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Colorless and Transparent high – Temperature-Resistant Polymer Optical Films – Current Status and Potential Applications in Optoelectronic Fabrications

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Additional information is available at the end of the chapter

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Abstract

Recent research and development of colorless and transparent high-temperature-resistant polymer optical films (CHTPFs) have been reviewed. CHTPF films possess the merits of both common polymer optical film and aromatic high-temperature-resistant polymer films and thus have been widely investigated as components for microelectronic and optoelectronic fabrications. The current paper reviews the latest research and development for CHTPF films, including their synthesis chemistry, manufacturing process, and engineering applications. Especially, this review focuses on the applications of CHTPF films as flexible substrates for optoelectrical devices, such as flexible active matrix organic light-emitting display devices (AMOLEDs), flexible printing circuit boards (FPCBs), and flexible solar cells.

Keywords: colorless polymer films, high temperature, synthesis, flexible substrates

1. Introduction

Various polymer optical films have been widely applied in the fabrication of optoelectronic devices [1]. Recently, with the ever-increasing demands of high reliability, high integration, high wiring density, and high signal transmission speed for optoelectronic fabrications, the service temperatures of polymer optical films have dramatically increased [2, 3]. For instance,

in the fabrication of new-generation flexible thin-film transistor-driven active matrix liquid crystal display devices (TFT-LCDs) or active matrix organic light-emitting display devices (AMOLEDs), the processing temperature on the flexible plastic substrates might be higher than 300°C [4-6]. Most of the common polymer optical films would lose their optical and mechanical properties at such high processing temperatures. Thus, colorless and transparent high-temperature-resistant polymer optical films (CHTPFs) have attracted increasing attentions from both the academic and engineering aspects in the past decades.

According to the different servicing temperatures or glass transition temperatures (T_g), the polymer optical films could be roughly classified into three types, including conventional optical films ($T_g < 100^\circ\text{C}$), common high-temperature optical films ($100 \leq T_g < 200^\circ\text{C}$), and high-temperature optical films ($T_g \geq 200^\circ\text{C}$), as shown in Figure 1. The typical chemical structures for the polymer optical films are illustrated in Figure 2. Main physical and chemical characteristics for the typical optical polymers were tabulated in Table 1 [7, 8]. It can be clearly seen that conventional polymer optical films, such as polyethylene terephthalate (PET, T_g : $\sim 78^\circ\text{C}$) or polyethylene naphthalate (PEN, T_g : $\sim 123^\circ\text{C}$), possess excellent optical transparency. However, they are facing great challenges in advanced optoelectronic fabrication due to their limited service temperatures. On the other hand, high-temperature-resistant polymer films such as wholly aromatic polyimide films (PI) exhibit excellent thermal stability up to 300°C. However, they suffer from deep colors and poor optical transmittance in optoelectronic applications. Thus, achieving a compromise between the pale color and high thermal stability for the polymer optical films is one of the most challenging projects for optoelectronic polymeric films development.

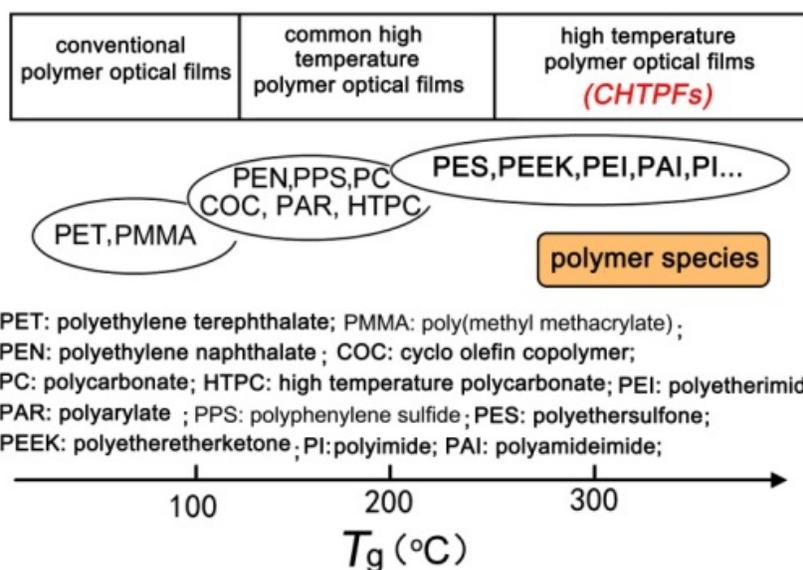


Figure 1. Classification of polymer optical films

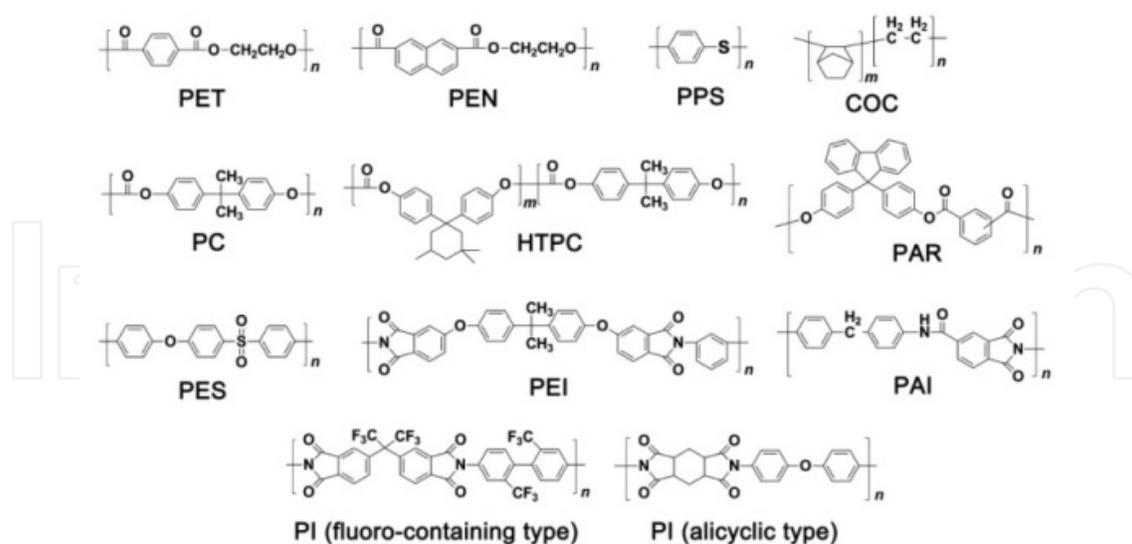


Figure 2. Typical chemical structures for polymer optical films

Item ¹	Unit	PET	PEN	PC	PPS	PEI	PES	PI	CPI ²
Density	g/cm ³	1.40	1.36	1.20	1.35	1.27	1.37	1.43	1.23
Transmittance	%	90	87	92	85	80	89	30-60	90
T_m	°C	256	266	240	285	365	380	NA ³	NA
T_g	°C	78	123	150	90	217	223	>300	303
WVTR	g/m ² day	21	6.9	60	8	43.5	73	64	93
OTR	cm ³ /m ² day	6	2	300	6	220	235	22	NA
Water uptake	%	0.3	0.4	0.2	0.05	1	0.5	1.3	2.1
σ	MPa	225	275	98	250	130	95	274	112
E_b	%	120	90	140	50	70	70	90	12
D.S.	V/ μ m	280	300	250	250	250	260	280	NA
ϵ	-	3.2	3.0	3.0	3.0	3.5	4.0	3.3	2.9

¹ T_m : melting point; T_g : glass transition temperature; WVTR: water vapor transmission rate; OTR: oxygen transmission rate; σ : tensile strength; E_b : elongation at break; D.S.: dielectric strength; ϵ : dielectric constant; ² Data from colorless PI film Neopulim® L-3430 developed by MGC, Japan; ³ Not available.

