THERMAL RESISTANT POLYMERS FOR MICROELECTRONIC APPLICATIONS

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ABSTRACT

Few materials are commercially available that exhibit thermal resistance sufficient to be used in electronic manufacturing. High temperature processing in semiconductor and panel making operations includes plasma deposition, dielectric curing, and annealing of polycrystalline silicon. In some cases, there is a desire to maintain transparency, measured as %T in UV/VIS.[1] Common choices of engineering polymers include polybenzimidazole (PBI) and polyimide (PI) due to their high glass transition temperature (Tg).[2] Although limited polymer choices exist to resist temperatures beyond 400C (752F), careful formulating of nanocomposite coatings can extend >500C (>932F). In our studies, we have been successful in demonstrating coatings sufficient to withstand 600C (1,112F) and able to support manufacturing. This paper discusses several formulated products using filled polymers to offer rigid support for high speed grinding, plasma etching, and temperatures beyond 450˚C used in thermal oxide deposition in 3D packaging and displays. These same special properties drive the use of polymers in washable coatings for laser dicing of chips leading to stacking.[3]

1. INTRODUCTION

The combined semiconductor and display industries generate over $600b in annual revenue. A key driver is the growth in smart phones and tablets that demand higher power devices, functionality, miniaturized, and at lower costs. This forces creative packaging with thin substrates, solder bumps, stacking chips, and screens that are thinner and compact (flexible displays). Wafer level packaging (WLP) is driving growth at 2X faster than the industry (Fig. 1).

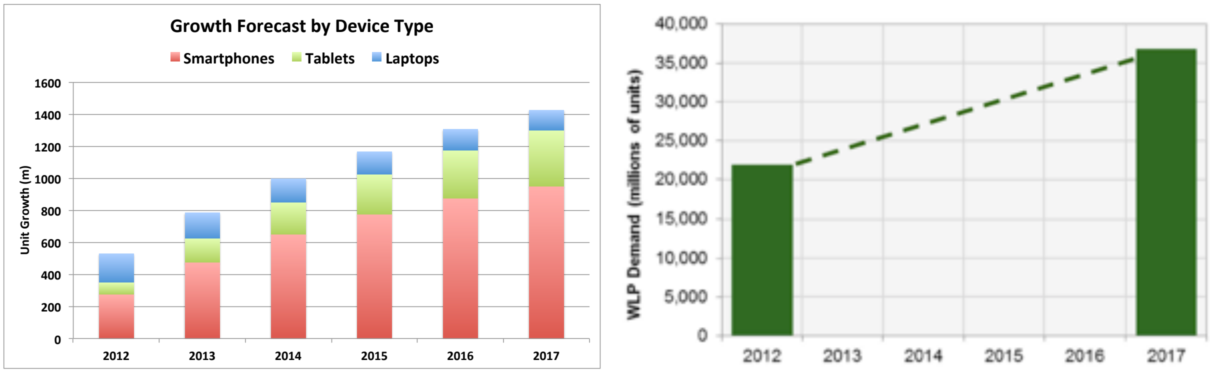


Fig. 1. Growth of electronic devices (left) and demand for WLP units (right).

This demand requires new thermal resistant polymers. Making three-dimensional integrated circuits (3DIC) requires multiple processes to prepare wafer substrates such that thin die can be stacked and connected. Thermal resistant polymers must sustain temperatures exceeding 300˚C for periods of several hours. The 3DIC market and making flexible displays represents some of the top challenges to the industry.[4]

1.1 Materials & Properties

Photoresist polymers in lithography generate annual sales >$1.5b, yet are rarely used in processes exceeding 250˚C. High temperature candidates include aromatic PBI and PI, both exhibiting Tg values of 427˚C and 370˚C, respectively. These materials are used as equipment o-rings and device dielectrics. PBI and PI exhibit a high temperature index on the performance triangle used to compare properties of unfilled engineering polymers (Fig. 2).

