

Solution Properties and Imidization Reaction of Polyimide Precursors: Polyamide Acid, Polyamide Acid Esters.

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Abstract

Solution properties and the imidization reaction of polyimide precursors (polyamide acid, polyamide acid esters) for low thermal expansion polyimide (PI(BPDA/PDA)) were investigated. Viscosity of the polyamide acid solution in NMP is much higher than that of the polyamide esters at the same concentration. The difference in the radius of gyration of the two precursors well explains the difference in the solution viscosity. Thermal expansion coefficients (TEC) of the resulting polyimide films are strongly affected by structure of the precursors. The esters give larger TEC than the polyamide acid does. TECs of polyimide films from polyamide acid depend on imidization conditions. TECs are minimized when the films were dried at 100 C and the values increase with increasing drying temperature. Interactions between the precursors and solvent (NMP) cause large differences in properties of the precursor solution and resulting films.

1. Solution Properties of the Precursors

Fig.1 shows logarithmic plots of the concentration dependence of viscosity for polyamide acid (PAA) and polyamide acid ethyl ester (PAE) in NMP solutions. Critical concentration, i.e. the concentration polymer chains start to overlap each other, can be obtained as a cross point of tangents of the slopes. Radius of gyration and persistence length can be obtained from the critical concentration. Characteristic values obtained are listed in Table 1. Although the length of rigid segment of the precursors is the same (17A), a large difference in their correlation length is observed. The value of PAA (46A) is almost twice that of PAE. Activation energies for viscosity of PAA and PAE are 35.6 and 15.5KJ/mole, respectively. The value of PAA is more than

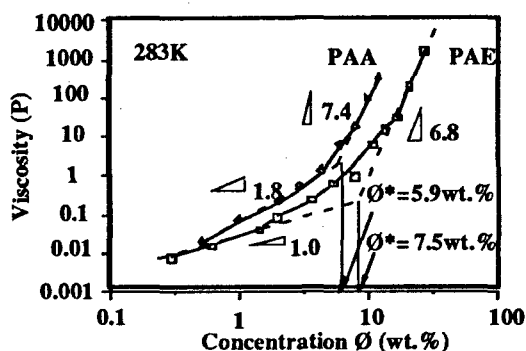


Fig. 1 Critical Concentration and Concentration Dependency of Viscosity of Precursor Solutions in NMP at 283K

Table 1 Characteristic Values of PAA and PAE

	$\langle S^{1/2} \rangle^2$		A	Mw	l_0	θ^*	n	
	(Å)	(Å)					$\theta < \theta^*$	$\theta > \theta^*$
PAA	123	109*	46	43000	17	5.9	1.8	7.4
PAE	175		26	160000	17	7.5	1.0	6.8

*: Light scattering

twice that of PAE.

A specific interaction between, NMP and carboxylic groups of PAA resulting in formation of a 1:2 molecular compound of repeating unit PAA and NMP has been reported.^{1) - 4)} The activation energy for decomposition of this molecular compound has been estimated as 109 KJ/mole. Strongly solvating NMP molecules swell the PAA chain and increase the activation energy.

2. Thermal Expansion Coefficient of Polyimide Films

Mechanical properties and TEC of PI(BPDA/PDA) films from the precursors were investigated. Difference in tensile strength and elongation at the break is not clear. The TECs of films from PAEs are much larger than those from PAA. (Table 2)

Formation of the molecular compound with NMP might affect properties of resulted films formed. Possible formation of the 1:2 compound during the imidization reaction was examined regarding its effect on TECs of the films. Fig. 2 shows imidization conditions. The spin coated precursor films are placed in an oven at each drying temperature (80, 100, 150, 200°C) for 1h and then imidization conditions are applied. Two drying temperature are below the decomposition temperature of the molecular compound (120°C) and the other two are above it. All the properties discussed in this section are for fully imidized films.

As expected, TECs of polyimide films from PAA are affected by drying temperature(Fig.3). The values are minimized when the PAA film is dried at 100°C and then increase with increasing drying temperature. TECs of polyimide films from PAE

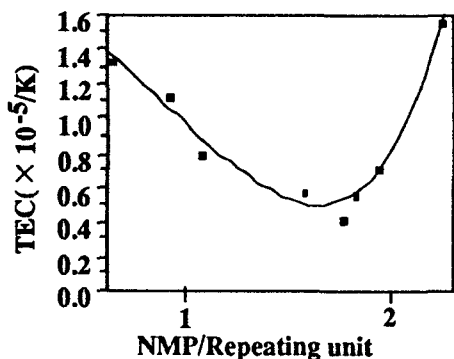


Fig.4 Effects of Residual NMP on Thermal Expansion Coefficient of PI (BPDA/PDA)

Table 2 Properties of Polyimides from Polyamide acid and Polyamide acid esters

Precursor	T.E.C. ($\times 10^{-5} K^{-1}$)	TS (MPa)	Elongation (%)
PAMe	1.8	400	20
PAEt	2.0	390	20
PAPr	2.0	360	18
PABu	2.2	370	16
PAA	0.5	400	25

PAMe:methylester, PAEt: ethylester, PAPr: propylester, PABu: butylester, PAA:Polyamide acid.TS: Tensile strength.

