

# THERMAL RESISTANT POLYMERS FOR MICROELECTRONIC APPLICATIONS

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## ABSTRACT

As electronic devices are designed thinner and more compact for improved performance, there is a greater demand upon their materials of construction for thermal and abrasion resistance, low stress, and in some cases, the ability to be washed away.[1-2] Coatings are simple choices for substrate protection. Aromatic polybenzimidazole (PBI) exhibits a high Tg value ( $T_g = 427^\circ\text{C}$ ) and may be prepared into a high solids matrix producing thick coatings which can be cured in seconds by UV to achieve a thermal stability  $>300^\circ\text{C}$ .[3,4] Polyimide (PI) coatings may be cast and cured onto a range of substrates to achieve thermal stability  $>400^\circ\text{C}$ . Nanoparticle filled polymers offer rigid support for high speed grinding and plasma etching in 3D packaging. The same polymers mentioned here can be formulated to sustain temperatures beyond  $450^\circ\text{C}$  to support thermal oxide deposition while remaining transparent, two key requirements for display applications. Finally, water washable polymers which can sustain the impact of laser processing are important for chip dicing.[5] This paper discusses several polymers and their characterization practices used to support a range of electronic manufacturing applications.

## 1. INTRODUCTION

Microelectronic manufacturing requires the use of thermal resistant polymers. PBI and PI exhibit desirable properties, including high glass transition ( $T_g$ ), the temperature where a glassy state changes to amorphous. These materials are represented at the top of the maximum temperature index of the polymer performance triangle used to compare properties of unfilled substances used for industry's most complex challenges (Fig. 1).

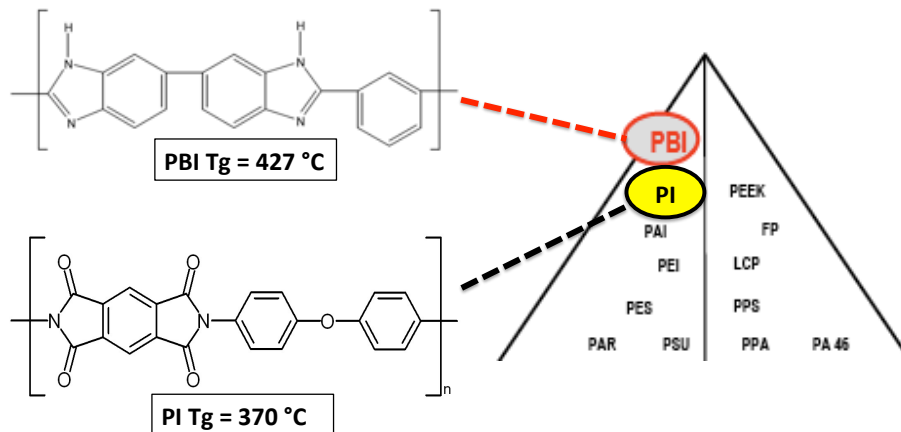


Fig. 1. Polymer performance triangle showing engineering products with a temperature index of  $>150^\circ\text{C}$ . Products on the left are amorphous while partially crystalline materials are on the right. Chemical structures of PBI and amorphous PI are shown.

Although thermal resistance may be a key consideration for a polymer's use in electronics, it is only a part of several properties that define the use of a material for temporary or permanent applications. Transparency and chemical compatibility are other measured characteristics for integration into manufacturing. The ability to build a system with combinations of these characteristics will define a polymer product for use as temporary adhesives in chip stacking, flexible substrates as displays, and dielectrics.

### 1.1 Thermal Resistance

All polymers used in electronics will have some thermal budget as defined by the tool or operation. Electronic manufacturing processes that require thermal resistance are usually defined by a thermal treatment or plasma exposure. Thermal examples include an anneal, outgas, or dielectric cure, while plasma may be used for a substrate and/or metal etch and/or deposition. In this context, the definition of thermal stability can begin at 300°C for a desired length of time.

Characterizing thermal resistance is most commonly done by thermogravimetric analysis (TGA), where a material is subjected to a thermal program in air or inert conditions while measuring its change in weight. An onset of thermo degradation is shown as a weight loss and the inflection (change in slope) is reported. However, weight loss is not the only measure for thermal resistance. For example, TGA values of coatings for PBI and a vinyl-silicone are presented as 617 °C and 405 °C, respectively (Fig. 2), while the appearance of coatings for these specimens are dark brown (PBI) and transparent (silicone).