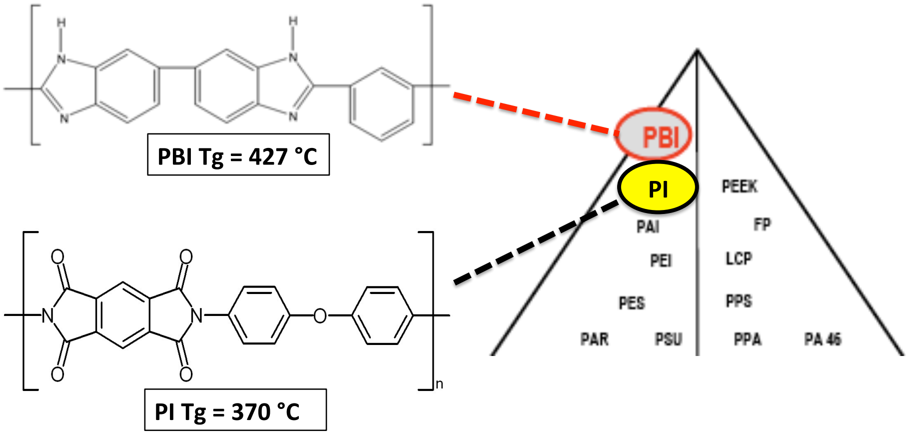


Fig. 2. Polymer performance triangle showing engineering products with a temperature index of >150 °C, as amorphous (left) and crystalline (right), with structures of PBI and amorphous PI.

Thermal resistance is 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 (Fig. 3).

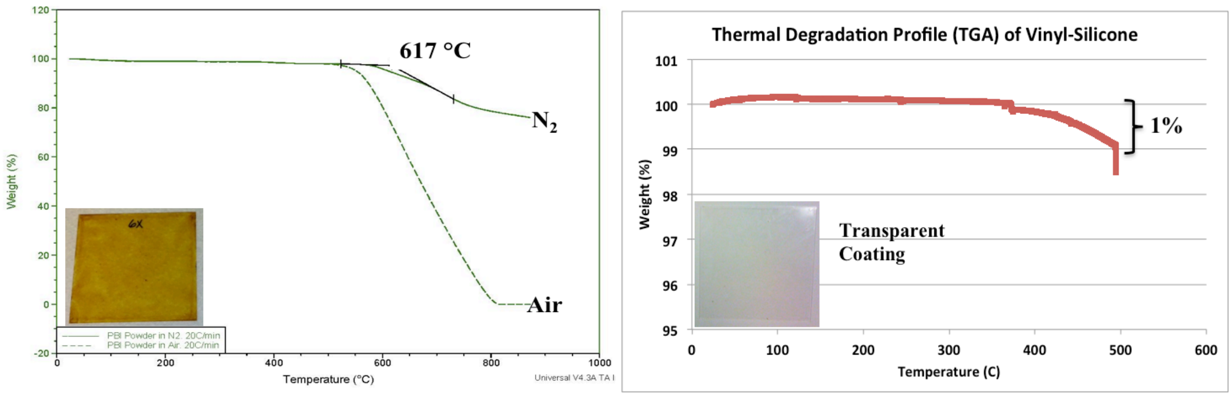


Fig. 3. TGA curves and coating images of PBI polymer (left) and vinyl silicone (right) showing thermal resistance >600 °C in N2 and up to 500°C, respectively.

Material degradation by TGA is seen as a change in slope with corresponding weight loss, but it is not the only measure for thermal resistance. As seen in Fig. 3, the TGA for PBI appears more favorable over a vinyl-silicone, yet the specimens are dark brown and transparent, respectively. Flexible substrates that maintain thermal resistance as >90% transparency at <400nm are in demand for optical applications such as solar panels and displays. Color development may be triggered by polymer chemistry, impurities, or oxygen content. Examples include polyimide and silicone taken to 450°C where a polyimide transparency drops to near zero at 400nm while a filled silicone maintains above 90% (Fig. 4).