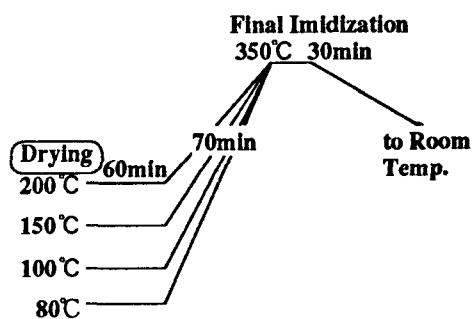


Fig. 2 Imidization Conditions

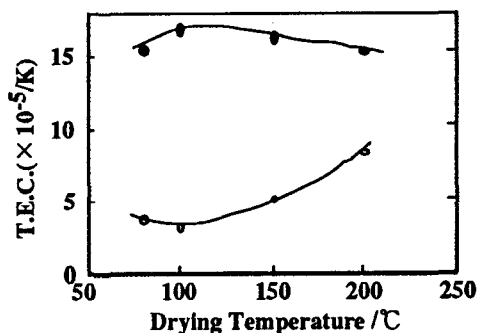


Fig. 3 Effects of Drying Temperature on Thermal Expansion Coefficient of PI(BPDA/PDA)

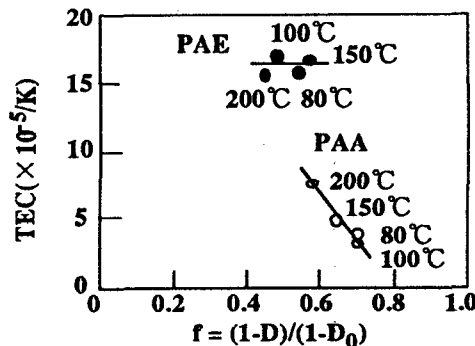


Fig.5 The In-plane Orientation Factor f Dependence of Thermal Expansion Coefficient of PI(BPDA/PDA) Films from PAA and PAE

that does not make the 1:2 compound, are not affected by drying temperature. Fig. 4 shows the importance of forming the molecular compound on TECs of polyimide films. The TEC is a minimum when PAA forms the 1:2 complex quantitatively.

Strong effects of in-plane orientation of polyimide films on TECs have been reported.⁵⁾ Fig. 5 shows the relation between the in-plane orientation factor and TECs of the films. TEC of PI(BPDA/PDA) films from PAA show a good correlation with in-plane orientation factor. But for PI(BPDA/PDA) films from PAE, no relationship appears.

Fig.6 shows the X-ray diffraction patterns of PI(BPDA/PDA) films from PAA. The diffraction peak around 20° is due to the plane distance of imide rings. Based on diffraction intensity, crystallinity of films dried at 80 and 100°C is larger than that of the film dried at 150°C. Since the position of the diffraction peak shifts slightly toward the lower angle region, a larger distance of imide ring is expected for the film dried at 150°C.

Fig. 7 shows the X-ray diffraction patterns of PI(BPDA/PDA) films from PAE. The change in diffraction intensity is small and peak positions are identical for all drying conditions.

There is a clear relation between crystal structure and TECs of the films. Films with higher crystallinity and shorter plane distance of imide rings give lower TEC.

The results of this investigation will be useful for designing low thermal expansion polyimides.

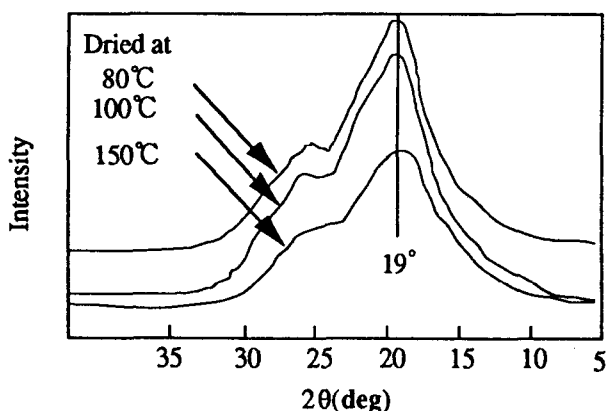


Fig.6 X-Ray Diffraction Patterns of PI(BPDA/PDA) Films from PAA

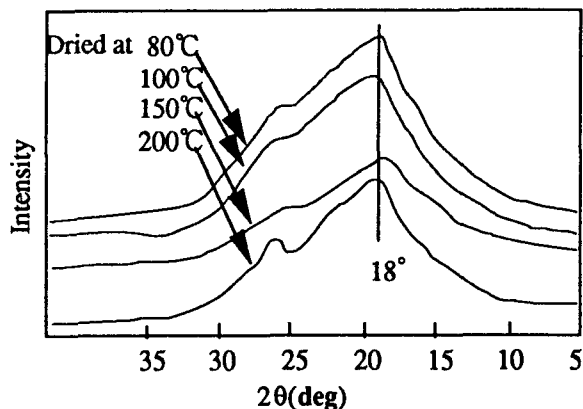


Fig.7 X-Ray Diffraction Pattern of PI(BPDA/PDA) Films from PAE

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