การสังเคราะห์และวิเคราะห์ลักษณะเฉพาะของพอลิอิไมด์แบบไวแสงชนิดบวกที่มีส่วนผสมของไซเลนสำหรับการใช้งานเป็นวัสดุปิดคลุม

นางสาวภัทริน โมรา

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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Synthesis and Characterization of Positive-type Photosensitive Silane-Containing Polyimide for Cover Layer Materials Application

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ภัทริน โมรา : การสังเคราะห์และวิเคราะห์ลักษณะเฉพาะของพอลิอิไมด์แบบไวแสงชนิดบวกที่มีส่วนผสมของไซเลนสำหรับการใช้งานเป็นวัสดุปิดคลุม (Synthesis and Characterization of Positive-type Photosensitive Silane-Containing Polyimide for Cover Layer Materials Application) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร.ศราวุธ ริมดุสิต, 86 หน้า.

ในงานวิจัยนี้มีจุดมุ่งหมายเพื่อพัฒนาวัสดุปิดคลุมสำหรับใช้งานในแผ่นวงจรชนิดอ่อน โดยโคพอลิอิไมด์ที่ใช้สามารถเตรียมได้จากมอนอเมอร์ 3 ชนิด ได้แก่ s-BPDA, NTDA และ ODA โดยปฏิกิริยาควบแน่นแบบ 2 ขั้นตอนในตัวทำละลาย NMP ซึ่งได้ทำการศึกษาผลของสัดส่วนของมอนอเมอร์ต่อสมบัติทางความร้อน ทางกล และทางไฟฟ้า โดยผลที่ได้โคพอลิเมอร์ที่เหมาะสมสำหรับการนำไปพัฒนาแสดงสมบัติที่ดีในด้านต่างๆ ดังนี้ มีความสามารถในการดัดโค้งสูง มีสมบัติทางความร้อนที่ดี ได้แก่ อุณหภูมิการเปลี่ยนสถานะคล้ายแก้ว (T_g) อยู่ในช่วง 307-355 องศาเซลเซียส อุณหภูมิการสลายตัวทางความร้อนสูงกว่า 560 องศาเซลเซียส ค่าคงที่ไดอิเล็กทริกต่ำอยู่ในช่วง 2.95-3.31 และมีค่าสัมประสิทธิ์การขยายตัวทางความร้อน (CTE) ใกล้เคียงกับของแผ่นทองแดงด้วย (27.7 ppm/^{o}C) นอกจากนี้ยังได้ทำการพัฒนาพอลิอิไมด์แบบไวแสงชนิดบวกที่เพิ่มการยึดเกาะโดยใช้สารคู่ควบไซเลนและใช้นิเฟดิพีน (nifedipine) เป็นสารไวแสง โดยเตรียมพอลิอิไมด์แบบไวแสงจากพอลิเอมิกเอสิด (poly(amic acid), PAA) s-BPDA/NTDA(70/30mol%)-ODA ผสมกับนิเฟดิพีน 20% โดยน้ำหนักของ PAA และผลที่ได้พอลิอิไมด์แบบไวแสงยังสามารถแสดงสมบัติที่ดีในด้านต่างๆ ดังนี้ มีสมบัติทางความร้อนที่ดี ได้แก่ อุณหภูมิการเปลี่ยนสถานะคล้ายแก้ว (T_g) เท่ากับ 360 องศาเซลเซียส อุณหภูมิการสลายตัวทางความร้อนมีค่า 474 องศาเซลเซียส ค่าคงที่ไดอิเล็กทริกต่ำมีค่า 3.01 มีค่าสัมประสิทธิ์การขยายตัวทางความร้อน (CTE) ใกล้เคียงกับของแผ่นทองแดง (28.5 ppm/^{o}C) และมีค่าความไวแสงเท่ากับ 200 mJ/cm^2 นอกจากนี้พอลิอิไมด์แบบไวแสงสามารถเพิ่มการยึดเกาะได้ดีขึ้น เมื่อเติมสารคู่ควบไซเลนที่ 0.5% โดยน้ำหนัก และแสดงความความแข็งแรงในการลอก (peel strength) ที่ดี มีค่าเท่ากับ 0.80 N/mm ซึ่งจากผลดังกล่าวนั้น พอลิอิไมด์แบบไวแสงชนิดบวกที่มีส่วนผสมของสารคู่ควบไซเลนสามารถนำไปใช้เพื่อพัฒนาเป็นวัสดุปิดคลุมในแผ่นวงจรชนิดอ่อนได้นั่นเอง

ภาควิชา	วิศวกรรมเคมี	ลายมือชื่อนิสิต	....
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A novel cover layer material for flexible printed circuit (FPC) applications is developed in this research. Cover layer film based on copolyimide was prepared from three monomers, i.e. 3,3',4,4'-biphenyl tetracarboxylic dianhydride (s-BPDA), 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA) and 4,4'-oxydianiline (ODA), by a two steps polycondensation reaction in n-methyl pyrrolidone (NMP). The obtained copolyimide films were characterized at varied comonomer compositions for their thermal properties i.e. glass transition temperature (T_g), degradation temperature (T_d) and coefficient of thermal expansion (CTE), as well as their tensile strength and dielectric constant since these properties are crucial for a successful use as a cover materials for FPC. A positive working photosensitive copolyimide based on poly(amic acid) (PAA) and nifedipine as a photoreactive compound has been developed. The PAA was prepared from s-BPDA/NTDA(70/30mol%)-ODA by a two steps polycondensation reaction in NMP. The obtained photosensitive copolyimide film (PSPI) exhibited high thermal stability with T_g of 360°C, T_d up to 474°C and low dielectric constant of 3.01. The relatively low CTE of the resulting PSPI film was found to be closed to that of copper foil (i.e. 28.5 ppm/^{o}C). Positive-type patterns could be obtained from nifedipine containing the PSPI with a sensitivity of 200 mJ/cm^2. In addition, A positive type photosensitive silane-containing copolyimide film was improved adhesion property with peel strength of 0.80 N/mm with an addition of silane coupling agent at 0.5% by weight. The results revealed that the present PSPI system is a promising candidate as a novel cover layer material for flexible printed circuit board.

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Finally, I would like to dedicate this paragraph to my parents and special one who give their understanding, generous encouragement and unconditional love during my studies.

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CHAPTER I

INTRODUCTION

Flexible printed circuit (FPC), which is fabricated by copper-patterning of a copper clad laminated sheet (CCL) and subsequent protection with a cover layer (CL), is a very important component in microelectronic devices such as cellular phones and mobile personal computers. [1]

Photosensitive polyimides (PSPIs) are widely used as protection and insulation layers of multi-chip modules for computers, telecommunications and flexible printed circuit board due to their high flexibility, high thermal properties as well as high glass transition temperature (T_g), high thermal stability as well as high degradation temperature (T_d), low dielectric constant and low coefficient of thermal expansion (CTE) close to that of copper foil (18–20 ppm/K) [2] as a conductive layer or a considerably lower modulus. In addition to these advantages of photosensitive polyimides (PSPIs), they simplify processing and do not need a photoresist used in the microlithography, also make this material as excellent cover layer film.

Aromatic polyimides such as poly(4,4'-oxydiphenylene biphenyltetracarboximide) (s-BPDA/4,4'-ODA polyimide) have marked thermal stability, excellent mechanical and electrical properties suitable for applications in the fabrication of microelectronic devices as inter-dielectric layers, passivation layers and alpha particle protection layers [3-5]. However, s-BPDA/4,4'-ODA polyimide system have CTE values ranging 28-43 ppm/K [6-8]which is much higher than that of copper foil (18–20 ppm/K). In general, soluble PIs possess linear/stiff chain backbone structures which disturb the in-plane orientation responsible for lower CTE. The combinations of 1,4,5,8-Naphthalenetetracarboxylic dianhydride (1,4,5,8-NTDA) and sulfonated diamines are known to give heat resistant proton-conductive membrane [9, 10]. Naphthalenetetracarboxylic dianhydride (NTDA) is a useful dianhydride monomer which provides unique PIs possessing lower CTE, lower water absorption, and higher T_g, which are advantageous for flexible copper clad laminates (FCCL) applications. However, the commercially available 1,4,5,8-NTDA consisting of thermodynamically stable six-membered anhydride groups had very poor poly(amic acid) (PAA) polymerizability. But, it was possible to copolymerize with other dianhydride when a minor portion of 1,4,5,8-NTDA was used [9]. Therefore, s-BPDA, 1,4,5,8-NTDA and 4,4'-ODA were chosen as a major component of copolyimide in this study.

However, their very stiff/rod like polyimide backbones has insufficient adhesion to copper. Coupling agents find their largest application in the area of polymers. Since any silane that enhances the adhesion of a polymer is often termed a coupling agent, regardless of whether or not a covalent bond is formed, the definition becomes vague [11]. Silane coupling agents have the ability to form a durable bond between polymer and metal materials [11]. 1-[3-(Trimethoxysilyl)propyl]urea has better stability than others silane in reactive polymer systems, like phenolic, epoxy or polyurethane [12]. It has good adhesion between the inorganic filler and the polymer. The polymer laminate comprising a 1-[3-(Trimethoxysilyl)propyl]urea does not contain any intermediate adhesive layer, and the polymer layer combines the benefits of adhesion to a metal materials [13]. Therefore, we provide a polyimide laminate comprising a silane coupling agent to solve the adhesion problem in this study.

Photosensitive polyimide (PSPI) consist of poly(amic acid) (PAA) and photosensitive compound. Most PSPIs reported so far are a negative-working type and need organic solvents as the developer [14, 15]. However, negative PSPI swells during development, because the developer is an organic solvent. Thus, it limits the pattern resolution. In order to overcome these problems, positive-working PSPIs that can be developed with base solutions have been attracting great interest [16]. 1,4-dihydropyridine (DHP) derivatives such as nifedipine known as a medicine were also utilized in PSPI systems [17-19]. 1,4-dihydro-2,6-dimethyl-4-(nitrophenyl)-3,5-pyridinedicarboxylic acid dimethyl ester (nifedipine) is converted into the corresponding pyridine derivative in the exposed area so that it can solubilize in alkaline developer to formulate a positive-working PSPI and exhibits a good sensitivity, high contrast and resolution [20].

In this work, we developed s-BPDA/1,4,5,8-NTDA/4,4'-ODA polyimide cover layer material which can be directly formed on the printed circuits by the simple casting process of the polyimide solution and displays a high flexibility, high thermal properties, high thermal stability, low dielectric constant and low coefficient of thermal expansion (CTE) close to that of copper foil. Moreover, the present paper describes the preparation and properties of the positive-type photosensitive s-BPDA/1,4,5,8-NTDA/4,4’-ODA containing 1-[3-(Trimethoxysilyl)propyl]urea (silane coupling agent) polyimide using nifedipine as photosensitive compound.

CHAPTER II

THEORY

2.1 Flexible Circuit Technology

The advance of electronic systems into our everyday lives is evidence of a major digital technology revolution. The success stories of the personal computer and the mobile phone serve to demonstrate that consumer and business demand for innovative products are significant. Increasingly electrical and electronic systems are entering our lives in many unanticipated ways. They can be found in our homes in the form of cordless phones and digital TVs, in our cars in the form of hands-free communications and telematics, and in business in the form of notebook computers and mobile personal data assistants (PDAs) (Figure 2.1). [21]

Figure 2.1 Application of flexible printed circuit [22].

Importantly, and also covertly, within the above applications flexible printed circuits have also been entering our lives. Traditionally employed in the role of wire replacement, removing the need for complex wire harnesses, and replacing costly and increasingly complicated wired assemblies, flexible circuits offer a much simpler and often significantly more cost-effective interconnection method.

However, alongside increasingly innovative applications flexible-circuit technology is branching out significantly from this initial role and it is poised to be a technology that will provide enormous design freedoms for electronic engineers and product designers over the coming years. As the demands of modern electronic systems call for increasing functionality, greater circuit density, higher connectivity, better environmental performance, and all at lower cost, flexible circuitry is poised to deliver on the promise of twenty-first century electronics.

2.2 Flexible-Circuit Materials

As discussed initially, flexible circuits (Figure 2.2) typically represent a composite (laminate) of materials, chosen to work together to deliver a desired overall combination of electrical and mechanical performance [21]. However, these criteria are not alone in enabling the determination of an appropriate combination of circuit materials. Other typical factors that play heavily on the selection of suitable materials are:

- Application environment
- Volumes
- Reliability requirements
- Dynamic or static flexing required
- Duration of flexing or dynamic operation (cycles)
- Additional electrical requirements of the circuit-e.g. impedance
- Connections to components and other circuitry
- Method used for component assembly
- Costs

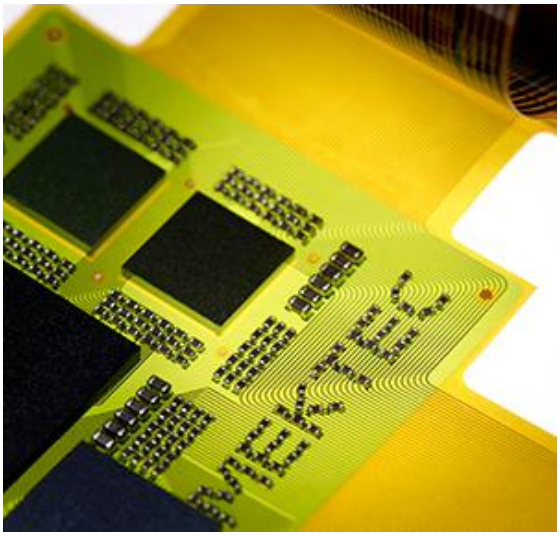


Figure 2.2 Flexible printed circuit board [23].

2.3 Material Configuration

Within a typical flexible circuit [21], four distinct classes of materials are used:

- Base material (dielectric film/flexible substrate)
- Conductors (foil or conductive coating)
- Adhesive (optional)
- Cover lay (film or coating)

Other materials utilized include numerous surface finishes and anti-tarnishing coatings, and integral stiffeners or backing substrates, all designed to give additional properties and performance capabilities to the circuit assembly or enhance the ease of manufacture. A simple typical circuit make-up is detailed in Figure 2.3 below.

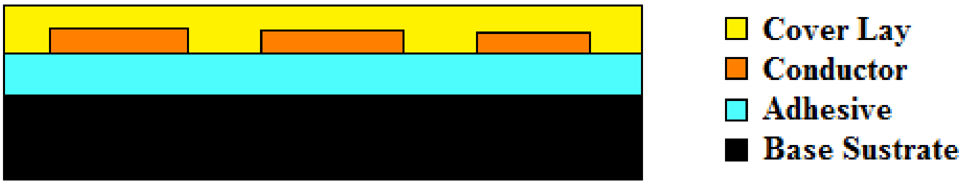


Figure 2.3 Flexible-circuit make up [21].

2.3.1 Base Materials

A suitable base material [21] has to perform a variety of important functions. It must electrically insulate the conductive circuit tracks from one another and it must be compatible with any adhesives used for conductor or cover-lay bonding. Under normal circumstances the base material will also provide the circuit with much of its mechanical characteristics, such as its flexing strength and durability. In the case of adhesiveless laminates, which will be discussed later, the base substrate provides all of the circuit's strength. Typically, the major criteria and properties required of a suitable substrate are:

- High dimensional stability
- Good thermal resistance
- Tear resistance
- Good electrical properties
- Flexibility
- Low moisture absorption
- Chemical resistance
- Low cost
- Consistency from batch to batch
- Wide availability

There are many materials that have been used as substrate materials with varying degrees of success over recent decades. Materials that have been widely used for various FPC applications include:

- Polyimide
- Polyester
- Fluorocarbon films
- Aramid papers
- Composites

These materials present a range of differing properties (see Table 2.1), which are called upon by circuit designers where their blend of electrical and mechanical performance capabilities and costs best suit the application at hand. As previously discussed, the two materials that receive by far the most attention are polyimide and polyester films.

Table 2.1 Typical properties of dielectric materials [21].

Property	Polyester	Polyimide	Fluorocarbon	Composite	Aramid
Tensile strength	Excellent	Excellent	Fair	Good	High
Flexibility	Excellent	Excellent	Excellent	Good	Fair/Good
Dimensional stability	Fair/Good	Good	Fair	Good	Excellent
Dielectric strength	Good	Good	Excellent	Very Good	Good
Solderability	Poor	Excellent	Fair	Excellent	Excellent
Operating temperature	105–185°C	105°C	+220 °C	150–180°C	220°C
Coefficient of thermal expansion	Low	Low	High	Moderate	Low
Chemical resistance	Good	Good	Excellent	Very Good	Fair
Moisture absorption	Very Low	High	Very Low	Very High	Low
Cost	Low	High	High	Moderate	Moderate

2.3.2 Conductor Materials

Material considerations for FPC conductors are similar to those of rigid circuit boards. The conductor material must survive processing and provide adequate electrical and mechanical performance in the application environment. The list of conductor candidate materials includes elemental metal foils, such as copper and aluminum, and metal mixtures including stainless steel, beryllium-copper, phosphor-bronze, copper-nickel and nickel-chromium resistance alloys. Both silver and carbon polymer thick-film (PTF) inks are also used [21].

Copper is the material of choice for flexible-circuit conductors. In practice, of the wide variety of possible conductor materials, only a selected few have found use within volume applications. As well as providing the electrical connectivity and electrical performance features of flexible circuits, conductor properties greatly influence the fatigue life, stability, and mechanical performance of FPC assemblies. In many static applications bending is limited to installation and general servicing. In dynamic applications, the assembly is flexed or folded repeatedly during normal use. As a general rule, for dynamic applications, conductors should be of the minimum acceptable thickness and their material of construction must be carefully chosen, along with their grain orientation and deposition technique, to match the performance levels required [21].

2.3.2.1 Copper

The relatively low cost of copper, its high workability, good plating and good electrical characteristics make it an excellent material for flexible-circuit conductors. It is also the case that there are several different kinds of copper available, which can be matched by the circuit designer to specific applications.

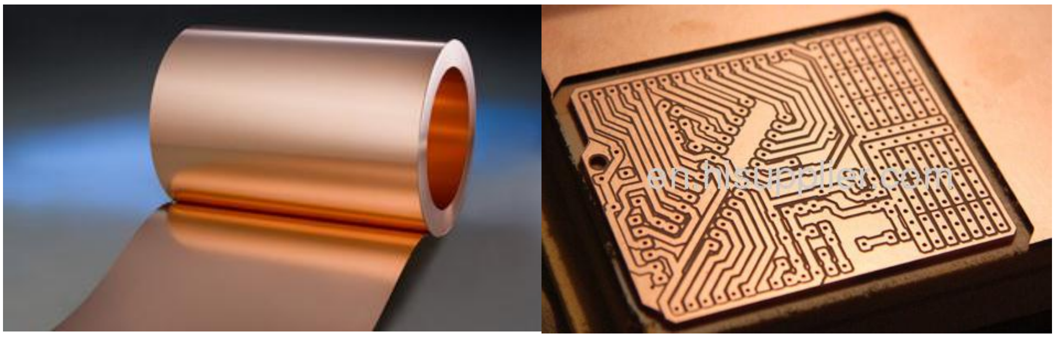


Figure 2.4 Copper foils [24].

Copper foils (Figure 2.4) suitable for use in flex circuits typically fall into two categories-electrodeposited (ED) or wrought (W). The IPC standard IPC-MF-150 (‘Metal Foil for Printed Wiring Applications’) [25] details these categories and defines four types of copper within each, giving flex designers eight types of copper to select from. Table 2.2 is a guide to the common grades of copper available [21].

Table 2.2 Summary of IPC-MF-150 copper foil categorization [25].

Copper foil category	**Number**	**Designator**	**Description**
Electrodeposited (E) copper foils	1	STD – (E)	Standard electrodeposited
	2	HD – (E)	High ductility electrodeposited
	3	THE – (E)	High-temperature elongation electrodeposited
	4	ANN – (E)	Annealed electrodeposited
Wrought (W) copper foils	5	AR – (W)	As rolled wrought
	6	LCR – (W)	Light cold rolled wrought
	7	ANN – (W)	Annealed wrought
	8	LTA (W)	As rolled wrought low temperature annealable

2.3.3 Adhesives

Adhesives play an important role in flexible circuits. They are used to provide a secure join between the substrate and the chosen conductor material, to join circuits together where multi-layer or rigid-flex constructions are required, and to provide a protective cover lay over exposed conductors once they are formed [21].

There are a number of methods for applying adhesives but generally they are coated onto the dielectric substrate and then laminated to the conductor foil. Depending upon the nature of the base this can be done via a heated press for sheet processed materials such as polyamides, or through heated rollers for roll-to-roll materials such as polyester. Some form of post curing at elevated temperature is usually required after roller lamination due to the relatively short contact time between roller and laminate [21].

Adhesives must be carefully chosen to offer compatibility with both substrate and conductor materials. They must be able to provide adequate mechanical strength, have good chemical resistance, and be able to withstand the conditions used in FPC manufacture without delamination [21]. Typical adhesives systems used for flexible-circuit manufacture include:

- Polyester
- Polyimide
- Acrylics
- Epoxies
- Fluoropolymers
- Phenolics

2.3.4 Cover Lays (Cover layers)

A cover lay (also known as a ‘cover layer’) (Figure 2.5) is usually a combination of a flexible film and a suitable pressure-sensitive or thermosetting adhesive. The most commonly used materials are polyester film coated with polyester adhesive, polyimide film with acrylic adhesive, and polyimide film with epoxy adhesive. As stated, in circuit design the usual practice is to match the cover-lay film to the material of the base substrate [21].

