Polyimide Film as a Vacuum Coating Substrate

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ABSTRACT

Polyimide film substrates offer performance at very high temperatures (400 °C and above). They have been used widely for flexible circuit constructions, for space applications, and are now finding use as substrates for flexible photovoltaic and display applications. Polyimide films are available in several chemistries and from several suppliers. This paper is presented from an experienced user's perspective. It seeks to consolidate data on these films from many sources, with a particular emphasis on their use as substrates for roll-to-roll thin film vacuum deposition. A major take-home message is that the high temperature performance of polyimide films and the resulting losses of mechanical properties are limited by decomposition not by softening or melting, as is the case for polyester (PET or PEN) or polypropylene (BOPP). This decomposition is largely an oxidative process, and thus the threshold temperatures for decomposition in vacuum (in the absence of oxygen) are substantially higher than that in air, the commonly reported ambient for high temperature data.

INTRODUCTION

Polyimide film is an important substrate for vacuum thin film deposition. Its bulk mechanical properties are among the highest for commercial available films, but it is most often selected for its excellent high temperature properties (to 400°C and above). By comparison, polyester (poly(ethylene terephthalate) or PET) films are limited to about 120°C, and poly(ethylene naphthalate (PEN) films are limited to about 180 °C.

The extraordinary high temperature properties are based on both chemistry and processing. The challenging properties of polyimide films result from the same sources. This paper will examine the chemistry and processing of various polyimide films to understand the origin of their properties.

Polyimide films are particularly important due to their growing use in flexible photovoltaic and display applications. They have a long history in flexible circuitry applications, including adhesiveless tape automatic bonding (TAB) tape, ink jet printer cartridges, and many others. They have enormous potential for other advanced applications as well. This paper seeks to consolidate data from a broad range of sources and references into one location, with a focus on polyimide films as vacuum coating substrates. A major take-home message is that polyimide films tolerate higher temperatures during vacuum processing than a casual read of the data sheets suggest.

POLYIMIDE CHEMISTRY OVERVIEW

Fundamentally all that is required for something to be called a polyimide is two carbonyl groups bonded to nitrogen, as shown in Figure 1a. But polyimide films currently in use for high temperature applications are all aromatic and heterocylic and have a chemical structure shown in Figure 1b.

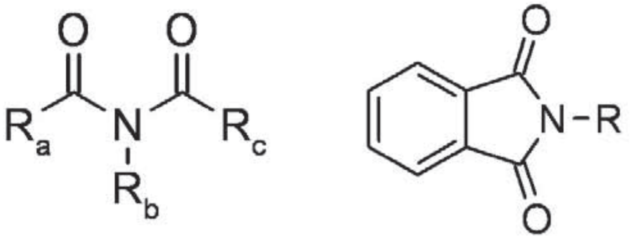

Figure 1: a (left) The generic chemical structure of a polyimide; b (right) the chemical structure of polyimides used in films [1].

The electron coupling resulting from the joining of the aromatic and heterocylic rings pushes the optical absorption edge to longer wavelengths, from the ultraviolet into the visible. The resulting blue absorption leads to the characteristic yellow to dark orange to brown color of polyimide films. If the ring system is fluorinated, the electron withdrawing character of the fluorine atoms moves the absorption edge back towards the UV, and thus some polyimide films can be colorless, although colorless films are not readily commercially available. Fluorination also reduces the moisture absorption and the dielectric constant of the films [2].

POLYIMIDE FILM PRODUCTION OVERVIEW

Polyimide films are formed by casting a solvent solution of a poly(amic acid) precursor onto a drum [1]. The poly(amic acid) precursor forms a film that is strong enough to be removed from the drum and that can be carried through an oven for curing, where the imidization reaction to form the polyimide takes place. It is the curing that leads to imidization. Some films may be oriented during curing, and some films are given extended heat treatment to drive the imidization reaction further towards completion.

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POLYIMIDE CHEMISTRY OVERVIEW

All the poly(amic acids) used in making polyimide films are formed from equimolar mixtures of one or more dianhydrides and one or more diamines. Chemical purity and balance between the two reactants types are critical for high performance films [1]. Nevertheless many choices for each component are possible [3]. Not surprisingly the choices affect the resultant film properties. In many cases the constituent compounds and their mixtures are held as proprietary by the film producers.

DuPont™ Kapton® H, Kapton® V, and Kaneka Texas Corporation Apical® AV share a common chemistry, as shown in Figure 2. PMDA stands for pyromellitic dianhydride, and ODA stands for oxydiphenylene diamine.

