

Synthesis and Characterization of Novel Photosensitive polysiloxaneimides

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ABSTRACT

Photosensitive polysiloxaneimides(PSPI) were prepared by adding the photosensitive monomer such as hydroxyethylacrylate(HEA) to copolyisoimides, which were synthesized by the polycondensation of pyromellitic dianhydride(PMDA) with oxydianiline(ODA) and bis(p-aminophenoxy) dimethylsiloxane(APDS).

A series of photosensitive polysiloxaneimides films were prepared, the desire structure-properties relationships about thermal expansion coefficient(TEC), Thermal stability and Tg, dielectric constants and moisture absorption were also discussed.

INTRODUCTION

Polyimides have been playing an important role in the electronics industry because they retain their excellent physical properties(dielectric, mechanical, and thermal properties) at high temperature up to 450 ~ 500 °C.¹ But the patterning of nonphotosensitive polyimides is very complicated. To reduce the number of patterning steps, considerable effort has been made to develop photopatternable polyimides.²⁻⁵ Of particular interests are photosensitive polyamic acid esters pioneered by R.Rubner, et al.⁶ It has been found that there are several disadvantages, especially the molecular weight control of the polymers is difficult and the reaction process introduces chloride ions.

In this paper, we introduced an improved process for the synthesis of photosensitive siloxane-containing copolyimide precursors. A series of photosensitive polysiloxaneimides films were prepared, the desired structure-properties relationships were discussed in this article.

EXPERIMENTAL

Synthesis of Photosensitive Polysiloxaneimide(PSPI) Precursor

PMDA 0.022mol was dissolved in NMP with stirring, APDS 0.002mol in NMP was added at room temperature for 3h, then a solution of ODA 0.020mol in NMP was added at the same temperature by overnight stirring, giving a polyamic acid solution. DCC 0.044mol was added to the polyamic acid solution with stirring for 2h, giving polyisoimide solution, and then HEA 0.05mol was added dropwise to this stirred solution at 50 °C for 10h. The mixture was filtered to remove by product and the filter liquid was precipitated into deionized water

with stirring. The product was washed with deionized water repeatedly until there was no solvent in the product, then dried at room temperature under vacuum.

Five copolyimide precursors are prepared with different contents of APDS, as shown in Table 1.

Table 1 The Code Names of PSPI precursors and the Molar Ratio of ODA and APDS

Polymer Code	PSPI-1	PSPI-2	PSPI-3	PSPI-4	PSPI-5
ODA:APDS	100:0	95:5	90:10	85:15	80:20

PSPI film Preparation

PSCOPi precursors solution was coated on the glass plate and softbaked at 70°C for 10h in air. The softbaked samples were then thermally imidized in a Heraeus oven with a nitrogen flow by a step-cure process: 150°C/1h, 200°C/30min, 250°C/30min, and 300°C/30min, 350°C/30min. The ramping rate for each step was 2 °C/min and cooling rate was 1 °C/min. The thickness of cured films was 20 ~ 40 μm.

RESULTS AND DISCUSSIONS

Thermal Expansion of Coefficient(TEC)

PSPI films were run in the tensile mode on the thermal mechanical analyser(TMA) in order to determine the average thermal expansion coefficient between 30 ~ 250 °C. As shown in Table 2, the TEC increased with increasing of siloxane moiety content. It is estimated that the cause was attributed to that the siloxane is flexible.

Table 2 The Thermal Expansion Coefficient of PSPI Films

Polymer Code	PSPI-1	PSPI-2	PSPI-3	PSPI-4	PSPI-5
TEC(× 10 ⁵ .K ⁻¹)	3.7	3.9	4.24	4.63	4.80

Thermal Stability and Tg

Figure 1 shows the TGA curves for the PSCOPi films. The TGA results indicate that the decomposition temperature at weight residue 95% occur at 430 ~ 550 °C in air. Polyimides generally have good thermal stability. However, as shown in Figure 1, somewhat reduction in the thermal stability of polymer was observed with increasing siloxane content because of the Si-CH₃ groups are susceptible to thermal degradation. It is found that the more the siloxane moiety content in main chain, the worse the thermal stability of the PSPI. This is thought to be due to the introduction of flexible spacer units(O-Si-O) that are randomly distributed in the backbone of the polymer.