The purpose of a cover lay is three fold: to provide circuit and conductor protection; to allow access to circuit pad and contact areas for further processing such as soldering and conductive adhesive bonding of components; and to enhance circuit flexibility and reliability.

To enable access to required conductor features beneath the cover lay, such as pads and contact points, registration holes are drilled, punched, or laser machined into the film. The cover lay is then registered over the conductor pattern and laminated using heat and/or pressure according to the adhesive's requirements [21].

To reduce conductor damage from frequent bending, the thickness of the cover lay should be the same as the thickness of the dielectric layer. This arrangement places the conductor traces near the neutral axis of the finished circuit assembly, in effect in the center of the layered construct, which significantly reduces conductor stress during flexing.

An increasingly popular alternative to pre-punched and drilled adhesive films is the photoimageable cover lay. A layer of light-sensitive material, either in film or liquid form, is placed over the top surface of the conductor trace layer. The layer is exposed to light through a photographic negative that acts as a mask, selectively exposing areas of the film to the light. The light-sensitive coating cures in the exposed areas and subsequent processing strips uncured material to leave a patterned covering which provides access to contact pads and soldering lands [21].

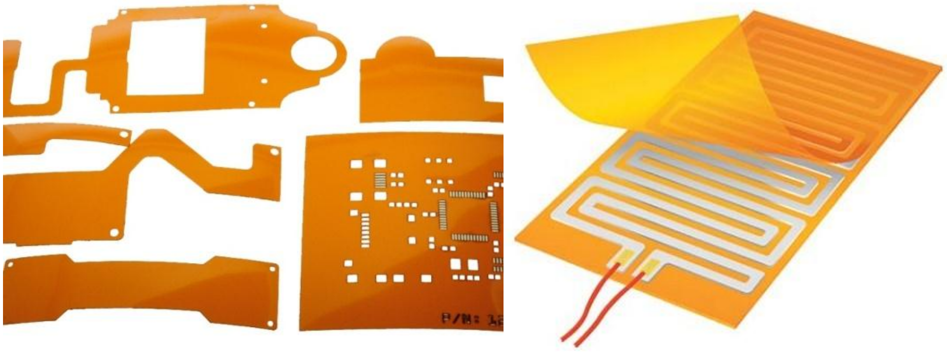


Figure 2.5 Polyimide film use as cover lay material [26].

2.4 Polyimides (PIs)

Aromatic polyimides, in general, are comprised of five-membered heterocyclic imide units and aromatic rings. The structure of these “cyclic chain” systems makes polyimides insoluble/intractable and, thus, not amenable to traditional solution/melt polycondensation reactions. Early attempts made at DuPont R & D in the 1950s utilizing direct reaction of dianhydrides and aromatic diamines in the melt or in solution resulted in precipitation of intractable low molecular weight polyimides. However, by 1956, Dr. A. Endrey at DuPont had successfully pioneered the invention of obtaining polyimides through reaction of soluble/processable intermediates known as poly(amic acid)s. This type of reaction consisted of two steps: the solution polycondensation of an aromatic diamine and a dianhydride to form poly(amic acid) which could be processed into a useful shape, followed by cyclodehydration of the amide-acid to form polyimide [27-29].

2.4.1 Classic Two-step Method of Polyimide Synthesis

In the classic two-step method of synthesizing aromatic polyimides [29], the initial step consists of preparing a solution of the aromatic diamine in a polar aprotic solvent, such as N-methyl pyrrolidone (NMP), to which is added a tetracarboxylic dianhydride.

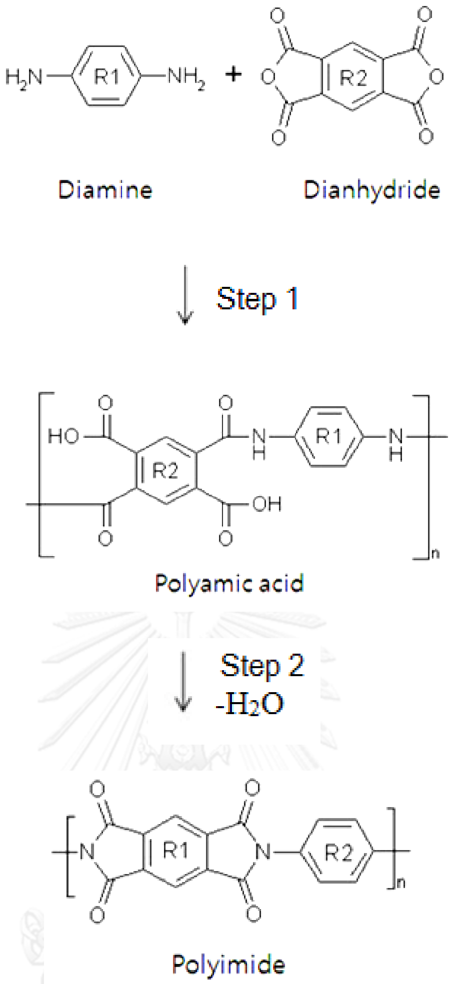


Figure 2.6 Classic two-step method of polyimide synthesis [30, 31].

The formation of poly(amic acid) occurs during this step at ambient temperature and is complete within 24 hours, depending on monomer reactivity. The high molecular weight poly(amic acid) produced is fully soluble in the reaction solvent and, thus, the solution may be cast into a film on a suitable substrate. The second step in this synthetic method is the cyclodehydration reaction (imidization) that is accomplished by heating the film to elevated temperatures, or by incorporating a chemical dehydrating agent [32]. The overall reaction scheme for the two-step method is depicted in Figure 2.6

2.4.2 Synthesis of Polyimides via Derivatives of Poly(amic acid)s

During classic poly(amic acid) synthesis, proton transfer by the o-carboxylic acid group initiates reversal of the polycondensation reaction. Derivatization has been utilized to convert the acid to a species incapable of releasing an acidic proton, such as an ester, under the standard reaction conditions. Ester-amide derivatives have been successfully prepared by utilizing diester-diacyl chloride monomers in solution polycondensation reactions with diamines [33-36].

These derivative polymers are useful as thin film dielectrics [36-38] and as photosensitive polyimide precursors [39, 40] in electronics applications. The improved hydrolytic stability and solubility of the poly(ester-amide) precursors allow for the isolated product to be stored and then reformulated in suitable solvents as needed for spin casting [36].

Imidization processing of the films is similar to that of poly(amic acid)s: (1) thermal, which requires somewhat higher temperatures than used for amide-acids, and, (2) chemical, using a base such as triethylamine to remove the amide proton [33]. FTIR studies indicate that chain scission side reactions involving decomposition of ester-amide to anhydride and amine groups are absent during thermal imidization of poly(amide ester)s [37]. This results in retention of high molecular weight and hydrolytic stability of the films [30].

2.4.3 Introduction to Structure-Property Relationships of Polyimides

The properties of polyimides [30], as for polymers in general, are governed by three fundamental characteristics: chemical structure, average molecular weight and molecular weight distribution [41]. The chemical structure relates to the chemical composition of the repeat unit and end groups. It also encompasses the composition of any branches, crosslink or defects in the structural sequence. The average molecular weight describes the average polymer chain size. The molecular weight distribution relates to the degree of regularity in the molecular size. Extensive literature has been published describing alterations in the structure and size of the polyimide backbone and how these changes affect the physical and mechanical properties. In the following sections, a sampling of this literature will be reviewed with particular emphasis on properties applicable to microelectronics packaging devices. To provide background information, the subject of microelectronics packaging is first addressed with regard to function, fabrication and the performance/property requirements for polymer dielectrics. The subsequent discussions on structure-property relationships of polyimides are divided into three major areas:

(1) Linear thermoplastic two-phase polyimides
(2) Linear thermoplastic amorphous polyimides
(3) Cross-linked amorphous polyimides.

2.4.4 Property Considerations and Requirements for Interlayer Dielectrics

Polyimides are prime candidates for high performance dielectrics due to the ease with which their thermal, electrical and mechanical properties can be tailored to specific requirements. The facile modification of polyimides arises not only from the large selection of monomer structures and combinations, but also from the wide variety of macromolecular sizes and architectures (i.e. branched, network, linear, etc.). Discussions of particular polyimide structures and their influence on physical properties will be provided in subsequent sections. First, however, a background description of the property considerations and requirements for interlayer dielectrics in MCM-D packaging will be provided [30].

2.4.4.1 Electrical Properties

1. Dielectric constant (ε'): A lower ε' value stands for a higher insulating ability. Polyimides have low dielectric constants, typically between 3.0 and 3.8. For comparison the value of a standard SiO_2 insulator is higher with a $\varepsilon'$of 4.0. This feature makes polyimides commonly used for dielectric films [30, 42].

2. Dielectric loss tangent ($\tan \delta$): the typical $\tan \delta$ value (or the dissipation factor) of polyimides is about 0.002. Low values of $\tan \delta$ indicate minimal conversion of electrical energy to heat, i.e. minimal overall power loss in the dielectric [23, 42].

3. Dielectric strength: this measures the ability of a material to withstand high voltages without breakdown or the passage of considerable amounts of current. Most polyimides have a dielectric strength of 10^5-10^6 V/mm [30, 42].

2.4.4.2 Thermal Properties

1. Coefficient of thermal expansion (CTE): the values of polyimides are relatively higher than those of inorganic materials, (see Table 2.3). This characteristic needs to be considered in processing the polyimide film when it contacts with an inorganic substrate, because the unconformity between two different materials leads to tensile internal stress.

Table 2.3 Coefficient of thermal expansion (CTE) of polyimide and other materials [30, 42]

Material	CTE value (ppm/°C)
SiO_2	4
Si, SiC	3
Alumina	6
Gold	14
Copper	17
Aluminum	24
Polyimide	40-50

2. Thermal stability: Typical aromatic polyimides are considered very thermally stable. Thermogravimetric analysis (TGA) measurements show polyimides have 5% weight loss in air and only 1% under nitrogen when exposed to 400 ^{o}C for 2 hours. The cyclic-chain structures, which are the substitute groups, have a decisive role in polyimide's thermal stability [30, 42].

3. Glass transition temperature (T_g): Due to their comparatively rigid structures, polyimides possess a high glass transition temperature. T_gs of aromatic polyimides are relatively high with exceeding 300^{o}C for the rigid ordered type [30, 42].

2.4.4.3 Mechanical Properties

The mechanical properties of polyimide are influenced by cure history as well as by its molecular architecture. In general, polyimide films have been found to have relatively high mechanical strengths. Tensile strengths of relatively flawless, free-standing film specimens typically range from 100-200 MPa and the elongation at break (EB) values range from 10-25%, as measured by DMA [30, 42].

2.4.4.4 Adhesion

Polyimide films show good adhesion to different inorganic and metallic surfaces such as copper, silicon and aluminum, which is important for reliable performance in applications of electronics. Additionally, self-adhesion is also a decisive factor where subsequent layers of polyimide come in contact with each other. There are many factors affecting adhesive failure of polyimides (Table 2.4), such as: insufficient interfacial wetting, high temperature, humidity or the presence of particulate contaminants etc can cause degradation of adhesion [30, 42].

Table 2.4 Comparision of properties of polyimide and silicone dioxide dielectrics [30, 42].

Properties	**Polyimide**	**SiO_2**
Process temperature, °C	300-350	350-450
Decomposition temperature, °C	> 450	1710
Dielectric strength, V/m	10^6	10^6-10^7
Volume resistivity, Ω·cm	10^{15}-10^{16}	$>10^{16}$
Dielectric constant	3.2-3.8	3.5-4
Dielectric loss tangent	0.001-0.002	0.001
Coefficient of thermal expansion (CTE), 10^{-6}/°C	20-70	0.3-0.5
Thermal conductivity, W/cm °C	0.0017	0.021
Young's modulus, Gpa	3	70
Tensile strength, Gpa	0.1-0.2	0.2
Planarization, %	60-100	0

2.7. Photosensitive Polyimide (PSPI)

The importance of photosensitive polyimides (PSPIs) as practical packaging and/or insulating materials in microelectronics has increased in recent years. For instance, buffer coatings, passivation layers, alpha particle barriers, interlayer insulations, and wafer scale packages, are widely used in the industrial manufactures including integrated circuits (ICs) and multi-chip packages (MCPs).

Advances in outstanding property of polyimides (PIs) as thermally stable polymers along with expanded sources of monomers, have established that PSPIs can function over much broader range. With regard to the synthesis of PIs, poly(amic acid) (PAA) as a PI-precursor is typically prepared by ring-opening polyaddition of two monomers; a tetracarboxylic dianhydride and a diamine, which produces no side products (Figure 2.7). This simple chemistry and environmentally benign process allow us to evaluate photolithographic characterization directly from the polymerization solution (varnish), prompting to employ in industrial manufacturing. The PI films are mostly formed by thermal treatment of PAA (up to 350 °C) after casting the solution on a substrate. Such thermal imidization process addresses recently another aspect to be considered and claims an improvement toward low-temperature cyclization. Giving photosensitivity onto PIs or PI precursors enables them to produce pattern formation that simplifies the process significantly. Some PSPIs have taken over excellent chemistries developed by photoresists for microlithography, some have been employed with dissolution inhibitors, and some others have been involved in characteristics of own PIs. The most significant difference between PSPIs and photoresists is that PSPIs remain in the final manufactured products whereas the photoresists would be removed after pattern transfer to under-laid materials [17].

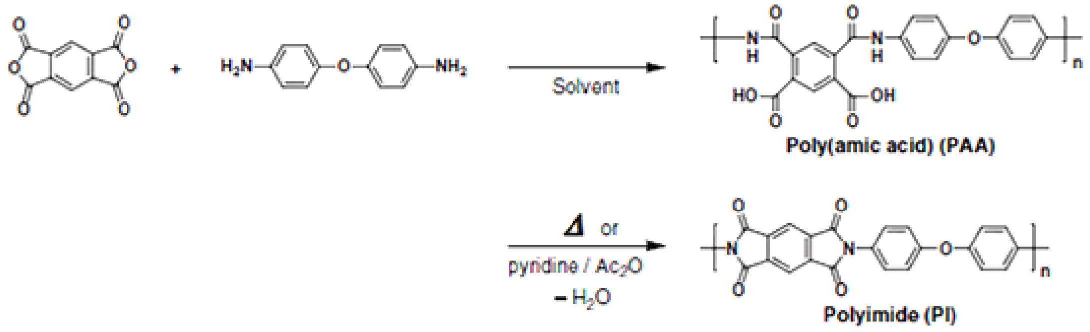


Figure 2.7 Synthesis of polyimide (PI) via poly(amic acid) (PAA) [17].

Thus, PSPIs are demanded mainly for two distinctive respects as shown in Figure 2.8; (i) photolithographic properties to make patterns; (ii) quality and durability required as final products. Imaging technique depends on photosensitivity introduced into a PSPI system as well as design of polymer structure which is also effective for the PI film properties. PSPIs should be consistent and satisfied with these factors simultaneously. Although PSPIs have been greatly contributed to the progress of microelectronics thus far, improving the versatility and robustness as well as resolution of the patterns is still crucial for expanding the utility of PSPIs in this important area. This review article highlights a recent progress of PSPIs including new concepts such as reaction development patterning, low-temperature imidization and mechanism-induced patterning etc. After brief introduction of a typical patterning process of PSPIs, various chemistries on PSPIs are described along with two major pattering methodologies; positive-, and negative-working PSPIs. The previously and/or originally developed PSPIs have been reviewed in the other literatures [17].

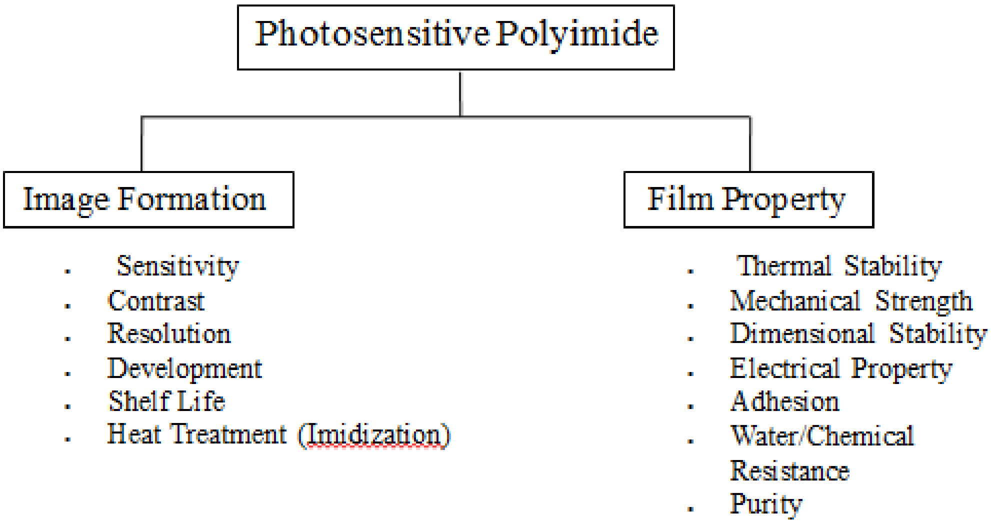


Figure 2.8 Requirement for development of PSPIs [17].

2.6 Photolithography of PSPIs

It is noteworthy that ‘‘PSPI’’ involves not only photopatternable PI with photoactive agents, but also photopatternable PI-precursor such as PAA or poly(amic ester) with photosensitive compounds. Thus, PSPI could be defined as that the origin of photosensitivity relies on either PI (or its precursor) matrix; or additives mixed with the matrix polymer. PI pattern formation by plasma etching through a patterned photoresist layer is not included in the PSPI system, which is known as a conventional fashion [17].

In this section, comparison of PI pattern formation in a conventional method and that using PSPI is described, followed by typical lithographic strategies-dissolution inhibitor, and chemical amplification (CA).

2.6.1 Patterning Process of PSPI vs. Conventional PI

Schematic representatives of photolithographic processes are shown in Figure 2.9. In a conventional method (Figure 2.9(a) and 2.9(b)), PIs are shaped into micropatterns by transfer of photolithographic patterns of an additional photoresist coated on a PI layer. Therefore, pattern formation of the photoresist and the following etching procedure are required. On the other hand, by incorporation of photosensitivity into PIs (or PI precursor), PSPIs enable to simplify a patterning process owing to elimination of a photoresist layer (Figure 2.9(c) and 2.9(d)). If a PI precursor is utilized for pattern formation, it is possible to convert the precursor pattern into the corresponding PI one by thermal imidization [17].

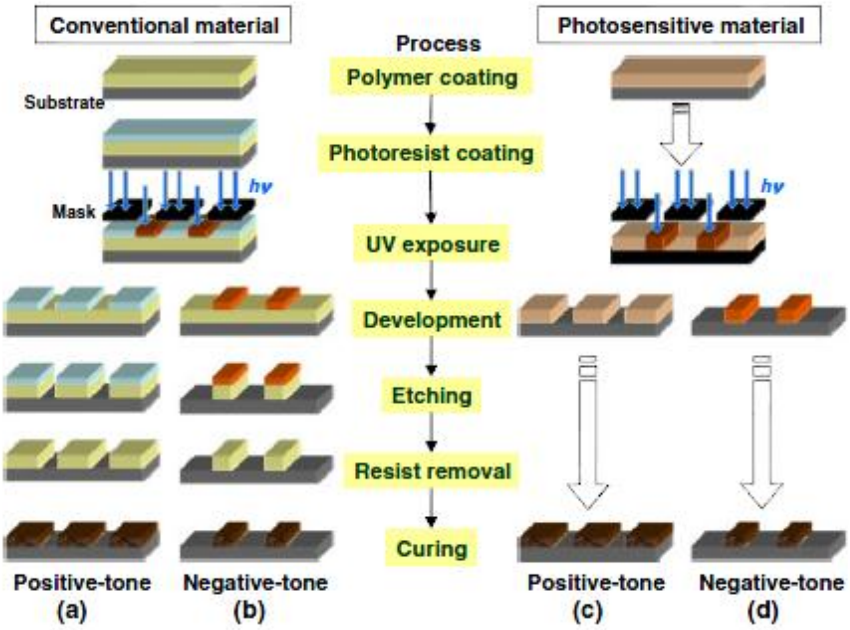


Figure 2.9 Photolithographic patterning processes in conventional methods using photoresists (a & b) and in advanced methods using photosensitive materials (c & d) [17].

After a photosensitive polymer is spin-coated onto a substrate of interest (e.g., a silicon wafer), this coated film is exposed to a UV light through a mask so that pattern information can be transferred to the film. As the source of UV light, wavelength at 436 nm (g-line) or 365 nm (i-line) is usually chosen for the lithography with PSPI materials. This photo-irradiation allows a coated polymer to undergo a chemical change such as deprotection, polarity change, chain-scission, cross-linking, imidization up on a post-exposure bake (PEB) (if necessary). In the following step of development, either the exposed or unexposed area is selectively removed resulting in a pattern formation. When the exposed area is washed out, that resist system is categorized in a positive-working (Figure 2.9(a) and 2.9(c)). On the other hand, a negative-working refers when the exposed area becomes insoluble in the developer (Figure 2.9(b) and 2.9(d)) [17].