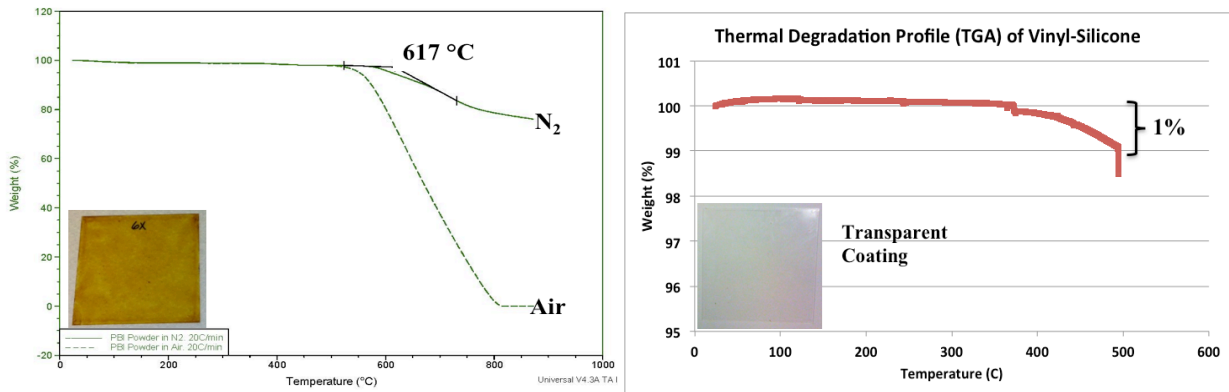


Fig. 2. TGA curves and coating images of PBI polymer (left) and vinyl silicone (right) showing thermal resistance >600 °C in N2 and up to 500 °C, respectively.

Thermal resistance may be represented in several ways, depending upon the final product needs. Although color change may indicate degradation, the final product may still retain many of its physical and chemical properties. In cases where temporary materials are being specified, changes in appearance are discouraged as it is the first indication of thermal oxidation, crosslinking, and a potential to leave residue and stains during its removal.

### 1.2 Transparency

Color development may be triggered by multiple sources to include the polymer chemistry, environment, or impurities from the casting solvent and container. For example, one PI chemistry of unique design is claimed to exhibit ~50% transmittance at 420nm and increasing in its clarity with increasing wavelength.[6] A transmission spectra is given for a clear PI, identified

as Novastrat 400, SRS ManTech (Fig. 3). Further efforts to improve transparency is likely to depend upon its fundamental chemistry, as most commercially available PI products exhibit color. Thin and flexible substrates that exhibit high thermal resistance and >90% transparency at <400nm is in demand for high yield optical devices, solar panels, and displays.

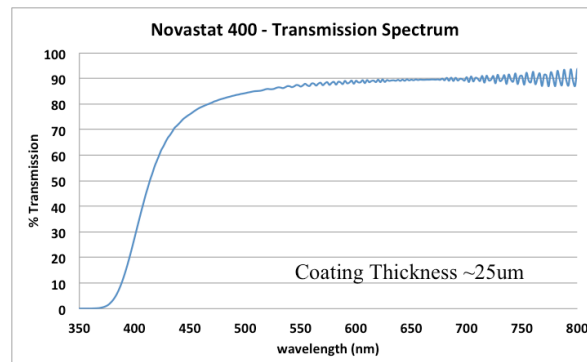


Fig. 3. Transmission spectra for a clear PI where %T = 27% at 400nm for a thickness of ~25 μm as coated and cured on glass (courtesy SRS Mantech, Nexsolve).

Dissolving PI is commonly done in aprotic solvents such as n,n-dimethylacetamide (DMAC), dimethylsulfoxide (DMSO), and n-methylpyrrolidone (NMP). Solvent solutions may be prepared at 20% solids with heating and mixing. Since many crosslinking PI systems proceed from polyamic acid, it is common for residual acid and monomer to remain. As curing continues, these trace impurities will contribute to color development.

### 1.3 Chemical Compatibility

A key property of a temporary polymer coating following an electronics application is its ability to be easily removed (cleaned) from the surface, leaving the substrate in a pristine condition. Usual cleans practices involve the application of solvents or aqueous mixtures followed by an alcohol or water rinse. Single-wafer cleaning tools are used for washing away coatings or adhesives from a taped film frame (Fig. 4).

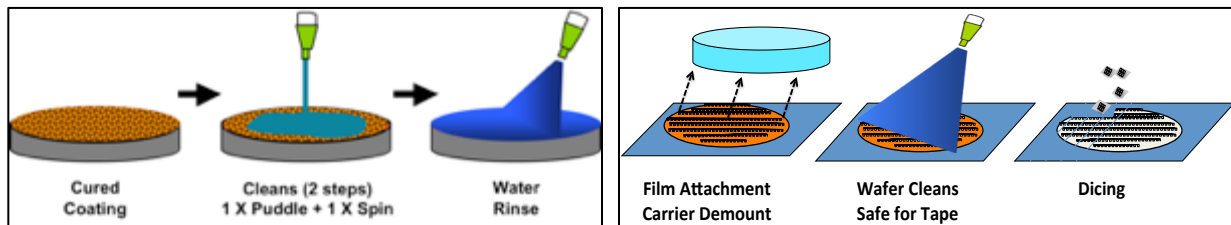


Fig. 4. Process flow for cleans of a protective coating (left) and an adhesive (right).

