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2011년 2월

主審

副審

委員
Abstract

Plasma polymerized methyl methacrylate (ppMMA) thin films having high optical transparency were prepared by rf plasma polymerization technique. For application to flexible organic light emitting diodes (OLEDs), the ppMMA thin films were deposited on poly ethyleneterephthalate (PET) substrate with ductility and flexibility. Thickness of the ppMMA on the PET were varied from 100nm to 400nm, where the plasma polymerization was carried out at the preparation conditions: Ar gas flow of 10sccm, rf plasma power of 150W. Water vapor permeation rate (WVTR) for the ppMMA thin films were measured by MOCON (water vapor transmission rate measurement device) to investigate the possibility to be analyzed as an encapsulation material in (flexible) OLEDs. After UV/Visible spectroscopy analysis, all the ppMMA thin films on PET substrates showed good enough optical transparency of 80%~90% in visible range. The ppMMA thin film with 400 nm thickness showed water vapor transmission rate of 5.6 g·day/m², which indicates the ppMMA studied in this thesis could be applied to OLEDs as a thin film encapsulation material with further improvements.
국문 요약

플라즈마 중합된 메틸메타 아크릴레이트 (ppMMA) 필름은 광학적 투과도를 가진 필름으로서 준비된 플라즈마 중합장비위에 MMA Monomer 를 기화시켜 만들었다. 역시 연성이 좋고 광학적 특성이 우수한 0.5mm 두께의 PET 위에 100nm부터 400nm 까지 Ar가스를 플라즈마 10 sccm을 흘려주고 캐패시터형 환형 전극 사이에 rf 플라즈마 150 W를 넣어주고, MMA Monomer의 안정된 증착과 증착된 막의 손실을 막기 위해 밑판 기판에 3V의 바이어스 전압을 하였다.

준비된 각각의 필름은 분투습도 측정 장비인 MOCORN 장비를 이용하여 측정, 400nm에서 5.6 g/day·m² 의 값을 보였고, ppMMA 중합막의 광투과도는 90% 이상의 높은 값을 보였다.

이는 OLED나 유기솔라셀 등의 유기소자 위에 같은 유기물의 수분 투과 방지막으로 제작과 PET기판위의 휘어짐이 가능한 투명기판 소자의 가능성을 보였다.
Optical transparency and humidity permeability of polymerized methyl methacrylate

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CHAPTER 1 INTRODUCTION

Since being introduced in 1987 by Vanslyke and Tang [1], Organic light-emitting devices (OLEDs) have been extensively studied due to their possible use in a wide range of display applications. Recently, the technologies for OLEDs have reached the commercial stage. First successful commercialized application of OLEDs were the Haptic AMOLED Phone for Samsung Electronics in 2009, and then followed by the Super AMOLED display for the smart phone Galaxy S.

Moreover, OLED technology, as an eco-friendly method of generating light, has attracted the interest of many big lighting companies such as Thorn, Philips, Osram, and General Electric (GE) in the last few years. But stability (especially in the life time) of OLED is still problem, which should be solved in order to realize the practical use of OLED. It has been demonstrated that some of organic materials used to form light-emitting layer of OLEDs are very sensitive to contamination, oxidation and humidity [2].

OLEDs once held have been gradually eroded. Nevertheless, the potential to be transparent or flexible still allows OLED technology distinguish itself from the others. So far, the most prominent manufacturers incorporating OLED’s, such as Sony and Samsung, have demonstrated their flexible OLED (FOLED) display
prototypes at some industrial exhibitions. While their examples may demonstrate that the OLED device can still emit light while being bent, the extent to which the luminescence efficiency and brightness would be affected because of bending, or how tightly it could be bent, has not been reported. The answer to both these questions constitutes the first step in evaluating the possibility of whether an OLED device could be made flexible [2].

<table>
<thead>
<tr>
<th>The goal of FOLED substrate use</th>
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<td>Thin</td>
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<td>Light weight</td>
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<td>Rugged</td>
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<td>Flexible</td>
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<td>Transparent</td>
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<td>Processible</td>
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<tr>
<td>Low cost</td>
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<tr>
<td>Solvent resistant</td>
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<tr>
<td>Impermeable to $h_2O$, $O_2$</td>
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To achieve an operating lifetime in excess of a few tens of hours however, improved isolation of the OLED from atmospheric O$_2$, H$_2$O is necessary. Simultaneously, good flexible encapsulation layer must have property of both transparency and anti barrier. Poly methyl methacrylate (PMMA) transmits up to 92% of visible light (3 mm thickness), and gives a reflection of about 4% from each of its surfaces on account of its refractive index [3,4].

