

Synthesis and Characterization of Imide-Oligosiloxanes Hybrid Nanocomposite (Imide HYBRIMER) by Reaction of Nano Amine Modified Oligosiloxane and Dianhydride

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ABSTRACT

Imide-oligosiloxanes hybrid nanocomposites (Imide HYBRIMER) were synthesized and their unique structure and thermal and mechanical properties were investigated. Imide HYBRIMER was made by reaction with nano-sized amine oligosiloxane (AO) and dianhydride, where oligosiloxane moieties were cross-linked by imide bonds to form three-dimensional nanocomposite. The AO were prepared from condensation reaction with aminopropyltrimethoxysilane (APTS) and diphenylsilanediol (DPSD) under base catalysts without water and solvents. The preparation of imide HYBRIMER was completed through the thermal imidization of amic acids, which were formed by reaction with amine groups in the AO and two different kinds of dianhydrides. The imide HYBRIMER were stable up to 400°C and thermal expansion coefficients measured by thermo-mechanical analysis (TMA) were varied from 33 to 80 ppm/°C. Higher thermal stabilities and mechanical strengths could be obtained by incorporating siloxane moieties in hybrid nanocomposites. The imide HYBRIMER, which has three dimensional network, could induce very low birefringence about 0.003, which was lower than that of linear typed polyimides.

INTRODUCTION

Polyimides are attractive for use of gate dielectrics in organic thin film transistor (OTFT) because of their intrinsic thermal stability and good insulating properties [1]. Gate insulating materials for OTFT need dielectric constant modulations and photo-patternability. Inorganic-organic hybrid materials can be good way to add new functionalities to conventional polyimides. Chemically bonded polyimide-inorganic hybrid materials have been reported for microelectronic and corrosion resistant applications where the organic and inorganic phases were able to mix at the molecular level [2,3]. By incorporation of the inorganic materials such as silica, polysiloxanes and polysilsesquioxanes into the polyimide, the polyimide-inorganic hybrid can have advantageous properties, such as higher thermal stability, higher mechanical strength,

higher transparency and lower birefringence compared to conventional polyimides. There were two different approaches to synthesize polyimide-inorganic hybrid materials in view of using inorganic moieties. The first method was to make the polyimide hybrids by sol-gel process, which inorganic components can be incorporated adding a precursor of silica such as TEOS [2]. Inorganic components were generated from molecules and covalently connected with polyimides matrix. The second method was to synthesize hybrid nanocomposites which covalently bonded imide or polyimide tethers coupled with inorganic species such as polysiloxane [4] and silicates [5]. In the present study, we used the nano-sized oligosiloxanes as an inorganic component and synthesized the imide-oligosiloxanes hybrid nanocomposites (Imide-HYBRIMER), which imide chain tethers coupled with nano-sized oligosiloxanes. The oligosiloxanes were modified with amine groups, which can produce the amic acids after condensation reactions with anhydrides. In this study, the nanostructures of amine-oligosiloxanes (AO) depending on their compositions and imide HYBRIMERS made from the AO and dianhydrides were investigated. In addition, their thermal and mechanical properties and birefringences were investigated.