For certain polymers used in electronics processes, their amorphous property must remain unchanged without crosslinking during thermal processing. One example includes water-washable coatings for laser dicing. Surface protection requires the application an aqueous soluble coating, rinsed after laser processing, to remove debris from the heat activation zone (HAZ).[7] Minimum interaction with the laser must occur with a polymer chemistry that is not susceptible to thermal crosslinking. Products are discouraged which contain polyvinyl alcohol (PVA) or polyvinyl pyrrolidone (PVP) due to their formation of thermally induced insoluble residues.

Instead, thermal resistant polymers exist which are cast by means of evaporative or UV cure.[8] Using a UV active polymer system that cures in seconds, laser debris is rinsed in water (Fig. 5).

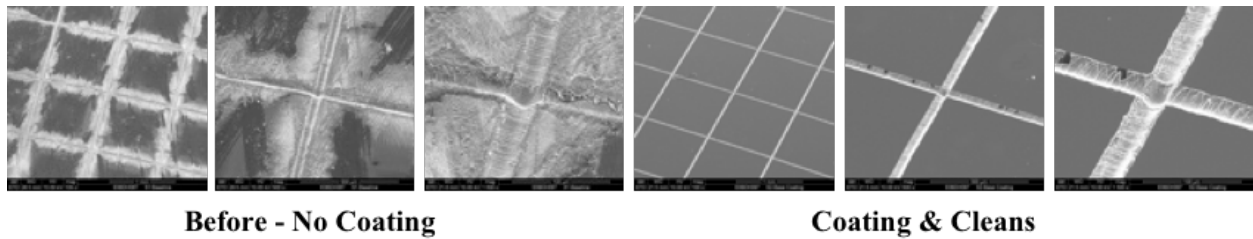


Fig. 5. SEM photos of thermally stable washable coating to support laser dicing, before – no coating (left) and coating and cleans (right).

Many are attracted to aqueous cleaning for reasons of environmental safety and cost reduction. Whether it be cleaning with water or detergents, the chemistries are non-flammable, non-toxic, and do not generate evaporative material to trigger air permit requirements. Subtleties exist in aqueous cleans, and many believe it to be more challenging to control than organic solvents. To improve results, detergents are being accepted for high performance stripping and selectivity, especially where large substrates are being processed. Certain companies are providing aqueous-washable temporary coatings and adhesives with simple cleaners in concentrated forms for semiconductor and other challenging markets [8].

#### 1.4 Polymers in 3DIC

A wide range of polymer types have been reportedly used in wafer bonding for three-dimensional integrated circuits (3DIC). These polymeric substances include rosin-urethane [9], silicone [10], rubber [11], and acrylic.[12] Wafers are bonded to carriers to prevent substrate bow and cracking during thinning and backside processing. The temporary adhesive is commonly applied to the wafer, bonded, processed, and then de-bonded and cleaned (Fig. 6)

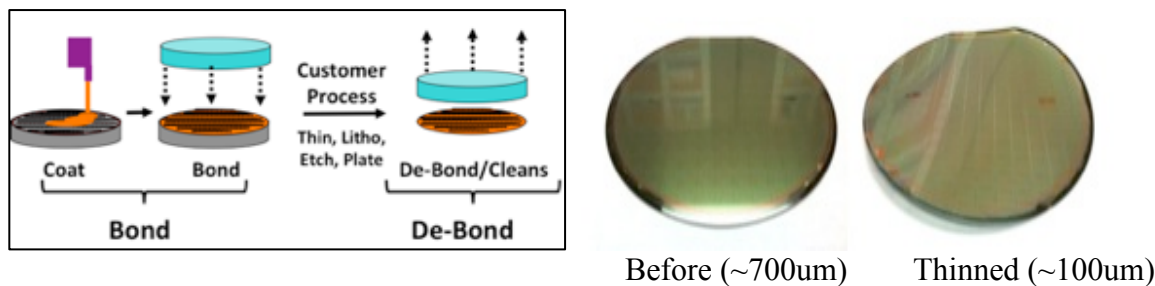


Fig. 6. Process of bond and de-bond is shown (left) and the effects of thinning are seen in a sapphire LED wafer at full thickness and thinned (right).

Thermal resistant polymers used for 3DIC are some of the most investigated systems in electronics. They are temporarily used and as such, must not become permanent while being exposed to a range of chemicals and thermal programs, for example, acidic plating baths and plasma etch used to construct through silicon vias (TSVs). The use of a carrier during bonding enables good surface planarity, low total thickness variation (low TTV), and reduces both internal stress and wafer bow during grinding.[13-16] Thinning uniformity TTV at  $\leq 0.5\%$  is maintained throughout processing.[9-10] De-bonding practices vary from chemical solvation, thermal slide, or laser ablation, lasting anywhere from 15min to several hours.