Plasma polymerized layer is generally pinhole–free and highly crosslinked and therefore are durable, thermally stable, chemically inert and mechanically tough. Thus, plasma polymerized methyl methacrylate (ppMMA) would be a good candidate as an encapsulation material for OLEDs. In this thesis, ppMMA thin films were prepared by a rf plasma polymerization technique and the properties of the ppMMA thin films were investigated considering the application to thin film encapsulation for OLEDs.
CHAPTER 2 THEORY

2.1 Methyl Methacrylate (MMA)

2.1.1 History

The first acrylic acid was created in 1843. Methacrylic acid, derived from acrylic acid, was formulated in 1865. The reaction between methacrylic acid and methanol results in the ester methyl methacrylate [5]. The German chemists Fittig and Paul discovered in 1877 the polymerization process that turns methyl methacrylate into poly methyl methacrylate (PMMA). In 1933 the German chemist Otto Röhme patented and registered the brand name PLEXIGLAS. In 1936 the first commercially viable production of acrylic safety glass began. During World War II acrylic glass was used for submarine periscopes, and windshields, canopies, and gun turrets for airplanes [6,7].

Figure 2.1 shows that chemical structure of methyl methacrylate
2.1.2 Synthesis

PMMA is routinely produced by emulsion polymerization, solution polymerization and bulk polymerization. Generally radical initiation is used (including living polymerization methods), but anionic polymerization of PMMA can also be performed. To produce 1 kg (2.2 lb) of PMMA, about 2 kg (4.4 lb) of petroleum is needed [8].

2.1.3 Processing

The glass transition temperature of PMMA ranges from 85 to 165 °C (185 to 329 °F); the range is so wide because of the vast number of commercial compositions. The forming temperature starts at the glass transition temperature and goes up from there. All common molding processes may be used, including injection molding, compression molding and extrusion. The highest quality PMMA sheets are produced by cell casting, but in this case, the polymerization and molding steps occur concurrently. The strength of the material is higher than molding grades owing to its extremely high molecular mass. Rubber toughening has been used to increase the strength of PMMA owing to its brittle behavior in response to applied loads.
2.1.4 Properties

PMMA is a strong and lightweight material. It has a density of 1.17–1.20 g/cm$^3$ [8,9], which is less than half that of glass [9]. It also has good impact strength, higher than both glass and polystyrene; however, PMMA’s impact strength is still significantly lower than polycarbonate and some engineered polymers. PMMA ignites at 460 °C (860 °F) and burns, forming carbon dioxide, water, carbon monoxide and low molecular weight compounds, including formaldehyde [15].

PMMA transmits up to 92% of visible light (3 mm thickness), and gives a reflection of about 4% from each of its surfaces on account of its refractive index (1.4914 at 587.6 nm) [11]. It filters ultraviolet (UV) light at wavelengths below about 300 nm (similar to ordinary window glass). Some manufacturers [13] add coatings or additives to PMMA to improve absorption in the 300–400 nm range. PMMA passes infrared light of up to 2800 nm and blocks IR of longer wavelengths up to 25 μm.

Colored PMMA varieties allow specific IR wavelengths to pass while blocking visible light (for remote control or heat sensor applications, for example). PMMA swells and dissolves in many organic solvents; it also has poor resistance to many other chemicals on account of its easily hydrolyzed ester groups. Nevertheless, its environmental stability is superior to most other plastics such as polystyrene and polyethylene, and PMMA is therefore often the material of choice for outdoor applications.
PMMA as maximum water absorption ratio of 0.3–0.4% by weight [14]. Tensile strength decreases with increased water absorption [17]. Its coefficient of thermal expansion is relatively high as $(5–10) \times 10^{-5}/K$ [15,16].

