

PREPARATION AND PROPERTIES OF POLY(URETHANE-IMIDE)

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ABSTRACT

Polymer blend consisting of polyimide (PI) and polyurethane (PU) was prepared by means of a novel approach. PU prepolymer was prepared by the reaction of polyester polyol and 2,4-toluenediisocyanate (2,4-TDI), and then end-capped with phenol. The prepolymer was blended with polyamide acid solution at room temperature in various weight ratios. The cast films were obtained from the blend solution and treated at various temperatures. The reaction between the two polymers and thermal stability of the blend films were measured by DSC and thermogravimetric analyses. Tensile measurement and viscoelastic analyses of the blend films showed that the films changed from plastic to brittle, then to elastic with the increase of polyurethane component.

INTRODUCTION

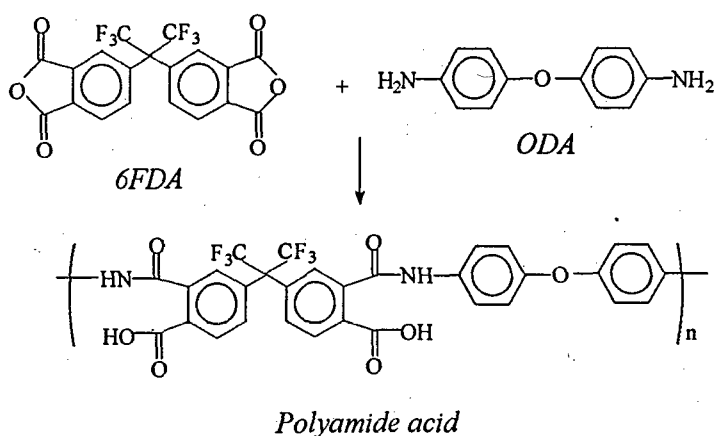
Polyurethanes and polyimides are two major kinds of polymer materials which are used in industries for high performance applications. Polyimides are an important class of heterocyclic polymers with remarkable heat-resistance and superior mechanical, electrical, and durable properties. Because of poor heat-resistance of polyurethane, its applications were limited. Introducing polyimide into polyurethane can improve the heat-resistance of polyurethane. It was reported that poly(urethane-imide)s were prepared by the intermolecular Diels-Alder (DA) reaction of 4-methyl-1,3-phenylenebis(2-furanylcarbamate) with various bismaleimides¹⁾, and that polyurethane prepolymer endcapped by isocyanate was reacted with dianhydride to prepare polyurethane having imide group in the backbone²⁾.

Here, we report a novel approach to prepare poly(urethane-imide) which is based on the reaction of polyurethane prepolymer and polyamide acid. Cast films were obtained, and the films were characterized by IR, DSC, TGA, viscoelastic analyses and tensile measurement.

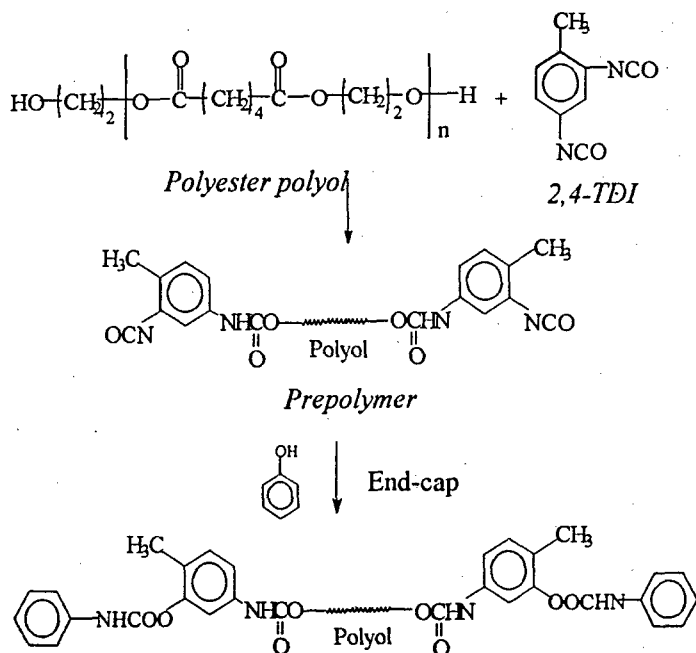
EXPERIMENTAL

Preparation of polyamide acid and prepolymer (Scheme 1)

Polyamide acid was prepared by the reaction of 2,2'-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) and oxydianiline (ODA) in N-methyl-2-pyrrolidone (NMP).



