

PROPERTIES OF POLYIMIDES CONSISTING OF BIPHENYLTETRACARBOXYLIC ACID MOIETIES AND THEIR APPLICATION

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ABSTRACT

UBE INDUSTRIES LTD. has produced biphenyltetracarboxylic dianhydride as the monomer for polyimides for about 15 years. There are two isomers, that is, 3,3',4,4'-biphenyltetracarboxylic dianhydride (*s*-BPDA) and 2,3',3,4'-biphenyltetracarboxylic dianhydride (*a*-BPDA). The polyimide particles derived from *s*-BPDA and *p*-phenylene diamine (PPD) are usefull for compression molding. However, the mechanical properties of the molding is not so high as compared with those of the corresponding film. The particles usefull for compression molding were obtained from the combination of *s*-BPDA, *a*-BPDA, and *p*-phenylenediamine (PPD). This particle had double layer structure. The flexural strength of the molding from the particles obtained from the molar ratio of *s*-BPDA/*a*-BPDA/PPD=90/10/100 was 1.6 times as high as that derived from equimollar monomers of *s*-BPDA and PPD.

INTRODUCTION

Aromatic polyimides are known as high heat resistant and high performance polymers. However, because of their poor solubility and difficulty fusible properties, they are usually shaped to basic materials such as film from polyamic acids solution as precursor. Polyimides are commonly synthesized from tetracarboxylic dianhydrides and diamines. UBE has produced biphenyltetracarboxylic dianhydride for about 15 years. Using this dianhydride, UBE supplies many sort of products correlated to polyimide such as film, varnish, coating agent, molding, etc.

UBE makes biphenyltetracarboxylic dianhydride utilizing oxidative coupling reaction of dimethyl-*o*-phthalate catalyzed by palladium compound¹⁾. There are two isomers in the final products, that is, 3,3',4,4'-biphenyltetracarboxylic dianhydride (*s*-BPDA) and 2,3',3,4'-biphenyltetracarboxylic dianhydride (*a*-BPDA). The monomer of *s*-BPDA is now commercially available. Polyimides derived from *s*-BPDA have been widely investigated. On the other hand, investigation of the polyimides using *a*-

BPDA is scarcely known. The properties of polyimides derived from *a*-BPDA are not so similar to those from *s*-BPDA. In the present study, we reveal the difference of properties between polyimides derived from *s*-BPDA and *a*-BPDA, and show the polyimide particles useful for compression molding as an example of practical use of *a*-BPDA.

EXPERIMENTAL

3,3',4,4'-Biphenyltetracarboxylic dianhydride (*s*-BPDA), 2,3',3,4'-biphenyltetracarboxylic dianhydride (*a*-BPDA), *p*-phenylenediamine (PPD), 4,4'-diaminodiphenyl ether (DADE), 2,2-bis(4-aminophenoxyphenyl)propane (BAPP), 1,3-bis(4-aminophenoxy)benzene (TPE-R) and hexamethylenediamine (HMDA) were used in the present study. The purity was at least 99% for all the monomers. The structures of these monomers are shown in Fig. 1.

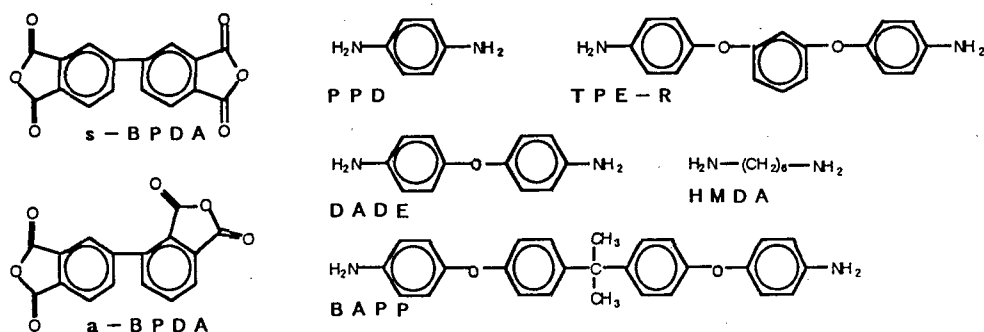


Fig. 1. Monomers used in the present study.

Polyimide films were obtained by casting method using the corresponding polyamic acid solutions. These films were finally treated at 350°C for 30 min. The thickness of the films was usually 25 μm. Polyamic acid solutions (concentration : 10-20 wt%) were obtained by the polyaddition of equimolar amounts of dianhydrides and diamines in the polar solvent such as *N*-methyl-2-pyrrolidone (NMP). Polyimide particles were obtained by heating polyamic acid solutions at 160-200°C for at least 3 hours.