Table 1. Typical properties of polymer optical films

In the past decades, considerable progress has been achieved in both the academic development and commercialization for novel CHTPFs. According to the classification in Figure 1, the leading materials, in terms of comprehensive properties and potential market volume, include colorless polyimide (PI) films, polyethersulfone (PES) films, polyetheretherketone (PEEK)

films, polyamide (PA), and polyamideimide (PAI) films. They have been the main components for CHTPF families. According to the statistics from Techno Create Corp. (TCC, an authoritative consulting agency in Japan), the market of CHTPFs in 2011 has been close to 1 billion Japanese yen and the market will see a rapid increase higher than 15% per year in the following years [9].

In this review, the state of art and future development of CHTPFs in optoelectronic fabrications has been reviewed. The molecular design, synthesis chemistry, and film fabrication techniques for CHTPFs were introduced first. Then, the applications of CHTPFs in several important optoelectronic fields including flexible display, flexible printing circuit boards (FPCBs), and flexible solar cells were presented.

2. CHTPF manufacturing technology

Generally, the overall production process for CHTPF products consists of several steps, including monomers synthesis, polymer resin preparation, and the film preparation. Technically, these three steps all have their own core technologies and are usually intertwined and interrelated. The reactivity and purity of monomers will definitely affect the physical and chemical properties of the derived polymer resins, including molecular weights and their distribution, inherent viscosities, solubility in organic solvents, appearance, color, and so on. The features of the resins have great effects on the properties of the final polymer films, including their color, optical transparency, mechanical strength, thermal stability, and dielectric properties. Meanwhile, the preparing technologies for the films, including casting procedure, the uniaxial or biaxial stretching process, high-temperature curing program, and even the final winding and rewinding process will also affect the features of the CHTPF products. Thus, the manufacture of CHTPFs is usually a multidisciplinary technology.

The manufacturing techniques for polymer films usually include several types, such as casting, melting extrusion, and blowing procedures. Extrusion is the process of forming a film continuously through an opening. Most extruders do this by rotating a screw inside a stationary heated cylindrical barrel, to melt the polymer resins and pump the melt through a suitably shaped slit. This is used for direct manufacture of finished film products. It may also be used to feed a second process such as injection molding, blow molding, coating, laminating, or thermo-forming process. Blowing procedure is usually performed from a single-screw extruder by extruding polymer resins, cooling it with external and/or internal air streams, stretching it in the machine direction (MD) by pulling it away from the die; stretching it in the transverse direction (TD) by internal air pressure, flattening it by passing through nip rolls, and winding it onto a cylindrical roll. Optional post-stretching operations may include flame or corona surface treatment for wettability, adhesion, and sealing.

Many factors influence the choice of suitable procedures for polymer film manufacture, including physical and chemical properties of the polymer resins, color and appearance demands, and the current abilities of film-producing equipment, and so on. For example, as shown in Figure 3, for crystalline polymer resins that have clear melting points, such as PET

and PEN, nonsolvent melting extrusion technique is mainly used. However, for amorphous polymers with low to moderate T_g values, such as PC and PES, both melting extrusion and solution casting techniques can be used. As for high- T_g amorphous polymers, such as PIs, solvent-casting procedure is usually the optimal choice.

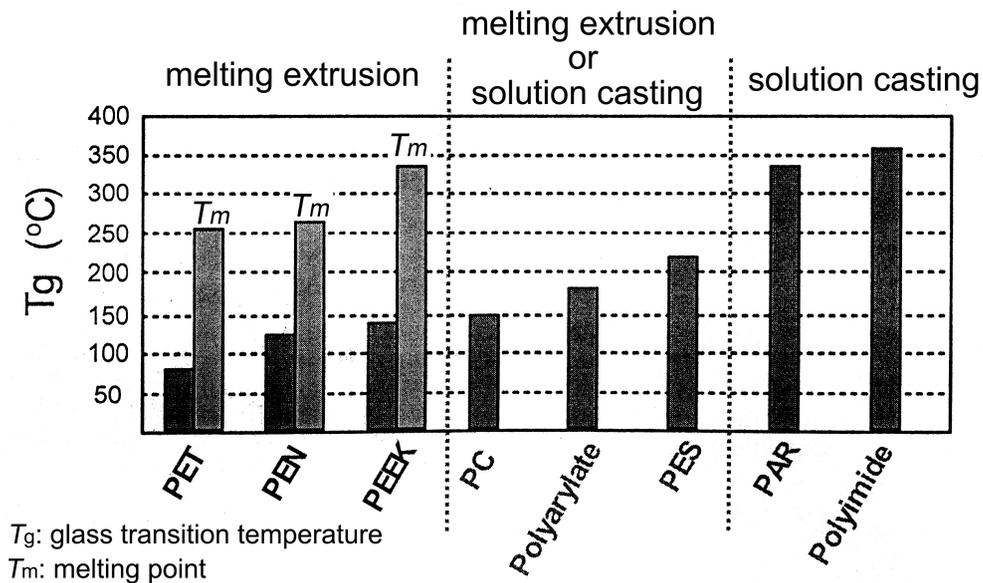


Figure 3. Processing methods for polymer films

The manufacturing techniques for CHTPF films have the similarities with the common optical films; however, they have their own uniqueness at the same time. This is mainly due to their relatively higher T_g values (or melting points) and lower solubility in common solvents caused by the more rigid molecular skeletons compared with the common optical polymers. Thus, for CHTPF films, solvent-casting procedure is most commonly used, especially in laboratory. For the solvent-casting procedure, it can be classified into two approaches: uniaxial stretching (machine direction, MD) and biaxial stretching (transverse direction, TD, and machine direction, MD) techniques. Biaxial stretching at temperatures above the T_g values of the CHTPF resins can usually improve the high-temperature dimensional stability of the obtained films.

Then, in the present paper, PI films are taken as examples to illustrate the development of lab-scale and industrial-scale manufacturing techniques for CHTPF films.

2.1. Laboratory preparation of PI films

Before industrial-scale manufacturing for CHTPF optical films, it is quite necessary to make a film prototype in laboratory so as to determine the optimal processing parameters. For PI films, the common fabrication techniques include two pathways: standard route via poly(amic acid) (PAA) and new route from organosoluble PIs, as illustrated in Figure 4. Both routes have their advantages and drawbacks. Generally speaking, the first standard PAA route is suitable to all kinds of PI films. In this procedure, dianhydride and diamine monomers will first polymerize

in *N,N*-dimethylacetamide (DMAc) to afford PAA solution. The obtained PAA solution is sensitive to heat and moisture, which is easily degrading when stored at room temperature. Thus, it had been better using the newly synthesized PAA for preparing PI films. The PAA solution is cast onto clean glass or stainless steel substrates, followed by thermally curing from room temperature to elevated temperatures. This curing process consists of not only the physical course of solvent evaporation but also the chemical course of imidization or cyclization with the elimination of water. It has been well established that the imidization temperatures as high as 300-350°C is necessary to finish the transition from PAA to PI. Such a high temperature will definitely affect the color of the produced PI films. On the other hand, during the elimination of water from the system, microscopic defects such as pinholes and crack might occur. Thus, the imidization condition should be deliberately controlled in order to produce high-quality PI films.

Technically, the second route is only useful for PI resins which are soluble in organic solvents (mainly DMAc). As we know, the solubility of PI resins is particularly associated with its structure. Introduction of flexible linkages (-O-, -CH₂-, etc.), bulky substituents (alkyl groups, phenyl, etc.), and unconjugated structure (aliphatic or alicyclic groups) are all beneficial increasing the solubility of PI resins in organic solvents. From this point of view, this route is quite useful for colorless PI films production, because most of the PI resins for colorless PI films are soluble in polar solvents. In addition, the curing procedure for preimidized PI solution is nearly pure physical course of solvent evaporation. Thus, the PI films can be produced at relatively low temperature and exhibit good surface smoothness. This is undoubtedly beneficial for the production of colorless PI films.