Figure 2.2 shows that Polymerization process of mma

Free radical Vinyl polymerization

methyl methacrylate

Poly (methyl methacrylate)
Poly(methyl methacrylate), which scientists call PMMA, is a clear plastic, used as a shatterproof replacement for glass. The clear barrier at the ice rink which keeps hockey pucks from flying in the faces of hockey fans is made of PMMA. The chemical company Rohm and Haas makes windows out of it and calls it Plexiglas®. Ineos Acrylics also makes it and calls it Lucite. Lucite is used to make the surfaces of hot tubs, sinks, one-piece bathtub/shower units, among other things.

When it comes to making windows, PMMA has another advantage over glass. PMMA is more transparent than glass. When glass windows are made too thick, they become difficult to see through. But PMMA windows can be made as much as 13 inches (33 cm) thick, and they’re still perfectly transparent. This makes PMMA a wonderful material for making large aquariums, with windows which must be thick in order to contain the high pressure of millions of gallons of water. In fact, the largest single window in the world, an observation window at California’s Monterrey Bay Aquarium, is made of one big piece of PMMA which is 54 feet long, 18 feet high, and 13 inches thick (16.6 m long, 5.5 m high, and 33 cm thick).

PMMA is also found in paint. The painting on your right, Acrylic Elf, was painted by Pete Halverson with acrylic paints. Acrylic "latex" paints often contain PMMA suspended in water. But PMMA is more than just plastic and paint. Often lubricating oils and
hydraulic fluids tend to get really thick and even gummy when they get really cold. This is a real pain when you’re trying to operate heavy construction equipment in really cold weather. But when a little bit PMMA is dissolved in these fluids it keeps them from getting thick in the cold, and machines can be operated down to −100°C (−150°F), that is, presuming the rest of the machine can take that kind of cold.
2.2 Plasma

2.2.1 Theory of Plasma

A plasma is a gas containing charged and neutral species, including some or all of the following: electrons, positive ions, negative ions, atoms, and molecules. On average a plasma is electrically neutral, because any charge imbalance would result in electric fields that would tend to move the charges in such a way as to eliminate the imbalance. As a result, the density of electrons plus the density of negative ions will be equal to the density of positively charged ions [18,19,20].

Plasma is often called the fourth state of matter. A solid substance in thermal equilibrium generally passes into a liquid state as the temperature is increased at a fixed pressure. The liquid passes into a gas as the temperature is further increased [21,22]. At a sufficiently high temperature, the molecules in the gas decompose to form a gas of atoms that move freely in random directions, except for infrequent collisions between atoms. If the temperature is further increased, then the atoms decompose into freely moving charged particles (electrons and positive ions), and the substance enters the plasma state. This state is characterized by a common charged particle density, \( n_e \approx n_i \approx n \) particles/m\(^3\) and, in equilibrium, a temperature \( T_e = T_i = T \). The
temperature required to form plasmas from pure substances in thermal equilibrium range from roughly 4000 K for easy-to-ionize elements like cesium to 20,000 K for hard-to-ionize elements like helium. The fractional ionization of a plasma is

\[ X_{iz} = \frac{n_i}{n_g + n_i} \]

Figure 2.3. state of matter versus temperature

where \( n_g \) is the neutral gas density, and \( n_i \) is the ionized gas density. \( X_{iz} \) is near unity for fully ionized plasmas, and \( X_{iz} \ll 1 \) for weakly ionized plasma [23].
2.2.2 Types of plasma

In commonly, plasma can be divided into equilibrium and non-equilibrium plasma. Equilibrium plasma is thermal plasma, is in local thermodynamic equilibrium and has almost same temperatures of electrons and ions \((T_e \approx T_i)\). In a non-equilibrium plasma, the electrons have high temperature more than the ions \((T_e >> T_i)\) and gas pressure is lower.

Equilibrium (thermal) plasma has a powerful energy to destruct stable chemicals and the chemical reaction is occurred in very short time. On the other hand, although it is not as strong as equilibrium plasma, non-equilibrium (non-thermal) plasma is convenient to control the chemical reaction [24,25].
2.3 Plasma polymerization

Plasma polymerization is a unique technique to fabricate thin polymer films (10 nm~1μm) from a variety of organic and organometallic starting materials. Plasma polymerized films are pinhole-free and highly crosslinked and therefore are endurable, thermally stable, chemically inert and mechanically tough. Furthermore such films are often highly coherent and adherent to a variety of substrates including conventional polymer, glass and metal surfaces. Due to these excellent properties they have been undertaken very actively in the last few years for a variety of applications such as permselective membranes protective coatings biomedicals, electronic, optical devices and adhesion promoters [26,27].

