

Thermal Dynamic Relaxation of an Aromatic Polyimide Based on Methyl-Substituted Benzidine

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Abstract

Two isomers of methyl-substituted Benzidine [o-tolidine (OTOL) and 2,2'-dimethylbenzidine (DMB)] were used to investigate how the methyl substituent position on Benzidine affect the dynamic mechanical properties of polyimides. From this result, the β -transition might be attributed to the motion of imide ring, which is affected by the steric hindrance of the bond rotation between the phenylene ring and imide ring, and the flexural modulus of polyimide are proportional to the activation energy of β transition.

Introduction

Aromatic polyimides have been widely used in high performance applications due to their excellent mechanical properties along with high thermal and thermo-oxidative stabilities. It has been reported that most polyimide and copolyimide exhibit three relaxation processes (α , β and γ processes) in their dynamic mechanical and dielectric behaviors. However, the origin of β relaxation process in polyimide recently still has received a considerable interest for many researchers. An early report indicated that the relaxation in PMDA-ODA is attributed to crystalline interplane slippage which is the mechanism of loss behavior in graphite^[1]. This mechanism was proposed because the β relaxation process was observed in oriented film and not observed in essentially unoriented molded samples. This conclusion is, however, in conflict with the crystallinity dependence of the magnitude of the β relaxation^[2,3]. Some researchers speculated that the β relaxation must be caused by the mobility of residual poly(amic acids) which remain in the incompletely imidized sample^[4-7]. However, later experimental results clearly showed that there is no direct correlation between amic acid content and the relaxation^[8,9]. Another explanation for the relaxation process was the so-called "rotational vibration"^[10-12]. It was proposed that the main type of motion is rotational vibration of small segments of a chain around quasi-equilibrium positions. Assignment of this vibration was to the motion of the phenylene and imide rings. Furthermore, it was suggested that the β relaxation involves the

mobility of phenylene groups in the diamine^[13,14]. On the other hand, the dianhydride portion of the polyimide can also affect the β relaxation process. The transition temperature of the relaxation was reported to be remarkably constant for various flexible diamines in polyimides, and decreased with the incorporation of flexible linkages in the dianhydrides^[15]. There are many factors would affect the β relaxation process in various polyimides, and sometimes they are not consistent and conflicting. For example, the factors arised from polymerization procedure like imidization process(either thermally or chemically) and curing history, which may inducing crosslinking and chain stiffening side reactions^[16].

In this study, an attempt has been made to discuss the origin of β -transition of polyimides, two isomers of methyl- substituted Benzidine [o-tolidine (OTOL) and 2,2'-dimethylbenzidine (DMB)] were used to investigate how the methyl position on Benzidine affect the dynamic mechanical properties of polyimides based on BPDA (3,3',4,4'-biphenyl tetracarboxylic dianhydride) and 6FDA(3,4-dicarboxyphenyl hexafluoropropane dianhydride). The relationship between the β relaxation and flexural modulus will also be discussed.

Experimental

General procedure for polyimide polymerization

The equivalent weight of the dianhydride (0.02 mol) was added to a diamine solution (0.02 mol) in the appropriate amount of m-cresol (15% w/w concentration) which contain isoquinoline as a catalyst at 160 °C under stirring with N₂ purge. Then, it was heated directly to reflux temperature (ca. 200°C) and maintained for 4 hours. The polymer was precipitated out and washed with 95% ethanol , and dried under reduced pressure at about 180°C to 240°C .

measurements

Seiko DMS 200 equipped with cooling tank was used to characterize dynamic mechanical properties, Tensile mode was employed in this experiment at 1Hz frequencies with the heating rate of 2°C/min. The flexural modulus measurements were carried out according to the ASTM D 790M-86. The double torsion (DT) fracture test was utilized to measure fracture energy .

Results and discussion

1. Inherent viscosity and thermal expansion behavior

As shown in table 1 , polyimides prepared from 6FDA dianhydride show less viscosity compare to these from BPDA dianhydride, it indicates that the structure of dianhydride appears to have greater effect on the viscosity of polyimide solution in NMP than that of diamine . In addition , the linear coefficient of thermal expansion(CTE) is also highly dependent of the dianhydride structure in this

system. These phenomenon are comprehensible that the energy barrier for torsional rotation within the biphenyl unit is higher than within the biphenyl hexafluoroisopropylidene unit, thus, BPDA based polyimides have low thermal expansion coefficients and high viscosity due to the linear conformation of the biphenyl skeleton of BPDA. while the polyimides based 6FDA lost linearity in the conformation of the molecular chain due to the presence of hexafluoroisopropylidene group (fig.1).

2. Dynamic mechanical relaxation

As shown in table 2, the temperature and activation energy of α -transition is higher for 6FDA based polyimides than that for BPDA based polyimides. It is clarity that the 6FDA based polyimides should has strong interaction between the polymeric chains due to the strongest electronegativity of fluorine, furthermore this results can be explained that the size of the unit in the 6FDA based polyimides moved cooperatively is probably larger than those in BPDA based polyimides, because the larger room for molecular chain motion is needed for trifluoromethyl pendant groups in 6FDA than diphenyl in BPDA. Different diamine shows no dependency on this transition for this system. However, the temperature and activation energy of β -transition were related with the structure of diamine. β -transition temperature was higher for OTOL based polyimides than that for DMB based polyimides. From this result, the β -transition might be attributed to the motion of imide ring, which is affected by the steric hindrance of the bond rotation between the phenylene ring and imide ring.