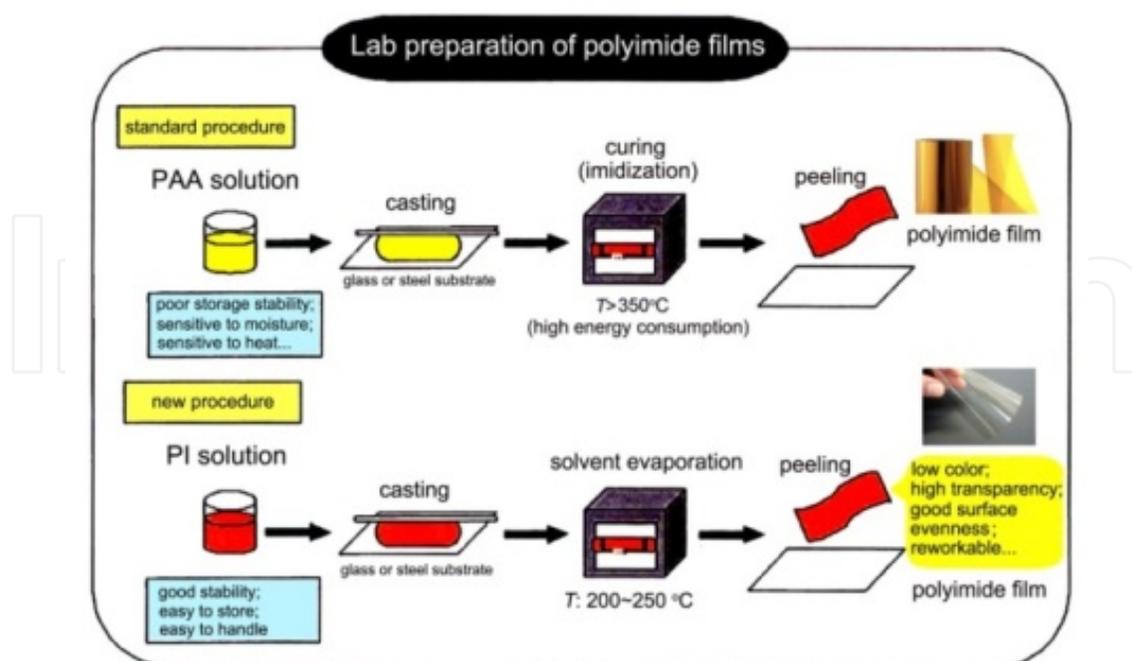


Figure 4. Lab-scale preparation of PI films

2.2. Industrial preparation of PI films

Ever since the commercialization of PI films with the trademark of Kapton® [poly(pyromellitic anhydride-oxydianiline), PMDA-ODA] in 1960s by DuPont Corporation in the USA, they have been becoming one of the most important basic materials for modern industry [10]. PI films have found various applications in civil and military high-tech fields. In 2011, the worldwide consumption for PI films is more than 8000 metric tons and this consumption is estimated to reach 13000 tons in 2016. The three major markets for PI film are flexible printed circuit substrates, high-temperature wire and cable wrapping, and magnetic wire insulation. The wide applications of PI films are mainly attributed to their excellent properties, including extreme servicing temperatures (-296-400°C for Kapton), high mechanical properties, excellent dielectric features, and good environmental stability. The superior property for PI films, on one hand, is associated with their heteroaromatic molecular structures, and on the other hand, owes to their unique producing techniques.

Compared with the lab-scale preparation, the greatest difference for industrial manufacturing of PI films is the stretching process [11]. Stretching process, either uniaxial or biaxial stretching of the gel-like PAA films, will result in the full orientation and extension for the PI molecular chains. The gelation of PAA films can be achieved either by partially evaporating the solvent or by chemical treatment with a dehydrating agent (acetic anhydride, dicyclohexylcarbodiimide, etc.) and its catalyst (pyridine). From a viewpoint of polymer physics, stretching will greatly enhance the mechanical properties of the obtained PI films. For example, the values of elongations at break for the lab-making PI films without any stretching treatment are usually below 20%. However, this value can be increased several times after stretching treatments.

A diagram of the biaxial stretching production line for PI films is shown in Figure 5. In this procedure, the monomers are first feed into the polymerization reactor containing fully dried DMAc solvent. After polycondensation, the obtained PAA solution is deaerated and cast from the slit die in the form of a continuous film onto the surface of a heated rotating stainless steel drum. The solvent in PAA is partially evaporated and a portion of imidization reaction occurs in PAA at the same time. Thus, a self-supporting PAA film is formed. Alternatively, the PAA solution on the rotating drum can pass through a bath containing dehydrating agent and cyclization catalyst to afford a gel-like PAA film. Then, the gel-like PAA film is peeled from the metal drum and first stretched in the machine direction (MD) while controlling the stretching rate using nip rolls. The stretching ratio can usually be regulated by the drive source and a speed regulator. The gel film stretched in the machine direction is subsequently introduced into a tenter frame where it is gripped at both transverse edges. Various means may be employed to grip the film, including pins, clips, clamps, and rollers. The gel film is then stretched in the transverse direction due to outward movement of the tenter clips, the volatile organic solvent is removed by evaporation, and the film is heat-treated by means of hot air or radiant heat from an electrical heater to give a biaxial oriented polyimide film (BOPI). The transverse stretching is carried out at temperatures around 350°C to facilitate the imidization of PAA. Such a procedure has been widely used for PI film production and there has been significant patent activity in the past half century since the commercialization of PI films

in 1960s. Up to now, most of the commercially available wholly aromatic PI films have been produced by such kind of procedure.

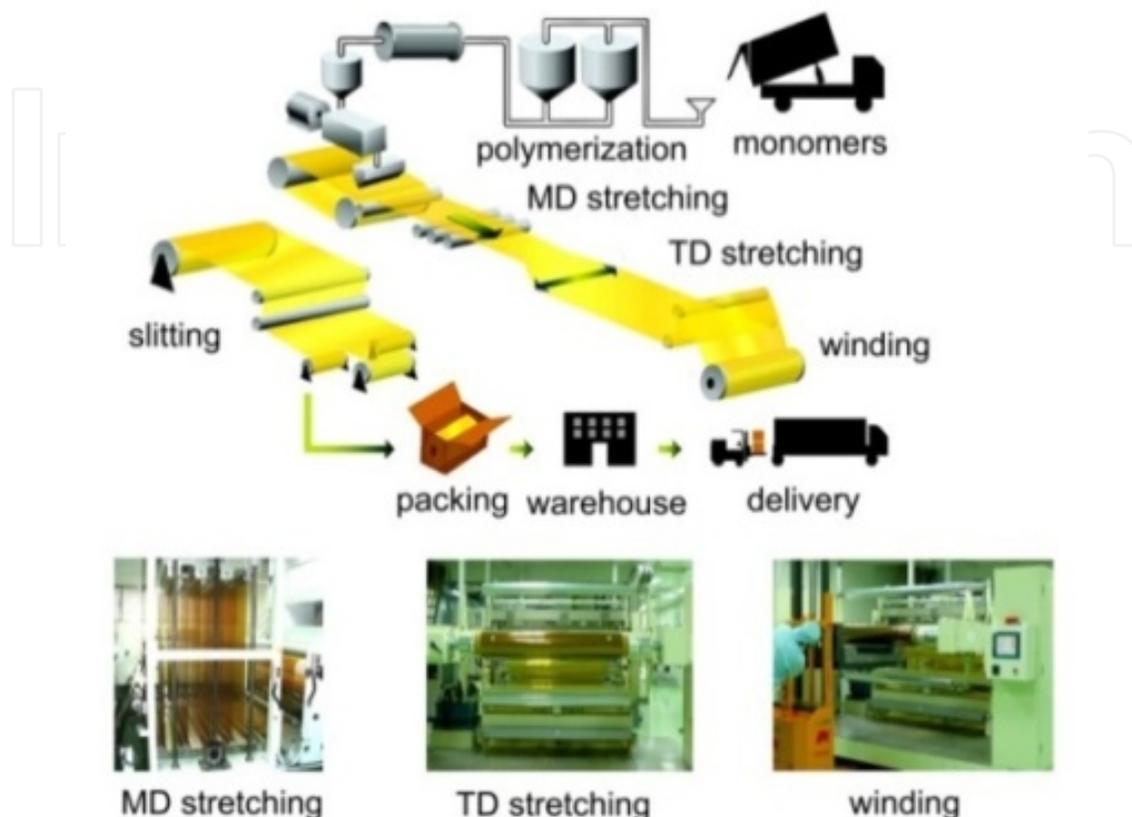
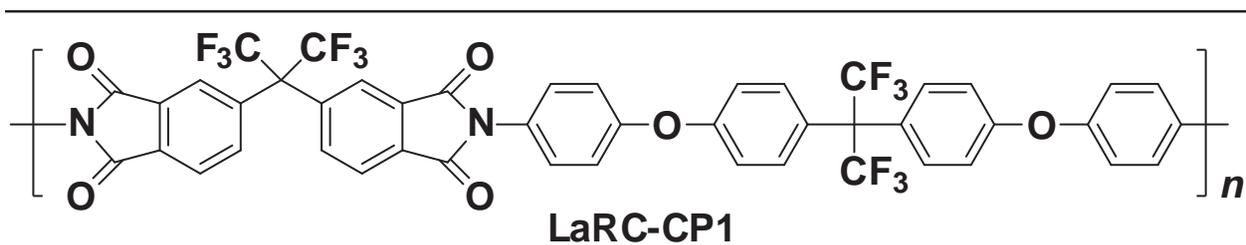


