

Preparation and Characterization of Poly(urethane-imide) Films Prepared from Reactive Polyimide and Polyurethane Prepolymer

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ABSTRACT

A novel type of poly(urethane-imide) was obtained by a reaction of polyurethane prepolymer and soluble polyimide containing hydroxyl functional group. Cast films obtained from a blend solution of the polyurethane prepolymer and the polyimide were thermally treated at various temperatures to give a series of poly(urethane-imide)s. The obtained poly(urethane-imide) films were transparent. By changing the ratio of polyurethane and polyimide components, poly(urethane-imide) films having various properties from plastic to elastomer were prepared. Thermogravimetric analyses studies showed that the introduction of polyimide component improved the thermal stability of polyurethane.

INTRODUCTION

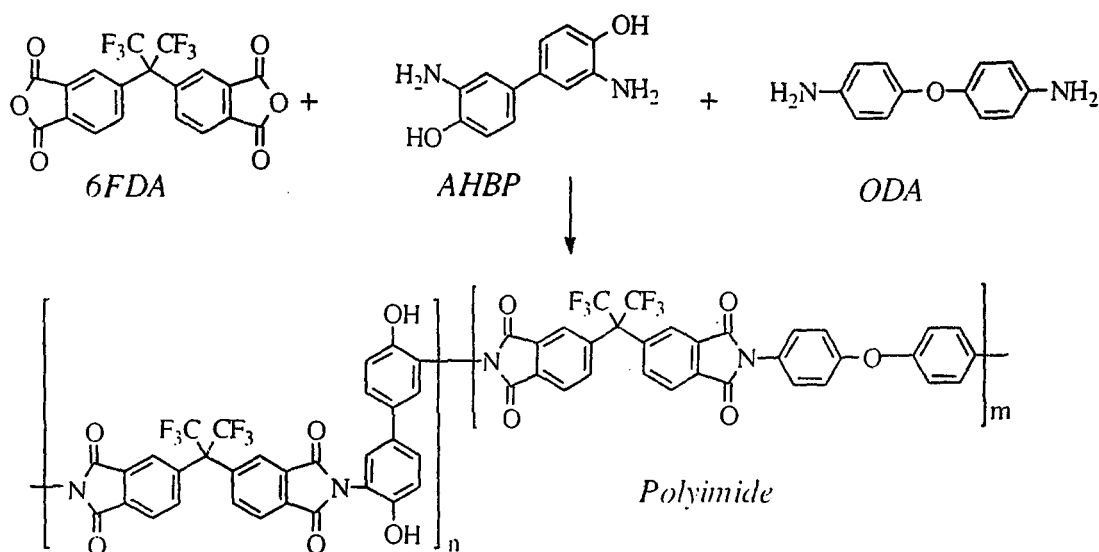
Polyurethane is becoming more and more important as engineering materials, because it has excellent abrasion resistance and properties of both elastomer and plastics. The conventional polyurethane, however, are known to exhibit poor resistance to heat. The poor heat-resistance of polyurethane limits its applications. Research focused on improving the thermal stability of polyurethane has been tried by various ways. The introduction of polyimide or oligoimide unit into polyurethane has been attempted by various approaches. Poly(urethane-imide)s obtained by reported methods are linear, which should result in poor solvent-resistance to ordinary organic solvents. Very recently, we reported a novel approach to prepare a series of poly(urethane-imide)s [1,2]. Our approach is based on the reaction of polyurethane prepolymer and poly(amide acid) which is a precursor of polyimide. The prepared poly(urethane-imide)s have network structure and showed improved thermal stability and excellent solvent-resistance. The films were elastic or plastic depending on the ratio of the two components.

In this report, we intended to prepare poly(urethane-imide)s that have well-defined structure via simple reaction. For that purpose, we examined another novel approach which is based on the reaction between terminal isocyanates in the polyurethane prepolymer and pendent hydroxyl groups in polyimides that are soluble in organic solvents.

EXPERIMENTAL

1. Preparation of polyimide

Various kinds of soluble polyimides were prepared by the reactions of equimolar amount of 2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and 3,3'-diamino-4,4'-dihydroxybiphenyl (AHBP) in NMP, as shown in Scheme 1. The content of hydroxyl groups in the polyimide was controlled by adjusting the ratio of diamine monomers, AHBP and oxydianiline (ODA) as 1:0, 2:1, 1:1 and 1:2 (in molar ratio). Here, we designated the polyimides as PI₁₀, PI₂₁, PI₁₁ and PI₁₂ to indicate the ratio of diamines. Dried powder of poly(amide acid) was imidized in vacuo at 100°C and 200°C for 1h each. Formation of polyimide with hydroxyl groups was confirmed by IR from the absorptions of the imide function at 1780, 1380, 720cm⁻¹ and hydroxyl group at 3400cm⁻¹.



Scheme 1 Preparation of polyimide

2. Preparation of polyurethane prepolymer

Polyurethane (PU) prepolymer was prepared as follows. 2,4-Tolylene diisocyanate was added into dehydrated polyethylene adipate, and reacted at 80°C for 2hrs under nitrogen atmosphere to give PU prepolymer as a viscous liquid. Phenol was added into the liquid at 80°C for 3hrs to endcap the PU prepolymer.