## 1.5 Polymers in Display

As thinning and miniaturization influences display operations, the handling of thin and flexible glass is presented with many challenges. Many facilities are now exploring organic substrates as polymers to replace glass. A fundamental part of this evolution is the application of low temperature polysilicon (LTPS), indium tin oxide (ITO) or other plasma deposited material used to build the transistor.[17] At the time of this publication, several facilities are investigating this topic and how to integrate thin polymers, including their de-bonding.[18] Example process flows involve the application and cure of a polymer coating to glass, processing that material until device completion, and de-bonding it by laser cutting and peeling (Fig. 7).

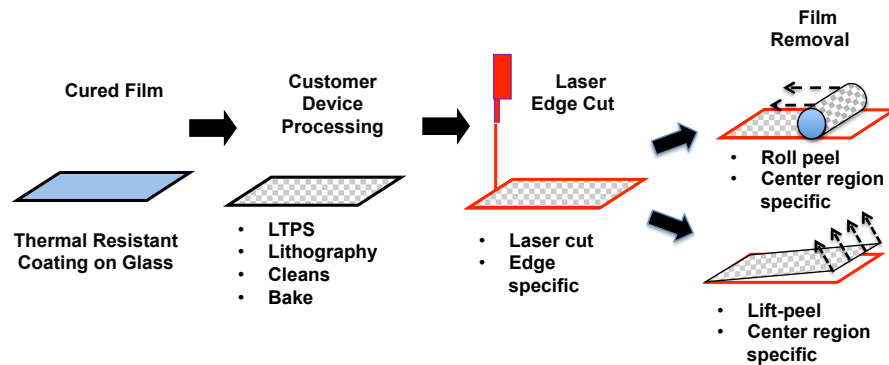


Fig. 7. Example process flow for thermal resistant polymer films for use in LTPS transistor device displays.

Mechanisms for peeling materials from substrates exist and is a standard practice for characterizing tape. [19] The removal of large-area substrate materials using peel methods becomes a physics problem with the different interacting forces represented as vectors and peel force measured by gages (Fig. 8).

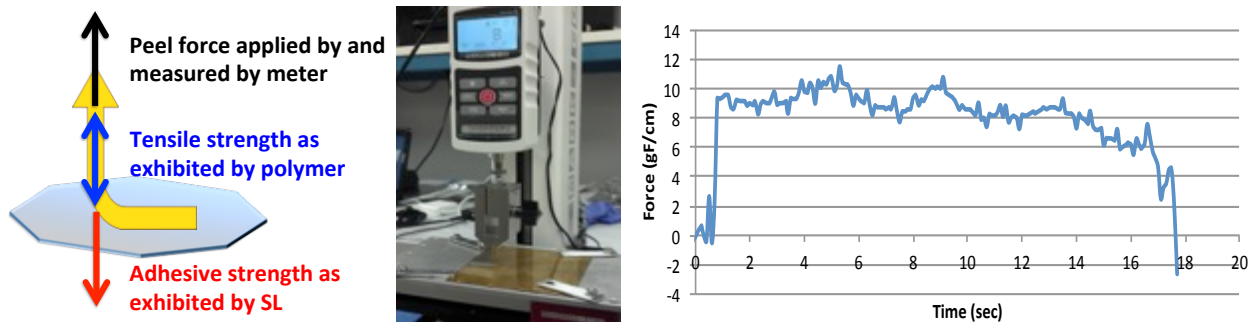


Fig. 8. Peel mechanism model (left) with process and graph of peel force (right).

Investigations of new materials for the manufacture of displays are continuing, beginning with a material's thermal resistance and transparency. Knowing that a material provides such properties is only part of its qualification. It must sustain the customer's process and be able to removed, de-bonded, without damage to its integrity or that of the devices built upon its surface.

## 2. EXPERIMENTAL

### 2.1. Materials

For expanded analytical evaluation, quartz substrates are chosen and prepared at Daetec along with 100-200 mm (4-8") silicon wafers (1-0-0, ~525  $\mu\text{m}$ , Wollemi Technical, Inc.), and glass

(10cm X 10cm X 0.5mm, Fitek Industrial, Inc.). Several polymers were procured for this work: polyimides include Novastrat 400 (SRS Mantech Nexolve, [www.mantechmaterials.com](http://www.mantechmaterials.com)), polyimide P84 (HP Polymer, Inc., [www.hppolymer.com](http://www.hppolymer.com)), U-varnish (UBE Industries, Ltd., [www.ube-ind.co.jp](http://www.ube-ind.co.jp)), and PI-2611 (HD Microsystems, [www.hdmicrosystems.com](http://www.hdmicrosystems.com)). Formulated and proprietary materials as silanols and water washable systems are produced at Daetec [20]. Where applicable, UV-cure applications are conducted with *n,n*-dimethylacrylamide (DMAA) available from San-Esters and various photoinitiators under the tradename *Irgacure*, available from BASF, as Irgacure 2022 (BAPO/ $\alpha$ -hydroxykeone). Solvents as DMAC, DMSO, NMP, *n*-ethylpyrrolidone (NEP), 1,3-dioxolane, and gamma-butyrolactone (BLO) are used for solvation, viscosity reduction, and fixing.