Figure 5. Industrial-scale manufacturing for PI films via PAA precursors

Because the full imidization temperature for PAA is usually higher than 350°C , the manufacturing procedure mentioned above might be difficult for colorless PI film production, whose color and transparency is highly sensitive to high temperatures. Thus, a new manufacturing technique has been developed in recent years [12].

As illustrated in Figure 6, the new procedure uses soluble PI resins as the starting materials instead of PAAs. The key elements for this procedure include: (a) the PI resin must be soluble in a volatile solvent; (b) a stable PI solution with a reasonable solid content and viscosity should be formed; and (c) formation of a homogeneous film and release from the casting support must be possible. In the procedure, PI resins are first dissolved in polar solvents to afford the PI solution, which are purified by filtration through screen mesh. Then, the PI solution is cast onto stainless steel belt, followed by thermally drying at high temperatures to remove the solvent. This drying procedure is only to remove the solvent in the PI solution. Thus, the temperature is usually lower than the common imidization temperature ($300\text{--}350^{\circ}\text{C}$). Similarly, the PI films can also be stretched at an appropriate solvent content. For instance, NASA (National Aeronautics and Space Administration, USA) Langley research center investigated the molecularly oriented colorless PI films for space applications [13]. In large space structures

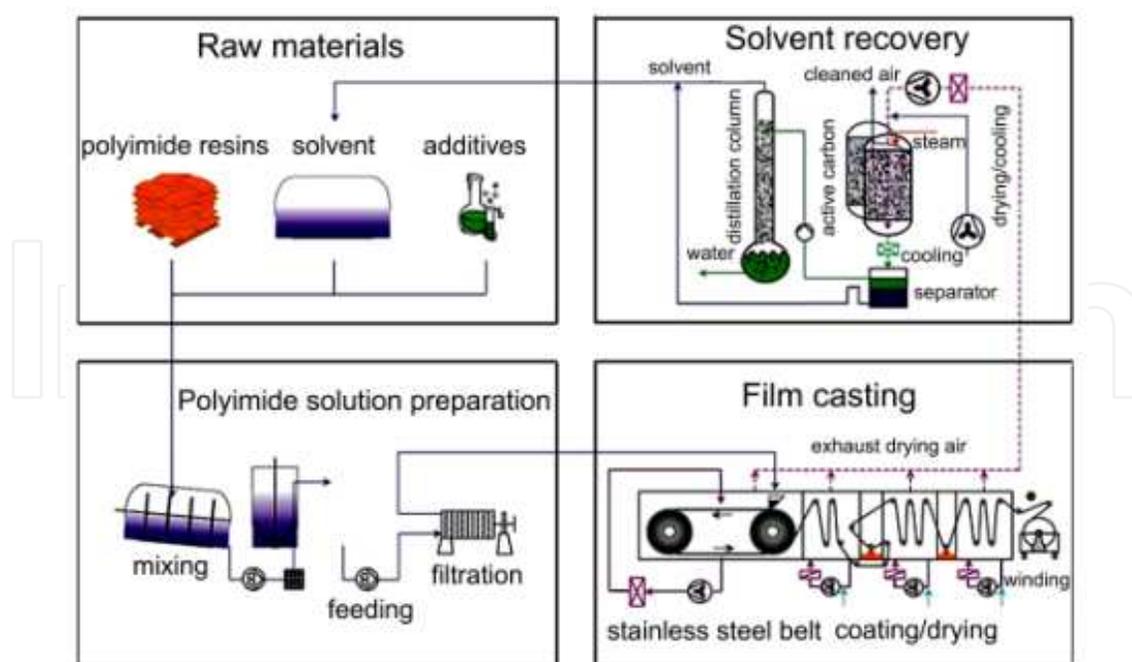
with designed lifetimes to be 10-30 years, there exists a need for high-temperature (200-300°C) stable, flexible polymer films that have high optical transparency in the visible light region. For this purpose, a colorless and transparent PI film, LaRC-CP1, derived from 6FDA and fluoro-containing diamine, 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (BDAF), has been developed in NASA. This film is prepared from soluble PI resin. The LaRC-CP1 film was uniaxially stretched at 1.5, 1.75, and 2 times the original length of the film. Table 2 shows the influence of stretching on the physical and mechanical properties of LaRC-CP1 film. Apparently, the tensile properties of the film increased with increased stretching ratio. For example, the tensile strength of 2.0× stretched film increased from 93.0 to 145.4 MPa after stretching treatment; and the elongations increased from 16% to 65%. After stretching treatment, the dimensional stability, stiffness, elongation, and strength of the film were greatly enhanced, which are crucial for the applications in space environments.



Stretch ratio	CTE (ppm/°C)	Tensile strength (MPa)	Modulus (GPa)	Elongation (%)
None	50	93.0	2.0	16
1.5×	42	88.9	1.7	20
1.75×	44	107.5	1.8	49
2.0×	46	145.4	2.1	65

Table 2. Characterization of stretched LaRC-CP1 film

US Patent 8357322 assigned to Mitsubishi Gas Chemical Company describes a method for producing colorless and transparent PI films by a solution casting procedure. The biaxially stretched colorless PI films exhibit excellent optical transparency, heat resistance, and reduced dimensional changes [14]. The films were produced with the soluble PI resin as the starting materials, which were derived from 1,2,4,5-cyclohexanetetracarboxylic dianhydride and aromatic diamines by one-step high-temperature polycondensation route. The PI film was biaxially stretched in the machine direction by 1.01 times and in the transverse direction by 1.03 times at 250°C for 11 min under a stream of nitrogen. Then, the PI film was dried by blowing nitrogen containing 1000 ppm oxygen at a flow rate of 3.3 m/sec at 280°C for 45 min. The obtained PI film had a thickness of 200 μm, a total light transmittance of 89.8%, a yellow index of 1.9, and a haze of 0.74%. The solvent residual ratio in the film was 0.5% by weight. By virtue of these properties, the colorless PI films might find various applications in optoelectronic applications, such as transparent conductive film, transparent substrates for flexible



adapted, modified, and reprinted from ref. [12]

Figure 6. Industrial-scale manufacturing for PI films via soluble PI resins

display, flexible solar cells, and flexible printing circuit board (FPCB). Similar procedures were also reported by the company [15].

In addition, US Patent 7550194 assigned to DuPont Company [16] and US patent 8846852 to Kolon Industries [17] report the low-color PI films derived from the copolymers of fluoro-containing dianhydride, 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA), 3,3',4,4'-biphenyl-tetracarboxylic dianhydride (BPDA), and fluoro-containing diamine, 2,2'-bis(trifluoromethyl)-benzidine (TFMB). The copolymers were prepared via PAA precursors, followed by chemical imidization of the PAAs to afford the gel-like PAA films or soluble PI resins. Then, the PI films were produced from these intermediates at high temperature up to 300°C. Flexible and tough PI films with low color and high transparency were obtained.