In this regard, photolithographic evaluation involves many aspects, in other words, many flexibility to optimize for the best performance of patterning. For instance, the sensitivity of PSPIs depends on the transmittance of the polymer as coated on the substrate and the quantum yield of photosensitive units at the exposure wavelength, whereas the contrast is a function of the rate of cross-linked network formation for a negative resist and the rate of deprotecting reaction for a positive resist at a constant input dose. Furthermore, the rate of change of solubility with the proportion of the deprotection is dependent on the developer. Thus, there is a variety of the photosensitive polymer matrices incorporating additives such as photosensitizers (e.g., diazonaphthoquinones (DNQs) and photoacid generators (PAGs)) or cross-linkers, etc. [17]

2.7 Photosensitive Compound

2.7.1 Nifedipine

1,4-dihydropyridine (DHP) derivatives such as nifedipine (Figure 2.10) known as a medicine were also utilized in PSPI systems. Nifedipine (1,4-dihydro-2,6-dimethyl-4-(nitrophenyl)-3,5-pyridinedicarboxylic acid dimethyl ester) acts as a dissolution inhibitor in poly(amic acid) after a post-exposure bake (PEB) [17-19].

Figure 2.10 Nifedipine [43].

The two types of the photochemical reactions with DHP were proposed as follows: (1) When the temperature for PEB is low, DHP is converted into the corresponding pyridine derivative in the exposed area so that it can solubilize in alkaline developer to formulate a positive-working PSPI (Figure2.11). On the other hand, (2) when the PEB temperature is high (ca. 160 °C or higher), the dissolution behavior is reversed because the photo-generated pyridine derivative functions as a base catalyst promoting the thermal imidization to produce a negative-working PSPI [17-19].

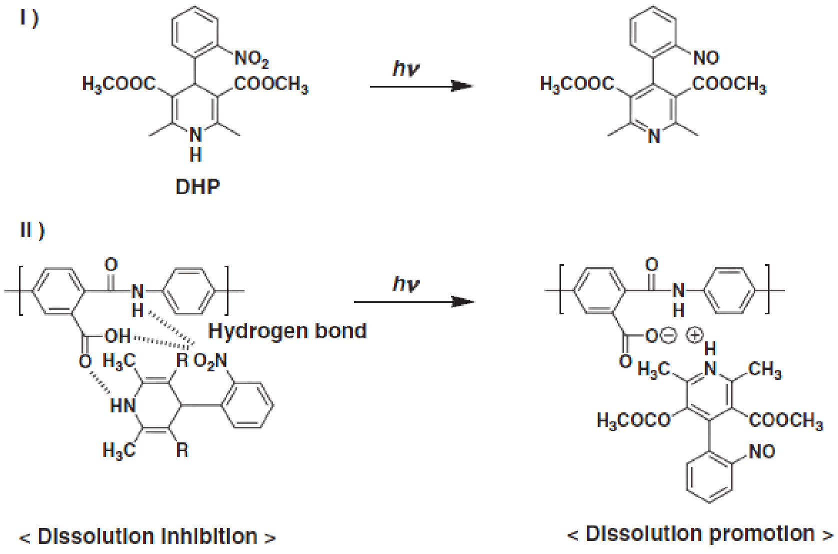


Figure 2.11 Dissolution inhibition mechanism with DHP [17].

2.8 Silane Coupling Agent

The value of silane coupling agents was first discovered in the 1940s in conjunction with the development of fiberglass reinforced polyester composites. When initially fabricated, these composites were very strong, but their strength declined rapidly during aging. This weakening was caused by a loss of bond strength between the glass and resin. In seeking a solution, researchers found that organo-functional silanes – silicon chemicals that contain both organic and inorganic reactivity in the same molecule – functioned as coupling agents in the composites. A very small amount of an organo-functional alkoxy silane reacted at the glass-resin interface did not only significantly increase initial composite strength but also resulted in a dramatic retention of that strength over time. Subsequently, other applications for silane coupling agents were discovered (e.g., mineral and filler treatment for composite reinforcement; adhesion of paints, inks and coatings; reinforcement and cross-linking of plastics and rubber; cross-linking and adhesion of sealants and adhesives; and in the development of water repellents and surface protection) [44].

2.8.1 Organosilane Chemistry

Monomeric silicon chemicals are known as silanes. A silane that contains at least one carbon-silicon bond (Si-C) structure is known as an organosilane. The organosilane molecule (Figure 2.12) has three key elements:

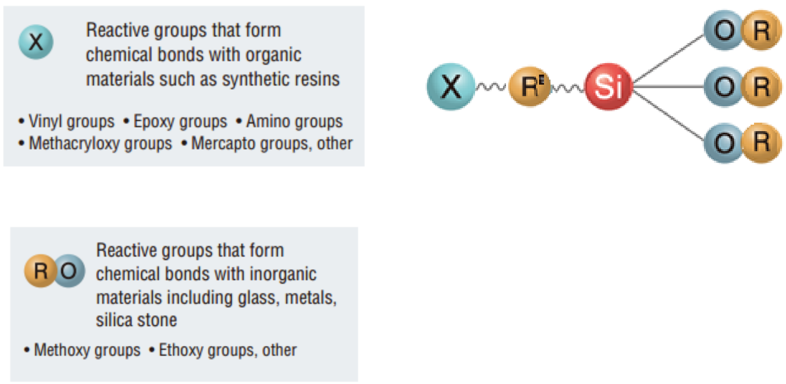


Figure 2.12 The organosilane molecule [45].

$X-R'-Si(OR)_3$
X = Organic (e.g., Amino, Vinyl, Alkyl…)
R = Methyl, Ethyl, Isopropyl…
R' = Aryl or Alkyl $(CH_2)_n$ with $n = 0, 1$ or 3

X -a non-hydrolyzable organic moiety. This moiety can be reactive toward another chemical (e.g., amino, epoxy, vinyl, methacrylate, sulfur) or non-reactive (e.g., alkyl).

OR - a hydrolyzable group, like an alkoxy group (e.g., methoxy, ethoxyisopropoxy) or an acetoxy group that can react with various forms of hydroxyl groups present in mineral fillers or polymers and liberates alcohols (methanol, ethanol, propanol) or acid (acetic acid). These groups can provide the linkage with inorganic or organic substrates.

R’ - a spacer, which can be either an aryl or alkyl chain, typically propyl, Through their dual reactivity, organosilanes serve as bridges between inorganic or organic substrates (such as minerals, fillers, metals and cellulose) and organic/ polymeric matrices (such as rubber, thermoplastics or thermosetting) and, hence, can dramatically improve adhesion between them. See Figure 2.13.

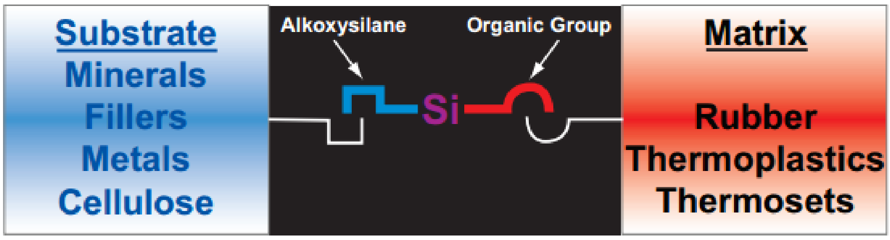


Figure 2.13 How organosilane molecules work [44].

2.8.2 Typical Silane Applications

Adhesion Promoter (Figure 2.14): Organosilanes are effective adhesion promoters when used as integral additives or primers for paints, inks, coatings, adhesives and sealants. As integral additives, they must migrate to the interface between the adhesive layer and the substrate to be effective. As a primer, the silane coupling agent is applied to the inorganic substrate before the product to be adhered is applied. By using the right organosilane, a poorly adhering paint, ink, coating, adhesive or sealant can be converted to a material that will frequently maintain adhesion even if subjected to severe environmental conditions (e.g., high temperature, underwater immersion or UV radiation) [44].

Figure 2.14 Adhesion promoter [46].

Dispersing/Hydrophobing Agent: Organosilanes with hydrophobic organic groups attached to silicon will impart that same hydrophobic character to a hydrophilic inorganic surface. They are used as durable hydrophobing agents in concrete construction applications, including bridge and deck applications. They are also used to hydrophobe inorganic powders to make them free flowing and dispersible in organic polymers and liquids. They also improve cure (by reducing catalyst inhibition) and electrical properties [44].

Coupling Agent: Organosilanes are used couple organic polymers to inorganic materials (Figure 2.15). Typical of this application are reinforcements, such as fiberglass and mineral fillers, incorporated into plastics and rubbers [44].

Figure 2.15 Silane coupling agent [47].

2.8.3 1-[3-(Trimethoxysilyl)propyl]urea (γ –Ureidopropyltriethoxy silane)

1-[3-(Trimethoxysilyl)propyl]urea (Figure 2.16) is known as a commercial silane coupling agent (Table 2.5). It has better stability than others silane in reactive polymer systems, like phenolic, epoxy or polyurethane. It has good adhesion between the inorganic filler and the polymer. The polymer laminate comprising a 1-[3-(Trimethoxysilyl)propyl]urea does not contain any intermediate adhesive layer, and the polymer layer combines the benefits of adhesion to a metal materials [11-13].

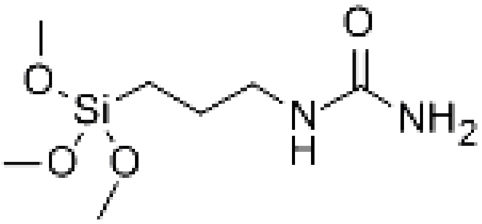


Figure 2.16 Chemical structure of 1-[3-(Trimethoxysilyl)propyl]urea [48].

Table 2.5 Commercial silane (silane coupling agent) [44]

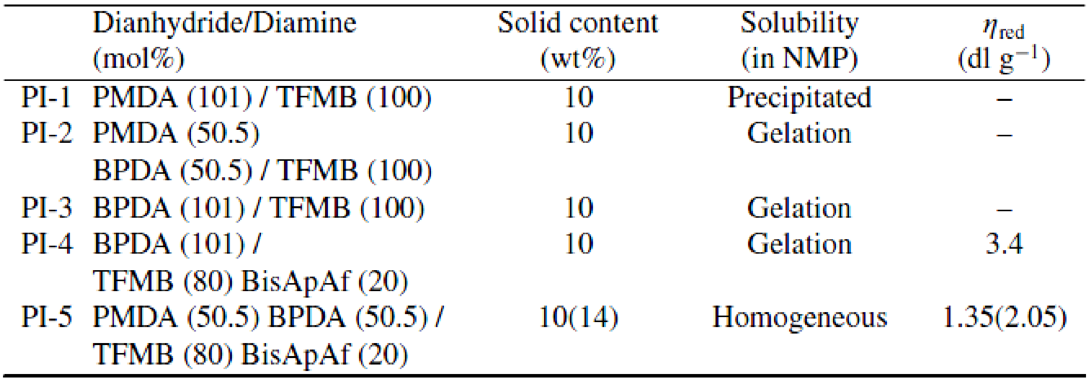
Silane	Organic Reactivity X	Alkoxy Group OR	Chemical Name
XIAMETER® OFS-6030 Silane	Methacrylate	Methoxy	γ-Methacryloxypropyltrimethoxy silane
XIAMETER® OFS-6040 Silane	Epoxy	Methoxy	γ -Glycidoxypropyltrimethoxy silane
XIAMETER® OFS-6076 Silane	Chloropropyl	Methoxy	γ -Chloropropyltrimethoxy silane
Dow Corning® Z-6376 Silane	Chloropropyl	Ethoxy	γ -Chloropropyltriethoxy silane
Dow Corning® Z-6300 Silane	Vinyl	Methoxy	Vinyltrimethoxy silane
XIAMETER® OFS-6075 Silane	Viny	Acetoxy	Vinyltriacetoxy silane
Dow Corning® Z-6910 Silane	Mercapto	Ethoxy	Mercaptopropyltriethoxy silane
XIAMETER® OFS-6920 Silane	Disulfido	Ethoxy	Bis-(triethoxysilylpropyl)-disulfide
XIAMETER® OFS-6940 Silane	Tetrasulfido	Ethoxy	Bis-(triethoxysilylpropyl)-tetrasulfide
Dow Corning® Z-6675 Silane	Ureido	Methoxy	γ -Ureidopropyltriethoxy silane
XIAMETER® OFS-6106 Silane	Epoxy/melamine	Methoxy	Epoxy silane modified melamine resin

CHAPTER III

LITERATURE REVIEWS

Junichi I. and Tadashi A. (2009) [1] studied organo-soluble low CTE polyimides and their applications to photosensitive cover layer materials in flexible printed circuit boards. First, they synthesis a high molecular weight of polyimide composed of PMDA, BPDA, TFMB and BisApAf (Table 3.1), which was prepared by the one-pot polycondensation in NMP without precipitation and gelation.

Table 3.1 Polymerization conditions and reduced viscosities of polyimides [1].



	Dianhydride/Diamine (mol%)	Solid content (wt%)	Solubility (in NMP)	η_{red} (dl g^{-1})
PI-1	PMDA (101) / TFMB (100)	10	Precipitated	–
PI-2	PMDA (50.5) BPDA (50.5) / TFMB (100)	10	Gelation	–
PI-3	BPDA (101) / TFMB (100)	10	Gelation	–
PI-4	BPDA (101) / TFMB (80) BisApAf (20)	10	Gelation	3.4
PI-5	PMDA (50.5) BPDA (50.5) / TFMB (80) BisApAf (20)	10(14)	Homogeneous	1.35(2.05)

The excellent solubility in common organic solvents for this PI (PI-5; PMDA 50.5 mol%, BPDA 50.5 mol%, TFMB 80 mol% and BisApAf 20 mol%) allowed solution-casting. Unexpectedly, the obtained PI film showed a low CTE without thermal imidization process in addition to other combined properties, a low CTE, a high T_g, high thermal stability, low water absorption, comparatively good transparency and sufficient film flexibility (Table 3.2). Furthermore, fine positive-tone patterns could be obtained from DNQ (10 phr) containing PI-5 (PSPI-5) with a sensitivity of 238 mJ/cm^2 (Figure 3.1). Both PI-5 and PSPI-5 also achieved excellent insulation properties and non-flammability (Table 3.3). The results revealed that the present PI system is a promising candidate as a novel cover layer material (Figure 3.2) [1].

Table 3.2 Film properties of PI-5 and PSPI-5 [1].

Cover material	T_g (°C)	CTE (ppm K^{-1})	[1]Curling (mm)	W_A (%)	Tensile modulus (GPa)	Elongation (%)	Tensile strength (MPa)	T%	T_d^5 in N_2 (°C)
PI-5	280	14.3[ave. 100–150°C] 18.1[ave. 150–200°C]	h = –14.5	0.1	1.98	6.00	151	0.01 [365nm] 54.4 [405nm] 83.6 [436nm]	443.5
PSPI-5	292	19.1[ave. 100–150°C] 23.9[ave. 150–200°C]	h = –1.75	0.3	2.57	5.25	156	–	354.7

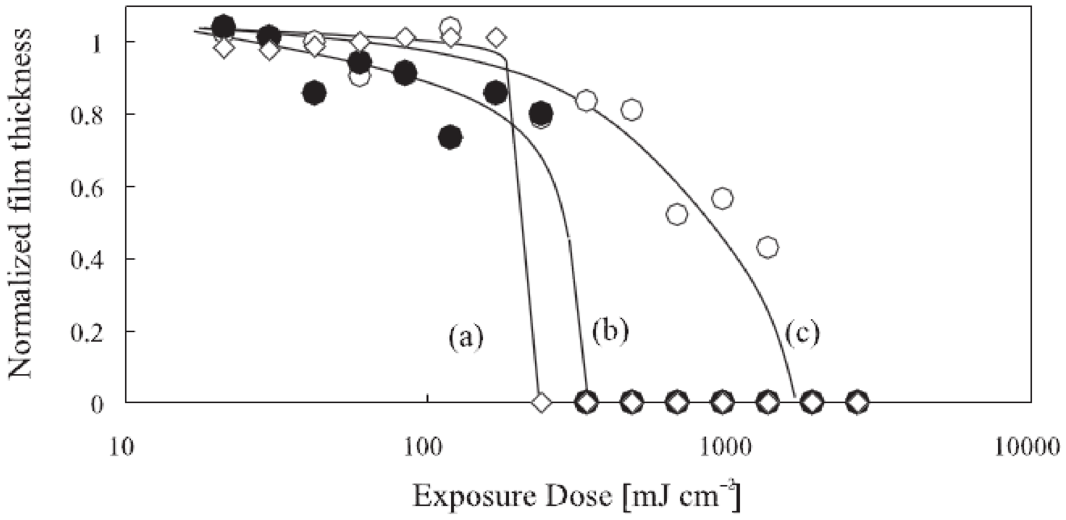


Figure 3.1 Photosensitivity curves for PSPI-5 film as a function of DNQ content: (a) 9.09 wt% (10 phr), (b) 16.6 wt% (20 phr), and (c) 23.1 wt% (30 phr) [1].

Table 3.3 Insulation properties and non-flammability for cover materials [1].

Sample	Insulation resistance (Ω)	Non-flammability
PI-5	7.49×10^{13}	UL-94, V-0
PSPI-5	3.83×10^{13}	UL-94, V-0

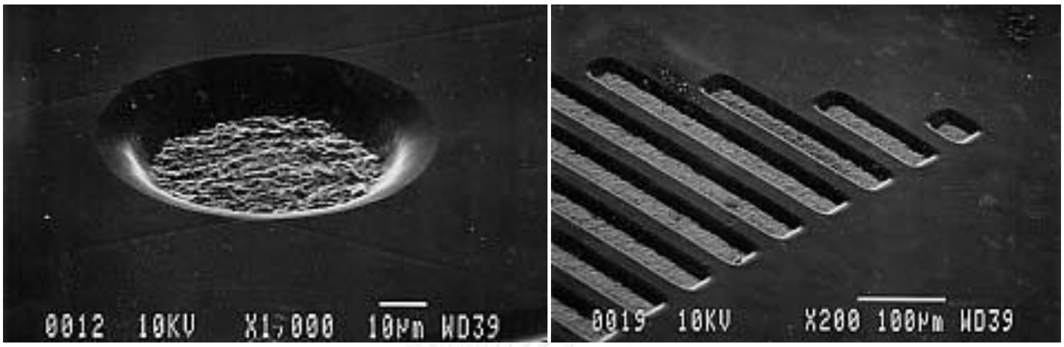


Figure 3.2 SEM photographs of positive-tone fine patterns obtained from PSPI-5 (10 μm thick, DNQ: 9.09 wt%): (a) dot and (b) line and space patterns. Developed using a 3 wt% NaOH aqueous solution at 40°C for 150 s and rinsed in water at 40°C for 120 s after irradiation of 1500 mJ/cm^2 [1].

Sheng-Huei H. and Yu-Jen C. (2002) [8] interested structure-property of aromatic polyimides derived from PMDA and BPDA dianhydrides with structurally different diamines. Typical examples are Du Pont's Kapton type polyimide, derived from pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA), and Ube's Upilex type polyimides, i.e., Upilex R from 3,4,3',4'-biphenyltetracarboxylic dianhydride (BPDA) and ODA and Upilex S from BPDA and p-phenylene diamine (PDA). Several systematically varied aromatic polyimides having high molecular weights were prepared by the classic two-step procedure from dianhydrides PMDA and BPDA with various structurally different diamines, and almost all the polymers afforded flexible and tough films by successive heating the poly(amic acid) films to elevated temperatures.

In Table 3.4, the PMDA/ODA polyimide revealed a higher T_g in comparison to that of the corresponding BPDA/ODA polyimide because of a higher rigidity of the polymer chain. Both of ODA-based polyimides exhibited high thermal stability. However, the BPDA/ODA polyimide has CTE much lower than PMDA/ODA polyimide. It was proposed that the low thermal expansion coefficient appeared when the conformation of the molecular chain became linear.

Table 3.4 Characterization of 4,4'-ODA based polyimide [8].

Dianhydride	**Diamine**	**Viscosity (dl/g)**	**film quality**	**T_g (°C)**	**T_d (°C)**	**Char yield (%)**	**CTE (ppm/°C)**
PMDA	4,4'-ODA	2.44	flexible	352	614	58	50
BPDA	4,4'-ODA	2.02	flexible	270	612	64	28

M. Ree et al. (2000) [6] studied on self-adhesion of poly(4,4'-oxydiphenylene biphenyltetracarboximide) (s-BPDA/4,4'-ODA polyimide) and its adhesion to substrates. The s-BPDA/4,4'-ODA polyimidewas synthesized in N-methyl pyrrolidone (NMP) from biphenyltetracarboxylic dianhydride (s-BPDA) and 4,4'-oxydiphenylene (4,4'-ODA), and then converted to the polyimide in films by thermal imidization at 400°C. The polyimide exhibits high T_g (313°C) (Figure 3.3), exceptionally good self-adhesion (814–1187 J/m^2) and also good adhesions (>687 J/m^2) to inorganic substrates such as silicon wafer and glass ceramic (see Table 3.5). An oxygen plasma treatment enhances the self-adhesion highly, whereas a silane primer treatment improves the adhesions to the substrates. In addition, the morphological structure and some other properties were investigated.

