at T_g and the shift of the T_g's of the soft and hard segments.

In this study Polyuretanes were synthesized by two-step solution polymerization with BHPP chain extender. Phase separation was studied by the theoretical assessment and thermal and dynamic mechanical properties were investigated.

2. EXPERIMENT

Materials

4,4-diphenylmethane diisocyanate (MDI, Aldrich) and polytetramethylene glycols(PTMG, MW=2000, 1400, 1000 and 650) supplied by Aldrich were dried overnight under vaccum before use. BHPP was dried under vaccum and used as

received without further purification. DMAc(dimethylyacetamide), Aldrich, was dried over 3Å molecular seives for 5days.

Methods

The polyurethanes were synthesized by the two-step polymerization method using DMAc as the solvent. The dried PTMG was placed in a three-necked round-bottom flask fitted with a dry nitrogen inlet, condenser and mechanical stirrer and was heated 70~80℃. MDI of excess 5% was added to the molten PTMG under nitrogen. The mixture was kept for 2 hrs. with stirring to end-cap the polyol with isocyanate. DMAc was added to the prepolymer at room temperature. A stoichiometric amount of BHPP (solution of DMAc) was then added and the reaction continued for 20hrs. at room temperature with mechanical stirring. The total concentration of Polyurethane was 30wt%. The polymer was precipitated in H2O and dried under vaccum at 70 and casted on the glass at 70℃ to yield film.

DSC measurement was carried out on a Rheometric DSC instrument in the range of -120℃ and 250℃ at a scanning rate of 20℃/min. under 20mL/min. flow of dry nitrogen as a purge gas was used on sample about 5mg. The second run was used for interpretation.

The dynamic mechanical measurement was obtained at 110 H z using Rheovibron DDV-25FP with a heating rate of 2℃/min. over a temperature range of -130℃ to 15 0℃. Film samples of 0.4 mm thick × 0.3mm wide ×20mm long were prepared.

3. RESULT AND DISCUSSION

3.1 Differential Scanning Calorimetry

DSC thermograms of the polyurethanes based on PTMG 2000 with different hard segment contents were represented in Fig.1. The soft segment glass transition is well defined around -65℃. All sample clearly show the soft segment cold crystallization and soft segment melting but not melting of hard segments. The crystallinity in the soft segment results from the highly regular and symmetrical PTMG with higher molecular weight, suggesting a high level of immiscibility between hard and soft segment and rapid crystallizability of PTMG.

It is appeared that with increasing hard segment content T_g of soft segment increase. Such deviation of T_g and broad transition are generally considered to result from partial mixing between hard and soft segment and the restriction of rotation of the soft segment linked to the hard domain.

The effect of soft segment chain length on the thermal behavior were investigated

varying the soft segment molecular weight from 1000 to 2000 at a fixed hard segment content(28wt%).(Fig.2)

The glass transition temperature of the soft segments increases with the decreasing molecular weight of the soft segments. The trends of the thermal behavior in the polyurethanes with the same composition(PTMG:MDI:BHPP = 2:3:1) are found similar.

It is Polyurethane based on PTMG 650 with hard segment content 55wt% that had a broad melting endotherm of hard segment. It is well known that polyurethane with hard segment content above 35% had detectable crystalline regions by DSC.

It is likely that chain extender BHPP inhibit crystallization of hard segment through hydrogen bond. It may be due to the less effective packing and steric hindrance of BHPP with long chain.

Finally, this indicates that the polyurethanes made from lower molecular weight PTMG and higher hard segment content have more miscibility between the hard and soft segments. The more hard segments are dispersed in the soft segments, the more restrictive the soft segments. Evidence to support this is also seen in the dynamic mechanical result.