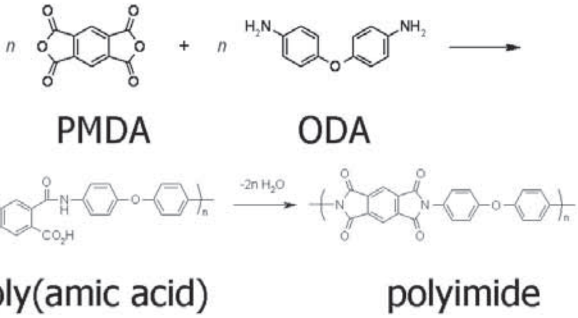

Figure 2: The chemical structures and reaction sequence to form PMDA-ODA type polyimide [4].

It is important to note that the PMDA component makes the resulting films susceptible to base catalyzed hydrolysis. Specifically PMDA-based films can be etched by exposure to a strong base. Several flexible circuit producers have used etching in basic solution for patterning vias and windows in polyimide films.

DuPont™ Kapton® E is a polyimide film specifically developed for flexible circuitry applications. It consists of a mix of two dianhydrides, PMDA and BPDA (biphenyltetracarboxylic acid dianhydride), and two diamines, ODA and PPD (paraphenylenediamine), in unspecified ratios. The BPDA component (shown in Figure 3) adds structural rigidity, resulting in greater dimensional stability and flatness in flexible circuitry applications when compared to Kapton H. Specifically Kapton E offers reduced coefficient of thermal expansion (CTE), reduced moisture absorption, and reduced coefficient of hydroscopic expansion (CHE) compared to Kapton H (see Table 1). It should be noted that the CTE of Kapton E is a good match to that of copper, reducing the strain as copper coated polyimide flexible circuits are cycled through temperature extremes in processing and/or in use (i.e., wave soldering).

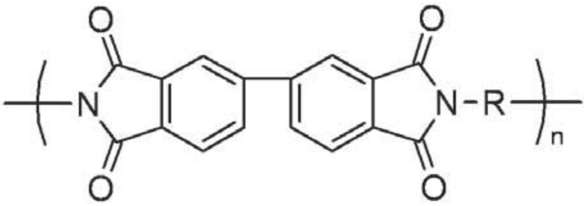

Figure 3: The chemical structure of BPDA.

Upilex S, from Ube Industries, Ltd., is based on a precursor formed from the dianhydride BPDA (shown in Figure 3) plus an unspecified diamine. It offers still lower CTE and a higher modulus compared to Kapton E (see Table 1).

CURING AND ANNEALING OF POLYIMIDE FILMS

This brief introduction to the chemistry of polyimide films demonstrates how the component chemistries impact the film properties. Curing and annealing also affect properties strongly but can be complicated, as described in this excerpt:

> "The cure cycle for poly(amic acid) resins is complicated by the simultaneous evaporation of solvents, the closure of the imide ring, the loss of water formed from the imidization reaction, and internal chain rearrangements. All of this is compounded by the fact that as imidization proceeds, the molecular chains become more rigid as [the] plasticizing solvent is removed, causing the chains to lose the mobility necessary for further imidization. The result is that the reaction occurs rapidly when the temperature is initially increased above the imidization threshold and the molecular mobility is not hindered. As the temperature stabilizes, the reaction slows down markedly since the chains have become more rigid and demand more energy to overcome this rigidity. If the temperature is increased further, imidization will continue, but at a slower rate since it is now hindered by decreased mobility. If the solvent is removed before imidization can occur, the reaction takes place in a glassy phase, leading to a slow and possibly incomplete cure. In addition, since crystallization requires the diffusion of polymer chains, the lack of mobility will also inhibit the development of crystalline order" [5].

Subsequent thermal annealing enables increased imidization, leading to changes in density, crystallinity, birefringence, in-plane coefficient of thermal expansion, and biaxial stress. The structural origins for these changes are discussed elsewhere [5].

Note that the film surface cures before the bulk and thus may have different properties (skinning). Note also that the side cast against the drum may be different than the air side, and that any high temperature processing by users may further imidize or crystallize the film and thus also change the film properties.

Table 1: A summary of polyimide film properties.