After a brief review of the plasma polymerization mechanisms, the surface modification of polymers will be discuss both by non polymer forming plasmas and by deposition of plasma polymerized thin films on their surface by appropriate plasma surface treatments, new properties such as optical reflection, adhesion, friction coefficient, surface energy, permeability, surface conductivity and biocompatibility of conventional polymers can be obtained [28,29,30].
Figure 2.4 plasma polymerization combination structure.
Figure 2.5 Difference modeling of monomer, conventional polymer plasma polymer.
Comparison of the structures of plasma polymers and conventional polymers are given in Fig.5. Out of this origination mechanism from plasma polymers there results special layer characteristics that are qualified for a multitude of applications:

[31]

1. excellent coating adhesion on almost all substrates
2. chemical, mechanical and thermal stability
3. high barrier effect
2.4 WVTR (water vapor transmission rate)

2.4.1 Definition of WVTR

WVTR (water vapor transmission rate) is the steady state rate at which water vapor permeates through a film at specified conditions of temperature and relative humidity. Values are expressed in g/100 in²/24 hr in US standard units and g/m²/24 hr in metric (or SI) units. Test conditions vary, but Exxon Mobil has standardized to 100°F (37.8°C) and 90% RH, which is the most common set of conditions reported in North America.

2.4.2 Relevance to package performance

A critical function of flexible packaging is to keep dry devices (OLED, solar cell packing about electrical devices, etc.). Without protective packaging, products will quickly gain or lose moisture until they are at equilibrium with the environmental relative humidity. At this point, anti encapsulation is very important. WVTR is the standard measurement by which films are compared for their ability to resist moisture transmission. Lower values indicate better moisture protection. Only values reported at the same temperature and humidity can be compared, because transmission rates are affected by both of these parameters.
One of the most valued properties of OPP is its exceptional moisture barrier. As shown in Table 9, gauge for gauge, OPP provides the best WVTR of all common polymer packaging films. (For homogeneous films like these, you can calculate the WVTR for a particular thickness by dividing the values in the table by the desired gauge in mils.)

2.4.3 Measurement

The rate at which water vapor will pass through a material under specified conditions and specimen geometry. The volume of water vapor that will pass through a unit thickness of material per unit area per unit time per unit barometric pressure. The test specimen is held such that it separates two sides of a test chamber. The "wet side" of the specimen is exposed to a high relative humidity atmosphere, while the "dry side" is subjected to a zero relative humidity atmosphere. Infrared sensors on the "dry side" detect the amount of water vapor present. Testing is complete when the concentration of water vapor in the dry side atmosphere is constant.
2.5 AFM

2.5.1 History of AFM

The atomic force microscope (AFM) is the most popular and powerful instrument to measure the structure of a surface in nanometer scale [35–37]. The Atomic Force Microscope was developed to overcome a basic drawback with STM – that it can only image conducting or semiconducting surfaces. The AFM, however, has the advantage of imaging almost any type of surface, including polymers, ceramics, composites, glass, and biological samples. Binnig, Quate, and Gerber invented the Atomic Force Microscope in 1985. Their original AFM consisted of a diamond shard attached to a strip of gold foil. The diamond tip contacted the surface directly, with the interatomic van der Waals forces providing the interaction mechanism. Detection of the cantilever’s vertical movement was done with a second tip – an STM placed above the cantilever [36,37].
2.5.2 AFM probe deflection

Today, most AFMs use a laser beam deflection system, introduced by Meyer and Amer, where a laser is reflected from the back of the reflective AFM lever and onto a position-sensitive detector. AFM tips and cantilevers are microfabricated from Si or Si3N4. Typical tip radius is from a few to 10s of 1nm.

Figure 2.6  Beam deflection system, using a laser and photodector to measure the beam position [32,33].
2.5.3 Measuring forces

Because the atomic force microscope relies on the forces between the tip and sample, knowing these forces is important for proper imaging. The force is not measured directly, but calculated by measuring the deflection of the lever, and knowing the stiffness of the cantilever. Hook’s law gives $F = -kz$, where $F$ is the force, $k$ is the stiffness of the lever, and $z$ is the distance the lever is bent.