Table 3 gives the T_g data of PSPI films measured on a DSC. The glass transition temperature(T_g) of PSPI films decreased with increasing the content of siloxane moiety. This phenomenon was caused by two possible reasons. One is the change in molecular polarity. Since O-Si-O is a relatively weak-polar group, the interaction among the polar group of polymers would decrease with increasing the content of O-Si-O and then the molecular chains become more flexible. The another reason is the change of regularity of macromolecule. The PSPI precursor is a random copolymer composed of more than two monomers. The chains arrangement is loss due to the poor regularity of molecule, which causes the increase of free volume fraction in polymer.

Table 3 The Glass Transition Temperature(T_g)

Polymer Code	PSPI-1	PSPI-2	PSPI-3	PSPI-4	PSPI-5
$T_g(^{\circ}\text{C})$	285 $^{\circ}\text{C}$	272 $^{\circ}\text{C}$	255 $^{\circ}\text{C}$	248 $^{\circ}\text{C}$	242 $^{\circ}\text{C}$

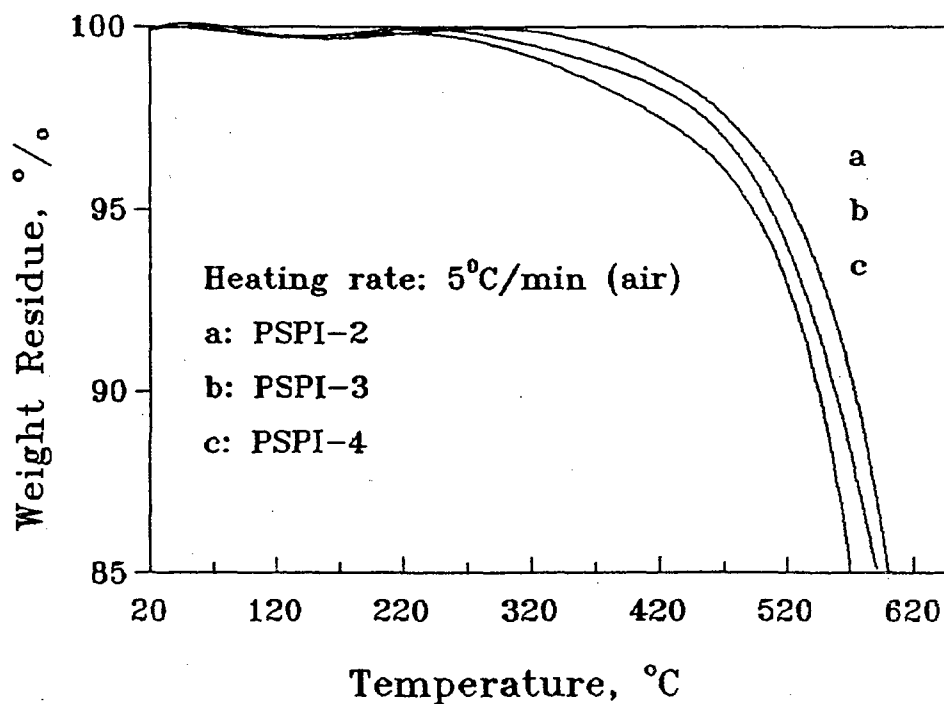


Fig. 1 TGA curves for PSPI films

Dielectric Constants

The dielectric constants (ϵ) were determined using dielectric constant detector. The measured dielectric constants values of PSPI films are listed in Table 4. It is observed that the dielectric constants reduced proportionally with the amount of siloxane content in PSPI films, it may be the result of the decrease of PSPI polarity when the siloxane groups were introduced.