	Kapton			Apical		Upilex
Property	H or V	K	E	AV	NP	S
Sample film thickness (μm)	25	75	75	25	25	25
Modulus 23 ºC (GPa)	2.7	4.3	5.5	3.2	4.1	9.0
H_2O absorption (%)	3.0	3.7	2.4	2.9	2.1	1.2
CHE (ppm/%RH)	17	16	9	20	9	12
CTE 100-200ºC (ppm/ºC)	35	17	17	32	16	9.5

A BRIEF HISTORY OF COMMERCIALLY AVAILABLE POLYIMIDE FILMS

DuPont first commercialized Kapton H in the 1966. It was first used commercially in adhesiveless flexible circuits in 1978. Kapton E, Apical, and Upilex became available in the 1980s, and others may now be available.

POLYIMIDE FILM PROPERTIES

A summary of polyimide film properties is given in Table 1 [6].

Note that the component chemistry of Kapton H and V and Apical AV are the same (PMDA-ODA), yet their properties differ, presumably due to the differing curing cycles used in production.

Due to the complexity of the chemistry and curing effects, the author suggests that the published properties should be thought of at some level as "generic," rather than presumed to accurately reflect the properties of any particular film sample.

As noted above, the CTE of copper (used in flexible circuits) is 17 ppm/ºC, a good match to that of Kapton E, Kapton K, and Apical NP; the CTE of molybdenum (commonly used in CIGS solar cells) is 5 ppm/ºC which is lower than that of any of the polyimide films but a best match to Upilex S.

A major take-home message is that polyimide films will tolerate higher temperatures during vacuum processing than a casual read of the data sheets suggest. High temperature performance of polyimide films is limited by decomposition not melting. The decomposition process is mostly oxidative, and oxidation is reduced or eliminated in vacuum. Moreover oxidation is a kinetic process: it takes time. Well above the threshold for oxidation in the presence of oxygen, the reaction occurs quickly; with very low levels of oxygen the decomposition is much slower and leads to embrittlement, not softening. Since polyimide films display outstanding mechanical properties, a loss of a few percent in any given attribute may not result in compromised performance. A DuPont technical service representative indicated that handling should be OK, even with some embrittlement, and that the maximum temperature tolerated will be HIGHER in vacuum than atmospheric data indicate, esp. for limited times at temperature. He said that 400ºC would be the typical maximum in air, but that certainly 450ºC maximum in vacuum could be tolerated and maybe 500ºC could be tolerated for a few minutes. He added that when tested in a helium environment, the useful life of a polyimide film was at least an order of magnitude greater than that in air [7].

One measure of the degradation of polyimide films at high temperatures is the weight loss. Figure 4 gives the weight loss for a temperature ramp rate of 3ºC / min for polyimide films in dry air and in dry helium. Note the much reduced weight loss for polyimide films heated in helium compared to those heated in air and that the sample heated in dry air oxidizes completely.

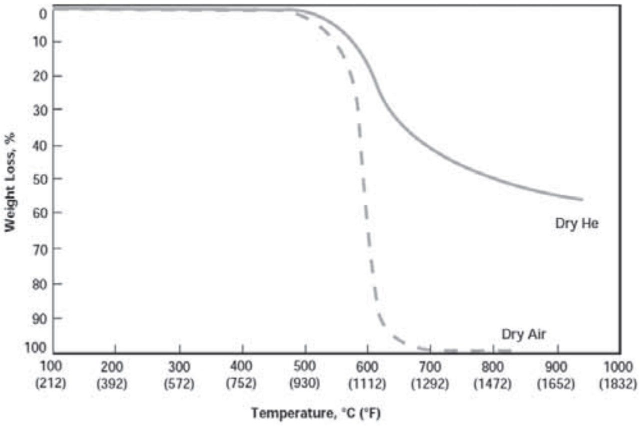

Figure 4: Weight loss as a function of temperature [8].

Another source [9] shows data that suggests that the onset for significant weight loss for PMDA-ODA materials heated in argon at 4ºC / minute is almost 600ºC.

The isothermal weight loss for Kapton HN films is shown in Figure 5. The data are given for a range of temperatures and with samples held in helium or air. Note the very low weight loss at very extended times for 450ºC in helium, and the low rate of weight loss for 500ºC in helium, especially at short exposure times.

