Preparation of Nanopatterned Polyimide by Imprinting and Curing Phenylethynyl-terminated Imide Oligomer

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Addition-type phenylethynyl-terminated imide oligomers were synthesized from 4,4'-diaminodiphenyl ether(ODA), 4-phenylethynylphthalic anhydride (PEPA) and 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) or 4,4'-hexafluoroisopropylidene)-dianhydride (6FDA), and preparation of nanopatterned polyimide was examined by imprinting the melted phenylethynyl-terminated imide oligomer and crosslinking the ethynyl groups. Crosslinked polyimide films were prepared by pressing the melted phenylethynyl-terminated imide oligomers and curing them under pressure at 370 °C afterward, and the properties of the polyimide films were studied for comparison. The crosslinked polyimide films had high glass transition temperature (T_g) above 320 °C, and showed excellent tensile strength more than 100 MPa. Nanopatterned polyimide was prepared by imprinting the melted imide oligomer with a metal mold and curing it under pressure at 370 °C afterward. ZEONOR[®] film could be imprinted using the imprinted and cured imide oligomer as sub-mold instead of the metal mold.

Keyword: imprint, phenylethynyl-terminated imide oligomer, crosslink, nanopatterned polyimide

1. Introduction

In the nanoimprint lithography (NIL), a mold with nanopattern on its surface is pressed into a thin resist cast on a substrate [1-4]. The resist, a thermal plastic, is deformed readily by the mold when heated above T_g due to low viscosity. After the resist is cooled below T_g , the mold is removed. The surface of the resist is changed into the shape opposite to the mold pattern. We investigated to form nanopattern on polyimide surface by NIL using metal mold and application of the nanopatterned polyimide to sub-mold for formation of the nanopattern on other polymer surface.

Aromatic polyimides are well known to have high dimensional stability, low thermal expansion, outstanding thermal and mechanical properties, as

well as environmental stability [5]. Therefore, nanopattern formed on polyimide is expected to be tough and durable. Recently, the nanopatterns have been fabricated on polyimide films to use in various fields, such as microelectric devices [6], biological applications [7] and displays [8], and their application could be further extended to other fields if they can be easily patterned at micro or nanoscale. Aromatic polyimide, Pyralin 2525 (HD Microsystems PI2525), has been imprinting by three approaches; imprint as its uncured soft state and cure it afterwards; imprint another low T_g polymer, then form the pattern on polyimide surface by oxygen reactive ion etching; and direct imprint on polyimide surface at temperature higher than its T_g [9]. Since aromatic polyimides do not exhibit high molecular mobility even at

temperatures higher than their T_g , the processing conditions for molding are extremely severe, or polyimide films are prepared by conversion of soluble polyamic acids, the precursors of polyimide [5]. Nanoimprinted Kapton-type-polyimide has already been obtained by imprinting the polyamic acid film and thermal imidation afterward [10]. Though a shrinkage took place during thermal imidation, it did not damage the nanopattern. The optimized nanoimprinting process was proposed by investigating the thermal and dynamic mechanical properties of the polyamic acid and polyimide carefully.

In this study, preparation of nanopatterned polyimide was examined by imprinting addition-type phenylethynyl-terminated imide oligomer. Fluid melted imide oligomer was imprinted and cured under pressure to crosslink the ethynyl groups. The imprinted and cured imide oligomer was evaluated as sub-mold for imprinting ZEONOR[®] film.

2. Experimental

2.1. Materials

3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA), 4,4'-hexafluoroisopropylidene-dianhydride (6FDA) and 4,4'-diaminodiphenyl ether(ODA) were purchased from Wako Pure Chemical Industry and purified by sublimation under reduced pressure. 4-Phenylethynyl-phthalic anhydride (PEPA) was kindly supplied from Manac Incorporated. *N*-Methyl-2-pyrrolidone (NMP, dehydrated grade) was purchased from Kanto Kagaku and used as received. Upilex R was purchased from Ube Industries LTD. ZEONOR[®] was purchased from Zeon Corporation.