Table 4 Dielectric Constant of PSPI Films Under 1KHz at room temperature

Polymer Code	PI	PSPI-1	PSPI-2	PSPI-3	PSPI-5
Dielectric Constant(ϵ)	3.80	3.69	3.08	2.78	2.49

Moisture Absorption

Figure 2 displays the moisture absorption for PSPI films by monitoring capacitance change on exposure to pre-set moisture room, the linear decrease of the moisture absorption with increasing content of randomly incorporated O-Si-O moieties. The reduction in moisture absorption is thought to be due to the introduction of the O-Si-O units that reduces the polarity of PSPI, so it decrease moisture absorption.

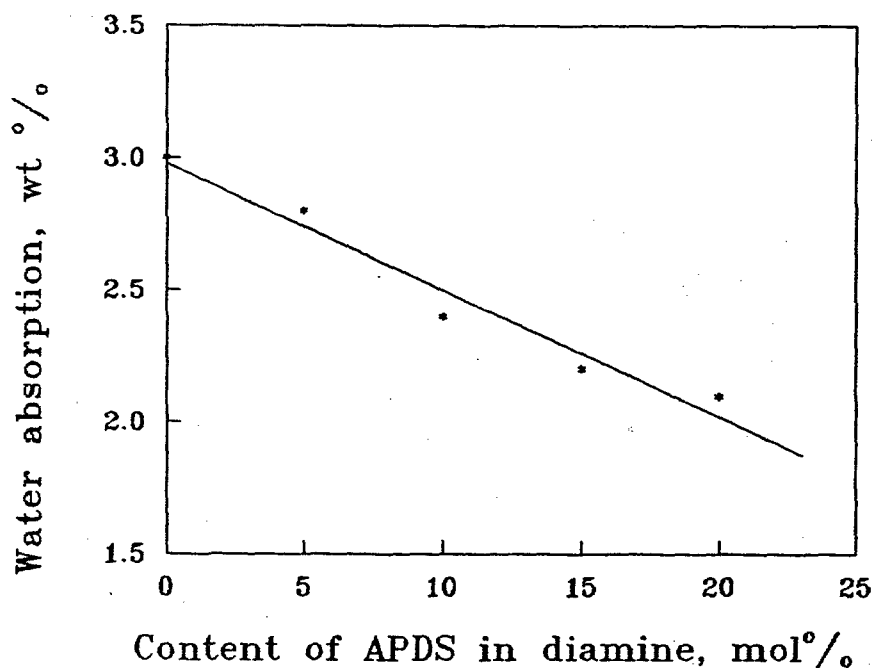


Figure 2 Moisture Absorption of PSCOPI films

Adhesion Properties

The adhesion strengths between one siloxane-free PSCOPi, four siloxane-containing PSCOPi and substrates are listed in Table 6. Substrates are Fe, Si and SiO₂ wafers.

All the samples were prepared by spin-coated on the substrate at 2000 rpm and followed by soft bake in a Haraeus oven by a step-cure process: 150 °C /30min, 200 °C /30min, 250 °C /30min, 300 °C /30min, 350 °C /30min. The heating rate for each step is 2.0 °C /min and the cooling rate is 1.0 °C/min. The thickness of cured films are 20 ~ 40 μm.

Table 5 indicates that the adhesion strength increases with the increasing siloxane moiety content. Relatively small fractions of siloxane reduces the rigidity of imidized polymer chains and plays an important role to tight connect the polymer to the substrate. From Table 5, it is also found that the SiO₂ is a better substrate than the others.

Table 5 The Adhesion of Various PSPI Films to Different Substrate

Polymer Code	PSPI-1	PSPI-2	PSPI-3	PSPI-4	PSPI-5
Fe	2	2	1	1	1
Si	2	2	2	2	1
SiO ₂	2	1	1	1	1

* The higher the grade shown in above table is, the worse the adhesion is.

CONCLUSIONS

In the present study, photosensitive copolysiloxaneimide precursors are successfully prepared from corresponding polyamic acid using DCC as a dehydrating agent to produce polyisoimide, and then photosensitive monomer HEA can be incorporated into polymer chain easily.

The thermal stability, dielectric constant and moisture absorption of siloxane-containing PSCOPi decreased with increasing siloxane moiety content.

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