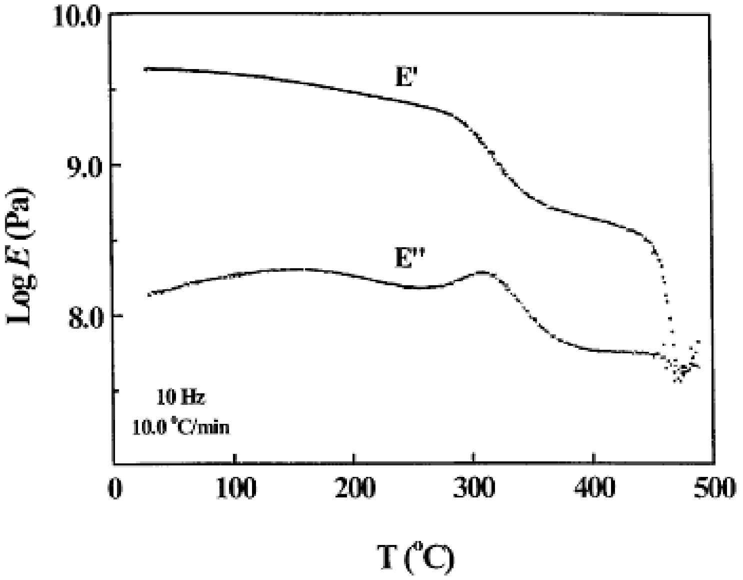
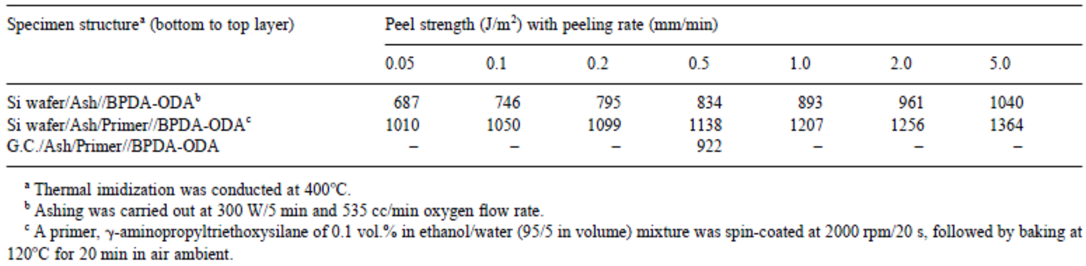


Figure 3.3 Variations of dynamic moduli (storage modulus E′ and loss modulus E″) of BPDA-ODA polyimide film as a function of temperature. The employed frequency and heating rate were 10 Hz and 10.0 K/min, respectively [6].

Table 3.5 Adhesion of BPDA-ODA polyimide to substrates: silicon wafer with oxidized surface and glass ceramic (GC) substrate [6].



Specimen structure[a] (bottom to top layer)	Peel strength (J/m^2) with peeling rate (mm/min)						
	0.05	0.1	0.2	0.5	1.0	2.0	5.0
Si wafer/Ash//BPDA-ODA[b]	687	746	795	834	893	961	1040
Si wafer/Ash/Primer//BPDA-ODA[c]	1010	1050	1099	1138	1207	1256	1364
G.C./Ash/Primer//BPDA-ODA	–	–	–	922	–	–	–

[a] Thermal imidization was conducted at 400°C.

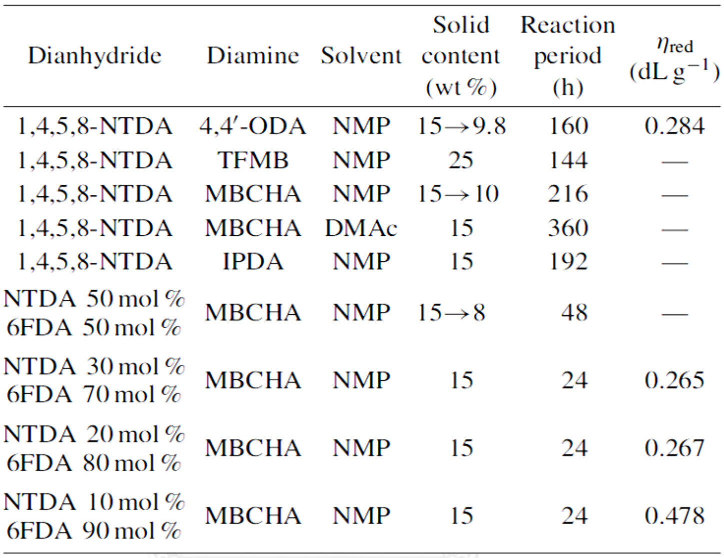
[b] Ashing was carried out at 300 W/5 min and 535 cc/min oxygen flow rate.

[c] A primer, γ-aminopropyltriethoxysilane of 0.1 vol.% in ethanol/water (95/5 in volume) mixture was spin-coated at 2000 rpm/20 s, followed by baking at 120°C for 20 min in air ambient.

M. Hasegawa and S. Horii (2007) [9] studied in low-CTE polyimides derived from 2,3,6,7-naphthalenetetracarboxylic dianhydride. They told that naphthalenetetracarboxylic dianhydride (NTDA) can be a candidate monomer in achieving both of low CTE and low water absorption. The combinations of 1,4,5,8-NTDA and sulfonated diamines are known to give heat resistant proton-conductive membrane. The commercially available 1,4,5,8-NTDA consisting of thermodynamically stable six-membered anhydride groups had very poor PAA polymerizability. But, the precipitate could be dissolved upon mild heating around

80°C to form a clear solution. The inherent viscosity of PAA (1,4,5,8-NTDA/4,4’-ODA) was 0.284 dL/g (see Table 3.6). However, it was possible to copolymerize with other dianhydride such as 6FDA when a minor portion of 1,4,5,8-NTDA (≤30 mol %) was used, because of its poor PAA polymerizability under the common conditions.

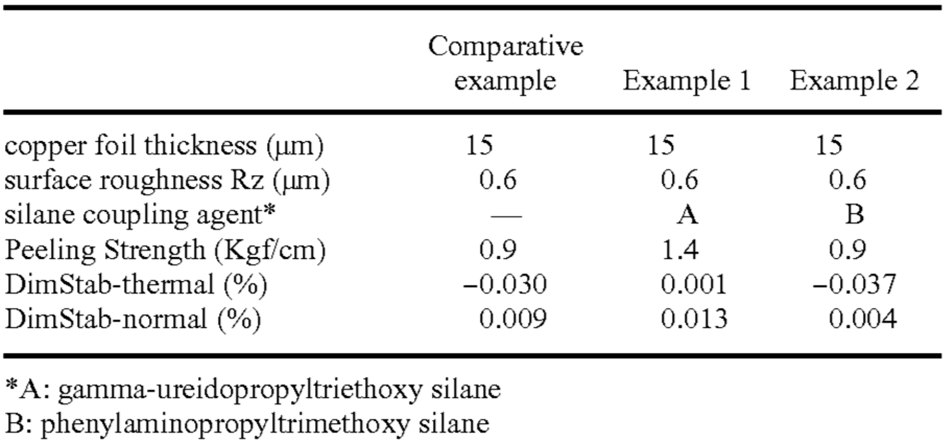
Table 3.6 Polymerization conditions and inherent viscosities of PAAs in 1,4,5,8-NTDA systems [9].



Dianhydride	Diamine	Solvent	Solid content (wt %)	Reaction period (h)	η_{red} (dL g^{-1})
1,4,5,8-NTDA	4,4′-ODA	NMP	15→9.8	160	0.284
1,4,5,8-NTDA	TFMB	NMP	25	144	—
1,4,5,8-NTDA	MBCHA	NMP	15→10	216	—
1,4,5,8-NTDA	MBCHA	DMAc	15	360	—
1,4,5,8-NTDA	IPDA	NMP	15	192	—
NTDA 50 mol % 6FDA 50 mol %	MBCHA	NMP	15→8	48	—
NTDA 30 mol % 6FDA 70 mol %	MBCHA	NMP	15	24	0.265
NTDA 20 mol % 6FDA 80 mol %	MBCHA	NMP	15	24	0.267
NTDA 10 mol % 6FDA 90 mol %	MBCHA	NMP	15	24	0.478

Yu-Jen C.et al. (Patent US2009/0197104) [13] provides a BPDA/BTDA/PDA/ODA polyimide laminate comprising a 1-[3-(Trimethoxysilyl)propyl]urea (silane coupling agent) 1 wt% or less of the total weight of the polyimide precursor to solve the adhesion problem (Table 3.7). The laminate does not contain any intermediate adhesive layer, and the polyimide layer combines the benefits of strong adhesion to a copper foil, high transparency, good mechanical properties and thermal stability.

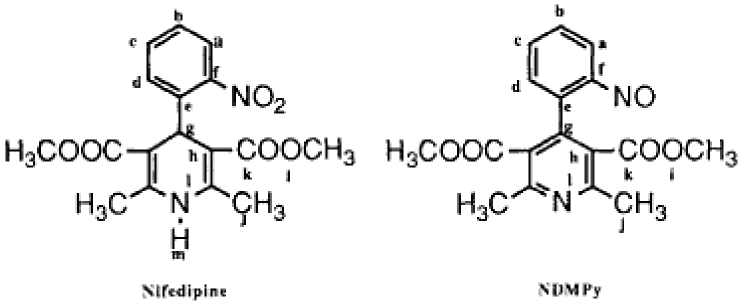
Table 3.7 Comparative of peeling strength of polyimide [13].



	Comparative example	Example 1	Example 2
copper foil thickness (μm)	15	15	15
surface roughness Rz (μm)	0.6	0.6	0.6
silane coupling agent*	—	A	B
Peeling Strength (Kgf/cm)	0.9	1.4	0.9
DimStab-thermal (%)	−0.030	0.001	−0.037
DimStab-normal (%)	0.009	0.013	0.004

*A: gamma-ureidopropyltriethoxy silane
B: phenylaminopropyltrimethoxy silane

T. Omote and T. Yamaoka (1992) [20] showed positive-type polyimide precursor (BPDA/DDE) has been developed and examined. It is synthesized by the polycondensation of biphenyltetracarboxylic dianhydride and 4,4'-diamino-diphenyl ether, based on systems composed of dimethyl 1,4-dihydro-2,6-dimethyl-4-(2-nitrophenyl)-3,5-pyridinecarboxylate (nifedipine). Nifedipine photoconverted quantitatively to 4-(2'-nitrosophenyl)-2,3-dicarboxymethyl-3,5-dimethylpyridine (NDMPy) in a polyimide precursor film (Figure 3.4-3.5). It has been confirmed that nifedipine and NDMPy in the film act as a dissolution inhibitor and as a dissolution promoter, respectively.



Nifedipine NDMPy

Figure 3.4 Chemical structure of nifedipine and 4-(2'-nitrosophenyl)-2,3-dicarboxymethyl-3,5-dimethylpyridine (NDMPy) [20].

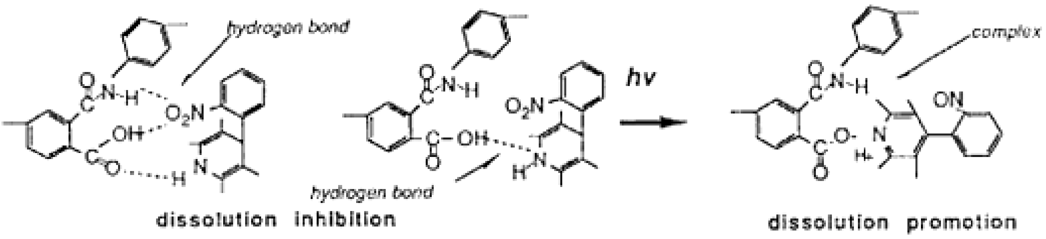


Figure 3.5 Nifedipine photoconverted quantitatively to NDMPy in a polyimide precursor film [20].

This system is positive-working and developable with 1.5% TMAH aqueous solution. The sensitivity and contrast of the system were evaluated by the characteristic curves (Fig. 12). The characteristic curves were prepared from the films containing 20 to 30 wt% nifedipine. With increasing concentration of nifedipine, the solubility inhibition increases and sensitivity slightly decreases. The values of sensitivity and contrast are listed in Table 3.8. The photoreactive polyimide precursor (BPDA/DDE), including 25wt% nifedipine, shows a 170 mJ/cm^2 sensitivity and a 5.5 γ value.

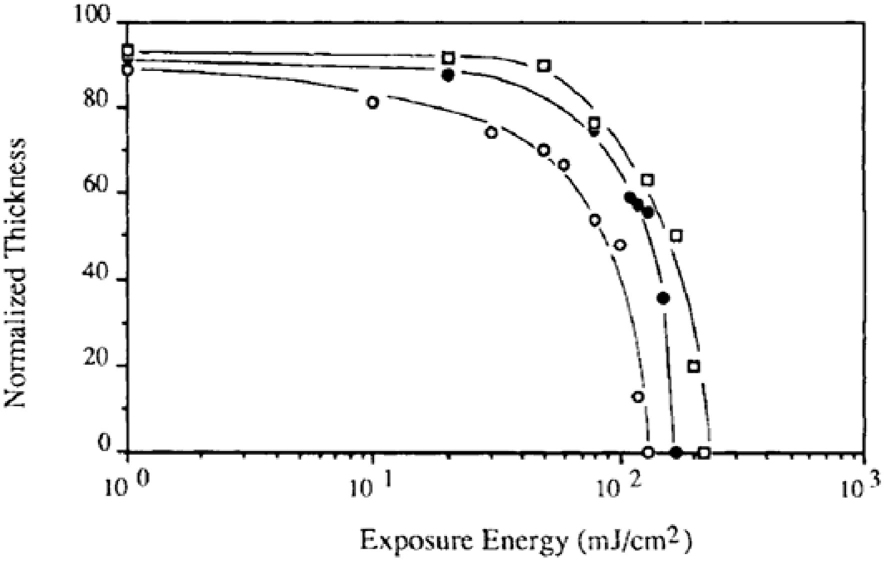


Figure 3.6 Characteristic curves of the film with nifedipine. Nifedipine concentration (wt%): (○)20; (●)25; (□)30 [20].

Table 3.8 Lithographic characteristics of the system [20].

Content of Nifedipine (wt%)	Sensitivity (mJ/cm^2)	Contrast (γ)
20	130	4.4
25	170	5.5
30	220	4.3

CHAPTER IV

EXPERIMENT

4.1 Materials

The chemicals used in this work were purchased from commercial sources listed in Table 4.11 and used as-received.

Table 4.1 Sources and purity of chemicals used.

Monomer	Source	Purity (%)
3,3′,4,4′-Biphenyltetracarboxylic dianhydride (s-BPDA)	Aldrich	99.0
1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTDA)	Aldrich	99.5
4,4′-Oxydianiline (4,4’-ODA)	TCI	98.0
Nifedipine	Aldrich	98.0

4.2 Synthesis of poly(amic acid) (PAA)

A solution of 4,4’-oxydianiline (ODA) (0.6007 g, 3.0 mmol) in NMP (3.5 ml, 8.4 g) was added with stirring s-BPDA (0.7943 g, 2.7mmol or 90% of 3.0 mmol) and NTDA (0.0815 g, 0.3 mmol or 10% of 3.0 mmol). The mixture was stirred at room temperature for 2 h and 80ºC for 30 min to form homogeneous poly(amic acid) (PAA) solution. The poly(amic acid) (PAA) solution obtained was dried at 100ºC for 1 h, followed by annealing at 300ºC for 2 h in air oven to form PI films.

4.3 Synthesis of photosensitive polyimide (PSPI)

The poly(amic acid) (PAA) obtained was mixed with nifedipine (20 wt% of PAA). The mixture was stirred at room temperature for 30 min to yield homogeneous photosensitive PAA solution.

4.4 Synthesis of silane-containing photosensitive polyimide (si-PSPI)

The poly(amic acid) (PAA) solution obtained was added with stirring nifedipine (20 wt% of PAA) and 1-[3-(Trimethoxysilyl)propyl]urea (0, 0.5 and 1.0wt% of PAA). The mixture was stirred at room temperature for 2 h to form homogeneous photosensitive polyimide precursor. The photosensitive polyimide precursor was coated onto a copper foil and baked at 85ºC for 10 min. The resultant 30 μm thick photosensitive polyimide (PSPI) films were exposed on a UV lamp through a photo mask, then developed in a 10wt% potassium hydroxide aqueous solution at 40^{o}C 1 min and then rinsed with 40^{o}C hot water 20 seconds, followed by post-exposure baked and cured at 300ºC for 2 h in air oven to form an adhesive photosensitive polyimide copper clad laminate.

4.5 Dissolution rate determination

The PSPI was coated onto a copper foil and baked at 85ºC for 15 min. The resultant 30 µm thick PSPI films were exposed on a 250W UV lamp through a photo mask. The exposed films were post-baked at 130-160^{o}C for 20 min then developed in 10wt% potassium hydroxide aqueous solution at 40^{o}C and 1 min and then rinsed with 40^{o}C hot water for 20 seconds. The dissolution rates (Equation 4.1) were calculated from the film thickness before and after developing in the KOH solution, followed by dividing the decreased thickness by the developing time. [49]

$$\text{Dissolution rate} = \frac{T_i - T_f}{t_{dev}} \qquad (4.1)$$

When T_i is film thickness before development

T_f is film thickness after development

t_{dev} is developing time

4.6 Photosensitivity and contrast evaluation

The 30μm PSPI films on copper foil were exposed to the filtered UV lamp, and were developed in 10wt% potassium hydroxide aqueous solution at 40^{o}C 1 min and then rinsed with 40^{o}C water for 20 seconds. The characteristic exposure curve was obtained by plotting the normalized film thickness against exposure energy. The normalized film thickness and the contrast of film were calculated using Equation 4.2 [50] and 4.3 [51], as expressed below.

$$\text{Normalized film thickness} = \frac{\text{Thickness of exposed film}}{\text{Thickness of unexposed film}} \qquad (4.2)$$

$$\text{Contrast}(\gamma) = \frac{1}{\log_{10}\left(\frac{D_f}{D_o}\right)} \qquad (4.3)$$

When D_o is the highest exposure dose that has the normalized film thickness as 1.0

D_f is the lowest exposure dose that has the normalized film thickness as 0.0

4.7 Characterizations of the resulting PI cover films

4.7.1 Differential scanning calorimeter (DSC)

Glass transition temperature (Tg) was measured with a differential scanning calorimeter (Perkin Elmer DSC 8000) at a heating rate of 10°C/min in a nitrogen flow. The sample mass used is 5-10 mg.

4.7.2 Dynamic mechanical analysis (DMA)

DMA was carried out on PI film specimens (23.7 mm long, 5 mm wide, and 50-60 μm thick) on a Rheometrics Solids Analyzer RSA II instrument at a heating rate of 5ºC/min with a load frequency of 1 Hz in a nitrogen atmosphere.

4.7.3 Thermomechanical analysis (TMA)

The CTEs of the PI specimens (10 mm long, 5 mm wide, and typically 30 μm thick) were measured at a heating rate of 5°C/min as an average value within 100–200°C for the film plane direction on a thermomechanical analyzer (Bruker-AXS, TMA 4010) with a fixed load of 5 mN (0.5 g) in a nitrogen flow.

4.7.4 Thermogravimetric analysis (TGA)

A Diamond TG/DTA Thermogravimetric/Differential Thermal Analyzer (TGA) was conducted to evaluate the thermal stability of the PI films at a heating rate of 10 °C/min in nitrogen and air. The 10% weight loss temperatures (T_{d10}) were compared.

4.7.5 Fourier transform infrared spectroscopy (FTIR)

Nicolet 6700 FTIR spectrometer was used in this research to monitor the imidization reaction. The spectrum is reported from 400 to 4,000 cm^{-1} and scanning times of 64 at a resolution of 4 cm^{-1}.

4.7.6 Instron universal testing machine

Tensile strength and tensile modulus of the polyimide films were determined using a universal testing machine. The sample dimension is 10×100×0.05 mm^3 (L×W×T) with a test speed of 5 mm/min following ASTM D 882-02.

4.7.7 LCR meter

Dielectric constants of the polyimide and copolyimide films were determined by LCR meter. The measurement was performed at room temperature and at a frequency of 1 kHz with Agilent E4980A Precision LCR meter.

4.7.8 Confocal microscope

Confocal microscope could be analyzed surface characteristic and lithographic formed on surface of polyimide. The polyimide films were characterized using a confocal laser scanning microscope with model of Olympus OLS3000. In this research, the morphology of the polyimide films was measured by Confocal Microscope with magnification of 5x.

4.7.9 Optical microscope

Relief patterns formed by development under an optimum condition were observed by optical microscopy (model Nikon ECL1PSE E600 POL).