Polyurethane prepolymer was prepared by the reaction of toluene-2,4-diisocyanate (TDI) and polyethylene adipate (L-4002) at 80°C for 2hrs under nitrogen atmosphere. Finally, prepolymer was endcapped by phenol.



Preparation of the blend solutions and cast films

Polyamide acid and prepolymer were mixed in various weight ratios. The blend solutions were cast on a glass plate, then solvent (NMP) was evaporated under vacuum at 50°C for 16 hrs. The cast films were thermally treated at 100°C and 200°C for 1 hr, respectively.

Scheme 1. preparation of polyamide acid and prepolymer.

Measurements

Dynamic viscoelastic measurement was carried out with a Rhevibron Model DDV-01FP from -50°C to 400°C. Differential scanning calorimetry (DSC) was performed with a Rigaku Thermal Analysis Station, TAS 100, equipped with a DSC cell base at a heating rate of 10°C/min under nitrogen atmosphere. Thermogravimetric analyses (TGA) were carried out with a SEIKO I TG/DTA 300, at a heating rate of 5°C/min under Ar. Tensile properties were investigated using a IMADA Seisaku-sho Model SV-3 at room temperature.

RESULTS AND DISCUSSION

Preparation of the blend solution of polyamide acid and polyurethane prepolymer

Polyurethane prepolymer was mixed with polyamide acid solution in NMP. All the blend solutions were clear and transparent in any weight ratios. After drying, the cast films became opaque which means phase separation. After heat treatment, the cast films became transparent for PI/PU 1/9. But others still remained opaque.

Tensile properties of poly(urethane-imide)

Tensile properties of poly(urethane-imide) in various ratios are shown in Table 1. The modulus for pure polyimide treated at 200°C was 1.37GPa. With the increasing of polyurethane prepolymer ratio, the modulus decreased greatly and properties of films changed from plastic to brittle (PI/PU ratio at 5/5), then elastic (PI/PU ratio at 1/9). It is clearly shown in Fig. 1 that the film has become typical elastomer at PI/PU ratio of 1/9.

Viscoelastic properties of poly(urethane-imide)

The viscoelastic analysis showed glass transition temperature (T_g) at 320°C for pure 6FDA/ODA polyimide treated at 200°C. As shown in Fig. 2, T_g for poly(urethane-imide) film at PI/PU ratio of 1/9 was found at -25°C from E'' and 10°C from $\tan \delta$. At around T_g , modulus decreased greatly, and film behaves as elastomer up to above 200°C.