Figure 2.7  AFM probe distance from Sample (Z distance)[32,33]
2.5.4 AFM Modes of operation

Because of AFM’s versatility, it has been applied to a large number of research topics. The Atomic Force Microscope has also gone through many modifications for specific application requirements.

2.5.4–1 Contact Mode

The first and foremost mode of operation, contact mode is widely used. As the tip is raster-scanned across the surface, it is deflected as it moves over the surface corrugation. In constant force mode, the tip is constantly adjusted to maintain a constant deflection, and therefore constant height above the surface. It is this adjustment that is displayed as data. However, the ability to track the surface in this manner is limited by the feedback circuit. Sometimes the tip is allowed to scan without this adjustment, and one measures only the deflection. This is useful for small, high-speed atomic resolution scans, and is known as variable-deflection mode [37]. Because the tip is in hard contact with the surface, the stiffness of the lever needs to be less that the effective spring constant holding atoms together, which is on the order of 1 – 10 nN/nm. Most contact mode levers have a spring constant of < 1N/m.>
2.5.4-2 Lateral Force Microscopy

AFM measures frictional forces on a surface. By measuring the “twist” of the cantilever, rather than merely its deflection, one can qualitatively determine areas of higher and lower friction.

2.5.4-3 Noncontact mode

Noncontact mode belongs to a family of AC modes, which refers to the use of an oscillating cantilever. A stiff cantilever is oscillated in the attractive regime, meaning that the tip is quite close to the sample, but not touching it (hence, “noncontact”). The forces between the tip and sample are quite low, on the order of pN (10⁻¹² N). The detection scheme is based on measuring changes to the resonant frequency or amplitude of the cantilever.

2.5.4-4 Dynamic Force / Intermittant-contact / “tapping mode” AFM

Commonly referred to as “tapping mode” it is also referred to as intermittent-contact or the more general term Dynamic Force Mode (DFM). A stiff cantilever is oscillated closer to the sample than in noncontact mode. Part of the oscillation extends into the repulsive regime, so the tip intermittently touches or “taps” the
surface. Very stiff cantilevers are typically used, as tips can get “stuck” in the water contamination layer.

The advantage of tapping the surface is improved lateral resolution on soft samples. Lateral forces such as drag, common in contact mode, are virtually eliminated. For poorly adsorbed specimens on a substrate surface the advantage is clearly seen.

2.5.4–5 Force Modulation

Force modulation refers to a method used to probe properties of materials through sample/tip interactions. The tip (or sample) is oscillated at a high frequency and pushed into the repulsive regime. The slope of the force–distance curve is measured which is correlated to the sample’s elasticity. The data can be acquired along with topography, which allows comparison of both height and material properties.

2.5.4–6 Phase Imaging

In Phase mode imaging, the phase shift of the oscillating cantilever relative to the driving signal is measured. This phase shift can be correlated with specific material properties that effect the tip/sample interaction. The phase shift can be used to differentiate areas on a sample with such differing properties as friction, adhesion, and viscoelasticity. The techniques is used simultaneously with DFM mode, so topography can be measured
2.6 PET (Poly ethylene terephthalate)

2.6.1 Definition of PET

Polyethylene terephthalate polyester (PETP) is the most common thermoplastic polyester and is often called just “polyester”. This often causes confusion – not only is the chemically similar polybutylene terephthalate (PBT) also a (thermoplastic) polyester, the most common resin system used in GRP is also a polyester system – and also often called just “polyester”. (In this latter case, however, the polyesters are chemically unsaturated and are “free–radical polymerized” into a thermoset).

2.6.2 General Properties

Polyethylene terephthalate (PET) is a hard, stiff, strong, dimensionally stable material that absorbs very little water. It has good gas barrier properties and good chemical resistance except to alkalis (which hydrolyze it). Its crystallinity varies from amorphous to fairly high crystalline. It can be highly transparent and colourless but thicker sections are usually opaque and off–white. Polyethylene terephthalate films are widely known in the form of biaxially oriented and thermally stabilized films usually...
referred to by their main brand names Mylar, Melinex or Hostaphan. Strictly speaking, these names should be used only for this type of film whose properties are different from, and in several respects superior to, those of “ordinary” polyethylene terephthalate (PET) film.