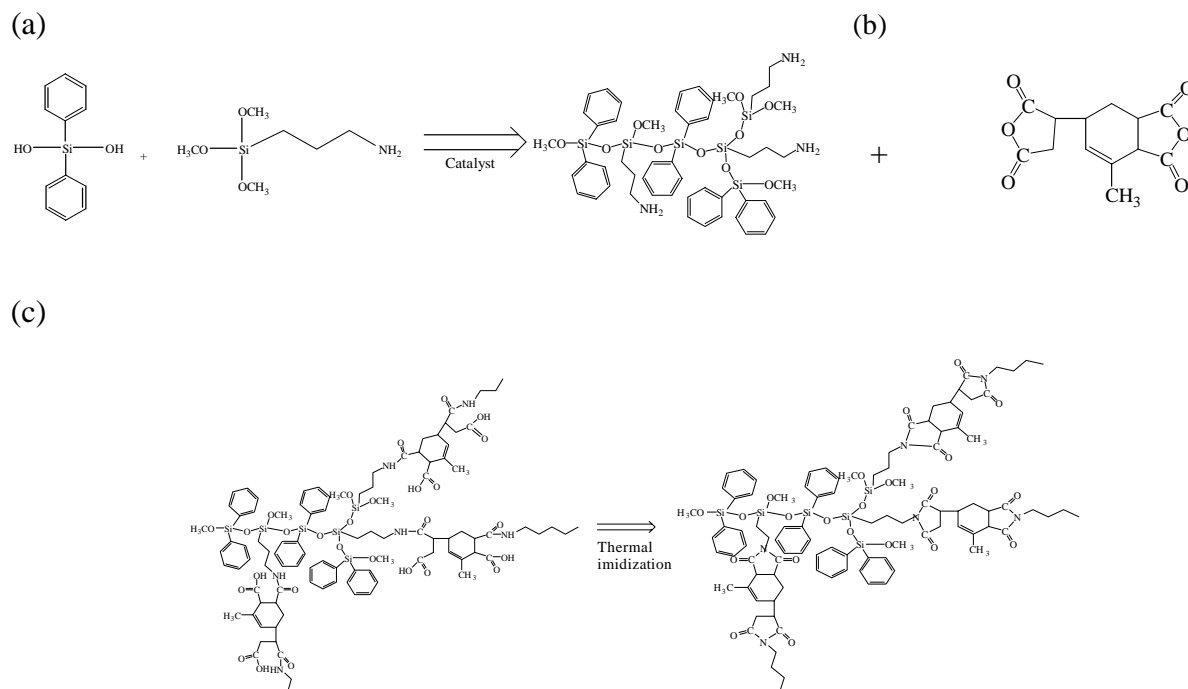


Figure 1. Synthesis scheme of the imide HYBRIMER. (a) Condensation reaction of APTS and DPSD, (b) DODCA(didanhydride) (c) Imide HYBRIMER by thermal imidization of poly(amic acid) synthesized from condensation reaction (a) and (b).

EXPERIMENT

The amine-oligosiloxane (AO) were synthesized from condensation reaction with aminopropyltrimethoxysilane (APTS) and diphenylsilanediol (DPSD) under base catalysts. Barium hydroxide monohydrate ($\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$) was used as a catalyst to promote a condensation reaction. APTS and $\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$ were mixed at 80°C , and DPSD was added to the mixture continuously for two hours to prevent self-condensation of DPSD and phase separation. The formulations and notations of the AO depending on their compositions were summarized in Table I. The sizes and molecular weights of the AO were measured by small angle neutron scatterings (SANS) and matrix-assisted laser desorption–time of flight mass spectroscopy (MALDI-TOF MS).

Imide HYBRIMER was prepared from thermal imidization of poly(amic acids), which were formed by reaction the AO with a dianhydride. In this study, 5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride (DODCA) and pyromellitic dianhydride (PMDA) were used as the dianhydride precursors. The molar ratio of amine/anhydride groups was kept at 1:1. AO and the dianhydride were dissolved separately in N-methylpyrrolidinone (NMP) and their solid contents were 5 wt%. Two solutions were mixed at $0\sim 5^\circ\text{C}$ and stirred for 6 hours under nitrogen atmosphere. The film and bulk samples were prepared by solution casting on glass substrate. All the samples were cured at 120°C for 6 hours in air and another 3 hours at 330°C for 3 hours under N_2 . The formations of imide and amic acid in nanocomposite were confirmed by fourier transformed infrared spectroscopy (FT-IR).

Thermal and mechanical properties of imide HYBRIMER were characterized by thermogravimetric analysis (TGA) and thermo-mechanical analysis (TMA). Birefringence and refractive index of imide HYBRIMER were measured by the prism coupling method. The close relations between all measured properties and nanostructures of imide HYBRIMER depending on the AO will be investigated.

Table I. Formulation of amine-oligosiloxanes (AO) depending on precursor composition

Notation	APTS(mol%)	DPSD(mol%)	$\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$ (mol%)
AD 33	33.3	66.7	0.01
AD 41	41	59	0.01
AD 50	50	50	0.01

RESULTS AND DISCUSSIONS

Synthesis of amine-oligosiloxanes

APTS is quickly reacted with water and easy to be precipitated during sol-gel process. In order to restrict rapid condensation reactions of the hydrolyzed APTS, the AO is synthesized under no water and solvents conditions. Siloxane bonds is successfully formed without precipitation and phase separation under barium hydroxide monohydrate ($\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$) catalysts. Siloxane bonds can be formed by the condensation reaction between the silanol group of DPSD and the methoxy group of APTS. As this condensation reaction proceeds, amine-oligosiloxanes are formed. Figure 2 shows the FT-IR spectra of the AO with various precursor compositions. It is found that the siloxane bonds ($1000\sim 1200\text{ cm}^{-1}$) are formed and the methoxy groups (2840 cm^{-1}) are remained but very low Si-OH ($3200\sim 3600\text{ cm}^{-1}$) exists in all the composition.