The chemical structure and torsion angles of DMB and OTOL are shown in Fig 2 . it is clearly shown that the bond rotation between imide ring and phenylene ring is less freedom for OTOL based polyimieds than that for DMB based polyimides due to the methyl substituent at 3-position on the phenylene ring of OTOL, the steric hindrance of the methyl substituent inhibits variation of ω 'torsion angles in OTOL based polyimides, so that essentially only oscillations in a range of 60° - 120° are possible⁽¹⁷⁾. Moreover, there is no direct correlation between β transition temperature and dianhydride, which suggests that dianhydride in this system would not affect much on β relaxation process.

3. β - transition and flexural modulus

The flexural modulus are the most important small-strain mechanical property. It is the key indicator of the "stiffness" or "rigidity" of specimens made from a materials. It quantifies the resistance of the specimens to mechanical deformation, in the limit of infinitesimally small deformation⁽¹⁸⁾. The flexural modulus is approximately proportional both to the strengths of the links between the atoms in a material and to the number of links per unit of cross-sectional area. (The use of the term "link" refer to the meaning including chemical bonding and physical interactions such as hydrogen bonds and van der Waals interactions.) The flexural module of polymer (i.e., the rigidities of macroscopic specimens) thus generally

increase with increasing chain stiffness and cohesive energy density. As shown on table 3, the flexural modulus of polyimide are proportional to the β transition temperature. It demonstrated that the flexural modulus of 6FDA based polyimide is decreased by incorporating DMB diamine, which showed the lower β transition temperature owing to the more freedom on chain motion between the imide ring and phenylene ring. Consequently, it can be explained that the rigidities and/ or stiffness of macroscopic polymer was decreased due to the β relaxation process of polyimides occurred in DMB/6FDA. (i.e., the motion of the links of units were inhibited by the methyl substitutes in OTOL diamine). It is reasonable that a similar relationship was also observed for the yielding stress, because the stress in uniaxial tension is roughly proportional to Young's modulus⁽¹⁷⁾.

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Table 1 Glass transition temperature and viscosity measurement of polyimides

Polyimides	* η_{inh} (dl/g)	**T _g (°C)	#CTE $\times 10^{-5}$
DMB/BPDA	9.72	328	0.19
DMB/6FDA	1.24	325	3.70
O-Tol/BPDA	6.48	310	0.74
O-Tol/6FDA	2.75	347	3.40

* η_{inh} : inherent viscosity for polyimides were measured at 0.5 wt% in p-chlorophenol at 60°C.

** T_g were measured from TMA at 15°C/min under nitrogen purge at 40 ml/min.

CTE is stand for the linear coefficient of thermal expansion .

Table 2 Dynamic mechanical properties of methyl-substituted benzidine based polyimides

Polyimides	α		β	
	ΔE (KJ/mol)	*Temp. (°C)	ΔE (KJ/mol)	Temp. (°C)
DMB/ BPDA	424	379	105	125
DMB/6FDA★	771	374	115	132
O-Tol/ BPDA	504	358	142	168
O-Tol/6FDA★	683	399	130	158

* T_g measurement was taken under 2 °C/min at 1 Hz

Table 3 Mechanical properties and fracture toughness of neat polyimides

Polyimides	E(GPa)	* σ_y (MPa)	**K _{IC} (MPa $m^{1/2}$)	G _{IC} (J/m ²)
#DMB/BPDA	-	-	-	-
DMB/6FDA	2.9	83.8	2.0	1243
#O-Tol/BPDA	-	-	-	-
O-Tol/6FDA	3.5	106.1	2.1	1130

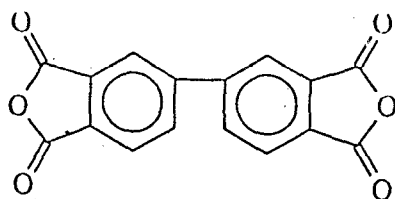
* σ_y : tensile yielding stress were performed on the Tensometer/T-10, Monsanto Co., under the crosshead speed of 5mm/min at room temperature.

** Fracture toughness were measured by using double torsion (DT) method at room temperature in compressive mode with crosshead speed 0.5mm/min.

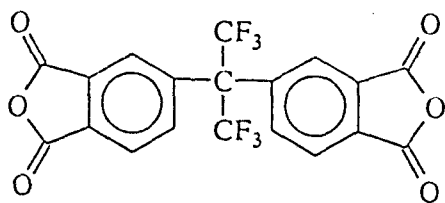
Polyimides composed of BPDA are difficult to be molded due to their high viscosity as well as poor flow ability

β 型の 2 系は、曲げ弾性率の相違が大きい。

Figure 1 The chemical structure of dianhydrides



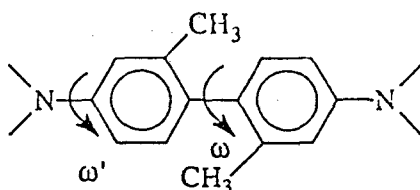
(3,3',4,4'-biphenyl tetracarboxylic dianhydride, BPDA)



(3,4-dicarboxyphenyl hexafluoropropane dianhydride, 6FDA)

Figure 2 The schematic drawing of the bond rotation for two diamine

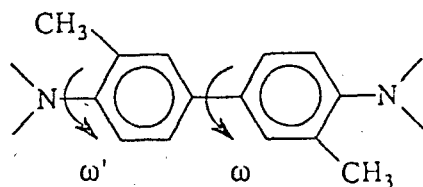
任意の
回転角に
関係.



DMB

$\omega' = 45^\circ$ $\omega = 90^\circ$
~~75°~~

(2,2'-dimethyl-4,4'-diaminobiphenyl, DMB)



O-tolidine
~~DMB~~

$\omega' = 76^\circ$ $\omega = 180^\circ$
~~44°~~

(3,3'-dimethyl-4,4'-diaminobiphenyl, O-Tolidine)