<table>
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<tr>
<td>Acids - concentrated</td>
<td>Good</td>
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<tr>
<td>Acids – dilute</td>
<td>Good</td>
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<tr>
<td>Alcohols</td>
<td>Good</td>
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<tr>
<td>Alkalis</td>
<td>Poor</td>
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<tr>
<td>Aromatic hydrocarbons</td>
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<td>Halogens</td>
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<td>Ketones</td>
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Table 2.1 Chemical Resistance property of PET [38]
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Table 2.2 Electrical Properties of PET [38]

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<tr>
<td>Aromatic hydrocarbons</td>
<td>Fair</td>
</tr>
<tr>
<td>Greases and Oils</td>
<td>Good</td>
</tr>
<tr>
<td>Halogens</td>
<td>Good</td>
</tr>
<tr>
<td>Ketones</td>
<td>Good</td>
</tr>
</tbody>
</table>

Table 2.3 Physical Properties of PET [38]
CHAPTER 3 EXPERIMENTS

3.1 Surface pretreatment and deposition process

In any thin film deposition process, substrate cleansing is essential for better thin film adhesion to substrates and thin film property assurance. Therefore, prior to thin film deposition of ppMMA, the PET substrates were cleansed throughly using ultrasonic cleaner: isopropyl alcohol → D.I water → nitrogen gas dry

Figure 3.1 Ultrasonic cleaner

Originally, cleaning process sequence is firstly done with an Acetone for organic dust remove, but PET is dissolved by Acetone inevitably. So the cleaning process for the PET carried out in this thesis except of Acetone cleaning.
Plasma polymerized methyl methacrylate (ppMMA) film was deposited on the PET substrate by radio frequency (13.56Mhz) argon gas plasma. The conditions of plasma polymerization were as follows: flow rate of argon gas as 10sccm; rf plasma power as 150W; working vacuum as $5.0 \times 10^{-1}$ torr.

In order to investigate the deposition time-thickness relationship, thickness of the ppMMA thin films were measured by means of scanning electron microscopy (SEM). And after the SEM data (operate time-deposition thickness), the ppMMA thin films were deposited on PET substrates so that the thickness would be as 100nm, 200nm, 300nm, and 400nm.

Figure 3.2 Plasma polymerization equipment
Figure 3.3 Schematics of the rf plasma polymerization equipment
3.2 Film characterization and surface morphology analysis

Surface morphology of the ppMMA film was analyzed by atomic force microscopy (AFM, NS4A). The measurements were accomplished with a Si cantilever for contact AFM, in non contact mode, where specimen size was 5μm×5μm.

Figure 3.4 AFM equipment for thin film surface morphology analysis
The adhesion quality of the ppMMA coating was inspected by an adhesive-tape peel test according to the guideline of the American Society for Test and Materials (ASTM 3359-B),

- **temp set point**: 37.8°C
- **relative humidity auto**: 100%

Scanning electron microscopy were then used to study the cracks of ppMMA films on PET.

Optical transparency of the ppMMA film was analyzed by uv/vis spectroscopy (*Perkin Elmer*) the slit width was set at 2 nm.

Chemical combination of the ppMMA film was analyzed by
Fourier Transform Infrared (FTIR) spectroscopy (Bruker, Karlsruhe, Germany). For data processing, OPUS software v.6 (Bruker) was used.

Figure 3.6  Scanning electron microscope (SEM) equipment
Figure 3.7 Pt coating devices for SEM image photographing

Figure 3.8 FTIR equipment for chemical composition analysis
3.3 Optical transparency measurement.

Optical transparency of the ppMMA thin films was analyzed by UV/Vis spectroscopy *(Perkin Elmer)* with slit width set to 2nm.

1. Measurement range: visible wavelength (350nm~750nm)
2. Reference: bare *Corning* glass
3. Samples: ppMMA thin films of 100nm, 200nm, 300nm, and 400nm

![UV/Vis spectroscopy](image)
3.4 WVTR rate measurement

Water vapor transmission rate (WVTR) of the ppMMA thin films on PET substrate was measured by MOCON Test. The rate at which water vapor will pass through a material under specified conditions and specimen geometry. The volume of water vapor that will pass through a unit thickness of material per unit area per unit time per unit barometric pressure. The test specimen is held such that it separates two sides of a test chamber. The "wet side" of the specimen is exposed to a high relative humidity atmosphere, while the "dry side" is subjected to a zero relative humidity atmosphere. Infrared sensors on the "dry side" detect the amount of water vapor present. Testing is complete when the concentration of water vapor in the dry side atmosphere is constant. The WVTR of the ppMMA was measured in this thesis in g/m²/24hr for 100nm, 200nm, 300nm, and 400nm samples to investigate the effect of thickness and process condition of the ppMMA on their WVTR characteristics. Figure 3.10 and Figure 3.11 shows the MOCON test equipment and schematic of the MOCON test, respectively.