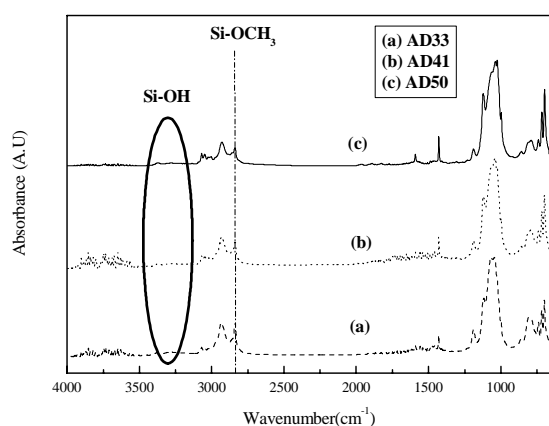


Figure 2. FT-IR spectra of the amine-oligosiloxanes of various precursor composition; (a) AD33, (b) AD41, (c) AD50

Table II. The sizes and the molecular weights of the amine-oligosiloxanes

	Size (nm)	Molecular weights	Estimated structure
AD 33	0.74	700~800	Linear tetramers
AD 41	1.21	700~800, 900~980	Linear tetramer and hexamer
AD 50	1.72	900~980	Linear hexamers

The sizes of the AO are determined by the SANS and molecular weights are analyzed by the MALDI-TOF MS. Table II summarizes results depending on precursors As DPSD content increases in AO, the size and molecular weight grows. The sizes of AO are from 1 to 2 nm and molecular weights are from 700~1000. From these results, we can estimate nanostructure of AO. In the AD33, linear tetramers, which consist of two APTS and two DPSD or three APTS and one DPSD, are mainly found. On the other hand, in the AD50, hexamers, which consist of three

APTS and three DPSD or four APTS and two DPSD, are detected. These structures in the AO are agreed with the size increment in the SANS results.

Synthesis of Imide HYBRIMER

As previously mentioned, the imide HYBRIMER is synthesized from the thermal imidization of the poly(amic acid) tethers which are connected to oligosiloxanes. The synthesis scheme is illustrated in figure 1. The formation of poly(amic acid) is easily checked by exothermic heats from the reaction of the AO and the dianhydride mixtures. In the FT-IR spectra of the imide HYBRIMER (not shown here), peaks around 1680 and 2800~3200 cm^{-1} reveal the existence of poly(amic acid) after just mixing. After heat-treatment over 330°C, the poly(amic acid) bonds change to the imide bonds by ring closure. The peaks around 1370 and 1780 cm^{-1} , which observed after thermal imidization, are typical imide peaks. In the present study, we used DODCA as alicyclic dianhydride and could obtain colorless film and bulk samples. Because siloxane bonds and alicyclic imide in the imide HYBRIMER has lower absorption around UV regions compared to aromatic rings in the conventional polyimides, imide HYBRIMER do not show the yellowish color, which are characteristics of aromatic polyimides. However, the imide HYBRIMER used the PMDA as precursor shows little yellowish color due to the aromatic rings in the PMDA.

Each AO unit has more than three amine groups, which are able to form imide tethers by reacting with dianhydrides. Thus, the structure of imide HYBRIMER is able to have a three-dimensional network shown as figure 1.

Properties of Imide HYBRIMER

TGA results of the imide HYBRIMER show that 5 % weight loss temperature increases by incorporation of highly condensed oligosiloxanes. The thermal stability of imide HYBRIMER is highly dependent on condensation degree in the AO. Table III summarizes 5% weight loss temperature depending on their compositions. Also, incorporation of highly condensed oligosiloxanes enhances the mechanical strength of imide HYBRIMER films. Thermal expansion coefficients (TEC) are raised as a function of DPSD concentration. Highly condensed AO produced more cross-linked network structure and more imide tethers in the nanocomposite. Higher chain packing density of the imide tethers had similar effect on the thermal stability and the mechanical strength. The imide HYBRIMER contained PMDA in place of DODCA has highest value of TEC and thermal stability because highly condensed AO and dianhydrides without bulky side groups increases thermal stability and TEC of the imide HYBRIMER.

The imide HYBRIMER is isotropic due to their 3-dimensional network structure. Thus they shows lower birefringence compared other polyimide and polyimide-silica hybrids. Table III showed refractive index of imide HYBRIMER at TE and TM mode. Birefringences of all the imide HYBRIMER are about 0.003, which are very small compared to other aromatic polyimides [6]. These low birefringences are due to their 3-dimensional structure and bulky side groups of DODCA. Thus, the imide HYBRIMER is easy to sue in application of optics and displays.

Table III. Properties of the imide HYBRIMER of various precursor compositions

Compositions	5% weight loss Temp.(°C)	Thermal expansion coefficient (ppm/°C)	Birefringence ($n_{TE}-n_{TM}$)
AD33-DODCA	370	79.8	0.003
AD41-DODCA	400	58.6	0.003
AD50-DODCA	430	37.8	0.002
AD50-PMDA	457	32.9	-

CONCLUSIONS

Nano sized amine-oligosiloxanes (AO) were synthesized by condensation reactions with APTS and DPSD. Their sizes and molecular weight are controlled by compositional changes. The imide HYBRIMER, which the AO were cross-linked by imide tethers are successfully prepared and had a three dimensional network structure. Imide HYBRIMER containing highly condensed AO showed higher thermal stability and mechanical strength. The imide HYBRIMER has low birefringence due to their isotropic structure and imide tether with bulky side groups.

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