CHAPTER V

RESULTS AND DISCUSSION

5.1 Copolymer film characterization

5.1.1 Kinetic of the imidization

The kinetics of imidization is measured by the degree of transformation of poly(amic acid) (PAA) into polyimide by given output parameters - temperature and time of reaction. Appropriate method for determination of imidization degree is FTIR spectroscopy. The band at 1380 cm^{-1} is called imide II (C–N–C vibration) band and using for qualitative and quantitative estimations of imidization degree in the present of internal standard at 1500 cm^{-1} (C-C Ar vibrations) [52, 53]. The imidization degree of poly(amic acid) (PAA) to polyimide (PI) was determined using equation (1).

$$\text{Degree of imidization}=\frac{(\text{peak area at 1380 cm}^{-1})_{\text{time}}/(\text{peak area at 1500 cm}^{-1})_{\text{time}}}{(\text{peak area at 1380 cm}^{-1})_{300^{\text{o}}\text{C}}/(\text{peak area at 1500 cm}^{-1})_{300^{\text{o}}\text{C}}} \qquad (1)$$

Degree of imidization is calculated from the IR spectrum is shown in Figure 5.1 that shows the spectra of the s-BPDA/NTDA(70/30)-ODA copolyimides post-cured at various temperatures. At curing 100 ºC 1 hour followed post-cured at 250, 280 and 300ºC 2 hours each, the shape of the spectrum changes significantly, indicating the thermal imidization reaction proceeds at this temperature range. The peak at 1380 cm^{-1} increases in intensity and cannot be distinguished above 280ºC. The spectra post-cured at 280ºC is similar to that of the spectra post-cured at 300ºC, suggesting that the films above 280ºC are almost fully imidized.

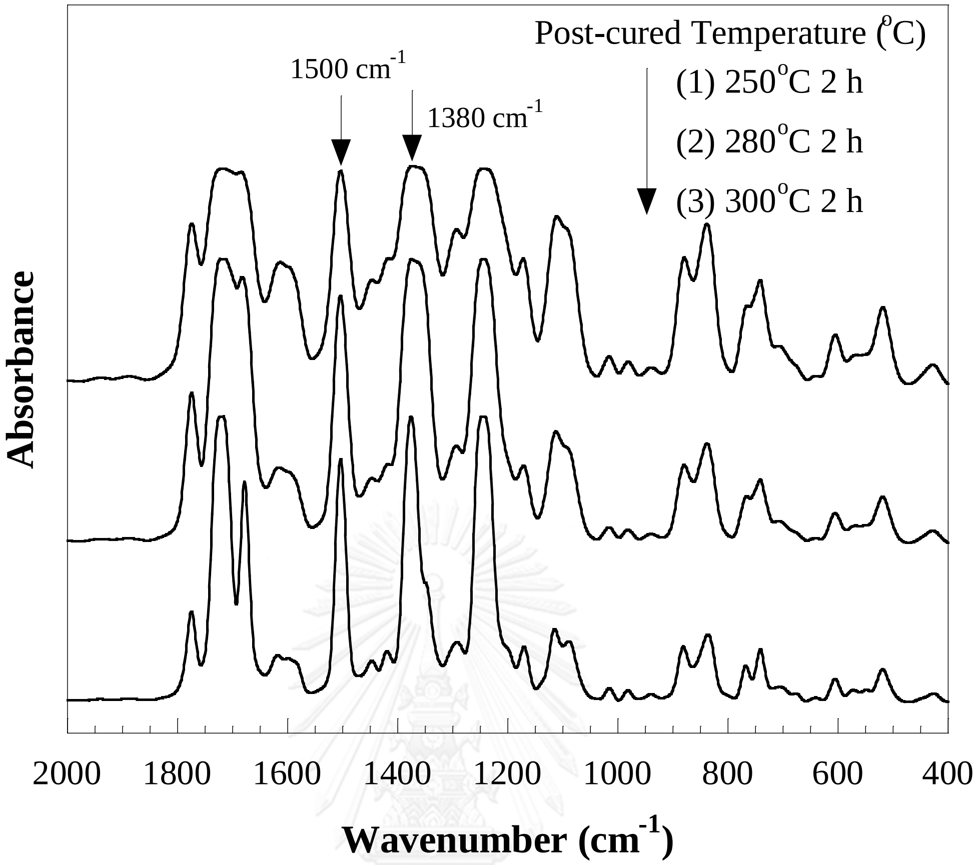


Figure 5.1 IR spectra of the s-BPDA/NTDA(70/30)-ODA copolyimides at curing 100ºC 1 h followed post-cured at temperature: (1) 250oC for 2 h, (2) 280oC for 2 h, (3) 300oC for 2 h.

The results from the calculations of the degree of imidization are presented in Table 5.1. The s-BPDA/NTDA(70/30)-ODA copolyimide thermally treated for 2 hours at 300°C displays fully imidized (100% of imidization degree). The s-BPDA/NTDA(70/30)-ODA copolyimide thermally treated for 2 hours at 280°C displays a higher degree of imidization than that thermally treated for 2 hours at 250°C. From this table, to achieve >90% imidization degree, post-curing temparature of >280ºC is necessary for the present curing condition (2 hours).

Table 5.1 Degree of imidization of the s-BPDA/NTDA(70/30)-ODA copolyimides at curing 100 ºC 1 h followed at various post-cured temperature.

Post-cured Temperature (°C)	Degree of Imidization (%)
250	85
280	97
300	100

5.1.2 Imidization of s-BPDA/ODA polyimide and its copolyimides with NTDA

The structures of s-BPDA/ODA polyimides were confirmed by FTIR. As presented in Figure 5.2, the completion of the imidization was confirmed by the absence of anhydride carbonyl peaks in the FTIR spectra in the regions of 1560 cm^{-1} and 1650 cm^{-1} and the appearance of the napthalimide carbonyl absorptions at 1713 cm^{-1} (asymmetric) and 1665 cm^{-1} (symmetric) [1, 10]. This is observed that the quantity and the intensity of the new bands (1713 and 1665 cm^{-1}) corresponding to the carbonyl group in NTDA increase when increasing NTDA contents [54, 55]. The C-N-C vibration of six-membered dianhydride was observed around 1344 cm^{-1} [10]. FTIR spectra of the obtained PIs showed intensive characteristic imide bands at 1776 cm^{-1} (imide C=O asymmetrical stretching), 1723 cm^{-1} (imide C=O symmetrical stretching), 1380 cm^{-1} (C–N–C vibration (imide II)), 1240 cm^{-1} (ether linkages (Ar-O-Ar)), 1140 cm^{-1} (C–H bend (imide III)), and 740 cm^{-1} (C=O bend (imide IV)), confirming the complete imidization of our films [55].

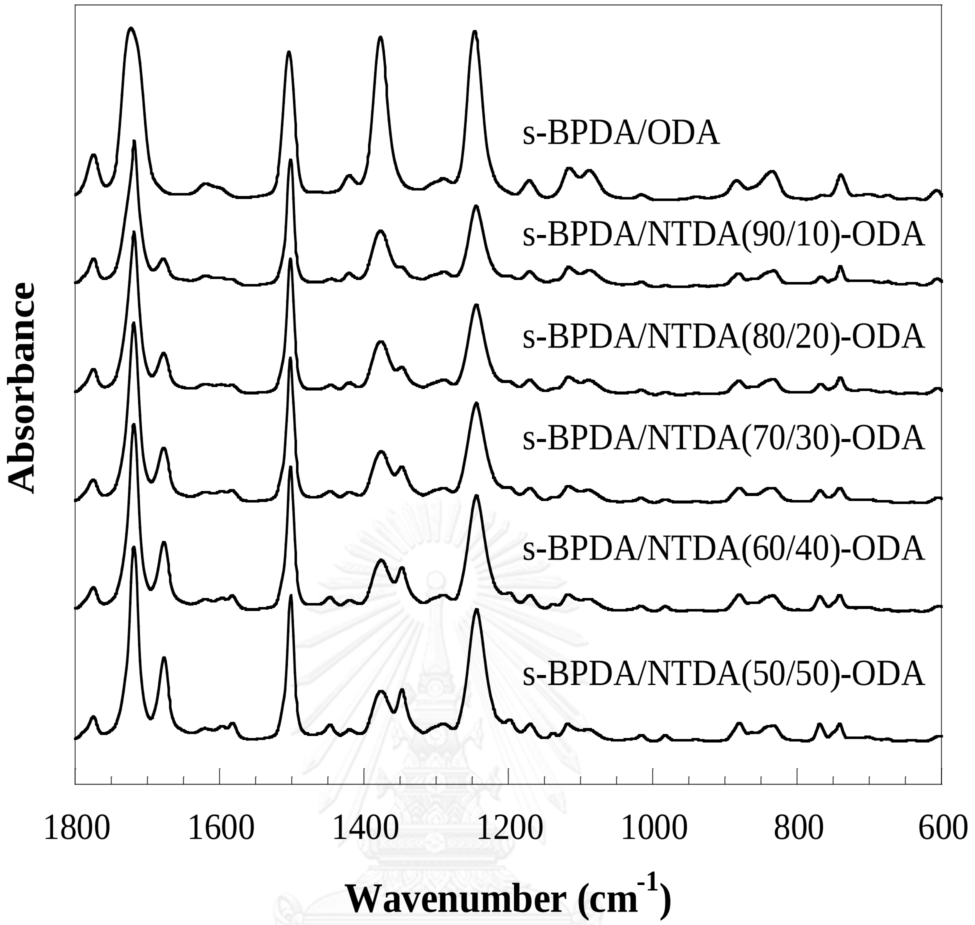


Figure 5.2 FTIR spectra of s-BPDA/ODA polyimide and its copolyimides with NTDA.

5.1.3 Polymerization

Polymerizability of s-BPDA/NTDA-ODA copolyimides was evaluated on the basis of the final inherent viscosities of the resultant PAAs. In this research, we use the term ‘polymerizability’ as a criterion representing how the polymerization of PAAs proceed smoothly, as a result, afford lower molecular weight (lower viscosity) PAAs. Therefore, polymerizability is supposed to be influenced by total effects of chemical and physical parameters: intrinsic monomer reactivity and the polymers (oligomers or intermediates) formed, since precipitation inhibits the progress of polymerization. Thus, the use of monomers possessing lower intrinsic reactivity gives lower molecular weight PAAs. In the systems using NTDA, lower intrinsic reactivity of monomers usually leads to lower molecular weight PAAs [9]. **Table 5.2** summarizes the viscosities of the PAAs obtained. First, one of the most reactive NTDA was used. The viscosity of PAA (1,4,5,8-NTDA/4,4'-ODA) was 0.192 dL g^{-1}, showing poor polymerizability. From the values in table 4.2, the viscosities of the PAAs were found to decrease as the NTDA content increased, i.e., from 1.978 dL g^{-1} of the s-BPDA/ODA PAA to the value of 1.782 dL g^{-1}, 1.389 dL g^{-1}, 1.008 dL g^{-1}, 0.605 dL g^{-1}, and 0.302 dL g^{-1} at the NTDA contents of 10, 20, 30, 40, and 50 mol%, respectively.

Table 5.2 The viscosities of s-BPDA/ODA polyimide, NTDA/ODA polyimide and their copolyimides.

Sample	Viscosity (dL/g)
s-BPDA/ODA	1.978
s-BPDA/NTDA(90/10)-ODA	1.782
s-BPDA/NTDA(80/20)-ODA	1.389
s-BPDA/NTDA(70/30)-ODA	1.008
s-BPDA/NTDA(60/40)-ODA	0.605
s-BPDA/NTDA(50/50)-ODA	0.302
NTDA/ODA	0.192

The poor polymerizability in the 1,4,5,8-NTDA/4,4'-ODA system is probably attributed to intrinsically low reactivity toward the ring-opening amide formation for the anhydride groups in 1,4,5,8-NTDA rather than its limited solubility in NMP commonly used for PAA polymerization, since s-BPDA, which is practically insoluble in these solvents, easily leads to high molecular weight PAAs by the reaction with ODA. The predicted poor reactivity of 1,4,5,8-NTDA arises from the thermodynamically more stable six-membered structure of the dicarboxylic anhydride groups in contrast to five-membered structure of s-BPDA

5.1.4 Effects of the s-BPDA/NTDA-ODA copolyimide compositions on glass transition temperature (T_g)

DSC thermograms of s-BPDA/ODA polyimide and its copolyimides at various % by mole from 0-50% are shown in Figure 5.3. From the thermograms, the T_gs of the copolyimides were found to increase as the NTDA content increased, i.e., from 290^{o}C of the s-BPDA/ODA to the value of 306^{o}C, 334 ^{o}C and 355^{o}C at the NTDA contents of 10, 20 and 30mol%, respectively. And then, the T_gs of the copolyimides were found to decrease from 351-338^{o}C when NTDA was added from 40-50% by mole. An increasing rigid molecular structure of the six-membered NTDA in backbone chain of the obtained copolyimides is attributed to the higher T_g values as a result of decreasing free volume of the copolymers. And, the decrease in T_g at high content (more than 30%) of NTDA can be explained considering the reduction of the molecular weights. The poor polymerizability in the NTDA/ODA system is probably attributed to intrinsically low reactivity leads to lower molecular weight PAAs [9]. As NTDA content increases more than 30%, molecular weight PAAs decreased, the mobility of molecular chain is increased and T_g thus shifts to lower temperature from 355 to 338°C.

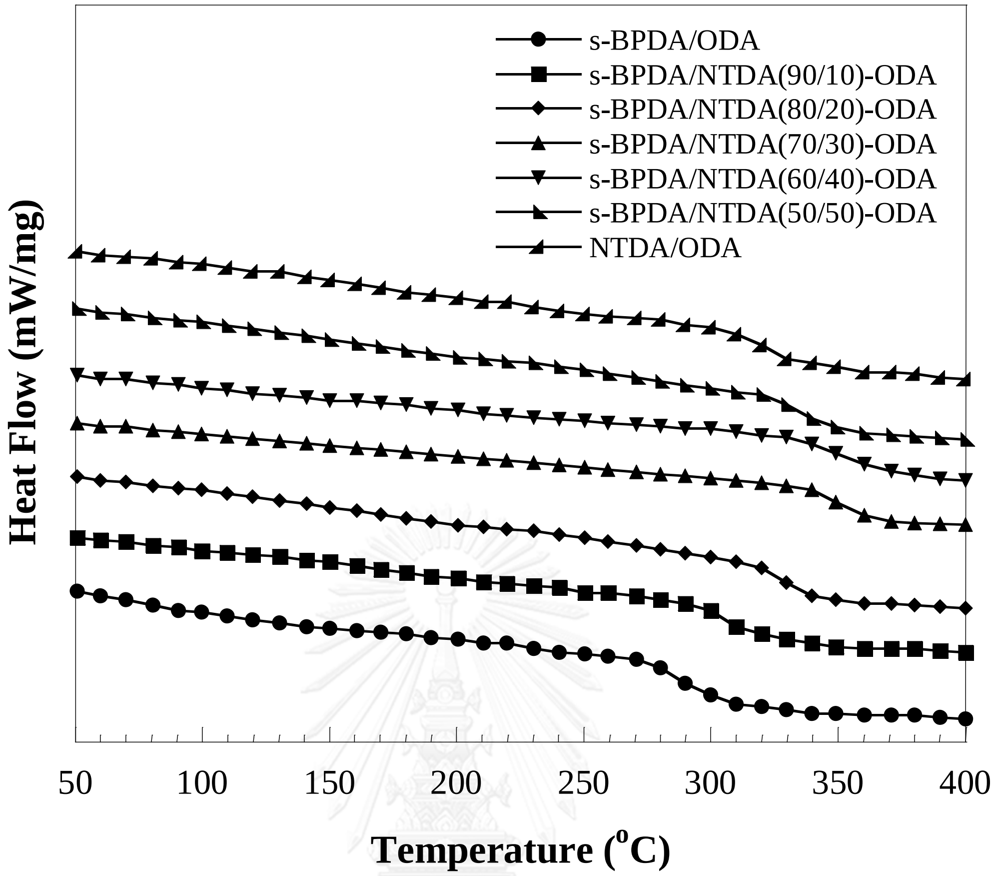


Figure 5.3 DSC thermograms of s-BPDA/ODA polyimide and its copolyimides.

5.1.5 Effects of the s-BPDA/NTDA-ODA copolyimide compositions on dynamic mechanical properties

Glass transition temperature (T_g) of the s-BPDA/ODA and the copolyimides were examined from loss modulus curves of the DMA thermograms. The maximum peak of the loss modulus can be used to identify glass transition temperature of a polymer. From the values in Table 5.3, the glass transition temperature (T_g) of the s-BPDA/ODA polyimide was determined to be 280^{o}C. The T_gs of all copolyimides were higher than that of s-BPDA/ODA polyimide ranging from 289 to 334°C. With the increasing NTDA content, the T_g expresses a trend of increasing in the beginning, and then, decreases slightly. It reaches the maximum value when 30 mol% NTDA was added; at this point, the T_g decreases from 334 to 321°C. These results are in agreement with the results from DSC thermograms.

The storage modulus of the s-BPDA/ODA polyimide film was 2.01 GPa. From the Table 5.3, it could be observed that the values of storage modulus were increased with increasing NTDA content ranging from 2.54-4.22 GPa. The increase in storage modulus could be attributed to the addition of rigid molecular structure of the six-membered NTDA dianhydride into the copolyimides.

Table 5.3 Dynamic mechanical properties of s-BPDA/ODA polyimide and its copolyimides.

Sample	T_g (DMA, ^oC)	Storage Modulus (GPa)
s-BPDA/ODA	280	2.01
s-BPDA/NTDA(90/10)-ODA	289	2.54
s-BPDA/NTDA(80/20)-ODA	316	3.18
s-BPDA/NTDA(70/30)-ODA	334	3.51
s-BPDA/NTDA(60/40)-ODA	330	3.87
s-BPDA/NTDA(50/50)-ODA	321	4.22

5.1.6 Effects of the s-BPDA/NTDA-ODA copolyimide compositions on thermal stability

Thermal stability of s-BPDA/ODA polyimide, NTDA/ODA polyimide and their copolyimides is shown in Figure 5.4. From the TGA thermograms, we can see that the s-BPDA/ODA polyimide exhibited the degradation temperature at 10% weight loss to be about 556°C whereas that of the NTDA/ODA polyimide showed the value of 570^{o}C. This suggests that the NTDA/ODA polyimide is more thermally stable than s-BPDA/ODA polyimide which is as expected [10, 56].

From these results, T_ds of the copolyimides increase from about 560°C to about 569°C with the increase of the NTDA content up to 30%. The presence of the NTDA in the copolyimides thus helps improving thermal stability of the resulting copolymers. And, T_ds of the copolyimides decrease from about 569°C to about 559°C with the increase of the NTDA content from 30-50%. These results are in agreement with the poor polymerizability in the NTDA/ODA system. The thermal stability of the copolymers thus tends to decrease with an addition of the NTDA comonomer (more than 30%).

Char yield of the s-BPDA/ODA polyimide reported at 800°C was found to be 42% by weight while that of the NTDA/ODA polyimide was determined to be 60% by weight. From Figure 5.4, the char yield of the copolyimides was found to increase from 51-59% with increasing % by mole of NTDA up to 30%. The thermal stability of the copolymers thus tends to increase with an addition of the NTDA comonomer. And, char yield of the copolyimides decrease from about 59-45% with the increase of the NTDA content more than 30%. These results are in agreement with thermal stability from T_ds [9, 10].

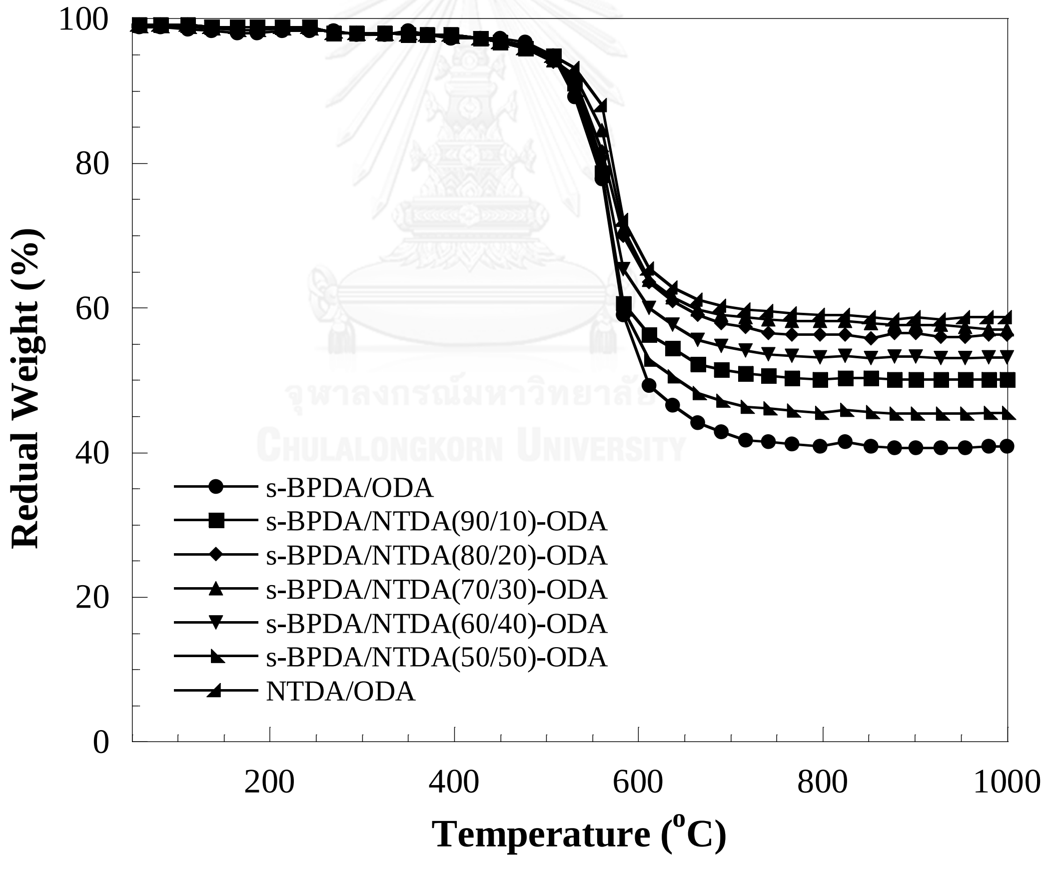


Figure 5.4 TGA thermograms of s-BPDA/ODA polyimide, NTDA/ODA polyimide and their copolyimides.