The adhesion quality of the coating was inspected by an adhesive-tape peel test according to the guideline of the American Society for test and materials (ASTM 3359–B),
[1] At least, mocon testing require square circle 5cm. aluminium foil cover film's outline 
(a) after thin film deposition, the ppMMA thin films were then treated with Ar plasma for each 3 min.
(b) then the ppMMA thin films were thermally treated on hot plate at 100℃ 5min long for each samples: thermal treatment temperature was decided considering the glass transition temperature (Tg) of the PET and MMA (Tg of the PET is 260℃; Tg of the MMA is 160℃)

[2] Side of the ppMMA thin films deposited with Al cover films was in contact with water vapor

[3] WVTR was then measured until equilibrium is reached
Figure 3.10 MOCON test equipment for WVTR measurement

Figure 3.11 A schematic of the MOCON test
CHAPTER 4 RESULTS AND DISCUSSIONS

4.1 Result of ppMMA film deposition thickness

In order to get the deposition time to ppMMA thin film thickness relationship, the plasma polymerization of MMA were done for 10min, 20min, 30min, 40min, 50min, and 60min. The deposition condition for the ppMMA were as follows: Ar gas (plasma discharge gas) flow rate of 10~15 sccm; plasma power of 150W; substrate bias power of 3W. Thickness of the ppMMA thin films were investigated in this thesis by SEM analysis, which is shown in Figure 4.1 The resulting ppMMA thin film thickness on the PET substrate is shown in the Figure 4.2.

In comparison to other plasma polymerized thin films such as plasma polymerized styrene (ppS) and plasma polymerized vinyl acetate (ppVA), and plasma polymerized thiophene (ppTh), the ppMMA showed relatively low deposition rate of 10nm/min. Thin film thickness of plasma polymerized polymer thin films is dependent on monomer vaporization degree and plasma polymerization condition. As the plasma polymerization condition for the ppMMA carried out in this thesis is similar to those of other plasma polymerized polymer thin films, the relatively low deposition rate of the ppMMA might be caused by MMA monomer vaporization rate. For the application to encapsulation material in OLEDs, optical transparency in visible range is essential, so the ppMMA thin films were studied in this thesis, despite the relative low deposition rate.
In addition, differences of the deposition rate for plasma polymerized polymer thin films are also dependent on vaporization pressure due to inherent material combining force and then thin film coalescence degree on the surface of substrates. The plasma polymerization for the ppMMA thin films were then decided to get an optimized condition for higher deposition rate.
Figure 4.1 SEM images of the ppMMA thin films

① 100nm, 10min  ② 200nm, 20min (approximate value)
③ 400nm, 40min  ④ 600nm, 60min
Figure 4.2 Deposition time–thickness relationship for the ppMMA thin films
4.2 Surface analysis

4.2.1 AFM Data (rms of ppMMA film surface)

Surface roughness of substrates is generally very important for any thin film deposition, and it is one of the critical issues especially for OLEDs fabrication. In case of flexible OLEDs, the substrate surface roughness is more severe problem, because polymeric flexible substrates have generally relatively inferior surface roughness. Therefore, surface roughness of the PET substrates were measured by AFM prior to the ppMMA deposition, and the compared with those of the ppMMA on the PET substrates. Figure 4.3–4.8 shows the AMF images of the bare PET substrates and the ppMMA thin films. Surface roughness of PET film is relatively bigger than the others. As the ppMMA thin film thickness increases, rms value, hence the surface roughness of the PET is getting small. It is thought that ppMMA of small density was deposited on the substrate. It is generally known that the ppMMA is hydrophobic, so the smaller the rms value of the ppMMA is, then it would be better for water vapor protection, hence the encapsulation performance independent of the WVTR property.
Figure 4.3 AFM 2D Data of PET roughness of PET (5um×5um size, non contact)
Rms : 1.211 nm

Figure 4.4 AFM 3D Data of PET roughness of PET (5um×5um size, non contact)
Rms : 1.211 nm
Figure 4.5  AFM 2D Data of ppMMA; 200nm on PET roughness of pmma 200nm on PET (5um×5um size, noncontact) Rms : 0.422 nm

Figure 4.6  AFM 3D Data of ppMMA; 200nm on PET
Figure 4.7  AFM 2D Data of ppMMA: 400nm on PET roughness of pmma 400nm on PET (5um×5um size, noncontact) Rms : 0.214 nm.