RESULTS AND DISCUSSION

Properties of Polyimide Films The properties of polyimide films derived from *s*-BPDA and *a*-BPDA are indicated in Table 1. Hereafter, the polyimide having *s*-BPDA moiety is abbreviated as PI-*s*-BPDA and that derived from *a*-BPDA is abbreviated as PI-*a*-BPDA. From the reason that *a*-BPDA has the asymmetric structure, PI-*a*-BPDA have relatively higher solubility for polar solvent such as NMP

as compared with PI-*s*-BPDA. The glass transition temperature of PI-*a*-BPDA is always higher than that of PI-*s*-BPDA in the case that the same diamines are employed. Since the PI-*a*-BPDA films usually fuse together at above glass transition temperature, those have the nature similar to thermoplastic polymers. On the other hand, the mechanical properties of PI-*s*-BPDA are superior than those of PI-*a*-BPDA. The polyimide consisting *s*-BPDA and PPD moieties has the highest tensile modulus and thermal stability. This polyimide film is commercially available as UPILEX S. The polyimide film derived from *s*-BPDA and DADE is also produced as UPILEX R. The films of PI-*a*-BPDA do not have so high performance.

Table 1 Properties of polyimide films

Polyimide (abbreviation)	T _g (°C)	T _m (°C)	T _d ^{3%} (°C)	solubility in NMP	Tensile Modulus Kg/mm ²	Tensile Strength, Yield Kg/mm ²
<i>s</i> -BPDA/PPD	(380-400)	—	600	insoluble	900	40 ^b
<i>s</i> -BPDA/DADE	285	(460)	550	insoluble	350	13.5 (25°)
<i>s</i> -BPDA/BAPP	246	—	495	slightly soluble	280	11.5
<i>s</i> -BPDA/TPE-R	230	(396)	530	insoluble	370	11.5
<i>s</i> -BPDA/HMDA ^a	145	340	485	insoluble	—	—
<i>a</i> -BPDA/PPD	—	—	600	insoluble	brittle	brittle
<i>a</i> -BPDA/DADE	330	—	550	slightly soluble	280	11.5
<i>a</i> -BPDA/BAPP	267	—	495	soluble	230	11.0
<i>a</i> -BPDA/TPE-R	250	—	530	soluble	270	11.5
<i>a</i> -BPDA/HMDA	150	—	485	soluble	190	7.5

T_g: glass transition temperature measured by DSC. T_m: melting point determined by DSC. T_d^{3%}: temperature at that 3% weight loss occurs. a; taken from Imai et al². b and c; ultimate

Polyimide particle Polyimide particles useful for compression molding are obtained by heating polyamic acid solutions at 150-200°C. Polyimide moldings are available from Du Pont (VESPEL) and UBE (Upimol). They are heat stable compounds and have high heat distortion temperature³. Recently the morphology and structure of polyimide particles obtained by the thermal imidization are investigated⁴. The molding of *s*-BPDA/PPD particles (Upimol S) has the highest heat resistance and stiffness. However, the tensile strength of Upimol S is not so high as compared with the corresponding film property. In general, it is desired that the crystallinity of the particles utilizing for moldings is relatively low⁵. The crystallinity of copolymers usually decreases as compared with the homopolymers.

In order to decrease the crystallinity, the copolymerization of *s*-BPDA, *a*-BPDA and PPD was carried out. The ratios of *a*-BPDA to the total dianhydride components were varied from 0.02 to 0.15. The results of polymerization are shown in Table 2. The crystallinity of the particles decreases with increasing *a*-BPDA component. The molecular weight of the particles was not so affected by the amounts of *a*-BPDA. The SEM photographs of the particles are shown in Fig 1. The morphology of *s*-BPDA/PPD particles (particle S) looks like a coral reef that is similar to a spherulite of the polymer. On the other hand, The morphology of the particles having *a*-BPDA moiety (particle SA-10) looks like a coral reef covered by a thin veil. The TEM