5.1.7 Effects of the s-BPDA/NTDA-ODA copolyimide compositions on mechanical properties

Tensile properties of the s-BPDA/ODA polyimide and its copolyimides are presented in Figure 5.5. The tensile strength and tensile modulus of the s-BPDA/ODA polyimide film were 128 MPa and 2.15 GPa, respectively. From the table, it could be observed that the values of tensile modulus were increased with increasing NTDA content. The increase in modulus could be attributed to the addition of rigid molecular structure of the six-membered NTDA dianhydride into the copolyimides. The values of tensile strength were increased with increasing NTDA content up to 30%. Therefore, they were able to improve the stiffness and strength of copolyimides. The tensile strength of copolyimides was decreased with increasing NTDA content from 30-50%. These results are in agreement with the poor polymerizability in the NTDA/ODA system. Therefore, they were able to reduce strength of copolyimides [9, 56].

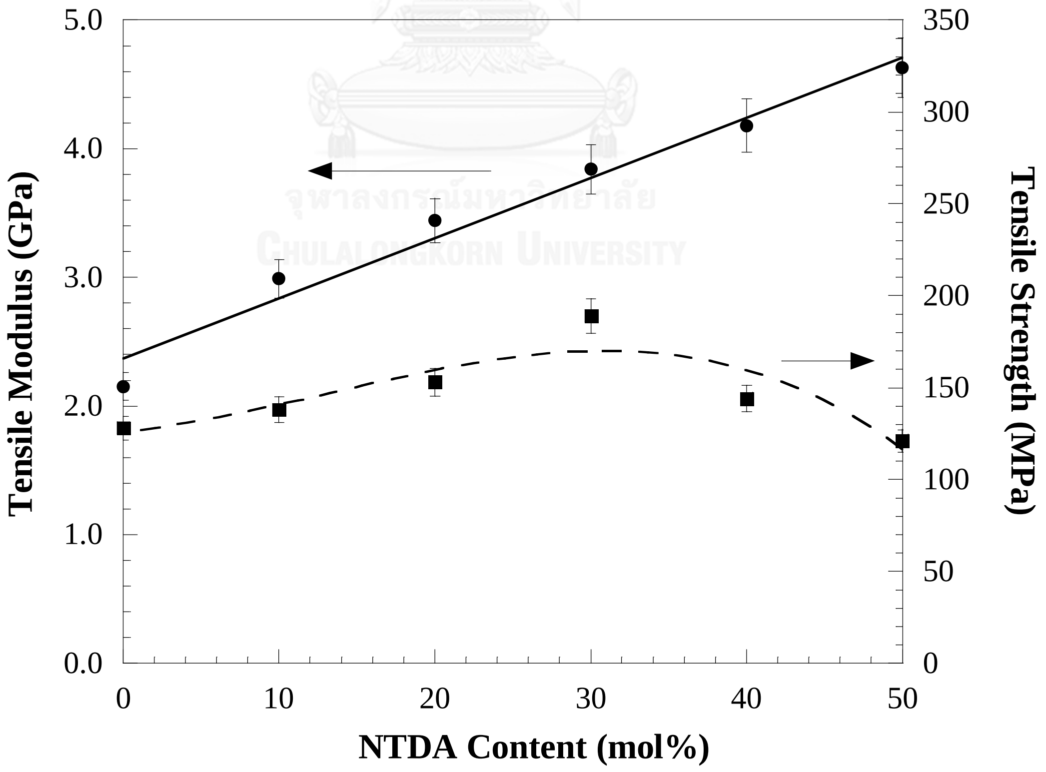


Figure 5.5 Tensile properties of the s-BPDA/ODA polyimide and its copolyimides.

5.1.8 Effects of the s-BPDA/NTDA-ODA copolyimide compositions on CTE

The CTE values estimated from the slopes of the TMA curves between 100°C to 200°C are also listed in Table 5.4. The CTE value of the s-BPDA/ODA polyimide was measured to be 48.4 ppm/°C. Whereas CTE values of the copolyimides were observed to be in a range of 22.7-33.8 ppm/°C. The CTE values tend to decrease with increasing amount of NTDA due to its more rigid/stiff chain backbone structures of this dianhydride moiety compared to others as explained in the previous section.

Table 5.4 Important film properties of s-BPDA/ODA polyimide and its copolyimide with NTDA.

Sample	CTE (ppm/ºC)	Dielectric Constant
s-BPDA/ODA	48.4	3.33
s-BPDA/NTDA(90/10)-ODA	33.8	3.31
s-BPDA/NTDA(80/20)-ODA	29.2	3.10
s-BPDA/NTDA(70/30)-ODA	27.7	2.95
s-BPDA/NTDA(60/40)-ODA	26.9	2.86
s-BPDA/NTDA(50/50)-ODA	22.7	2.52

5.1.9 Effects of the s-BPDA/NTDA-ODA copolyimide compositions on other electrical property

Dielectric constant of the copolyimides was also observed to decrease with an addition of the NTDA fraction (Table 5.4). This behavior is attributed to the lower polarity of the bulky NTDA group which reduces the efficiency of the dipole in reacting to polarity change during treatment in an alternating frequency in the dielectric constant measurement, thus the observed lowering in the obtained dielectric constant values of the resulting copolymers [9, 57].

5.2 Photolithographic evaluation

Nifedipine has been reported to effectively act as a dissolution inhibitor in a polyimide precursor after post-exposure bake (PEB) [20]. Upon UV exposure, nifedipine photoconverted quantitatively to 4-(2'-nitrosophenyl)-2,3-dicarboxymethyl-3,5-dimethylpyridine (NDMPy) in a polyimide precursor film. It has been confirmed that nifedipine and NDMPy in the film acts as a dissolution inhibitor and as a disolution promotor, respectively. The dissolution inhibition and promotion mechanisms were further investigated and subsequently expressed as follows:

1) Dissolution inhibition is due to resistivity of the polyimide precursor to an alkaline aqueous solution through intermolecular hydrogen bonding between -COOH in the polymer structure and -NH- in nifedipine [20].

2) Dissolution promotion is due to the hydrogen bond-breaking by photoconversion from nifedipine to NDMPy and the newly formed intermolecular complex between the COOH and -N= in NDMPy. The pattern making mechanisms were proposed in Figure 5.6 [20].

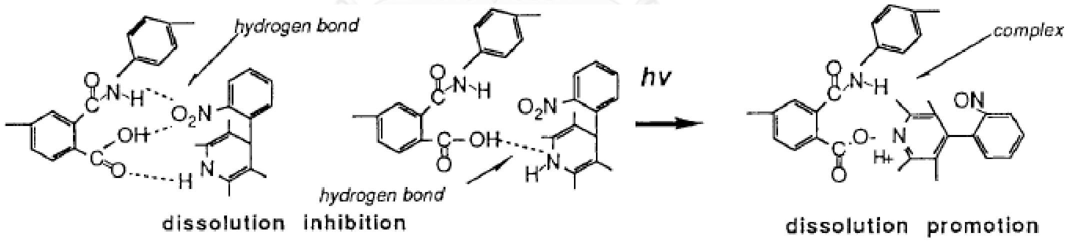


Figure 5.6 Chemical reactions or interactions occur through the exposure process between a polyimide precursor and nifedipine.

5.2.1 IR spectra of PSPI film with an increase in UV exposure doses.

Figure 5.7 shows IR spectral change for PSPI film upon UV irradiation from a UV lamp. The nifedipine absorption wavenumber at 3500 cm^{-1} decreased with an increase in exposure dose due to the photochemical reaction of nifedipine dispersed in the copolyimide film. The result indicated that the reaction was nearly completed with an exposure dose of 1000 mJ/cm^2 [1, 20].

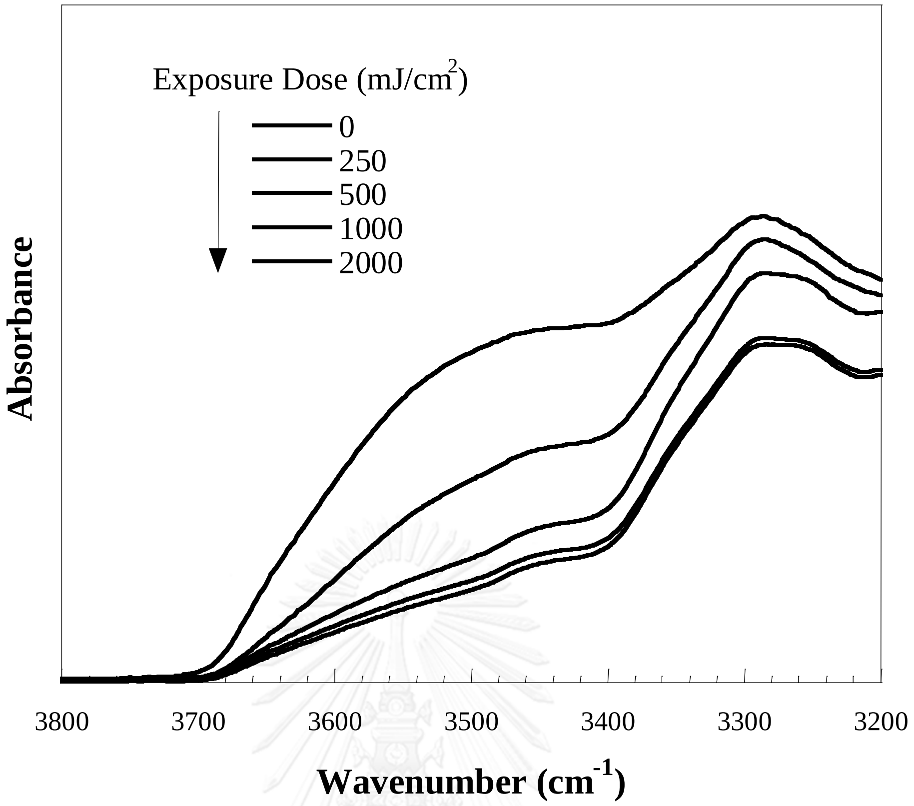


Figure 5.7 Change in IR spectra of PSPI film with an increase in UV exposure doses.

5.2.2 Effect of post-exposure baked (PEB) temperature on dissolution rate of photosensitive copolyimide (PSPI)

The relationship between the post-exposure bake (PEB) temperature (for 20 min) and the dissolution rate of PAA containing 20wt% of nifedipine is shown in Figure 5.8. The dissolution rate was estimated by measuring the film thickness after development. This was performed at 40°C by using 10wt% KOH aqueous solution as a developer. The exposed (1000 mJ/cm^2) film containing 20wt% of nifedipine dissolved faster than the unexposed film at all tested PEB temperatures. In the low PEB temperature regions, the dissolution rates of both exposed and unexposed areas were too fast to achieve good patterns. However, at 140°C of PEB temperature, the dissolution contrasts between the exposed and unexposed parts were large enough to obtain a good pattern image [58].

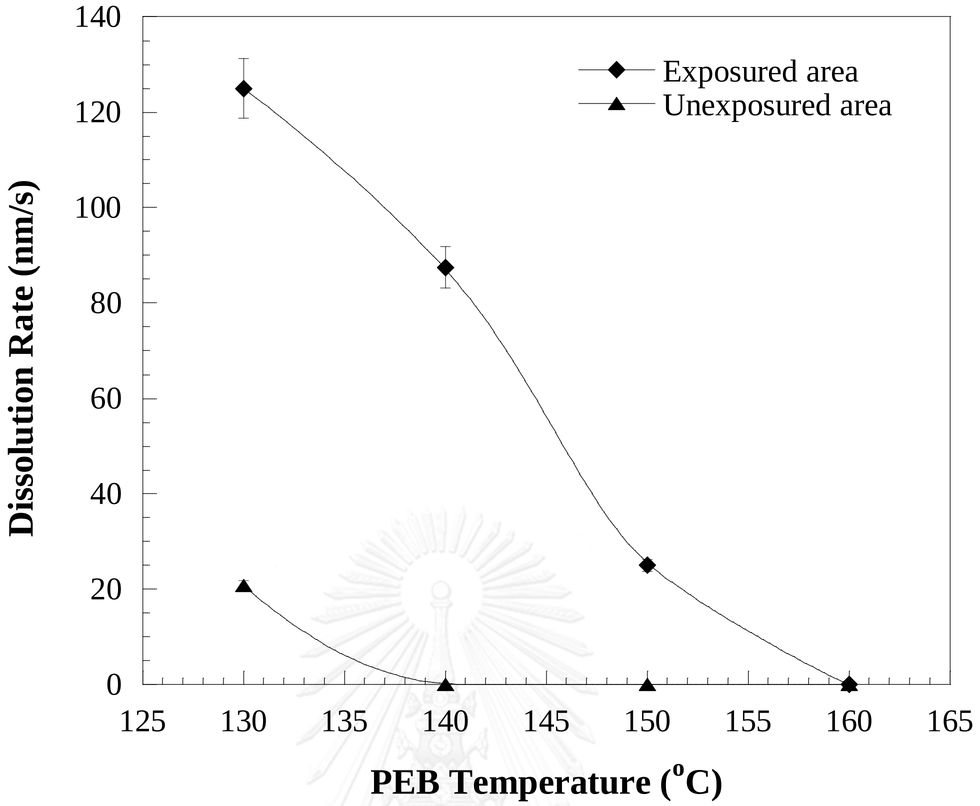


Figure 5.8 Relationship between the PEB temperature (for 20 min) and dissolution rate of a copolyimide containing 20 wt% nifedipine.

5.2.3 Effect of post-exposure baked (PEB) time on dissolution rate of photosensitive copolyimide (PSPI)

The relationship between the post-exposure bake (PEB) time and the dissolution rate of PAA containing 20 wt% of nifedipine at 140°C PEB temperature is shown in Figure 5.9. The dissolution rate was estimated by measuring the film thickness after development. This was performed at 40°C by using 10wt% KOH aqueous solution as a developer. The exposed (1000 mJ/cm^2) film containing 20 wt% of nifedipine dissolved faster than the unexposed film at all tested PEB times. In the low PEB time regions, the dissolution rates of both exposed and unexposed areas were too fast to achieve good patterns. However, at 12.5 min of PEB time, the dissolution contrasts between the exposed and unexposed parts were large enough to obtain a good pattern image.

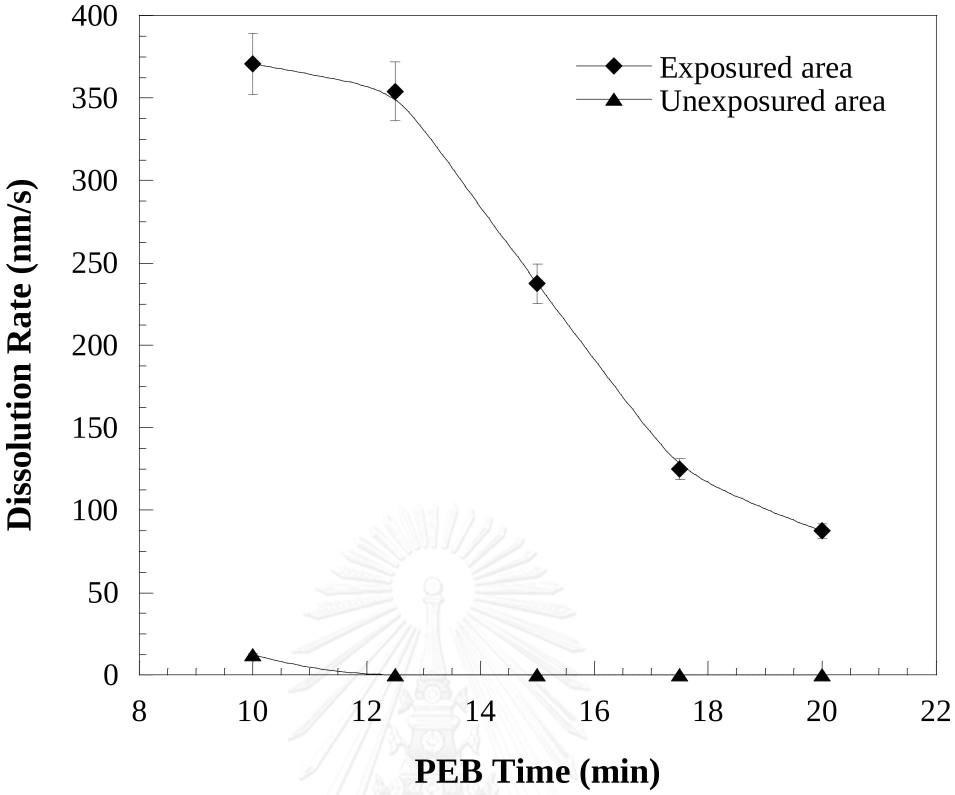


Figure 5.9 Relationship between the PEB time and dissolution rate of a copolyimide containing 20 wt% nifedipine at 140°C PEB temperature.

5.2.4 Effects of nifedipine composition on sensitivity and contrast of photosensitive copolyimide (PSPI)

The sensitivity and contrast of the PSPI system were further evaluated by using characteristic curves (Figure 5.10). All samples were prepared by the method described in the Experimental section through exposure at 140°C PEB for 12.5 min, and development in a 10%wt KOH aqueous solution. The characteristic curves were prepared from the films containing 20 to 30 wt% nifedipine.[20] The sensitivity, determined from the dose where the PSPI film was completely dissolved (the normalized thickness became zero), was found to increase with increasing nifedipine content, reflecting total photochemical conversion of nifedipine for each sample. It should be noted that even at a relatively low nifedipine content such as 20 wt%, the amount was enough for fine patterning.

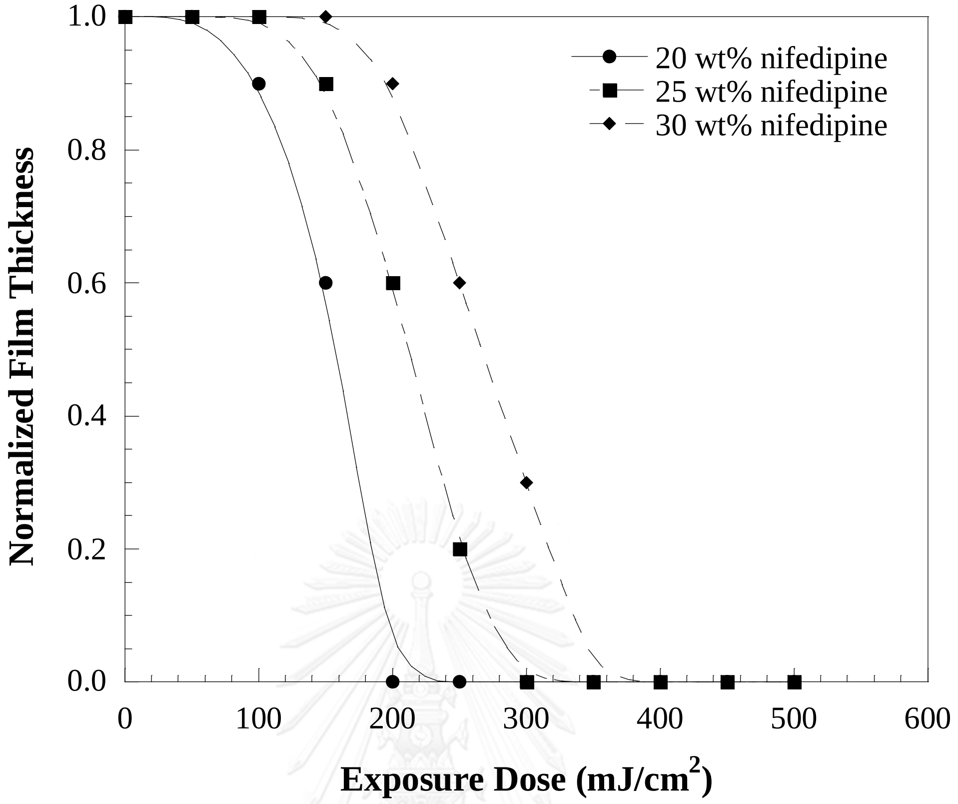


Figure 5.10 Characteristic curves of the PSPI films with various content of nifedipine.

The values of sensitivity and contrast are listed in Table 5.5. Those values suggest that these PSPI systems can be applied as photoimageable materials in FPC fabrication.[20] Figure 5.11 exhibits the optical micrographs of a positive-image fine patterns obtained from PSPI (30 µm thick, nifedipine 20 wt%) by post-baking at 140°C for 12.5 min after exposure of the film to UV light at 200 mJ/cm^2. This resist was capable of resolving a 400 µm feature when 30 µm thick films were used.