2.3. CHTPF films analysis and evaluation techniques

In practical applications for CHTPF optical films, various properties have usually been analyzed and evaluated. For different applications, specific properties might be specially emphasized. For example, in the fabrication of AMOLEDs, the water vapor transmission rate (WVTR) and oxygen transmission rate (OTR) of the flexible substrates are severely limited to be below 10^{-4} cm³/m² day and 10^{-6} g/m²/day, respectively, because the penetration of water and oxygen through the substrates might poison the emitting components, resulting in the reduced operating life of the devices [18]. In flexible solar cells, optical transmittance and yellowness might be the most concerned parameters because yellowness of the polymer substrates might

decrease the conversion efficiency of solar light to electricity. Thus, it would be helpful to understand the analysis and evaluation techniques for CHTPF films.

2.3.1. Optical properties

Common optical properties, such as yellow index (YI), haze, optical transmittance at specific wavelength, ultraviolet-visible cutoff wavelength, refractive index are usually needed to be evaluated for CHTPFs.

Yellowness index (YI) indicates the degree of departure of an object color from colorless or from a preferred white toward yellow. Haze value indicates the degree of cloudiness in a film. The YI and haze value of a film can usually be measured by a colorimeter and can be computed by a given procedure from colorimetric or spectrophotometric data [19]. Optical transmittance of a film indicates the percentage of incident light that is transmitted by the film. The reciprocal of optical transmission is the haze value, which increases as the percent of transmission decreases. As a general rule, 0% haze relates to complete transparency, up to 30% is translucent, and more than 30% haze is considered opaque. Optical transmittance of a film can usually be measured with an ultraviolet-visible light spectrophotometer.

Refractive index of a film indicates the ratio of the velocity of light in vacuum to that in a film. It is the ratio of the sine of the angle of incidence to the sine of the angle of refraction. Refractive index values can be measured with a prism coupler. Birefringence of a film indicates the difference in the refractive indices of two perpendicular directions in a film. When the refractive indices measured along three mutually perpendicular axes are identical, they are classified as optically isotropic. When the film is stretched, providing molecular orientation, and the refractive index parallel to the direction of stretching is altered so that it is no longer identical to what is perpendicular to this direction, the film displays birefringence. The common apparatus for optical parameters measurement of CHTPF films are shown in Figure 7.

2.3.2. Thermal properties

As mentioned before, the thermal stability of optical films is becoming increasingly important for their applications in optoelectronic fabrications. The thermal properties of an optical film include thermal decomposition temperature (T_d), glass transition temperature (T_g), coefficient of thermal expansion (CTE), and high-temperature dimensional stability. Generally, thermal analysis for an optical film indicates any analysis of physical or thermodynamic properties of the film in which heat is directly involved, with the heat either being added or removed. Different methods are used with each method providing certain useful data or information.

Thermogravimetric analysis (TGA) is an analysis by the measurement of weight changes of an optical film as a function of increasing temperature with time. Properties measured include thermal decomposition temperature and relative thermal stability. Dimensional stability of a polymer optical film indicates its ability to retain the precise initial shape and size. It is the temperature above which the films lose their dimensional stability. For most films, the main determinant of dimensional stability is their glass transition temperature.

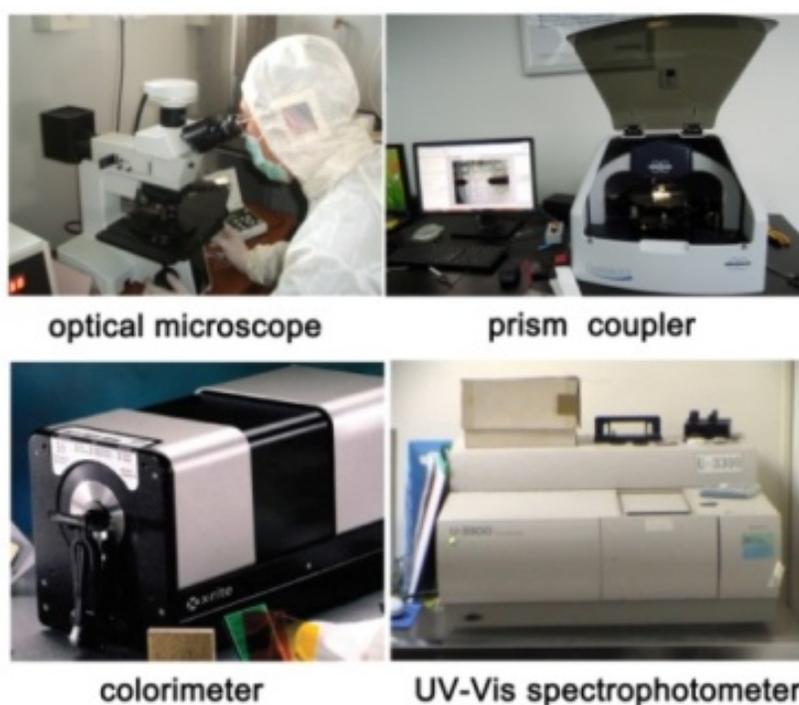


Figure 7. Optical properties measurement system

Below a certain temperature, polymer optical films will behave as hard glass-like substance. When heated above this temperature, individual segments of the polymer films will achieve large mobility; as a result the films become soft and elastic. The temperature at which this change happens is called the glass transition temperature (T_g). In other words, T_g indicates the reversible change in phase of a film from a brittle glassy state to viscous or rubbery state. At T_g , the film's volume or length increases, and above it, the properties of the film decrease. The T_g value of a film can be determined with specific equipment, such as differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and thermal mechanical analysis (TMA) and the obtained values depend on the method used. For crystalline polymer films, such as PET and PEN, the crystalline melting points are usually above T_g .

In a typical DSC measurement, two pans are placed on a pair of identically positioned platforms connected to a furnace by a common heat flow path. One pan contains the polymer film, the other one is empty (reference pan). Then, the two pans are heated up at a specific rate. The computer guarantees that the two pans heat at exactly the same rate, despite the fact that one pan contains polymer and the other one is empty. The polymer film sample will take more heat to keep the temperature of the sample pan increasing at the same rate as the reference pan. A plot is created where the difference in heat flow between the sample and the reference is plotted as a function of temperature. The inflection point in the heat flow plot is recorded as the T_g value for the film.

DMA indicates a technique in which either the modulus or the damping of a polymer film under oscillatory load or displacement is measured as a function of temperature, frequency, time, or other combinations. TMA indicates a test that measures the dimensional changes as

a function of temperature. The dimensional behavior of a film material can be determined precisely. Measurements made include coefficient of linear thermal expansion (CTE), T_g , and softening characteristic. CTE value of a film reflects the change in volume per unit volume resulting from a change in temperature of the material. The mean coefficient is commonly referenced to room temperature and expressed in mm/mm °C. CTE value is quite important for polymer optical films which are used with other heterogeneous materials, such as metal, glass, or ceramic. The unmatched CTE values between the polymer films with the other materials are thought to be one of the most important reasons for delamination, cracking, and other failures in the devices.

2.3.3. Gas permission properties

When a plastic substrate is used for the flexible OLED application, the water-vapor transmission rate (WVTR) and oxygen transmission rate (OTR) feature of the plastic substrate become critical because most high-performance semiconductor organic compounds show degraded performance when exposed to environmental moisture [20]. As mentioned before, WVTR and OTR of the flexible substrates are severely limited to be below 10^{-4} cm³/m² day and 10^{-6} g/m² day, respectively, for AMOLED and organic solar cells [21]. Unlike glass, plastic substrates usually cannot provide sufficient protection to the permeants. For example, general PI films have WVTR values of 10^0 - 10^2 g/m²/day dependent on the aggregation structures of their molecular chains. Addition of some specific additives, such as graphene [22], might improve their moisture barrier properties to a limited extent. Thus, inorganic thin films with extremely higher barrier properties have to be used on the substrate in practical applications. In order to evaluate the WVTR and OTR features of one polymer film, it is necessary to understand these two parameters. WVTR and OTR can now be measured with water vapor or oxygen gas permeation measurement systems produced by Mocon Corp., USA. The Mocon test has a measurement limit of $\sim 10^{-4}$ g/m² day. A lower WVTR measurement has to be measured by calcium test, which is able to measure up to $\sim 10^{-6}$ g/m² day.