## 2.2. Equipment

Coatings are produced on a Brewer Science, Inc. CB-100 spin-coater, while spray and encapsulation uses custom tooling designed at Daetec. Metrology data is generated by a XP-1 stylus profiler, AFP-200 atomic force profiler, and a Xi-100 optical profiler ([www.kla-tencor.com](http://www.kla-tencor.com)), using equipment settings 5 mg stylus load, minimum 4 mm distance, and a speed of 0.5 mm/sec. Modified thermogravimetric test methodology for outgas is conducted by typical laboratory scales (+/- 0.1mg). UV cure equipment includes the Intelli-Ray 400 microprocessor controlled light curing system ([www.uvitron.com](http://www.uvitron.com)). Furnace support uses box type #ST-1200C-121216 with microprocessor programming, nitrogen purge, and dispersion fan for chamber uniformity ([www.sentrotech.com](http://www.sentrotech.com)). FTIR Spectrum 100 and UATR Ir coating accessory ([www.perkinelmer.com](http://www.perkinelmer.com)) and UV/VIS spectrometer Cary 50 ([www.varian.com](http://www.varian.com)). Force gage M5-series with 90 degree sled and stand ESM301, fixtures, and software ([www.mark-10.com](http://www.mark-10.com)).

## 3. RESULTS

Evaluation for cure extent on thermoset polyimides U-varnish and PI-2611 were conducted using guidelines from HDI using FTIR. Wavelengths 1775cm<sup>-1</sup> and 1505cm<sup>-1</sup> to represent the extent of imidization as carbonyl and alkene bond, respectively, are compared at 250 °C and 350 °C. HDI's results of full cure at 250 °C were confirmed by the following plots (Fig. 9), as little or not difference is detected between the two temperatures held for 15min.

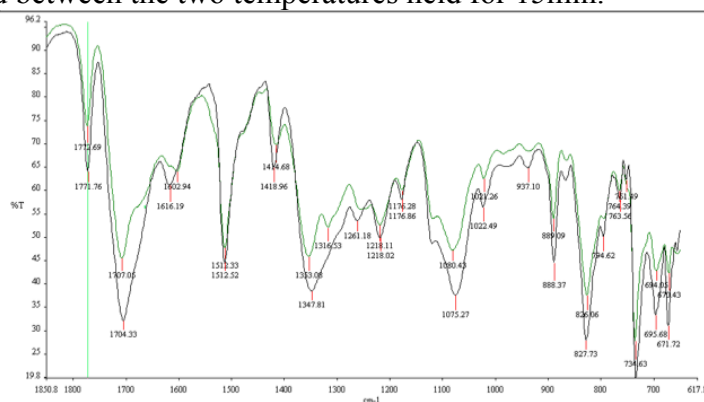


Fig. 9. FTIR scans of PI-2611 at 250 °C and 350 °C indicating full imidization (full cure).

The effects of solvent choice were tested with Novastrat 400 polyimide in DMAC, BLO, and NEP, as well as polyimide P84 in the same and BLO/dioxolane. The respective FTIR and UV/VIS scans were conducted on Novastrat 400 films cured onto glass at 350 °C, with FTIR insensitive to solvents, while UV/VIS identified a drop in % transmittance (%T) from the use of NEP (Fig. 10). Polyimide P84 showed similar shortcomings vs. casting solvent (Fig. 11).

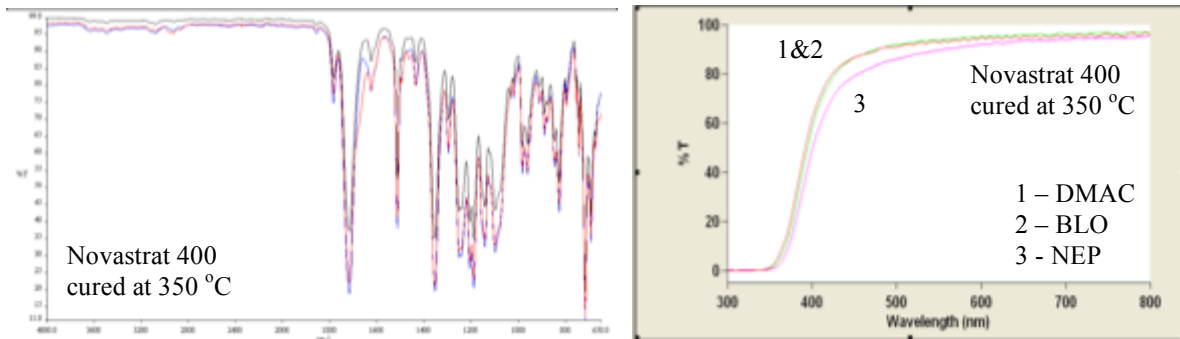


Fig. 10. FTIR and UV/VIS scans of Novastrat 400 cured on glass to 350 °C suggesting insensitivity to clarity issues by trace material by FTIR. UV/VIS detected a drop in % T of the polyimide cast from NEP.