Table 5.5 Lithographic characteristics of the obtained PSPI system in this work.

Content of nifedipine (wt%)	Sensitivity (mJ/cm^2)	Contrast (ɣ)
20	200	2.35
25	300	2.51
30	350	3.77

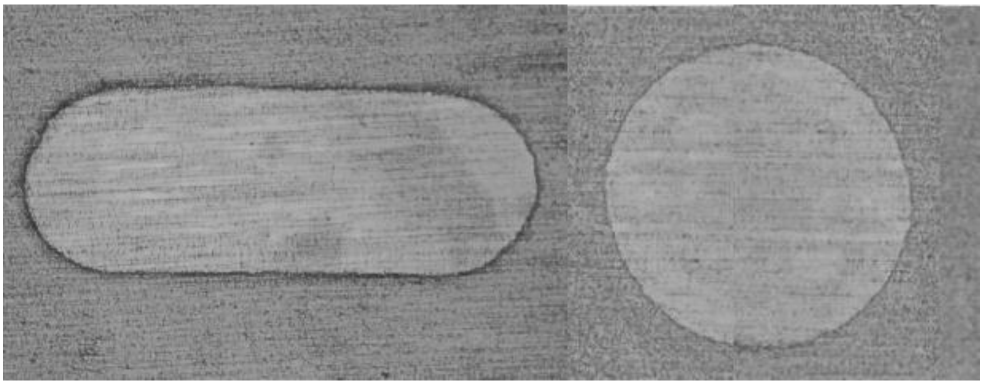


Figure 5.11 Optical micrographs of positive-type fine patterns obtained from our PSPI (30 µm thick, nifedipine 20 wt%).

5.3 Adhesive copolymer film characterization

Table 5.6 shows the contact angles of water deposited on s-BPDA/NTDA(70/30)-ODA copolyimide surface at various content of silane coupling agent in copolymer. The contact angles of water by Table 5.6 decreased by addition of silane coupling agent content in copolymer. Figure 5.12 shows a photograph of water contact angle for silane-containing copolyimide. The contact angles of si-PSPI decrease from 88^o for pure copolyimide, to 91^o for 0.5wt% of silane coupling agent in copolymer up to 93^o for 1.0wt% of silane coupling agent in copolymer. The contact angle of the silane-containing copolyimide decreases with increase in silane coupling agent content reflects the increases hydrophobicity of the polymeric surface. Those results showed that the surface character of si-PSPI was changed from hydrophilicity to hydrophobicity. That is owing to the existence of silane coupling agent on the surface of PSPI [59].

Table 5.6 The water contact angles on s-BPDA/NTDA(70/30)-ODA copolyimide surface and peel strength of copolyimide at various content of silane coupling agent in copolymer.

Sample	Contact Angle (Degree)	Peel Strength (N/mm)
s-BPDA/NTDA(70/30)-ODA (PI)	88	0.73±0.05
PI with 0.5 wt% of silane	91	0.80±0.06
PI with 1.0 wt% of silane	93	0.84±0.06

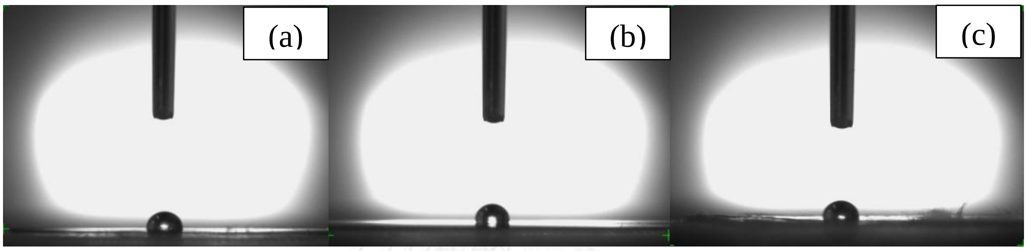


Figure 5.12 Photograph of water contact angle on s-BPDA/NTDA(70/30)-ODA copolyimide surface at various content of silane coupling agent in copolymer : (a) PI, (b) PI with 0.5 %wt of silane and (c) PI with 1.0 %wt of silane.

Referring to the papers on clay and silca [60, 61] modified by silane coupling agents, the reacting process of silane couping agent on PSPI is as follows: (1) The ethoxy groups of silane coupling agent hydrolyzed under the influence of ammonia and water, and silanols were formed. (2) The silanols associated and formed oligomers, and the oligomers adsorbed on the particle surface by hydrogen bonding and condensed with surface hydroxyls to form silane linkages during the evaporation of solvent. That is to say chemical bonds have formed between silane coupling agent and PSPI surface.

Figure 5.13 represents the interaction between silane-modified PI and copper surface. Silane unit and PI unit in the copolymer can form the covalent bond and the coordinated bond with copper surface, respectively. Since the covalent bond of silane is stronger than the coordinated bond of PI, silane-containing PI has a stronger interaction with copper surface than PI. [62]

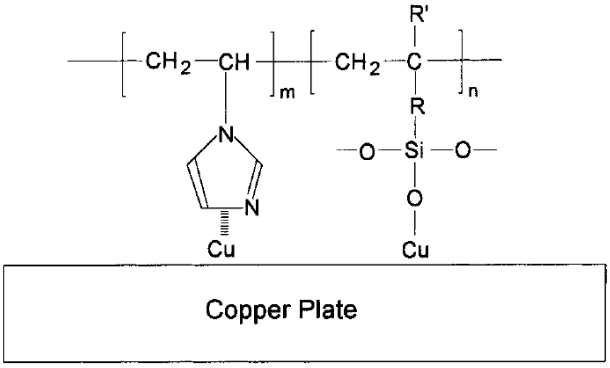


Figure 5.13 The interaction of the interaction between silane-modified PI and copper.

Table 5.6 shows the dependence of the peel strength of silane-containing copolyimide versus content of silane coupling agent. The peel strength for the Cu/PSPI system increased from 0.8 to 0.84 N/mm when the silane coupling agent content varied from 0.5 to 1.0 wt%.It is seen that the peel strength of silane-containing copolyimide increases with growth in silane coupling agent content. The fact that the strength of the silane-containing copolyimide increases with increase in silane coupling agent content reflects the increases hydrophobicity of the polymeric surface. The peel strength of silane-containing copolyimide diminished from 0.73 N/mm (pure copolyimide), to 0.8 N/mm (0.5wt% of silane coupling agent), and to 0.84 N/mm (1.0wt% of silane coupling agent). The presence of silane coupling agent in PSPI caused the more hydrophobic surface of copolymer. The peel strengths can be affected by the interfacial strength between copper surface and si-PSPI. Especially, silane-containing PSPI shows the remarkable improvement of the peel strengths in all silane coupling agent contents [63].

5.3.1 Effect of post-exposure baked (PEB) temperature on dissolution rate of silane-containing photosensitive copolyimide (si-PSPI)

In order to investigate the dissolution rate of an exposed (1000 mJ/cm^2) and an unexposed area, Figure 5.14 shows the relationship between the post-exposure bake (PEB) temperature and the dissolution rate of PAA containing 0.5wt% of silane coupling agent and 20wt% of nifedipine at 20 min PEB time. The dissolution rate of the exposed area decreased with increasing PEB temperatures, and the exposed film dissolved faster than the unexposed film at all PEB temperatures. Furthermore, the dissolution rates of the unexposed films for PEB temperature were almost identical. This result suggested that nifedipine can act as a dissolution promoter of silane-containing PI film with PEB temperature of 150°C being sufficient to achieve a good dissolution contrast [58].

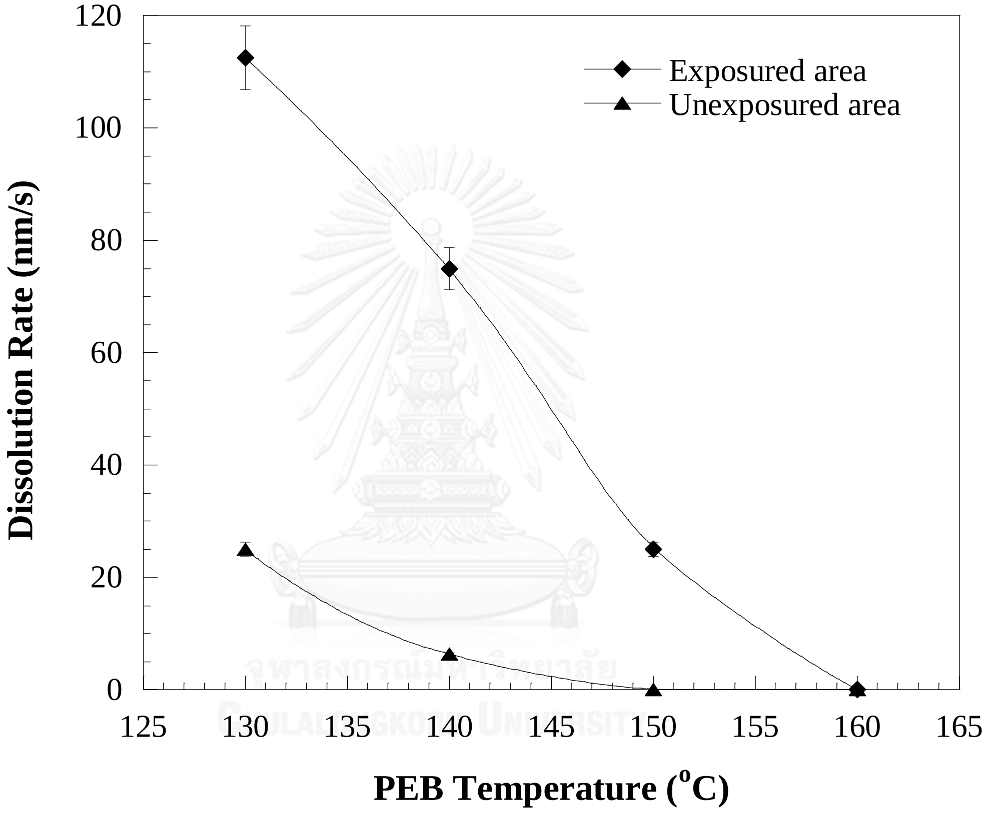


Figure 5.14 Relationship between the PEB temperature (for 20 min) and dissolution rate of a copolyimide containing 0.5wt% silane and 20 wt% nifedipine.

5.3.2 Effect of post-exposure baked (PEB) time on dissolution rate of silane-containing photosensitive copolyimide (si-PSPI)

In order to investigate the dissolution rate of an exposed (1000 mJ/cm^2) and an unexposed area, Figure 5.15 shows the relationship between the post-exposure bake (PEB) time and the dissolution rate of PAA containing 0.5wt% of silane coupling agent and 20 wt% of nifedipine at 150°C PEB temperature. The dissolution rate of the exposed area decreased with increasing PEB times, and the exposed film dissolved faster than the unexposed film at all PEB times. Furthermore, the dissolution rates of the unexposed films for PEB time were almost identical. This result suggested that nifedipine can act as a dissolution promoter of PI film with PEB time of 15 min being sufficient to achieve a good dissolution contrast [58].

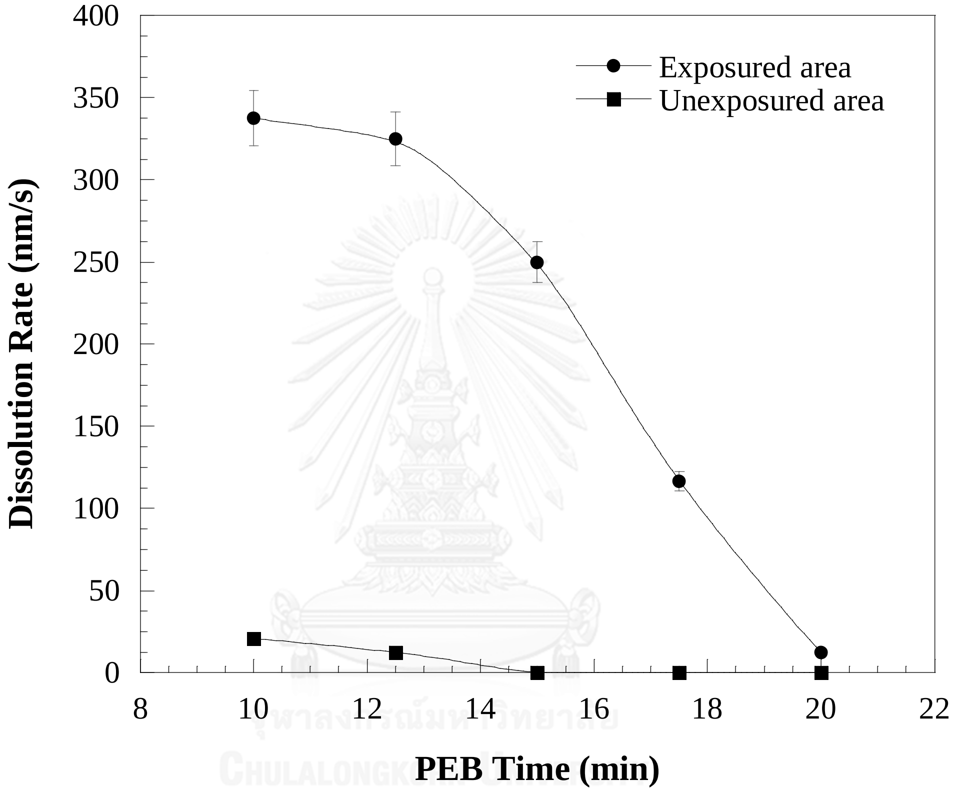


Figure 5.15 Relationship between the PEB time and dissolution rate of a copolyimide containing 0.5wt% silane and 20 wt% nifedipine at 150°C PEB temperature.

5.3.3 Effects of nifedipine composition on sensitivity and contrast of silane-containing photosensitive copolyimide (si-PSPI)

The sensitivity and contrast of the silane-containing PSPI system were further evaluated by using characteristic curves (Figure 5.16). All samples were prepared by the method described in the Experimental section through exposure at 150°C PEB for 15 min, and development in a 10%wt KOH aqueous solution. The characteristic curves were prepared from the films containing 20 to 30 wt%

nifedipine.[20] The sensitivity, determined from the dose where the silane-containing PSPI film was completely dissolved, was found to increase with increasing nifedipine content, reflecting total photochemical conversion of nifedipine for each sample. It should be noted that even at a relatively low nifedipine content such as 20 wt%, the amount was enough for fine patterning.

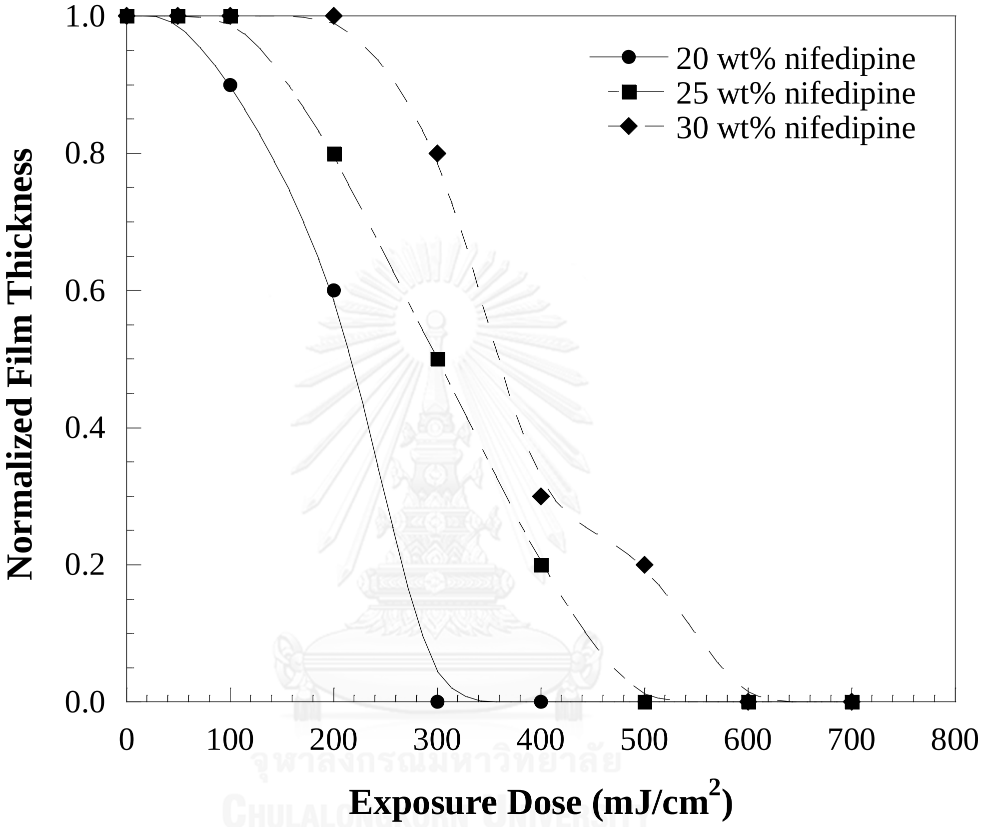


Figure 5 16 Characteristic curves of the silane-containing PSPI films with various content of nifedipine.

The values of sensitivity and contrast are listed in Table 5.7. Those values suggest that these silane-containing PSPI systems can be applied as photoimageable materials in FPC fabrication.[20] Figure 5.17 exhibits the optical micrographs of a positive-image fine patterns obtained from PSPI (30 µm thick, nifedipine 20 wt%) by post-baking at 150°C for 15 min after exposure of the film to UV light at 300 mJ/cm^2. This resist was capable of resolving a 500 µm feature when 30 µm thick films were used.

Table 5.7 Lithographic characteristics of the obtained silane-containing PSPI system in this work.

Content of nifedipine (wt%)	Sensitivity (mJ/cm^2)	Contrast (ɣ)
20	300	1.29
25	500	1.43
30	600	2.10

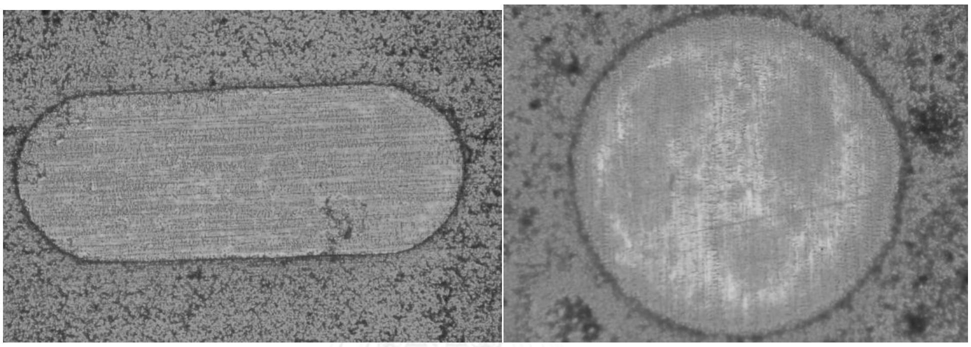


Figure 5.17 Optical micrographs of positive-type fine patterns obtained from our silane-containing PSPI (30 µm thick, nifedipine 20 wt%).

5.4 Photosensitive copolymer film characterization

5.4.1 Thermal properties of photosensitive copolymer film

DSC thermograms of copolyimide films (PI), photosensitive copolyimide film (PSPI) and photosensitive silane-containing copolyimide film (si-PSPI) are shown in Figure 5.18. From the thermograms, the glass transition temperature (T_g) of the copolyimide film (PI) was determined to be 355^{o}C. The T_g of photosensitive copolyimide film (PSPI) was slightly higher than that of the copolyimide film (PI) i.e. 360^{o}C. This is due to the fact that some crosslinking reaction took place between the OH groups in PI and nifedipine during annealing at 300^{o}C [64] thus resulting in the observed higher T_g value of the PSPI film. The T_g of photosensitive silane-containing copolyimide film (si-PSPI) was slightly lower than that of the photosensitive copolyimide film (PSPI) i.e. 358^{o}C. The T_g decreases with the flexibility of the backbone of the polymer chain. Consequently, the chain flexibility increases and T_g decreases [65].