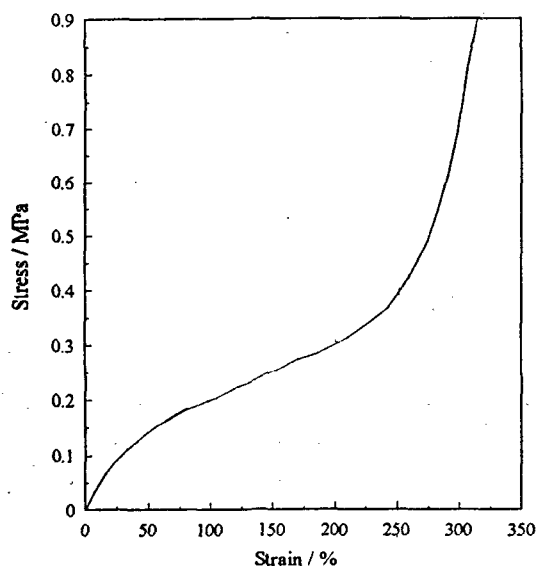


Fig. 1 Tensile properties of 6FDA/ODA-PU (1:9) film treated at 200°C

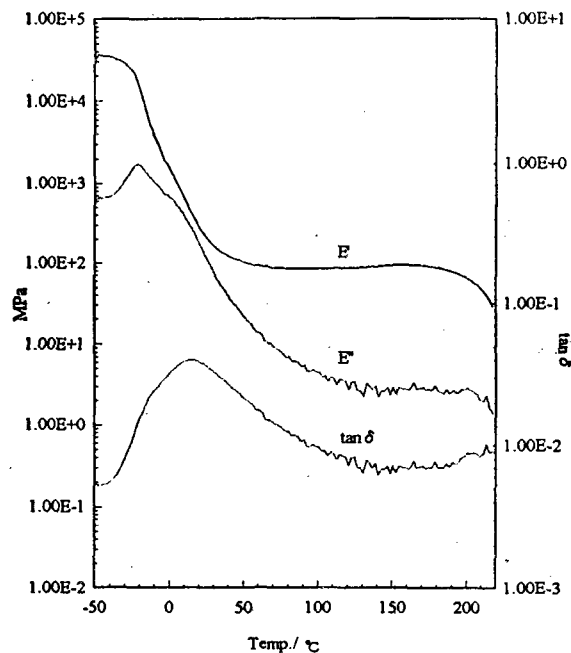


Fig. 2 Viscoelastic analysis of 6FDA/ODA-PU (1:9) film treated at 200°C

Table 1. Tensile properties of poly(urethane-imide).

PI/PU ratio	E (GPa)	σ (MPa)	Elongation (%)	
10/0	1.37	42.4	3.4	plastic
9/1	0.29	9.7	11.2	plastic
7/3	0.24	3.3	4.4	plastic
5/5	0.15	2.5	4.0	brittle
1/9	0.034	0.9	315	elastic

Thermal properties of poly(urethane-imide)

TGA of poly(urethane-imide) are shown in Figure 3. The TGA data show that the film for PI/PU ratio of 1/9 exhibited 5% weight loss at 290°C, which is 40°C higher than that of pure polyurethane. It is considered that heat resistance of polyurethane was improved by the introduction of polyimide. Films of other ratio showed the same tendency. These results were in good agreement with the decomposition temperatures observed by DSC.

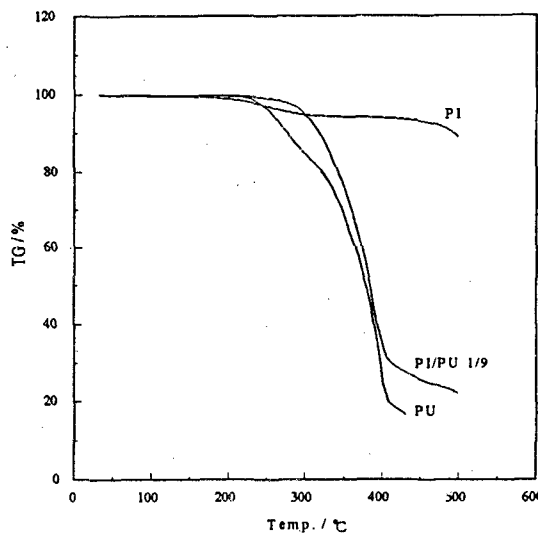


Fig. 3 TG curves of the 6FDA/ODA-PU films treated at 200 °C

CONCLUSIONS

- A series of blend of polyimide and polyurethane were prepared by mixing polyamide acid and polyurethane prepolymer solutions.
- Properties of poly(urethane-imide) changed from plastic to brittle, then to elastic with the increase of polyurethane component. Elastic modulus could be lowered significantly if the ratio of polyamide acid was lowered to less than 20%, depending on the ratio of NCO/OH in polyurethane prepolymer.
- Inclusion of polyimide between 10% and 20% improved decomposition temperature of polyurethane for more than 40°C.

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