3. Applications of CHTPF films in optoelectronics

3.1. Commercialization of CHTPF films

It is safe to say that the commercialization of CHTPFs is highly promoted by their potential applications for flexible optoelectronic devices, such as flexible light-emitting diodes (F-LED), flexible solar cells or photovoltaic cells (PV), flexible thin-film transistors (F-TFT), flexible printing circuit boards (FPCB), and so on. Many present and future applications of optical films make greater demands for higher properties, and especially combinations of properties, than are available from the commodity materials. To satisfy these requirements, organic polymer chemists and chemical engineers have developed and commercialized many types of polymers, offering improved properties. Table 3 briefly summarizes the commercially available and R&D CHTPF optical films in the world. Optical polymers containing various thermal-stable units, such as PI, PAI, PA, PES, and PS, have been extensively investigated and

commercialized. In addition, some kind of inorganic-organic hybrid optical films have also been developed. As mentioned before, a statistical date from Techno Create Corp shows that the market of CHTPF optical films in 2011 has been close to 1 billion Japanese yen and the market will see a rapid increase higher than 15% per year in the following years [9]. Some of the typical CHTPF optical films are shown in Figure 8.

Up to now, CHTPF optical films have found various applications as plastic substrate candidates for flexible optoelectronic devices, including FPCB, flexible display (TFT-LCDs or AMOLEDs, etc.), touch panel, electronic paper, and thin photovoltaic cells. Plastic substrates with both optical transparency and high-temperature resistance have great potential applications in these areas due to the superior flexibility, lightness, cost-effectiveness, and processability to their fragile and expensive glass analogs. For instance, in the fabrication of flexible bottom-emission AMOLED devices, the processing temperatures of light emitting-components on the flexible substrates usually precede 300°C. Under such processing conditions, only CHTPF optical films such as colorless PI films could meet the severe demands.

Company	Product name	Resin	Transmission %	T_g °C
Mitsubishi Gas Chemical	Neopulim®	PI	89–90	>300
DuPont-Toray	Colorless Kapton®	PI	87	>300
Kolon	NA ¹	PI	88	>300
Japan Synthetic Rubber	Lucera®	NA	88	280
Toyobo	HM type	Polyamideimide (PAI)	91	225
Nippon Steel Chemical	Sillplus®	Resin+glass	91–92	NA
Toray	Aramid®	Polyamide (PA)	NA	315
Sumitomo Bakelite	Sumilite® FS-1300	Polyethersulfone (PES)	89	223
Showa Electricity	Shorayal®	NA	92	250
Tosoh	OPS film	Polysulfone (PS)	93	220
Kurabo	Examid®	Polyamide (PA)	NA	220

¹ Not available.

Table 3. Commercialization of CHTPF optical films in the world

3.2. Applications of CHTPF films

There has been growing interest in the use of plastic film substrates in the fabrication of future electronic devices, such as flexible displays, photovoltaics, batteries, sensors, and antennas [23]. This developing trend provides great opportunities for the development of CHTPF optical films. As shown in Figure 9, CHTPFs have found widespread applications in optoelectronics as various substrates for flexible display devices, flexible solar cells, FPCBs, touch panels, and so on.

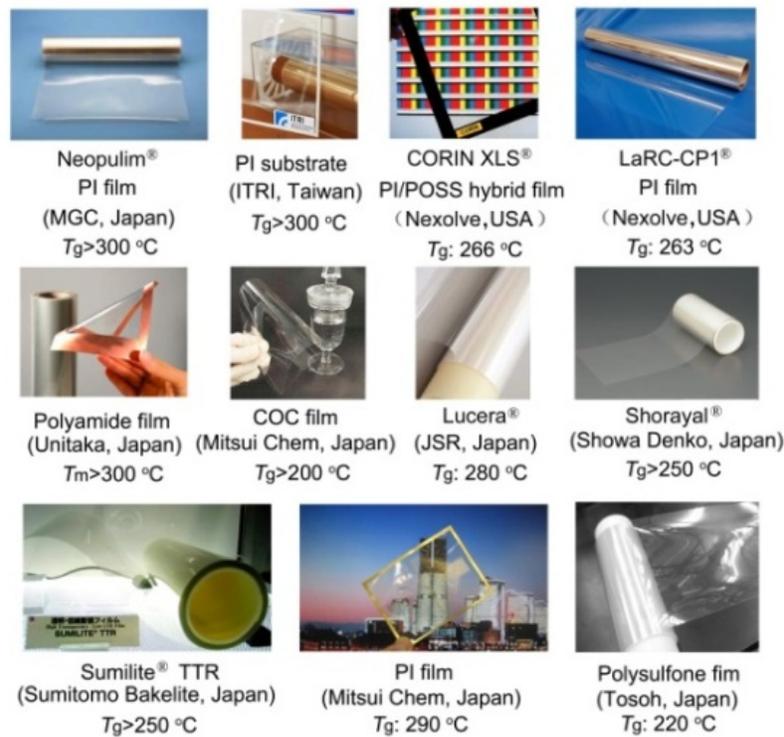


Figure 8. Commercially available or R&D CHTPF products in the literature



Figure 9. Potential applications of CHTPFs in optoelectronics

3.2.1. Substrates for advanced flexible display devices

As the structural support and optical signal transmission pathway and medium, flexible substrates are playing ever-increasing important roles in advanced optoelectronic display devices [24], the characteristics and functionalities of flexible substrates have been becoming



Figure 10. Roadmap for flexible products and substrates [24]

the important factors that affect the quality of flexible devices. Currently, there are mainly three types of substrates for flexible displays: thin glass, transparent plastic (polymer), and metal foil. Transparent plastic substrates possess good optical transmittance similar to that of thin glass; meanwhile the good flexibility and toughness comparable to those of metal foils. Thus, they are ideal for flexible display. A flexible display using a plastic substrate is considered to be one of the promising displays because of attractive features, such as thinness, lightweight, and good flexibility. For instance, as shown in Figure 10, the development of flexible substrates is experiencing a roadmap of plane (current) → bended (2015) → rollable (2018) → foldable (2020) in the following years. The radius of curvature of the highly transparent flexible substrates might reach below 3 mm in the year of 2020. At that time, transparent plastic substrates might be the best candidate that can meet the demands.

However, in order to achieve a practical application for transparent plastic substrates in flexible display, several issues have to be addressed. First, currently, the performance of thin-film transistors (TFTs) built on common optical films or sheets are limited by the low-temperature process caused by the low thermal stability of current plastic substrates, typically below 250°C. For instance, for flexible display devices, such as active matrix-driven organic light-emitting diodes (AMOLED) processing, fabrication of TFTs on flexible substrates is one of the most important procedure. Up to now, there have been four types of production technologies for TFT fabrications in AMOLED, including amorphous silicon (a-Si) TFTs, low-temperature polysilicon (LTPS) TFTs, oxide TFTs, and organic TFTs (OTFTs). The key features for the current TFTs are summarized in Table 4 [25].

It can be seen that LTPS TFTs technique exhibits the highest field-effect mobility and stable electrical performance. However, the procedure requires a high process temperature of about 500°C during silicon crystallization. Conventional polymer optical film substrates cannot meet the application. For a-Si TFTs process, it has been widely used for AMOLED devices owing to

uniform electrical characteristics over large areas, reasonable field-effect mobility, low-temperature process (< 300°C), and low cost compared to the other techniques.