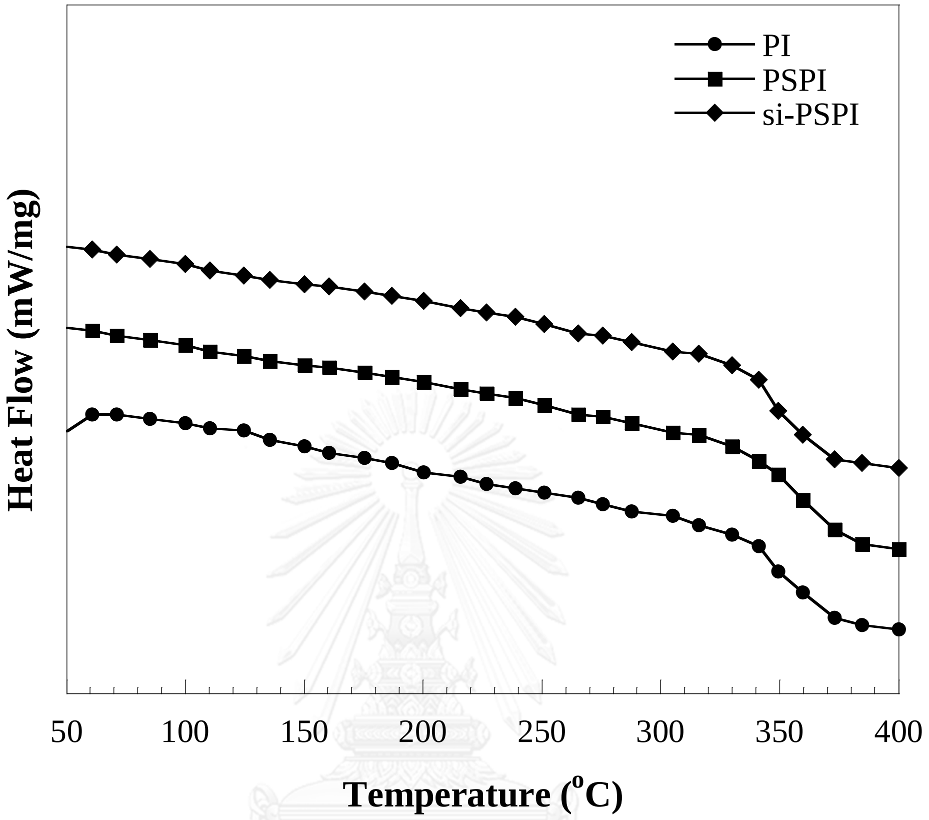


Figure 5.18 DSC thermograms of copolyimide film (PI) photosensitive copolyimide film (PSPI) and silane-containing photosensitive copolyimide film (si-PSPI).

TGA thermograms of copolyimide films (PI), photosensitive copolyimide film (PSPI) and photosensitive silane-containing copolyimide film (si-PSPI) after curing at 300°C for 2 hour are shown in Figure 5.19. The PSPI and si-PSPI curve exhibited slopes with two steps of weight loss being evident. The first weight loss starts at around 370°C indicating that both vaporization of residual solvent and degradation of the nifedipine begin at this temperature. The weight loss continues up to 450°C while the decomposition of the polyimide occurs at temperature higher than 500°C. The 10% weight loss temperature of PSPI film and si-PSPI film were 474°C and 464°C, respectively. On the other hand, the PI curve shows no weight loss below 370°C and the 10% weight loss temperature was 569°C. These results indicate that nifedipine as the photoreactive compound can be effectively removed with a 300°C post-development bake, and the PSPI exhibited relatively good thermal stability [16, 58].

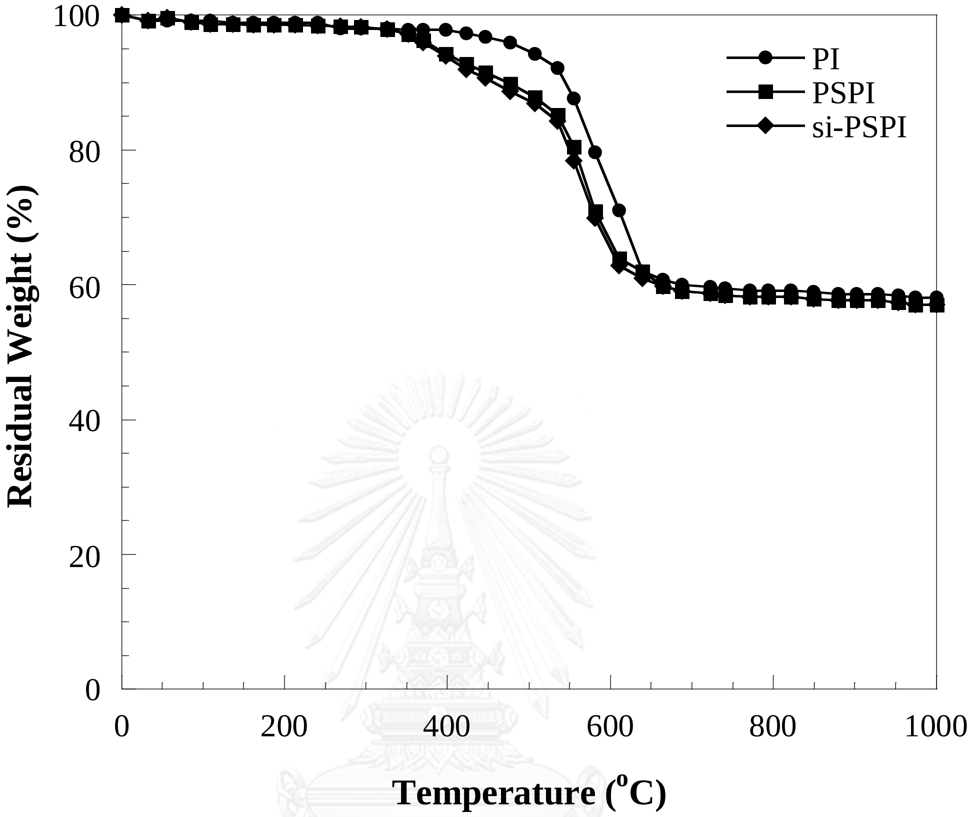


Figure 5.19 TGA thermograms of copolyimide film (PI) photosensitive copolyimide film (PSPI) and silane-containing photosensitive copolyimide film (si-PSPI).

The CTE values of PI and PSPI films measured by TMA (Table 5.8) were 27.7 and 28.5 ppm/^{o}C, respectively. Because of crosslinking reaction took place between the OH groups in PI and nifedipine during annealing [64], the CTE value of the PSPI film is slightly lower than that of the PI film. The CTE value of si-PSPI was measured to be 29.2 ppm/°C. The CTE values increase with existing amount of silane coupling agent due to its more flexibility chain backbone structures of silane coupling agent moiety compared to others as explained in the previous section [66]. This CTE value, however, is enough low for the next-generation PSPIs.

Table 5.8 Important film properties of copolyimide film (PI) photosensitive copolyimide film (PSPI) and silane-containing photosensitive copolyimide film (si-PSPI).

Sample	CTE (ppm/°C)	Tensile Modulus (GPa)	Tensile Strength (MPa)	Dielectric Constant
s-BPDA/NTDA(70/30)-ODA (PI)	27.7	3.84	189	2.95
PI with 20wt% nifedipine (PSPI)	28.5	3.92	195	3.01
PI with 20wt% nifedipine and 0.5 wt% of silane (si-PSPI)	29.2	3.87	204	3.09

5.4.2 Dynamic mechanical properties of photosensitive copolymer film

The thermal stability and mechanical properties of PI and PSPI were investigated by DMA. The DMA curves of PI film cured at 300°C for 2 h and PSPI film exposed to 1000 mJ/cm^2 and cured at 300°C for 2 h are shown in Table 5.9. The initial storage moduli of PI and cured PSPI at about 50°C are 3.51 and 3.65 GPa, respectively. The T_g of PI, determined from the peak temperature of the loss modulus plots, is observed at 334°C, whereas the T_g of PSPI is observed at 349°C. It is assumed that the T_g of PSPI is slightly higher than that of PI probably because of some crosslinking reaction took place between the OH groups in PI and nifedipine [64, 67].

As a result, the values in Table 5.9 clearly suggested that si-PSPI film were slightly more stable than the PSPI film. The decrease of the storage modulus of si-PSPI film, 3.54 GPa, due to the flexibility of the backbone of the polymer chain. Therefore, they were able to reduce the stiffness of PSPI. The T_g of photosensitive silane-containing copolyimide film (si-PSPI) was slightly lower than that of the photosensitive copolyimide film (PSPI) i.e. 346°C. These results are in agreement with the results from DSC thermograms [65].

Table 5.9 Dynamic mechanical properties of s-BPDA/ODA polyimide and its copolyimides.

Sample	T_g (DMA, ^oC)	Storage Modulus (GPa)
s-BPDA/NTDA(70/30)-ODA (PI)	334	3.51
PI with 20wt% nifedipine (PSPI)	349	3.65
PI with 20wt% nifedipine and 0.5 wt% of silane (si-PSPI)	346	3.54

5.4.3 Mechanical properties of photosensitive copolymer film

Tensile properties of PI film and PSPI film are presented in Table 5.8. The tensile strength and tensile modulus of PI film were 189 MPa and 3.84 GPa, respectively. And, the tensile strength and tensile modulus of PSPI film were 195 MPa and 3.92 GPa, respectively. From the table, it could be observed that the values of tensile modulus and tensile strength were increased with increasing nifedipine. The increase in modulus could be attributed to the occurrence of intermolecular crosslinking reactions in PI and nifedipine [64]. Therefore, they were able to improve the stiffness and strength of PSPI. The tensile strength and tensile modulus of si-PSPI film were 204 MPa and 3.87 GPa, respectively. It can be observed that the value of tensile modulus was decreased with increasing silane coupling agent [68]. These results are in agreement with the results from DMA thermograms. Tensile strength was decreased with increasing silane coupling agent. Therefore, they were able to improve the strength of si-PSPI.

5.4.4 Electrical property of photosensitive copolymer film

Dielectric constant of PSPI was also observed to decrease with an addition of nifedipine. This behavior is attributed to the lower polarity of nifedipine group which reduces the efficiency of the dipole in reacting to polarity change, thus the observed lowering in the obtained dielectric constant values of the resulting PSPI [57]. Table 5.8 shows the variation of dielectric constant with 0.5%wt of si-PSPI. The dielectric constant increased slightly with increase in silane coupling agent content for si-PSPI. The increase in dielectric constant can be attributed to the enhanced polarization from the dipole-dipole interaction, as compared with PSPI film [69].

CHAPTER VI

CONCLUSIONS

Copolymers of s-BPDA/NTDA/ODA were successfully prepared by a two-step polycondensation in NMP. The copolyimide films exhibited higher mechanical properties and thermal stability with tensile strength of 189 MPa, tensile modulus of 3.84 GPa, T_g of 355°C, T_d up to 569°C and a dielectric constant as low as 2.95 with an addition of the NTDA comonomer up to 30% by mole. The relatively low coefficient of thermal expansion (CTE) of the copolyimide film was also found to be closed to that of copper foil i.e. 27.7 ppm/ °C.

A photosensitive copolyimide synthesized from s-BPDA/1,4,5,8-NTDA(70/30 mol%)-4,4’-ODA poly(amic acid) (PAA) to be used as a cover material has been developed. The PAA containing 20 wt% of nifedipine was found to show a positive-type photosensitive polyimide precursor, in which nifedipine acts as the dissolution controller. This resist system is capable of being developed with aqueous alkaline solution. The relatively good sensitivity and contrast of the PAA with nifedipine i.e. 200 mJ/cm^2 and 2.35, were achieved. However, their very stiff/rod like copolyimide backbones has insufficient adhesion to copper. Coupling agents find their largest application in the area of polymers. Since any silane that enhances the adhesion of a polymer is often termed a coupling agent, regardless of whether or not a covalent bond is formed, the definition becomes vague. A positive type photosensitive silane-containing s-BPDA/1,4,5,8-NTDA(70/30 mol%)-4,4’-ODA copolyimide film was improved adhesion property with peel strength of 0.80 N/mm with an addition of silane coupling agent at 0.5% by weight. The relatively good sensitivity and contrast of the PAA with 0.5wt% silane and 20wt% nifedipine i.e. 300 mJ/cm^2 and 1.29, were achieved. Smallest dimension of the developed area of PSPI is 400 µm.

The obtained PSPI films also possess high mechanical properties and thermal stability with T_g of 358°C, T_d up to 464°C and a dielectric constant as low as 3.09

with an addition of silane soupling agent 0.5% by weight and nifedipine 20% by weight of s-BPDA/1,4,5,8-NTDA(70/30 mol%)-4,4’-ODA PAA. The relatively low coefficient of thermal expansion (CTE) of the silane-containing photosensitive copolyimide film was also found to be closed to that of copper foil i.e. 29.2 ppm/ °C. The results suggest this copolyimide film is a promising candidate as a novel cover layer material for FPC.

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APPENDICES

APPENDIX A

Characterization of copolyimide films

Appendix A-1 T_gs of s-BPDA/ODA polyimide and its copolyimides from DSC thermograms.

Sample	Tg (^oC)
s-BPDA/ODA	290
s-BPDA/NTDA(90/10)-ODA	307
s-BPDA/NTDA(80/20)-ODA	334
s-BPDA/NTDA(70/30)-ODA	355
s-BPDA/NTDA(60/40)-ODA	351
s-BPDA/NTDA(50/50)-ODA	338
NTDA/ODA	320

Appendix A-2 T_{d10}s and char yield of s-BPDA/ODA polyimide, NTDA/ODA polyimide and their copolyimides.

Sample	T_{d10} (^oC)	%Char yield
s-BPDA/ODA	556	42
s-BPDA/NTDA(90/10)-ODA	560	51
s-BPDA/NTDA(80/20)-ODA	564	57
s-BPDA/NTDA(70/30)-ODA	569	59
s-BPDA/NTDA(60/40)-ODA	562	52
s-BPDA/NTDA(50/50)-ODA	559	45
NTDA/ODA	570	60

Appendix A-3 Tensile properties of the s-BPDA/ODA polyimide and its copolyimides.

Sample	Tensile Modulus (GPa)	Tensile Strength (MPa)
s-BPDA/ODA	2.15	128
BPDA/NTDA(90/10)-ODA	2.99	138
BPDA/NTDA(80/20)-ODA	3.44	153
BPDA/NTDA(70/30)-ODA	3.84	189
BPDA/NTDA(60/40)-ODA	4.18	144
BPDA/NTDA(50/50)-ODA	4.63	121

APPENDIX B

Photolithographic evaluation

Appendix B-1 Relationship between the PEB temperature (for 20 min) and dissolution rate of a copolyimide containing 20 wt% nifedipine.

PEB Temperature (ºC)	Unexposure (mm)				Exposure (mm)				Time of development (s)	Dissolution rate unexposure (nm/s)	Dissolution rate exposure (nm/s)
	before		after		before		after				
130	0.030	0.030	0.028	0.028	0.030	0.030	0.020	0.020	80	20.8	125.0
	0.029		0.027		0.029		0.019				
	0.030		0.029		0.030		0.020				
140	0.030	0.030	0.030	0.030	0.030	0.030	0.023	0.023		0.0	87.5
	0.029		0.029		0.029		0.022				
	0.030		0.030		0.030		0.023				
150	0.029	0.029	0.029	0.029	0.029	0.029	0.027	0.027		0.0	25.0
	0.029		0.029		0.029		0.027				
	0.028		0.028		0.028		0.026				
160	0.029	0.029	0.029	0.029	0.029	0.029	0.029	0.029		0.0	0.0
	0.029		0.029		0.029		0.029				
	0.028		0.028		0.028		0.028				

Appendix B-2 Relationship between the PEB time and dissolution rate of a copolyimide containing 20 wt% nifedipine at 140°C PEB temperature.

PEB Time (min)	Unexposure (mm)				Exposure (mm)				Time of development (s)	Dissolution rate unexposure (nm/s)	Dissolution rate exposure (nm/s)
	before		after		before		after				
10.0	0.030	0.030	0.029	0.029	0.030	0.030	0	0.000	80	12.5	370.8
	0.029		0.028		0.029		0				
	0.030		0.029		0.030		0.000				
12.5	0.028	0.028	0.028	0.028	0.028	0.028	0.000	0.000		0	354.2
	0.028		0.028		0.028		0.000				
	0.029		0.029		0.029		0.000				
15.0	0.029	0.028	0.029	0.028	0.029	0.028	0.010	0.009		0	237.5
	0.028		0.028		0.028		0.009				
	0.028		0.028		0.028		0.009				
17.5	0.030	0.030	0.030	0.030	0.030	0.030	0.020	0.020		0	125.0
	0.030		0.030		0.030		0.020				
	0.029		0.029		0.029		0.019				
20.0	0.030	0.030	0.030	0.030	0.030	0.030	0.023	0.023		0	87.5
	0.029		0.029		0.029		0.022				
	0.03		0.03		0.03		0.023				

Appendix B-3 Characteristic curves of the PSPI films with various content of nifedipine.

Exposure Dose (mJ/cm^2)	Time of exposure (min)	Film thickness (mm)		Normalized film thickness	Film thickness (mm)		Normalized film thickness	Film thickness (mm)		Normalized film thickness
		20 phr			25 phr			30 phr		
		before	after		before	after		before	after	
0	0.0	0.006	0.006	1.0	0.008	0.008	1.0	0.007	0.007	1.0
50	2.5	0.011	0.011	1.0	0.005	0.005	1.0	0.005	0.005	1.0
100	5.0	0.010	0.009	0.9	0.004	0.004	1.0	0.010	0.01	1.0
150	7.5	0.010	0.006	0.6	0.004	0.0035	0.9	0.004	0.004	1.0
200	10.0	0.011	0	0.0	0.006	0.0035	0.6	0.004	0.0035	0.9
250	12.5	0.013	0	0.0	0.005	0.001	0.2	0.004	0.0025	0.6
300	15.0	0.010	0	0.0	0.006	0	0.0	0.004	0.001	0.3
350	17.5	0.012	0	0.0	0.004	0	0.0	0.004	0	0.0
400	20.0	0.016	0	0.0	0.022	0	0.0	0.006	0	0.0
450	22.5	0.014	0	0.0	0.015	0	0.0	0.006	0	0.0
500	25.0	0.016	0	0.0	0.006	0	0.0	0.006	0	0.0
550	27.5	0.015	0	0.0	0.007	0	0.0	0.006	0	0.0
600	30.0	0.016	0	0.0	0.006	0	0.0	0.006	0	0.0
650	32.5	0.015	0	0.0	0.009	0	0.0	0.006	0	0.0
700	35.0	0.014	0	0.0	0.007	0	0.0	0.006	0	0.0

APPENDIX C

Characterization of adhesive copolyimide films

Appendix C-1 Relationship between the PEB temperature (for 20 min) and dissolution rate of a copolyimide containing 0.5wt% silane and 20 wt% nifedipine

PEB Temperature (ºC)	Unexposure (mm)				Exposure (mm)				Time of development (s)	Dissolution rate unexposure (nm/s)	Dissolution rate exposure (nm/s)
	before		after		before		after				
130	0.030	0.031	0.028	0.029	0.030	0.030	0.020	0.021	80	25.0	112.5
	0.029		0.027		0.029		0.019				
	0.030		0.029		0.030		0.020				
140	0.030	0.032	0.030	0.032	0.030	0.030	0.023	0.024		6.3	75.0
	0.029		0.029		0.029		0.022				
	0.030		0.030		0.030		0.023				
150	0.029	0.030	0.029	0.030	0.029	0.030	0.027	0.028		0.0	25.0
	0.029		0.029		0.029		0.027				
	0.028		0.028		0.028		0.026				
160	0.029	0.030	0.029	0.030	0.029	0.029	0.029	0.029		0.0	0.0
	0.029		0.029		0.029		0.029				
	0.028		0.028		0.028		0.028				

Appendix C-2 Relationship between the PEB time and dissolution rate of a copolyimide containing 0.5wt% silane and 20 wt% nifedipine at 150°C PEB temperature.

PEB Time (min)	Unexposure (mm)				Exposure (mm)				Time of development (s)	Dissolution rate unexposure (nm/s)	Dissolution rate exposure (nm/s)
	before		after		before		after				
10.0	0.030	0.030	0.029	0.028	0.030	0.027	0	0.000	80	20.8	337.5
	0.029		0.028		0.029		0				
	0.030		0.029		0.030		0.000				
12.5	0.028	0.028	0.028	0.027	0.028	0.026	0.000	0.000		12.5	325.0
	0.028		0.028		0.028		0.000				
	0.029		0.029		0.029		0.000				
15.0	0.029	0.028	0.029	0.028	0.029	0.020	0.010	0.000		0.0	250.0
	0.028		0.028		0.028		0.009				
	0.028		0.028		0.028		0.009				
17.5	0.030	0.029	0.030	0.029	0.030	0.029	0.020	0.020		0.0	116.7
	0.030		0.030		0.030		0.020				
	0.029		0.029		0.029		0.019				
20.0	0.030	0.030	0.030	0.030	0.030	0.029	0.023	0.028			12.5
	0.029		0.029		0.029		0.022				
	0.030		0.030		0.030		0.023				

Appendix C-3 Characteristic curves of the silane-containing PSPI films with various content of nifedipine.

Exposure Dose (mJ/cm^2)	Time of exposure (min)	Film thickness (mm)		Normalized film thickness	Film thickness (mm)		Normalized film thickness	Film thickness (mm)		Normalized film thickness
		20 phr			25 phr			30 phr		
		before	after		before	after		before	after	
0	0.0	0.007	0.007	1.0	0.006	0.006	1.0	0.005	0.005	1.0
50	2.5	0.01	0.009	1.0	0.006	0.006	1.0	0.004	0.004	1.0
100	5.0	0.01	0.008	0.9	0.004	0.004	1.0	0.004	0.004	1.0
200	10.0	0.011	0.007	0.6	0.006	0.005	0.8	0.004	0.004	1.0
300	15.0	0.01	0	0.0	0.006	0.003	0.5	0.004	0.003	0.8
400	20.0	0.016	0	0.0	0.022	0.005	0.2	0.006	0.002	0.3
500	25.0	0.016	0	0.0	0.006	0	0.0	0.006	0.001	0.2
600	30.0	0.016	0	0.0	0.006	0	0.0	0.006	0	0.0
700	35.0	0.014	0	0.0	0.007	0	0.0	0.06	0	0.0

VITA

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