A NOVEL THERMAL CURABLE IMIDE OLIGOMER FOR PWB APPLICATION

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ABSTRACT

A novel type of matrix resin; a propargylether terminated thermal curable imide oligomer consisted from Aminophenyl propargylether(APE), Bis-phenol-A bis (trimellitate)dianhydride(ESDA), BTDA, and BAPP. Tgs of 251℃, moisture absorption of 0.45%(E-96/20/65), and dielectric constant of 3.1were showed. In this presentation, a possible curing mechanism, and other various properties of neat resin/composite will be also discussed.

1.Introduction

During the last two decades, in Japan, a high temperature resistance polymer has found increased application in various field, especially for a Printed Wiring Circuite Board(PWB) in an electronics.

A promising route developed in the late 1960's involved endcapping imide oligomers with norbornene, acetylene, and maleimide group which could be thermally polymerized through olefinic unsaturation and so on.

These are well known good candidates for high temperature resistant resins. But the improvement of a water absorption and dielectric properties related to a curcuit signal delaying, are strongly demaned for next generation's high speed curcuits in microelectronics.

For these demands, the propargylether terminated esterimide oligomer has been successfully developed as a composite matrix resin which improved both of a low water absorpotion and low dielectric properties with maintaining of a high temperature resistance by using following new technics.

In this presentation, we will discuss following fields; firstly, synthesis of two new monomers and the state-of-the-art of propargylether terminated esterimide oligomer, and secondly, preparation and characterization of a glass-fiber reinforced cupper-clad composite as an application.

2.Result and Discussion.

2.1 Monomer Synthesis.

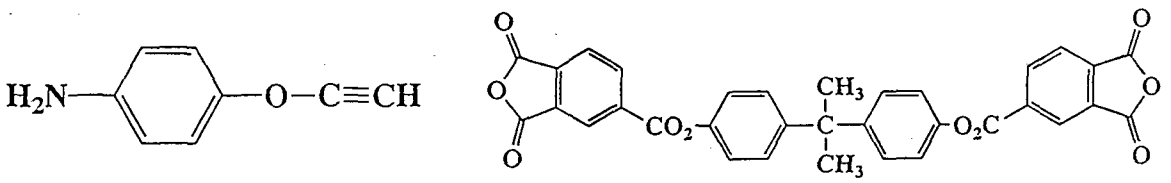
2.1.1 Aminoprenyl Propargylether(APE).

The title monomer was firstly synthesized by USSR gorup[1]. APE was synthesized by using propargyl halide with a good chemical yield.

2.1.2 Bisphenol-A Bis(trimellitate)dianhydride(ESDA).

ESDA was originally reported as a dianhydride for polyimide preparation by Loncrini[3] et al., in late 1960s. We reinvestigated ESDA as a possible dianhydride for a polyimide preparation[4].

ESDA was prepared from a trimellitic chloride(TMC) and Bisphenol-A with an excellent yield.



APE ESDA

Figure 1 Chemical structure of novel monomers

2.2 APE Terminated Esterimide Oligomer; Synthesis & Properties.

The propargylether group as an uncatalyzed thermal curing groups was firstly reported in 1988[5]. Dirlikov's group of Eastern Michigan University, has reported that dipropargyl bisphenol-A is one of certain candidates as high thermal resistant thermosets.

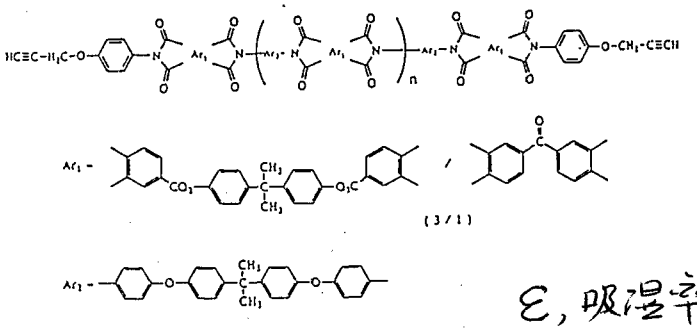
The authors has been individually investigated the possibility of propargylether group as a terminating group for a thermal curable polyimide. Then, we have been successfully developed the thermal curable propargylether terminated esterimide oligomer[6].

The oligomer was prepared from 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride(BTDA) and ESDA as a dianhydride and 2,2-bis(aminophenoxyphenyl)-1,3-dimethylpropane(BAPP) as a diamine and APE as an endcapping reagent. Properties are shown on Table 1.

DSC diagram shows that there are two exothermic peaks of 235 and 260°C . According previous reports[7], *2H*-1-benzopyran ring formation from an arylpropargylether around 220°C by an uncatalyzed reaction and subsequent polymerization were observed.

These two evidences shows that a propargylether end group of novel esterimide oligomer also has possibility of a formation of *2H* -1-benzopyran ring, and following polymerization. A possible curing mechanism will be discussed at presentation.

Table 1 Properties of the propargylether endcapped esterimide oligomer.



	Unit	condition	
Dielectric Constant; ε	-	E-24/50	3.1
		C-96/20/65	3.1
Dissipation Factor; tan δ	-	E-24/50	0.0056
		C-96/20/65	0.0074
Tm	℃		210 オリゴマー
Texo	℃		260
Td	℃		431
Tg	℃		251
△H	J/g		280
CTE; α	cm/cm/℃		4.2×10^{5}
Moisture Absorption		E-96/20/65	0.45
Flextual Strength	kg/mm²		3.0
Flextual Modulus	kg/mm²		241

2.3 Composite Application.

Three type composites were made by using different glass clothes; E-glass, T-glass, and D-glass.

Composite shows Tgs of 258℃ (DMA) and peel strengths of 1.0-1.3kg/cm at 20℃, 0.7-1.2kg/cm at 150℃, respectively.

A water absorption of 0.13-0.17% and a moisture absorption(C-96/40/90) of 0.17-0.32% are smaller than that of convensional one of 0.52, 0.79%, respectively. Figure 2 shows a water uptake percentage changing at 20℃ vs. treatment time. It shows that a water absorption of all of ours is smaller than that of convensional one and saturated under 1% within 200hrs.

All of E, T, and D-galss reinforced conposite's dielectric constants and dissipation facters at 1, 20MHz, and 2.45GHz are smaller than that of convensional one.

According above results, It was found that all our composites shows excellent properties incruding low dielectric properties and a low water absorption compared with convensional one.