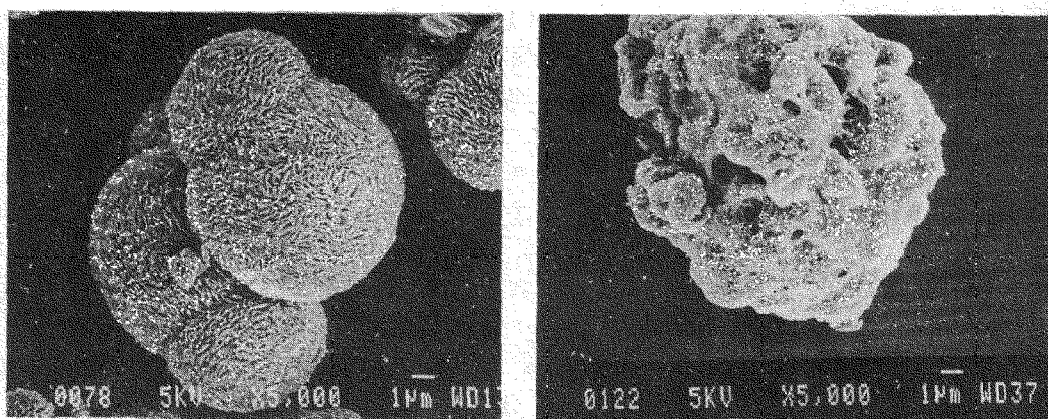
photographs of the particles are shown in Fig. 2. The crystallite of particle S seems to grow in a radial manner. The morphology of inner region of particle SA-10 is similar to that of particle S. Therefore, the major element of the inner region of particle SA-10 seems to be *s*-BPDA/PPD homopolymer. The surface region of particle SA-10 is regarded as *a*-BPDA/PPD homopolymer. Similar results were obtained for the series of SA particles. It is suggested that the particles consisting *s*-BPDA, *a*-BPDA and PPD moieties are not random copolymers, and that they have double layer structure.

Table 2 Characteristics of polyimide particles and their moldings

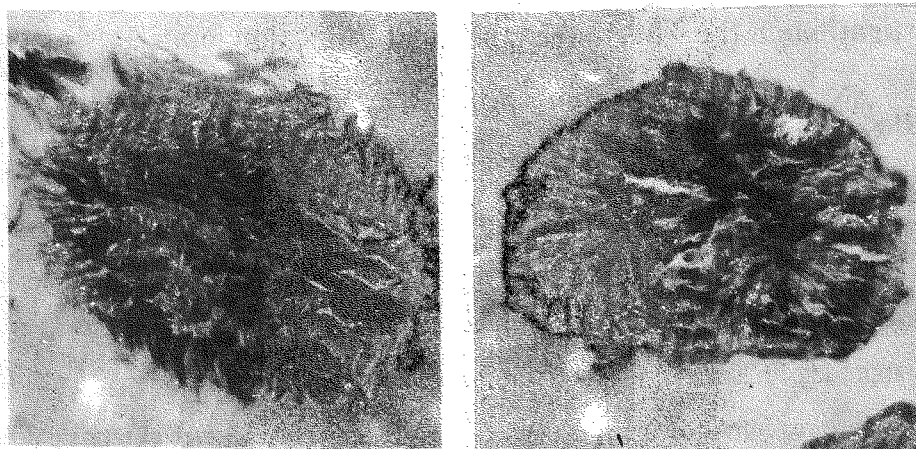
molar ratio (abbreviation)	diameter ^{a)}	inherent viscosity ^{b)}	crystallinity ^{c)}	flexural strength
<i>s</i> -BPDA: <i>a</i> -BPDA:PPD	μm	η_{inh}	%	Kgf/cm ²
100: 0:100 (S)	5-9	0.65	37.3	1040
98: 2:100 (SA-2)	5-8	0.62	36.1	1200
95: 5:100 (SA-5)	5-8	0.63	35.0	1500
90:10:100 (SA-10)	5-8	0.62	32.6	1730
85:15:100 (SA-15)	5-8	0.63	28.1	1570

All the polyimide particles were obtained in the same condition. a); determined by TEM measurement. b); sulfonic acid solution. (concentration; 0.5g/dl). c); measured by WAXS and analysed by Ruland method.

It is mentioned that PI-*a*-BPDA usually fuse together at above glass transition temperature. Since the particles of SA series seem to be covered by PI-*a*-BPDA, it is expected that the properties of molding of particle SA are superior to those of particle S. The mechanical properties of the moldings are also shown in Table 2. They were shaped by compression molding at 460°C. The properties of the molding derived from particles S are same as those of Upimal S. The flexural strength of the moldings indicates steep increase as the fraction of *a*-BPDA moiety in the starting particles increasing. These results are owing to the nature of PI-*a*-BPDA.



S SA-10
Fig.1. SEM photographs of S and SA-10 particles.



S

SA-10

Fig.2. TEM photographs of S and SA-10 particles.

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