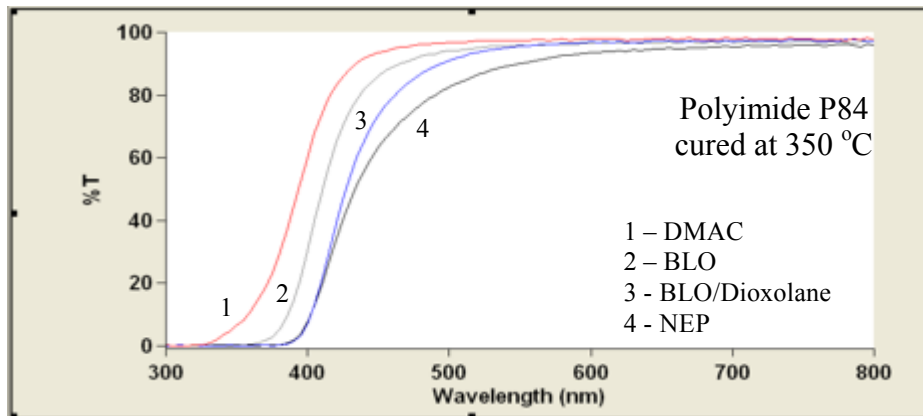


Fig. 11. UV/VIS of polyimide P84 indicating clarity differences with casting solvent.

Additional studies were conducted on Novastrat 400, polyimide P84, PI-2611, and U-varnish to investigate any clarity irregularities in cured films with increasing thermal exposure. Specimen films of each polyimide were cured on glass at 350 °C and 450 °C, and followed by UV/VIS analysis. Elevated temperature exposure indicated a sharp drop in %T at 450 °C, with the greatest drop observed from the amorphous PI materials, Novastrat 400 and polyimide P84 (Fig. 12), an inverse relationship of %T with thermal exposure for P84 (Fig. 13).

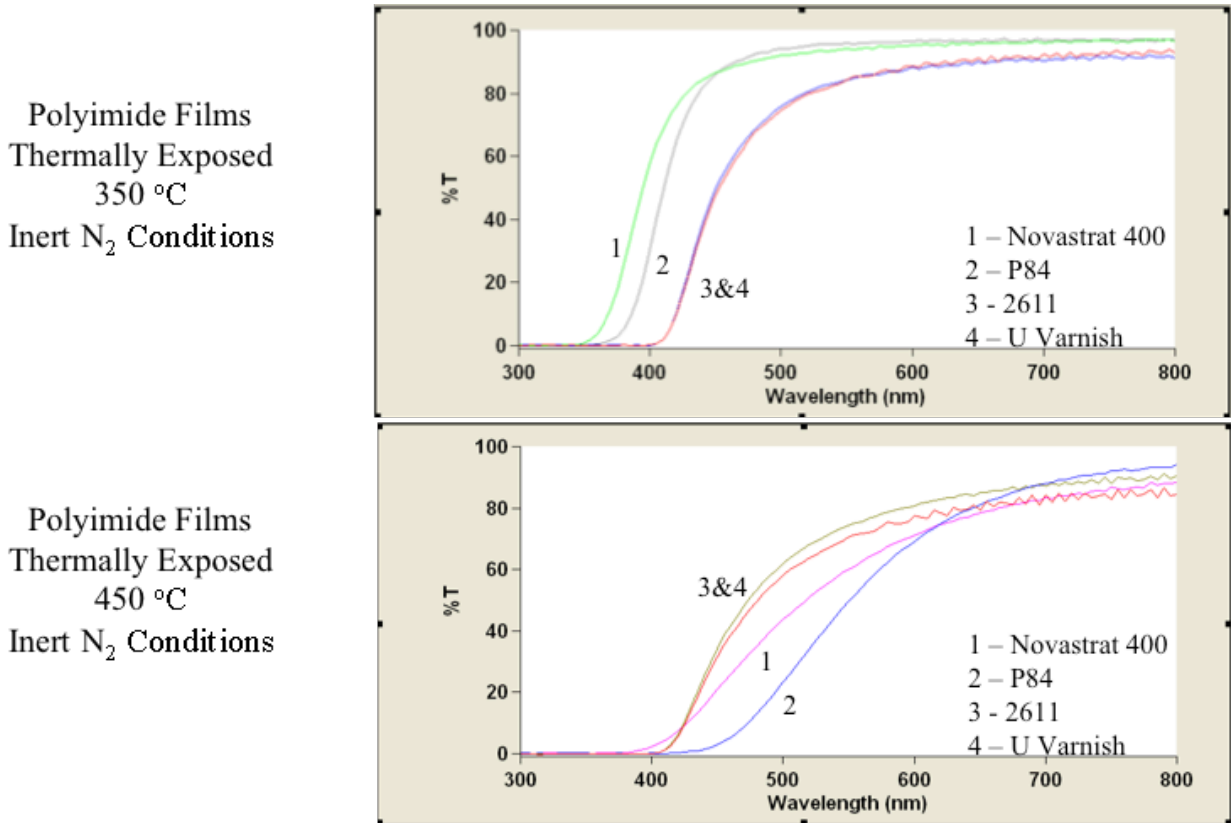


Fig. 12. UV/VIS of polyimides Novastrat 400, polyimide P84, PI-2611, and U-varnish, cured to 350 °C and 450 °C on glass indicating clarity differences as %T with thermal exposure.

