내열성 Polyimide 박막의 Different backbone Structures와 Photosensitive Precursor가 Water Sorption에 미치는 영향

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The Effect of Different Backbone Structures and Photosensitive Precursor on Water Sorption in High Temperature Polyimide Thin Films

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Introduction

Polyimides are formed from their corresponding various precursors: polyamic acid and photosensitive (DMAEM) or commercial photosensitive precursor . Due to volatilization of different volume by-products during curing process, the morphological structure of polyimide thin films can be changed. In addition, because of the nearness of the curing system to it's glass transition temperature, all the chain relaxation associated with volatilization may not coour. These may appear as imperfections in the stacking efficiency of the fully cured polyimide thin films. This study is to demonstrate that water diffusivity in different polyimide thin films depends on the degree to which the polyimide backbone structure can accommodate the large volume changes that occur during cure and how these processes affect the alignment or packing order of the rigid polyimide chains into perhaps a fringed micelle-like configuration[1,2].

To understand and classify these phenomena, the gravimetric technique for water diffusion kinetics in different backbone structure polyimide thin films prepared from various precursors was used. By using wide angle x-ray diffraction (WAXD) technique, the effect of different precursors on the morphology in polyimide thin films was investigated.

Experimental

The different backbone structure polyimides; poly(4,4'-oxydipheylene pyromellitimide): PMDA-ODA, Poly(p-phenylene biphenyltetracarboximide): BPDA-PDA, and Poly(4,4'-oxydipheylene benzophenonetetra carboximide): BTDA-ODA were used in the course of this work[6]. Three different amic acid precursor solutions; PMDA-ODA PAA(M_w 35,000 and 16.0 wt%), BPDA-PDA PAA(M_w 40,000 and 13.5 wt%), and BTDA-ODA PAA(M_w 40,000 and 18.0 wt%) were received from Du Pont Chemical Company. Specially, BPDA-PDA and PMDA-ODA photosensitive precursor solutions were prepared by adding a photocrosslinkable monomer, 2-(dimethylamino) ethyl methacrylate (DMAEM, Aldrich Chemical Co.), to the caboxylic acid function of the poly(amic acid) precursors through acid/amine ionic complexation. The prebaked samples were then placed in the curing oven and cured under flowing nitrogen by the following cure schedule: 150°C for 30 min, 230°C for 30 min 300°C for 30 min, and 400°C for 60 min[3,4,5].

Water sorption kinetics for cured polyimide thin films was investigated gravimetrically using a Cahn electrobalance. The experimental data are plotted with mass uptaking ratio M(t) /M(∞) as a function of $t^{0.5} L^{-1}$ (t (sec) is time, and L (cm) is thickness of film). Using Equation (1), various values of D were measured and the error between experiment and theoretical water sorption predicted from Equation (1) was minimized to produce the fitted apparent diffusion coefficient that is reported herein.

$$\frac{M(t)}{M(\infty)} = 1 - \frac{8}{\Pi^2} \Sigma \frac{1}{(2m+1)^2} \exp\left[\frac{-D(2m+1)^2 \Pi^2 t}{\lambda^2}\right] \qquad (1)$$

WAXD patterns were collected from the single polyimide films on a Rigaku CN 2155 powder diffractometer. One diffractormeter was set up for measurements in the transmission mode (i.e., reflections from lattice planes normal to the film surface) with a thin asymmetric cut (101) quartz plate monochromator bent to a section of a logarithmic spiral and located in the diffracted beam. The other was used for measurements in the reflections mode (i.e., reflections from lattice planes parallel to the film surface) with a curved graphite monochromator in the diffracted beam.

Results and Discussion

In table 1, water sorption results were given for three different polyimide films; BPDA-PDA, PMDA-ODA, and BTDA-ODA. The PMDA-ODA polyimide film exhibits high water diffusivity and high equilibrium sorption. BTDA-ODA and PMDA-ODA polyimide films are similar in their sorption characteristics. The BPDA-PDA polyimide prepared from amic acid precursor exhibits the lowest water diffusion and uptake. The corresponding value of water diffusion and water uptake in polyimide thin film were 1.4 x 10^{-10}cm^2/sec and 1.3%, respectively. It shows that BPDA group is significantly more hydrophobic (lower equilibrium water sorption) than that is the PMDA and BTDA group as shown in figure 1. However, linear structure BPDA-PDA polyimide thin film prepared from the large volume PSPI precursor showed a significantly higher diffusivity and water sorption than that does polyimide prepared from the amic acid precursor as shown in figure 2.

