NEW POLYIMIDES CONTAINING CARBONYL AND ETHER GROUPS IN BACKBONE

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ABSTRACT

Several aromatic diamines containing carbonyl and ether connecting groups between benzene rings were prepared from the reaction of nitrobenzoic acid chlorides with diphenyl ether and isophthalic acid chloride and the reduction of these dinitrocompounds. The polyimides resulted from the reaction of 4,4'-bis(3-aminobenzoyl)diphenyl ether **1** with PMDA, BTDA and ODPA provided transparent orange to yellow films with excellent tensile properties, exceptional resistance to solvents and strong base, and high thermooxidative stability. Glass transition temperature ranged between 205 and 273°C. The polyimide BTDA/**1** provided excellent strength for joining aluminium to aluminium and copper to copper.

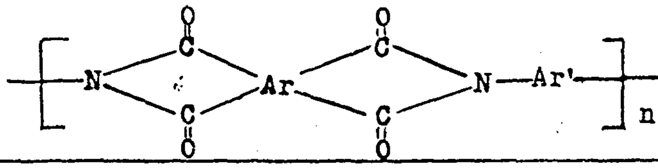
INTRODUCTION

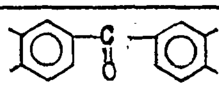
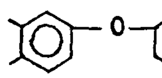
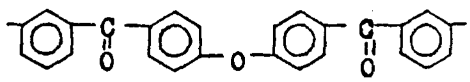
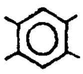
P. M. Hergenrother et al [1-3] had synthesized several aromatic diamines containing carbonyl and ether connecting groups between benzene rings. The polyimides prepared by the reaction of these diamines with dianhydrides have a strong tendency toward crystalline order, so they display some spectacular performances. Recrystallization of these crude diamines was difficult and the starting material for synthesis of them might to be very expensive. Our effort was to intend to synthesize some new similarities which can be pushed to commercial application.

SYNTHESIS

These new diamines ($(4\text{-}ArCOC_6H_4)_2O$ $Ar=3\text{-}H_2NC_6H_4$ **1**; $4\text{-}H_2NC_6H_4$, **2**; $3\text{-}H_2NC_6H_4$ and $4'\text{-}H_2NC_6H_4$, **3**. $1,3\text{-}(4,4'\text{-}ArCOC_6H_4OC_6H_4CO)_2C_6H_4$ $Ar=3\text{-}H_2NC_6H_4$, **4**; $4\text{-}H_2NC_6H_4$, **5**) were synthesized by the reaction of nitrobenzoic acid chlorides with diphenyl ether and isophthalic acid chloride, and the reduction of these dinitrocompounds. Yields of diamine were good. Recrystallization of **1** and **3** was very easy, but unnecessary. The polyamide acids were prepared by the addition of the dianhydrides PMDA, BTDA, ODPA and BPDA to DMAc solutions of diamines and the reactants were stirred for about 10 h under nitrogen at 15°C. The inherent viscosity of these polyamic acids are presented in Table 1.

Table 1, Polyimides Containing Carbonyl and Ether Groups



Polyimides Designation	Ar	Ar'	PAA η_{inh} (dL/g)	PI Tg(°C)
BTDA/1			1.2	239
ODPA/1			0.63	224
PMDA/1			1.1	273.5

FILMS

Polyamide acid films on plate glass were thermally cyclodehydrated to form the polyimide by stage heating to 300 or 350°C. The polyimide films resulted from the reaction of dianhydrides ODPA, BTDA, BFDA and PMDA with 1 or 3 were yellow to orange, tough, flexible and transparent Glass transition temperature (Tg) as determined by DSC on the cured films are listed in Table 1. A transparent orange film of the BTDA/1 polyimide provided tensile strength of 131.5 MPa, tensile modulus of 2.65 GPa and break elongation of 6~8% at 25°C. All film properties of polyimides are listed in Table 2.