3.2 Dynamic mechanical analysis

The storage modulus(E') of the investigated polyurethanes are given in Fig.3. Both series of samples exhibit a major relaxation(β relaxation) and one rubbery plateau corresponding to the two phase in the material. This is characterized by a significant decrease in the storage modulus and an increase in the loss modulus, which corresponds to the glass transition temperature of the soft segments. They shows that as the hard segment content increase a broadening in the β peak and an enhancement of the rubbery modulus is observed. This is due to an increase in the size and inter-connectivity of the hard segment domains as the sample has more hard segment content. The shift of β peak to higher temperature with increasing hard segment length can be attributed to a greater fraction of hard segments dissolved in the soft phase, indicating partial phase mixing between the hard and soft segment.

The temperature dependence of tan δ from the mechanical measurement is given in Fig.4. They illustrated loss peaks associated with the glass transition and damping capacity of the soft domains. The increase in the magnitude of β peak with increasing hard segment length results from the increase of amorphous regions in the hard segment. All sample display the most prominent damping peak, suggesting that they are all nearly amorphous. More phase separation can be expected as the soft segment molecular weight increase.

As the hard segment content increase and molecular weight of PTMG decrease peak of β relaxation shift to the higher temperature. The difference between the peaks of β relaxation of the soft segment is an indication of the relative number of hard blocks dissolved in the soft phase, suggesting degree of phase mixing.

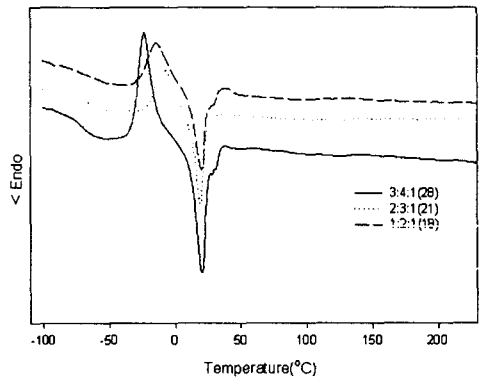

Fig.1.DSC thermograms of Polyurethanes Polyurethanes with PTMG 2000

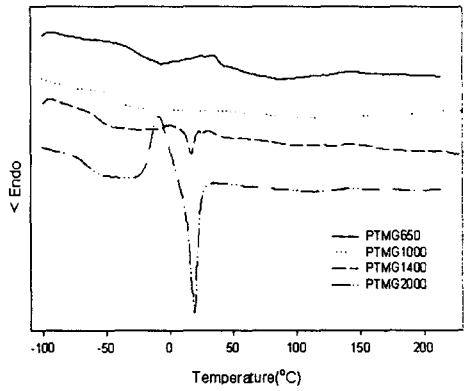

Fig.2 DSC thermograms of Polyurethanes with different MW of PTMG

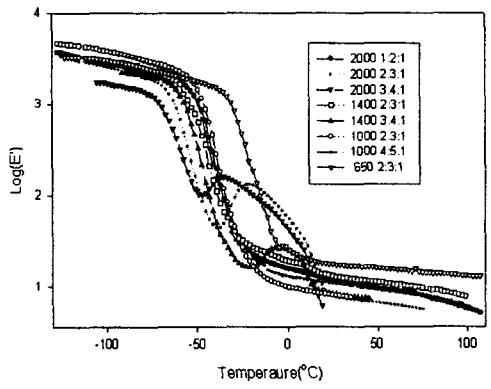

Fig.3. Storage modulus of Polyurethanes

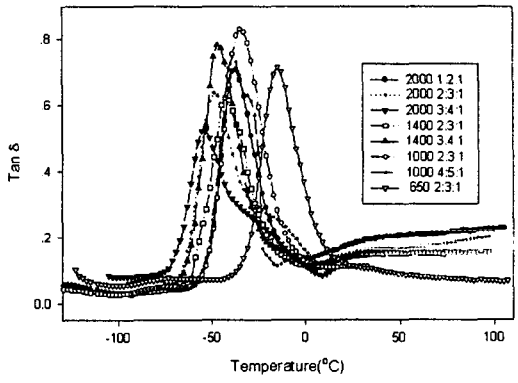

Fig.4 Tan δ as a function temp. for Polyuretnanes

4. REFERENCE

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