2.2. Synthesis of the imide oligomers (BPDA-PEPA-2)

In a three necked flask, 0.588 g (2 mmol) of BPDA was added to a solution of 0.600 g (3 mmol) of ODA in 20 mL of NMP, and stirred at room temperature for 5 h. 0.993 g (2 mmol) of PEPA was added to the homogeneous solution and stirred. After PEPA was dissolved, the reaction solution was stirred for 5 h. 0.612 g (6 mmol) of acetic dianhydride and 0.470 g (6 mmol) of pyridine were added to the solution in this order, and stirred for 5 h. The solution was poured into 800 mL of methanol. The precipitated polyimide oligomer was filtrated, washed with methanol and dried under vacuum.

2.3. Preparation of cured polyimide oligomer film

About 0.3 g of the imide oligomer powder (**BPDA-PEPA-*m***) was spread in film frame (80 mm × 50 mm × 50μm), and pressed under 2 MPa at 370 °C for 60 min. Cured film (**6FDA-PEPA-*m***) was prepared under 5 MPa. The cured oligomers were obtained as tough films.

2.4. Procedure of preparing nanopatterned cured imide oligomer

Six kinds of Si-molds having holes pattern with 1200 nm depth and different diameters were used for forming pillars patterns on polyimide surface. The diameters of holes were 1,000 nm, 500nm, 350 nm, 250 nm, 200 nm and 160 nm.

The Si-mold was treated with release agent as following. The mold was soaked in 0.1 wt% solution of Optool DSX (Daikin Industries, Osaka, Japan) in Demnumsolvent (Daikin Industries, Osaka, Japan) for 1 minute. After the Si-mold was baked at 120 °C for 5 min, it was washed with Demnumsolvent.

Imprinting and curing were carried out using 40TON vacuum press machine (Kitagawa seiki, Hiroshima, Japan). The powder of **BPDA-PEPA-2** was placed on silicon wafer, and heated. When the powder melted, the Si-mold was contacted and pressed. The temperature was ramped to 370 °C, and held at 370 °C for 1 h. The imide oligomer was held under 2 MPa between the Si-mold and the silicon wafer during the process. After cooling to room temperature, the patterned cured imide oligomer was removed from the Si-mold. Holes pattern opposite to that of the Si-mold was formed on the surface of the cured imide oligomer.

2.5. Procedure of imprinting ZEONOR[®]

Ni-mold having pillars pattern with 500 nm diameter and 1,000 nm height was used for preparing holes patterned cured imide oligomer. The Ni-mold was treated with the release agent as the Si-mold. Imprinting and curing were carried out using 40TON vacuum press machine. The powder of **6FDA-PEPA-3** was placed on silicon wafer, and heated. When the powder melted, the Ni- mold was contacted and pressed. The temperature was ramped to 370 °C, and held at 370 °C for 60 min. The imide oligomer was held under 5 MPa between the Ni-mold and silicon wafer during the process. After cooling to room temperature, the imprinted and cured imide oligomer was removed from the Ni- mold. The

cured 6FDA-PEPA film having holes pattern was prepared.

ZEONOR[®] film was placed on silicon wafer, and heated. The film was imprinted at 200 °C by the imprinted and cured 6FDA-PEPA, and held under 0.5MPa at this temperature for 1 min. After cooling to room temperature, ZEONOR[®] film was removed from the imide oligomer mold. The pillars pattern was formed on the surface of ZEONOR[®] film.

2.6. Measurement

Differential scanning calorimetry (DSC) was performed using a Shimadzu DSC-60 (Shimadzu Corporation, Kyoto, Japan) at a heating rate of 10 °C min⁻¹. Dynamic viscosity of polyimide oligomer and dynamic mechanical behavior of cured polyimide oligomer were performed with an Advanced Rheometric Expansion System (TA Instruments - Waters LLC, New Castle, Delaware, USA), and the measurements were carried out at 1 Hz at 5 °C min⁻¹. Dynamic viscosity and dynamic mechanical behavior were measured using parallel plate and film plate, respectively. The tensile tests of cured films were performed at a tensile speed of 10 mm min⁻¹ on specimens of 30mm × 5mm × 50 μm using Shimadzu AGS-100G (Shimadzu Corporation, Kyoto, Japan). Scanning electron microscopy (SEM) studies were performed using Hitachi S-2300 (Tokyo, Japan).