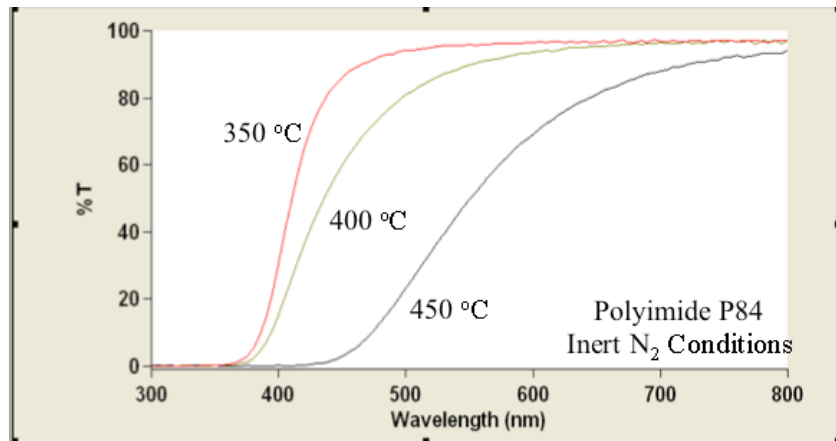


Fig. 13. UV/VIS of polyimide P84 showing drop in clarity as %T with thermal exposure.

Polyimide films were peeled from glass substrates and tested for tensile strength. In one experiment, U-varnish was exposed to temperatures up to 450 °C and held for a period of up to 10hrs and tested for tensile strength. The graphic relationship suggests a drop in tensile strength in polyimide with thermal exposure. This relationship for U-varnish is compared to the manufacturer’s information (Fig. 14).



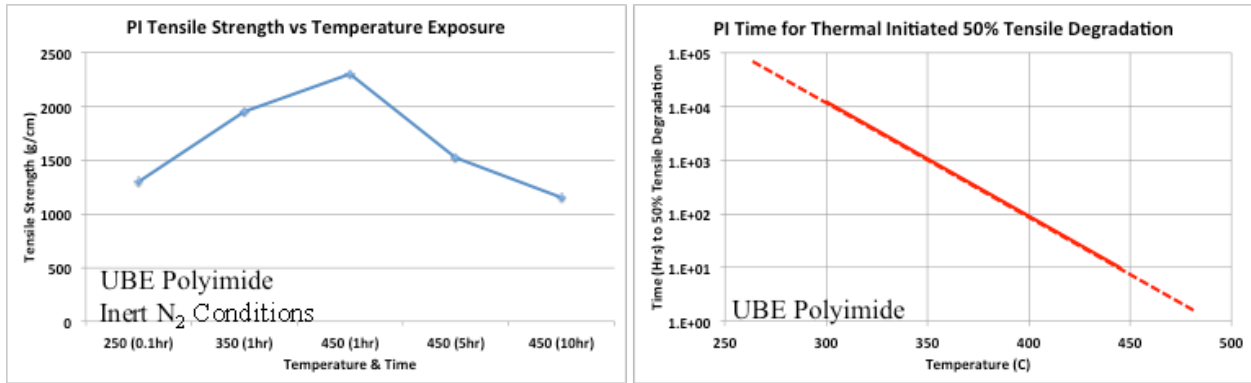


Fig. 14. Tensile strength of polyimide with heat exposure. U-varnish tensile strength of ~10um films exposed to 450 °C for up to 10hrs (left) is compared with manufacturer information (right).

Experiments with various vinyl-silicones suggest a high clarity and good thermal resistance (Fig. 2). In an effort to boost thermal resistance, different silicone families were explored with silanol chemistry included. Of key importance with such materials is the achievement of curing (crosslinking) without a drop in clarity. Catalysts were chosen from common sulfonic acid, benzylic amine, and nano sized ceramic and metal. Thermal exposures were conducted between 250-450 °C measuring condensation (crosslinking) as thermal outgas by weight change (Fig. 15) with improvements using nano materials (Fig. 16).