The morphological structure of thermally cured BPDA-PDA polyimide has been investigated by WAXD measurement. The WXAD results are shown in figures 3 and 4. The BPDA-PDA polyimide films showed three major peaks, regardless of precursor origin: (110), (200), and (210). As shown in figure 3, the peak (110) peak intensity was apparently increased by the bulky DMAEM groups, whereas the (200) peak intensity was decreased. The (200) peak was weakened in intensity by the photosensitive groups, but was not broadened in shape. This indicates slightly change in the intermolecular packing order in the resulting polyimide film prepared from PSPI (DMAEM) precursor. However, the transmission patterns were influenced by DMAEM precursor as shown in figure 4.

The WAXD patterns from the PMDA-ODA polyimide films prepared from amic acid and PSPI (DMAEM) precursors were investigated. the reflection WAXD patterns exhibit the poor intermolecular packing and irregularity in the broad halos. The comparison of the width of the broad peak indicates that the ordered chain molecules are more randomly In-Plane oriented but not vertical direction in the polyimide film prepared from PSPI (DMAEM) precursor than in the corresponding films from amic acid precursor. Comparison with water sorption kinetics of these polyimides, it shows a good agreement between morphological results and water sorption of PMDA-ODA polyimide films prepared from different precursors. In addition, the BTDA-ODA polyimides is similar to that observed for the hinged structure PMDA-ODA polyimides. The diffusivity and equilibrium water sorption is approximately the same regardless of precursor types. This suggests that BTDA-ODA polyimide is behaving more like PMDA-ODA polyimide than BPDA-PDA polyimide. It is more hydrophilic and the water is more mobile for BTDA-ODA and PMDA-ODA polyimides than that is for the BPDA-PDA polyimide.

Conclusion

Based upon our results, it shows that the semi-flexible PMDA-ODA polyimide has the ability and the chemical affinity to swell in the presence of 100 % relative humidity to the largest degree. In addition, the water diffusivity of the hinged structure PMDA-ODA polyimide is the greatest for these series of polyimides. It is significantly greater than that of BPDA-PDA polyimide. Specially, the large molecule PSPI precursor (DMAEM) distrupted the packing order in microstructure of linear structure BPDA-PDA polyimide during curing process. However, PSPI precursors did not give a significant effect on the water sortion kinetics and the morphology of hinged structure PMDA-ODA and BTDA-ODA polyimide films. With this regards, it suggest that the large molecule PSPI precursor (DMAEM) may give the increased chain mobility of polyimide films during curing process. Therefore, the hinged structure PMDA-ODA and BTDA-ODA polyimide thin films prepared from the large molecule PSPI precursor (DMAEM) might show more or less lower water difusivities than that does polyimides prepared from amic acid precursors

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Polyimide	Precousor	Thickness (micron)	Diffusivity $\times 10^{-10}$ (cm^2sec^{-1})	Equilibrium Sorption (wt %)
BPDA-PDA	Amic Acid	12.43	1.4	1.3
	PSPI (DMAEM)	13.10	5.0	1.8
PMDA-ODA	Amic acid	12.77	10.5	2.5
	PSPI (DMAEM)	11.19	8.7	2.6
BTDA-ODA	Amic Acid	12.40	10.0	2.2
	PSPI	13.65	9.0	2.6

Table 1. Designation of Polyimide Thin Film Structures and Measured Equilibrium Water Sorption and Water Diffusivity at 25°C.

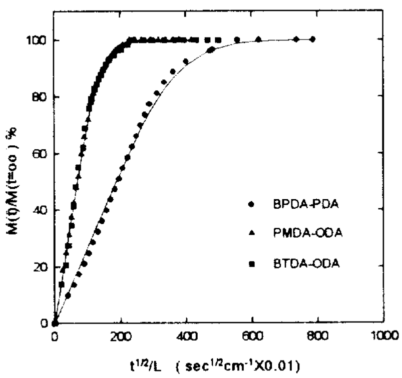

Fig 1. Dynamic Water Sorption at 100% Relative Humidity for Polyimide with Different Backbone Structure

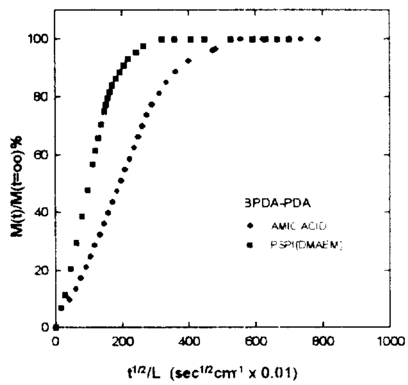

Fig 2. Dynamic Water Sorption at 100% Relative Humideity for BTDA-PDA Polyimide Prepared from Different Precursor Type