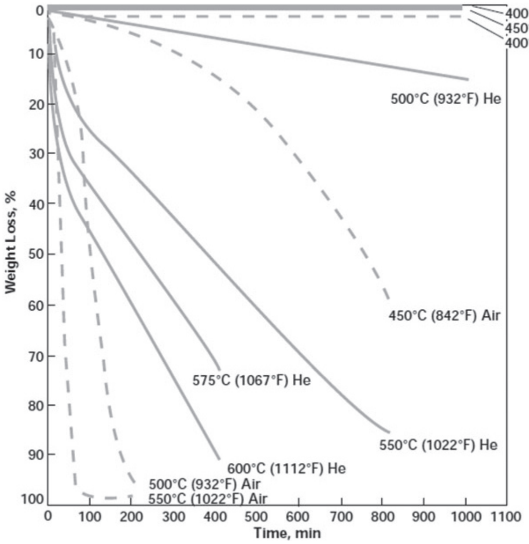

Figure 5: Isothermal weight loss for Kapton HN films as a function of temperature and gas composition [10].

It has been reported that a short sample of Apical NP film inadvertently held at 510ºC under vacuum for 5 minutes still performed well in the subsequent coating process [11].

COMMENTS FOR CIGS SOLAR CELL PRODUCERS

There are many paths being used for preparing flexible CIGS solar cells. Many require temperatures above 450ºC. While it is true that selenium and sulfur are oxidizing (they are in the same chemical family as oxygen, but they are not as strong oxidizing agents as oxygen itself), higher temperatures should be accessible, at least for limited times. Moreover the metal (Mo) electrode typically present is expected to protect the polyimide film from direct exposure to Se and S vapor.

Curling is often observed in the molybdenum deposition step. A major control variable is pressure during sputtering. The pressure can dramatically affect the deposited molybdenum film stress. Secondly, recognize that annealing of the polyimide film (as performed during cell processing) can also contribute to curling of the underlying polyimide film and thus the coated laminate. Pre-annealing may reduce curling from this cause.

POLYIMIDE FILM SURFACE SMOOTHNESS

The following data have been provide by the film manufacturers (all data in nm).

Kapton	200E		200H	
	air side	drum side	air side	drum side
Ra	6.07	25.6	14.0	28.8
Rmax	61.0	291	224	292
Rz	56.3	234	14	253
Upilex	25S		50S	
	A side	B side	A side	B side
Ra	2.3	2.3	2.0	1.9
Rmax	25.0	22.3	13.2	15.0
Rz	18.9	17.8	11.7	12.5

Ube specifies the A side as the inside of a film in roll and the B side as the outside of a film in roll.

MOISTURE IN POLYIMIDE FILMS

There are a number of statements about moisture content in polyimide, including several in the range of 4% and many as low as 1%. The moisture content at equilibrium depends on the relative humidity of the ambient in which the film came to equilibrium. The maximum moisture content occurs after immersion in water. Even then the reported results are inconsistent. One source [12] indicated that a Kapton HN film immersed in water for 24 hours at 23°C contains 2.8% water and another [13] indicated 4.0% water.

Moisture removal can be important for films to be processed in vacuum. The time for half of the moisture to leave selected films is given below (in data provided by DuPont). The experiment consisted of taking sheets of uncoated Kapton type HN and E conditioned at 23°C and 100% RH and then placing them in a 23°C, 0% RH dry box.

Film Thickness	**HN**	**E**
1 mil (25 µm)	3 minutes	9 minutes
2 mil (51 µm)	10 minutes	30 minutes
3 mil (76 µm)	21 minutes	--
5 mil (127 µm)	54 minutes	--

Note that in these experiments most of the moisture leaves through the upper and lower surfaces. Thus if one of the surfaces is coated or in contact with another surface, the equilibration times could be longer. Of course heat can dramatically reduce the time for moisture loss.

SPIN COAT-ABLE POLYIMIDE

There is an enormous amount of knowledge about PMDA-ODA based on its use in microelectronics as a spin coat-able interlayer dielectric. The material commonly used is DuPont Pyralin RC5878, a solution of 10-20% PMDA-ODA poly(amic acid) in N-methyl-2-pyrrolidone (NMP) [5].

SUMMARY

Polyimide films are available in differing chemistries, and these differing chemistries result in films with differing properties. The curing and annealing cycles that the films see are important in defining their properties. The high temperature performance of polyimide films is limited by decomposition and the resulting (often slow) loss of mechanical properties and not by softening or melting as is the case for PET or BOPP. The decomposition is largely an oxidative process, and thus the threshold temperatures for decomposition in vacuum (in the absence of oxygen) are substantially higher that those in air (with oxygen).

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