Table 2, Thin Film Properties of Polyimides

Polyimide	Exposure	Tensile Strength (MPa)	Tensile Modulus (GPa)	Elongation at Break (%)
BTDA/1*	none	131.5	2.65	6~8
	30% NaOH (24 h) at 30~35°C	116.2		5
	30% NaOH (50 h) at 30~35°C	68.5		6
ODPA/1	none	117.8		7
PMDA/1	none	124.8	2.29	8
BTDA/3	none	123.5		8
BTDA/4	none	105.0		brittle
BTDA/5	none	130.8		brittle

* stage heating to 350°C

It is noteworthy that the polyimide films of 1 presented excellent property of resistance to alkali. For example, the BTDA/1 polyimide film retained 116.2 MPa after 24 h in 30% aqueous sodium hydroxide at 30~35°C, while the 4,4'-ODA/PMDA (Kapton) polyimide film was rotten.

THERMAL PROPERTIES OF POLYIMIDES

The thermogravimetric behavior of the polyimides BTDA/1 and ODPA/1 is showing in Figure 1.

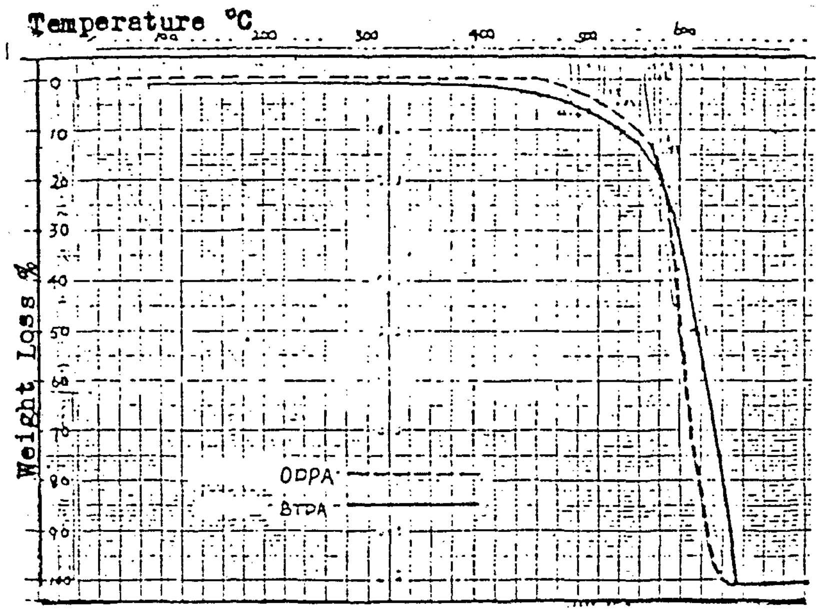


Figure 1. Thermogravimetric Analysis of Polyimides (BTDA/1= ———, ODPA/1= ------) in air

The corresponding temperatures and the weight loss after thermal degradation are listed in Table 3.

Table 3, Thermal Stability of the Polyimides*

Diamine	1				4
Dianhydride	PMDA	BTDA	ODPA	BPDA	BTDA
Initial Weight Loss (°C)	68	98	450	423	63
2% Weight Loss (°C)	450	424	486	478	400
5% Weight Loss (°C)	503		518	517	
15% Weight Loss (°C)	564		596	612	
50% Weight Loss (°C)	603		596	612	
10.3% Weight Loss (°C)	548	483	558	556	536

* in air

ADHESIVE PROPERTY

As adhesive, the coating of the precusor polyamic acid solution resulted from the reaction of BTDA with 1 can be fabricated at 200°C under 0.14 MPa pressure. The tensile shear strength for Al/Al bonding was 31 MPa. Polyamide acid solution of BTDA/1 can be filmed directly on copper foil with peel strength of more than 1.3 Kg/cm. Polyimide PMDA/1 also provided good adhesive performance.

CONCLUSIONS

Polyimides containing carbonyl and ether groups in backbone were prepared by using a variety of dianhydride and four new diamines. The potential availability of the polyimides resulted from diamines 1 and 3 can be film, moldings, composite materials, coats and adhesives.

REFERENCE

1, P. M. Hergenrother, N. T. Wakelyn and S. J. Havens, J. Polym. Sci. Part A: Polym. Chem. Ed. , 25, 1093 (1987).
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