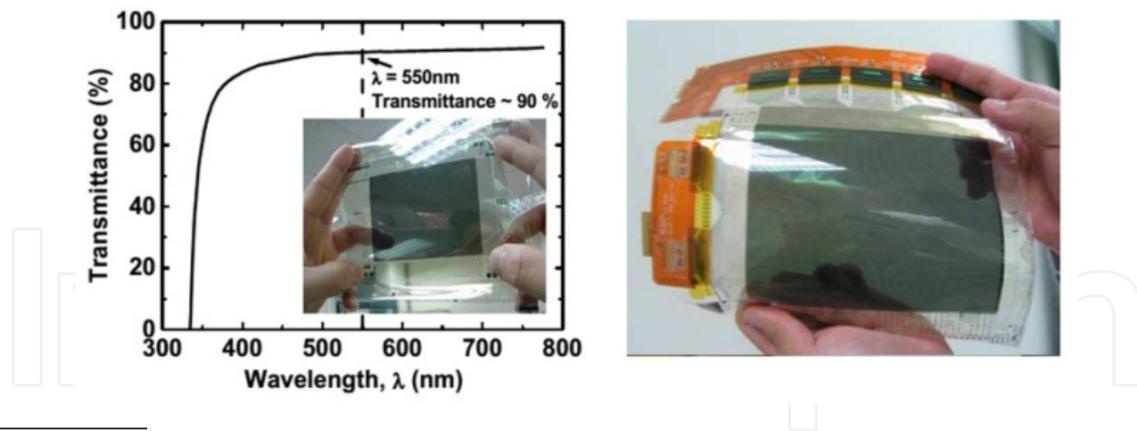
	a-Si TFTs	LTPS TFTs	OTFTs	IGZO TFTs
Field-effect mobility (cm ² /V-s)	< 1	50–100	0.1–1	10–30
Process temperature (°C)	<300	300–500	<300	<300
Device stability	Challenging	Good	Challenging	OK
uniformity	Good	Challenging	OK	OK
Manufacturability	Excellent	Maturing	Developing	Developing
cost	Low	Medium	To be determined	

Table 4. Key features for a-Si TFTs, LTPS TFTs, OTFTs, and IGZO TFTs [25]

ITRI (Industrial Technology Research Institute, Taiwan) developed a unique flexible-universal-plane (FlexUP) solution for flexible display applications [26]. This new technique relies on two key innovations: flexible substrate and a debonding layer (DBL). As for the flexible substrate, ITRI developed a colorless PI substrate, which exhibits good optical transmittance (90%), high T_g (>300 °C), low CTE (28 ppm/°C), and good chemical resistance. In addition, the PI substrate with barrier treatment shows a WVTR value less than 4×10^{-5} g/m²/day. Moreover, this barrier property suffered only to a minor drop, to 8×10^{-5} g/m²/day, after the flexible panel had been bent 1000 times at a radius of 5 cm. The substrate used a hybrid technique, which contains a high content (>60 wt%) of inorganic silica particles in the PI matrix. A 6-inch flexible color AMOLED display device was successfully fabricated using this substrate. By using this colorless PI substrate, flexible touch panel was also successfully prepared.

A 7-inch flexible VGA transmissive-type active matrix TFT-LCD display with a-Si TFT was successfully fabricated on the colorless PI substrate developed by ITRI [27]. The colorless PI substrate has the features of high T_g (>350°C) and high light transmittance (>90%), which ensure the successful fabrication of 200°C a-Si:H TFT in the flexible device, as shown in Figure 11. The flexible panel showed resolution of 640×RGB×480, pixel pitch of 75×225 μm, and brightness of 100 nit. This technique is fully a-Si TFT backplane compatible, which makes it attractive for applications in high-performance flexible display. Similarly, a-Si TFTs deposited on clear plastic substrates (from DuPont) at 250-280°C was reported [28]. The free-standing clear plastic substrate has a T_g value higher than 315°C and a CTE value below 10 ppm/°C. The maximum process temperature of 280°C has been close to the temperature used in industrial a-Si TFT production on glass substrates (300-350°C).

Toshiba Corp., Japan, successfully fabricated a flexible 10.2-inch WUXGA (1920×1200) bottom-emission AMOLED display device driven by amorphous indium gallium zinc oxide (IGZO) TFTs on a colorless and transparent PI film substrate, as shown in Figure 12 [29]. Firstly, a transparent PI film was formed on a glass substrate and then a barrier layer was deposited to prevent the permeation of water. Then, the gate insulator, IGZO thin film, source-drain metal,



adapted, modified, and reprinted from ref. [27]

Figure 11. Colorless PI substrate and the color VGA flexible TFT-LCD

and passivation layer were successively deposited to afford the IGZO TFT. Secondly, the flexible AMOLED panel was fabricated using the IGZO TFT, color filter, white OLED, and encapsulation layer. Finally, the OLED panel was debonded from the glass substrate to afford the final AMOLED panel. The threshold voltage shifts of amorphous IGZO TFTs on the PI substrates under bias-temperature stress have been successfully decreased to less than 0.03 V, which is equivalent to those on glass substrates. ITRI also reported high-performance flexible amorphous IGZO TFTs on transparent PI-based nanocomposites substrates [30].

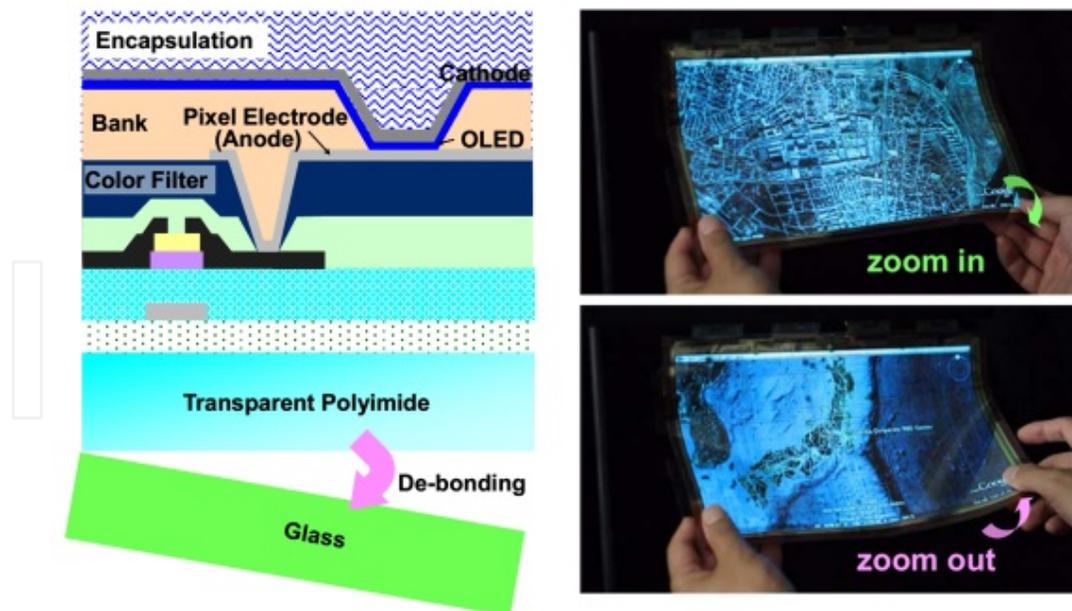


Figure 12. Flexible 10.2-inch AMOLED devices on transparent PI substrates [29]

Besides PI flexible substrates, other CHTPF substrates have also been developed. For instance, Teijin Ltd, Japan, developed novel high-temperature polycarbonate (PC) substrates for flexible

displays [31]. The PC base film was obtained by a solvent casting process from dichloromethane solution and exhibited high optical transmittance (91%), high T_g value (215 °C), ultra-low intrinsic birefringence and low retardation (1 nm), good elastic and dimensional stability, and an extremely smooth surface. The new substrates consisted of the high-temperature PC base film, silicon oxide gas barrier layer, and transparent indium zinc oxide (IZO) conductive film which showed promise in overcoming the obstacles in producing many kinds of thin, lightweight, and flexible display devices. Similarly, a high heat resistance PC film with the T_g of 240°C and optical transmittance higher than 90% in the visible light region has been reported by General Electric [32]. A transparent, high barrier, and high heat substrate for organic electronics was successfully prepared by the film.

In summary, with the development of CHTPF optical films, the fabricated TFTs have showed similar characteristics to those of industry-standard a-Si TFTs fabricated on glass in the 300-350°C range. This result represents an important step toward a generic TFT backplane on flexible and optically clear film substrates.