Figure 4.8  AFM 3D Data of ppMMA: 400nm on PET
4.2.2 Surface image (by SEM Data)

SEM measurement was done originally to measure the thickness of the deposited ppMMA thin films. But the SEM results could also be used to investigate the thin film property of the ppMMA such as mechanical cracks. It would be especially useful to investigate the flexible applications. As is shown in the Figure 4.9, the ppMMA deposited on the PET shows a microscopic crack after 90° bending, although it is an organic polymer thin film on the organic polymer substrate, namely, PET.

Figure 4.9 SEM image of the ppMMA thin film on PET substrate after 90° bending
4.2.3 FTIR Data

Composition of the ppMMA with 200nm, 300nm, 400 nm thickness on the PET substrate was analyzed with FTIR spectroscopy, of which the results are shown in the Figure4.10. Depending on the thin film thickness, difference of peak intensity is shown, but the films composition is almost similar for each samples.

![FTIR Data of the ppMMA thin films](image)
4.3 UV/Vis spectroscopy

For the application to thin film encapsulation material, the ppMMA should have high optical transparency in visible range as possible, because the light generated inside the OLED will be emanated to outside through the encapsulation material. The overall light emission efficiency of the OLED will also be then dependent of the optical transparency of the ppMMA thin films as encapsulation. Therefore, optical transparency of the ppMMA on PET substrates was measured by UV/Vis spectroscopy, of which the results are shown in the Figure 4.11 for the ppMMA thin films with thicknesses of 100nm, 200nm, 300nm, and 400nm, respectively. As is shown in the Figure 4.11, all the ppMMA thin films reveals good optical transparency in visible range, so that it could be used as transparent passivation thin films for OLED devices.

![Figure 4.11 Optical transparency Data of the ppMMA thin films](image)

Figure 4.11 Optical transparency Data of the ppMMA thin films
Figure 4.12 shows also, the ppMMA on PET substrate reveal acceptable optical transparency. For applications to transparent displays, optical transparency over 85% in visible range is needed. Therefore, the ppMMA thin films prepared in this thesis, could be used as transparent passivation thin film.

Figure 4.12 Transparent ppMMA thin films on the PET substrate
4.4 WVTR rate of ppMMA film

Water vapor transmission rate (WVTR) of the ppMMA thin films were measured by MOCON test, of which the results are shown in the Figure 4.13. The ppMMA film permeation of average is 7.344128 g / [ m²-day ] in 200nm and 6.267907 g / [ m²-day ] in 300nm and 5.274025 g / [ m²-day ] in 400nm. The WVTR values of the ppMMA should be improved for practical applications to OLEDs, but the ppMMA studied in this thesis shows possibilities of those applications.

![Figure 4.13 Time-H₂O permeation graph of the ppMMA thin films](image)

Figure 4.13 Time-H₂O permeation graph of the ppMMA thin films
CHAPTER 5 SUMMARY AND CONCLUSION

In this thesis, plasma polymerized methyl methacrylate (ppMMA) thin films were prepared on PET substrates considering the applications to flexible transparent displays based on OLEDs. The ppMMA thin films could be successfully prepared on flexible transparent PET substrates and showed pin-hole free features. In addition, all the ppMMA thin films revealed good optical transparency of over 90% in visible range. Among the ppMMA samples studied in this thesis, the sample with 400 nm thickness showed best WVTR value of 5.274025 g/[m²-day], although the value should be more improved for practical applications. But, the ppMMA proposed in this thesis showed possibilities of those applications and it is demonstrated that the plasma polymerization process could be an alternative technology for thin film encapsulation fabrication. Further process optimization like post-deposition thermal treatment, surface treatment by plasma, and plasma polymerization condition control would be needed to reduce the WVTR for the ppMMA thin films.
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