3. Results and Discussion

3.1. Direct imprint to Upilex-R polyimide

First, Upilex-R polyimide ($T_g = 300$ °C) film was examined to be imprinted directly. The nanopatterning PMMA ($T_g = 110$ °C) had been successfully carried out by imprinting at 175 °C under 4.4MPa [1]. The polyimide film was imprinted by a metal mold with holes pattern at 370 °C under 6 M Pa for 60 min. Figure 1 shows SEM photography of topography image on the surface. Straightforward pillars patterns could not be obtained on Upilex-R polyimide surface in spite of the severe conditions, and the heights of the pillars were much shorter than the depths of the holes of the mold. The mold patterns could not be imprinted sufficiently due to the low mobility. Upilex-R polyimide shows high modulus of 10^7 Pa

even at 370 °C, which is much higher than the T_g [11].

Figure 1. SEM photograph of pillars pattern formed by imprinting Upilex R directly with holles-patterned mold. Holles diameter; (a): 500 nm, and (b): 160 nm.

3.2. Preparation and properties of phenylethynyl-terminated imide oligomer

Sufficient mobility is required to form a pattern, which reflects sufficiently the mold pattern, by imprinting polyimide directly. We examined to imprint processable thermosetting-resin by a metal mold and crosslinking it afterward. Phenylethynyl-terminated imide oligomer¹²⁻¹⁶ was selected as such a resin. It has been examined to fabricate carbon fiber-reinforced plastic from various phenylethynyl-terminated imide origomers [17]. Phenylethynyl-terminated imide origomers were synthesized from the reaction of dianhydrides, ODA and PEPA as shown in Scheme 1. BPDA and 6FDA were used as dianhydride, and imide oligomers having various average degrees of polymerization (m) were synthesized by adjusting the molar ratio. Polyaddition to form polyamic acid, modification of phenylethynyl groups, and chemical solution imidation were carried out through one-pot procedure. The reaction solution was poured into methanol, and the imide oligomer was precipitated as powder. The thermal behaviors of imide oligomers were evaluated by DSC. The imide oligomers showed melting temperature (T_m) at 140-235 °C and the T_m values were higher as m increased.

Scheme 1. Synthesis of addition-type phenylethynyl-terminated imide oligomers.

Figure 2 shows temperature dependence the melt viscosities for the imide oligomers, **BPDA-PEPA-*m*** and **6FDA-PEPA-*m***. The imide oligomers ($m \leq 3$) had very low melt viscosities (10 Pa s) at 340 °C, and showed increase of the viscosities at about 360 °C due to crosslinking of the ethynyl groups.

Figure 2. Melting and curing behaviors of the oligomers: (a) **BPDA-PEPA-*m*** and (b) **6FDA-PEPA-*m***.

The properties of imide oligomers cured above 360 °C were examined. The powder of imide oligomer was placed in film frame, and held under pressure at 370 °C for 60 min. The cured oligomers were obtained as tough films. Figure 3 shows dynamic mechanical behaviors of the cured **BPDA-PEPA-*m*** and **6FDA-PEPA-*m***. For comparison, those of the corresponding polyimides without phenylethynyl groups, Upilex R and 6FDA-ODA are also shown. T_g values were observed as $\tan \delta$ peak temperatures (Table 1), and T_g values of the cured imide oligomers were higher than those of the polyimide without ethynyl groups. As m was lower, the T_g values were higher, the decrements in storage modulus at the glass transition were lower, and the effect of crosslinking was observed in the dynamic mechanical behaviors of the imide oligomers.

Figure 3. DMA behaviors of the cured oligomers: (a) **BPDA-PEPA-*m*** and (b) **6FDA-PEPA-*m***.

The mechanical properties of the cured imide oligomer films were evaluated using tensile tests. Table 1 shows the tensile strength (S), the elongation at break (E) and the tensile modulus (M). All the films had tensile strengths more than 100 MPa, and the elongation-at-break was longer with m .