3.2.2. Substrates for transparent Flexible Printing Circuit Boards (FPCBs)

Over the years, the FPCB applications have always been the largest market for high-temperature polymer films, such as PI, polyamideimide, and polyetherimide films. The flexible nature of FPCBs allows their convenient use in compact electronic equipment such as portable computer, digital cameras, watches, and panel boards. Generally, the traditional FPCB is mainly prepared from flexible copper-clad laminates (FCCLs), as shown in Figure 13. FCCLs consist of a layer of PI film bonded to copper foil. Depending on the intended use of the laminate, copper may be applied to one (single-sided) or both sides (double-sided) of the PI film. PI film almost completely dominates the portion of FCCL market in which heat resistance is needed to withstand the soldering temperatures. Recently, with the development of flexible displays, necessity for a transparent film substrate in place of glass substrate is increasing. Correspondingly, a transparent film substrate for FCCLs is increasingly desired. However, most of the all-aromatic PI films currently used in FCCLs show colors from yellow to deep brown, and thus cannot be used in transparent FCCLs.



Figure 13. FPCB industry chains from FCCL to final products

Toyobo Corp., Japan, recently patented a colorless and transparent FCCL and the derived FPCB based on a PAI film [33]. The PAI film was synthesized from 1,2,4-cyclohexanetricarboxylic anhydride (HTA) (Table 2) and aromatic diisocyanate monomers (Figure 6) and the curing procedure was 200°C/1 h, 250°C/1 h, and 300°C/ 30 min under nitrogen. The film exhibited good thermal stability with T_g of 300°C, light transmittance of 89%, good tensile properties with tensile strength of 140 MPa, elongation at break of 30%, tensile modulus of 3.9 GPa, and low CTE of 33 ppm/K. The single-side FCCL from the PAI film and copper coil showed good soldering resistance, high bonding strength (10.6 N/cm), and good dimensional stability under the condition of 150°C for 30 min. In addition, the FCCL showed good optical transparency with a transmittance of 75% at the wavelength of 500 nm.

Very recently, there has been vigorous activity in developing and commercializing transparent FPCB products in the world. This is mainly driven by the urgent needs of such products for mobile communication optoelectronics. Typical products reported by multiple manufacturers in public are summarized in Figure 14. Various optical films including PEN, PAI, and PI films have been used as the substrates in these new products. It can be anticipated that CHTPF optical films will play an increasingly important role for the future development of transparent FPCBs.

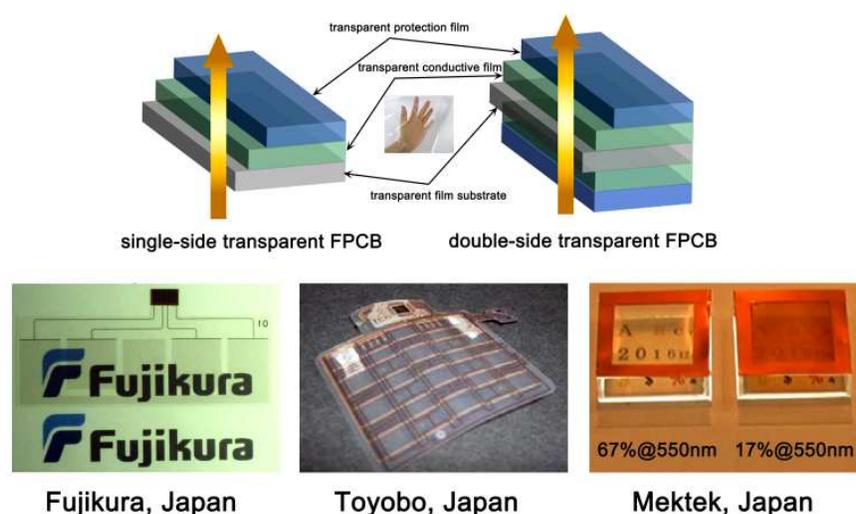


Figure 14. Application of CHTPF optical films in transparent FPCBs

3.2.3. Flexible substrates for thin-film solar cells

Solar cells or photovoltaics (PV) have been intensively studied in energy industries due to their potential ability to reduce the cost per Watt of solar energy and improve lifetime performance of solar modules [34]. Conventional thin film solar cells are usually manufactured on transparent conducting oxide coated 3-5 mm thick soda-lime glass substrates and offer no weight advantage or shape adaptability for curved surfaces. Fabricating thin-film solar cells on flexible polymer substrates seems to offer several advantages in practical applications, such as weight

saving, cost saving, and easy fabrication. The polymer substrates for thin-film solar cell fabrications should be optically transparent and should withstand the high processing temperatures. For example, for the current cadmium telluride (CdTe) cell fabrication techniques, the processing temperatures are in the range of 450-500°C. Most of the transparent polymers will degrade at such a high temperature. Undoubtedly, the lack of a transparent polymer which is stable at the high processing temperature of solar cells is one of the biggest obstacles for the applications of polymer substrates in flexible solar cells.

Wholly aromatic PI films, such as Kapton® (DuPont, USA) and Upilex® (Ube, Japan) can withstand a high temperature round 450°C. However, they exhibit deep colors and strongly absorb visible light. CdTe solar cells on such PI substrates will yield only low current due to large optical absorption [35]. The development of colorless PI film with good high-temperature stability makes it possible to produce high-efficiency solar cells. One of the most promising reports on the successful applications of colorless PI films in flexible solar cells fabrication might be the work carried out in Swiss Federal Laboratories for Materials Science and Technology (Empa) [36]. As one of the Empa's continuous work on developing high-efficiency thin-film solar cells aiming at enhancing their performance and simplifying the fabrication processes, they utilized colorless PI film (developed by DuPont) as the flexible substrate for CdTe thin-film PV modulus in 2011 (Figure 15). A conversion efficiency of 13.8% using the new substrates was achieved, which was the new record among this type of solar cells at that time.

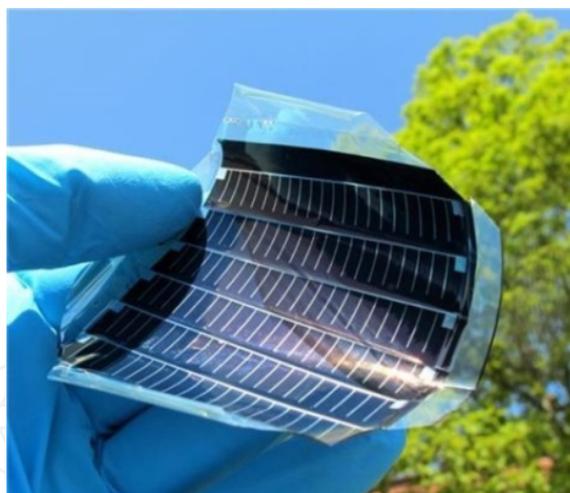


Figure 15. CdTe solar cells on colorless PI substrate (Source: Empa)

4. Conclusions

Undoubtedly, CHTPFs represent a class of new materials with both high technological contents and high additional value. High comprehensive properties make them good candidates for advanced optoelectronic devices. It can be anticipated that, with the ever-increasing

demands of optoelectronic fabrication, CHTPFs will attract more attentions from both the academia and the industry. For example, demand will continue to grow for displays of smart phones, tablet PCs, and other types of mobile electronic devices. Furthermore, these displays will be continuously improved in terms of visibility, flexibility, durability, and lightweight. In this context, CHTPF optical films are facing great developing chance. However, up to now, these still have several obstacles that should be overcome for the wide applications of CHTPFs in advanced fields. First, very limited commercially available CHTPF products greatly increase their cost, which lead to a very limited application only in high-end optoelectronic products. Low-cost CHTPFs are highly desired for their wide applications. Secondly, the combined properties of current CHTPFs should be further enhanced, such as further improving their optical transmittances at elevated temperatures, improving their mechanical and gas barrier properties. Thirdly, the manufacturing technology for CHTPFs should be further perfected in order to increase their uniformity, colorlessness, and dimensional stability at high temperatures.

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