RESULTS AND DISCUSSION

1. Preparation of poly(urethane-imide)s

Polyimide solution and PU prepolymer solution were mixed so that the amounts of hydroxyl functional groups in the polyimide and isocyanate groups in the PU

prepolymer are equal for the stoichiometric reaction. Thus, PI₁₀, PI₂₁, PI₁₁ and PI₁₂ were mixed with PU prepolymer in the ratios of P/PU as 20/80, 25/75, 30/70 and 40/60 in NMP. They were designated as PU/PI₁₀, PU/PI₂₁, PU/PI₁₁ and PU/PI₁₂. All the blend solutions were clear and transparent. The blend solutions were cast on a glass plate, and dried under vacuum at 50°C for 16 hr, followed by thermal treatment at 100°C and 200°C for 1 hr each. After drying, the cast films became opaque which means phase separation. But, the films became transparent after heat treatment at 100°C or 200°C.

The reaction between PU prepolymer and polyimide occurs at the interface of the separated phase. The progress of the reaction was followed from the IR of the cast films. After 200°C treatment, the absorption of hydroxyl groups in the polyimide disappeared and new absorptions appeared at 3340 and 1740cm⁻¹, which shows the formation of urethane linkage.

2. Solvent-resistance of the poly(urethane-imide)s

Solvent-resistance of the poly(urethane-imide) films was investigated. The films were immersed into various solvents as hexane, toluene, dichloromethane, acetone, THF and NMP for one week. All the polyimides used as one component were soluble in such solvents as THF and NMP, partially in acetone. As shown in Table 1, all the poly(urethane-imide) films did not change at all in hexane and toluene, but swelled in dichloromethane, acetone, THF and NMP. The only exception is PU/PI₁₂, which dissolved in NMP due to the low crosslink density. Therefore, it was shown that the poly(urethane-imide) films prepared by our method has excellent solvent-resistance.

Table 1 Solubility of polyimide and poly(urethane-imide)s.

Solvent	Solubility			
	PU/PI ₁₀	PU/PI ₂₁	PU/PI ₁₁	PU/PI ₁₂
Hexane	×	×	×	×
Toluene	×	×	×	×
Dichloromethane	◇	◇	◇	◇
Acetone	◇	◇	◇	◇
THF	◇	◇	◇	◇
NMP	◇	◇	◇	○

× insoluble; ◇ swelling; △ partially soluble; ○ soluble.

3. Tensile properties of poly(urethane-imide) films

Tensile properties of polyimides with various content of hydroxyl groups were examined. All the polyimides containing hydroxyl groups had higher tensile modulus (3.0~3.5 GPa) than 6FDA/ODA (1.9 GPa). Modulus increased with the increase of hydroxyl content. The rigidity of polyimide molecules depending on the ratio of

AHBP and ODA is the cause of the difference.

When polyimides with different amount of hydroxyl groups were used as polyimide component, poly(urethane-imide) films showed various properties. For example, the films were plastic for PU/PI₁₂, PU/PI₂₁ and PU/PI₁₀ and moduli for PU/PI₁₂, PU/PI₂₁ and PU/PI₁₀ were 297, 205 and 118 MPa. The film for PU/PI₁₁ was elastic and showed properties of elastomer. Elongation was more than 270% and it almost returned to original after break. The modulus of PU/PI₁₁ was 11.6 MPa, much lower than other poly(urethane-imide)s and stress-strain curve showed the pattern of a typical elastomer.

4. Viscoelastic properties of poly(urethane-imide) films

Viscoelastic analysis of the poly(urethane-imide) showed that T_g of the films were in the range of -8°C ~ 21°C depending on the PU component, and that T_g shifted to lower temperatures with the increase of PU component, as shown in Fig. 1. This suggests miscibility between PU and polyimide to some extent.

5. Thermal stability of poly(urethane-imide)s

TGA for poly(urethane-imide)s showed that the initial decomposition temperatures (5% weight loss) was about 260°C. The decomposition temperature did not change so much with the content of polyimide component. Conventional PUs are known to decompose at ca. 220°C. This indicates that the heat resistance of PU was improved by the introduction of polyimide.

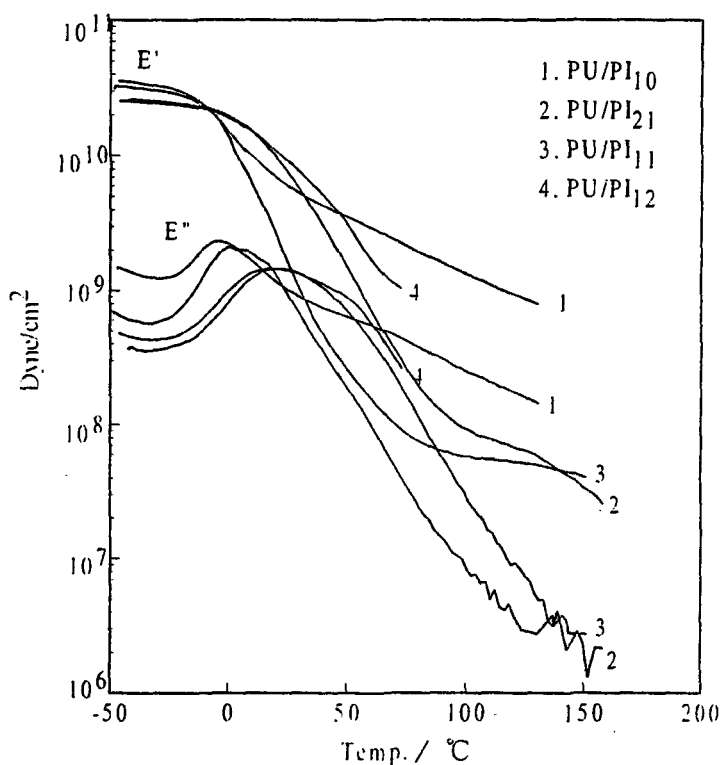


Fig. 1 Viscoelastic Analysis of Poly(urethane-imide)s

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2. M. Zuo, Q. Xiang and T. Takeichi, *Polymer*, in press.