Table 1. Properties of cured imide oligomer films.

Cured imide oligomer	T_g^a (°C)	S (MPa)	E (%)	M (GPa)
BPDA-PEPA-1	415	119	10	2.4
BPDA-PEPA-2	345	127	11	2.5
BPDA-PEPA-3	331	128	13	2.6
6FDA-PEPA-1	396	124	9	2.3
6FDA-PEPA-2	364	129	11	2.7
6FDA-PEPA-3	356	140	12	2.9
6FDA-PEPA-4	327	148	13	3.2

^a Determined by DMA at 5 °C min⁻¹.

3.3. Preparation of nanopatterned polyimide by imprinting and curing phenylethynyl-terminated imide oligomer

Since the cured imide oligomer films showed high T_g values and excellent mechanical properties, nanopatterned polyimide was prepared by the similar method. The procedure is shown in Figure 4. The powder of imide oligomer was placed on silicon wafer, and heated. When the powder melted, Si-mold was contacted and imprinted. The temperature was ramped to 370 °C, and held at this temperature for 1 h to cure the imide oligomer. The imide oligomer was held under pressure between the Si-mold and silicon wafer during the process. **BPDA-PEPA-2** and **6FDA-PEPA-3** were imprinted under 2 MPa and 5 MPa, respectively.

Figure 5 shows SEM photography of pillars patterns on the imprinted **BPDA-ODA-2** and **6FDA-ODA-3**. The diameters and heights of the pillars on the cured polyimide oligomer were agreement with diameters and depths of the holes on the Si-mold surface, and distortion of the pattern was not observed. It was suggested that the melted imide oligomer flowed into all the corners of the holes in the Si-mold and crosslinked without shrinkage.

3.4. Imprint to ZEONOR[®] film using nanopatterned cured imide oligomer as sub-mold

The patterned cured imide oligomer was evaluated as sub-mold for imprinting ZEONOR[®] film instead of the metal mold (Figure 7). The melted **6FDA-PEPA-3** was imprinted by Ni-mold with pillars pattern (diameter= 500 nm), and cured

Figure 4. Procedure for preparation of pillars-patterned cured imide oligomer.

Figure 5. SEM photograph of pillars patterns: (a) **BPDA-PEPA-2** and (b) **6FDA-PEPA-3**.

at 370 °C for 1h afterward (a). ZEONOR[®] (T_g = 150 °C) was imprinted by the cured **6FDA-PEPA-3**, and held under 0.5 MPa at this temperature for 1 min (b). Halls pattern, which was opposite to the Ni mold, was formed on the surface of the imprinted and cured **6FDA-PEPA-3**, and the same pillars pattern as the Ni-mold was formed on the surface of ZEONOR[®].

(a) Preparation of holes-patterned cured 6FDA-PEPA-3 **(b) Imprinting ZEONOR® by the cured 6FDA-PEPA-3**

Figure 6. Procedure for imprinting ZEONOR® by using patterned cured 6FDA-PEPA-3 as mold.

Figure 7 shows SEM photography of patterns on the imprinted and cured **6FDA-PEPA-3** and that of the imprinted ZEONOR® film. Though the height of the pillars was slightly longer (1720 nm), the diameter of pillar was agreement with that of the pillars on the Ni-mold surface, distortion of the pattern was not observed, and the Ni-mold pattern was be reflected sufficiently. The longer pillars is thought to be due to extension occurred in removing the imprinted ZEONOR® film from the mold.

Figure 7. SEM photograph of patterns: (a) patterned cured 6FDA-PEPA-3 and (b) imprinted ZEONOR®.

4. Conclusion

Addition-type phenylethynyl-terminated imide oligomers with a BPDA-ODA and 6FDA-ODA backbone structures were found to be have good processability for imprinting and conversion property to tough materials by curing them under pressure at 370 °C. Nano-patterns could be

formed on the surface by imprinting the melted imide oligomer and cured them under pressure at 370 °C afterward. The imprinted and cured imide oligomer could be used as sub-mold instead of metal mold for imprinting ZEONOR®.

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