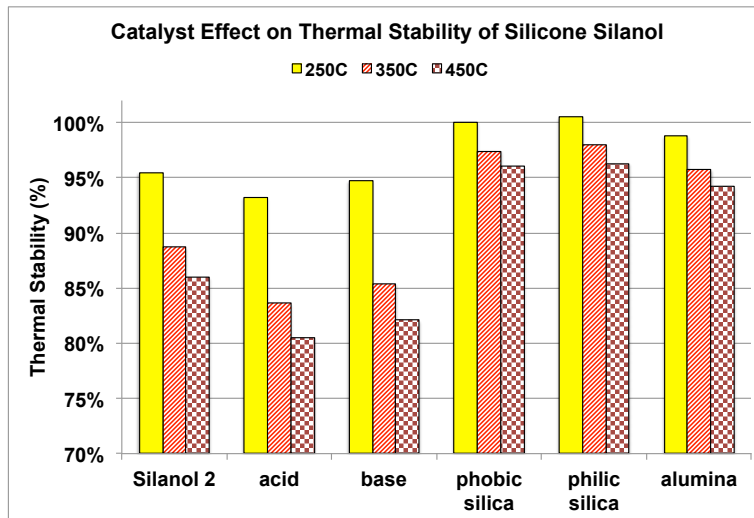


Fig. 15. Silanol chemistry testing for condensation by catalytic means from 250-450 °C measuring thermal stability as outgas as % weight change.

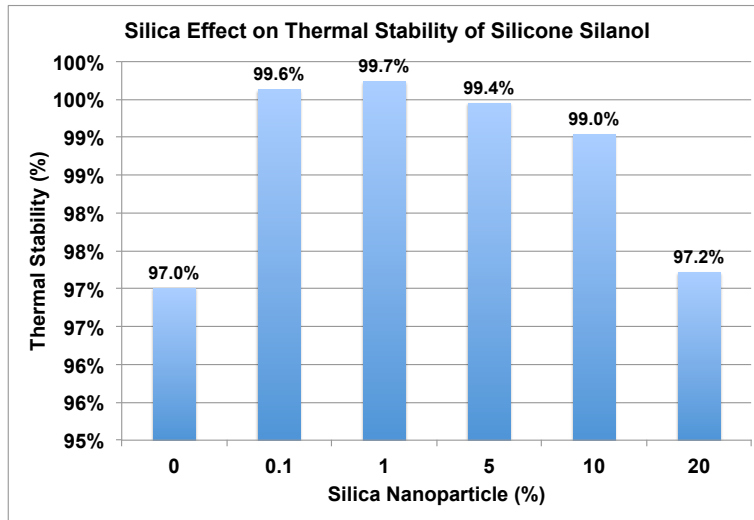


Fig. 16. Silanol chemistry testing to optimize catalytic condensation by silica nanoparticles taken to 450 °C showing good stability with as little as 0.1 % addition to achieve >99% stability.

Mixtures of silanol with catalyst were prepared into films on glass using similar cure programs as described earlier for polyimide. Once completed, the films were subjected to a number of thermal programs to demonstrate thermal stability and followed with UV/VIS (Fig. 17).

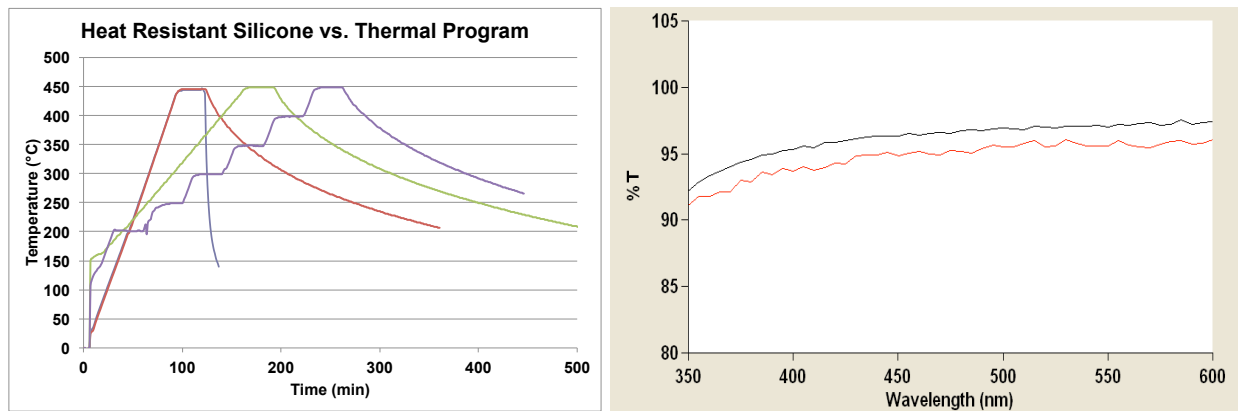


Fig. 17. Silanol chemistry upon thermal exposure to varying temperature programs for stability demonstration (left) and the representative films tested by UV/VIS (right).

#### 4. CONCLUSION

This paper introduces several challenges subjected to thermal resistant polymers used in electronics manufacturing. We observe that as various polyimides are exposed to temperature, they lose transparency and tensile strength. These two important properties are critical in the manufacture of displays. We find that silicones may show some promise for these applications. Silanols are shown to condense to a sufficient level to resist temperatures of 450 °C with greater than 99% stability and clarity >95% at 400nm. As our work continues with thermal resistant polymers, we believe that polyimide, silicones, as well as others, can be successfully integrated into electronics to achieve temperatures well beyond those currently tested.

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