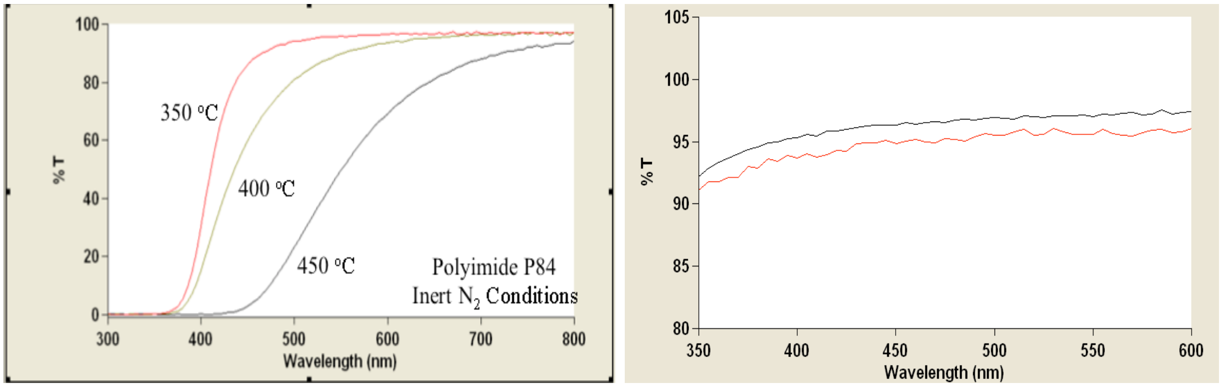


Fig. 4. UV/VIS of polyimide P84 showing drop in clarity as %T with thermal exposure.

Silicones used in electronics are cured from addition (vinyl) and condensation (silanol) reactions especially with nanomaterials that have been shown to increase thermal resistance (Fig. 5).[1]

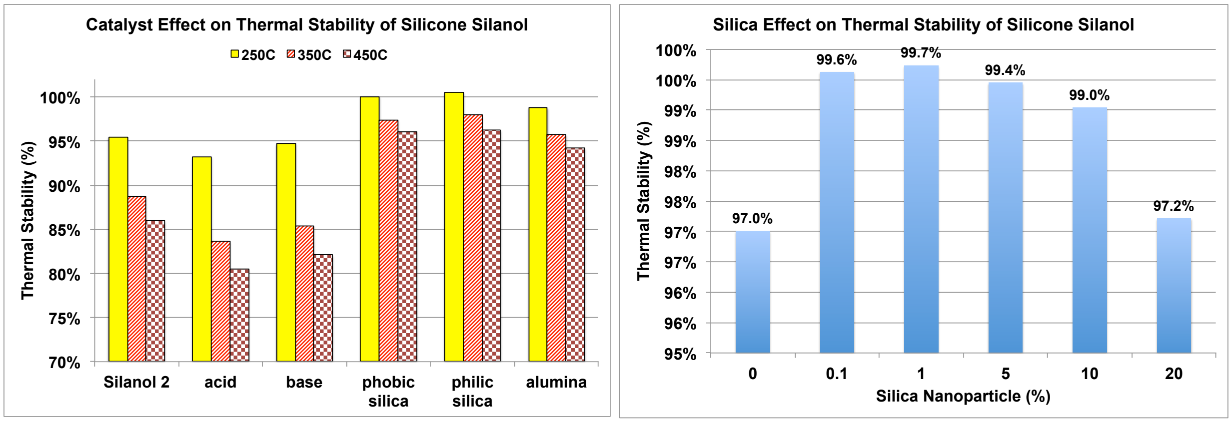


Fig. 5. Nanoparticles to improve silanol thermal stability in various forms (left) and silica (right).

Nanomaterial filled polymers are becoming more common as coatings to meet special properties. Similar results as that shown in Fig. 5 suggest a minimum amount of nanoparticles can cause important changes in mechanical properties when properly dispersed.[5]

Another key feature of electronic materials is the property of non-outgassing. Polymers that restrict the passage of gases, vapors, and liquids are commonly referred as barriers.[6]

Permeability is a measure of the quantity of a gas passing through a specific polymer film of given thickness per day at 1 atm pressure (cm^3-ml/day-atm). In the following figure, a comparison of different polymers to act as a barrier to water vapor and oxygen (O_2) is given with PBI over-lay to Nylon 6 (left) and outgas reduction by formulating with barriers (right).[2]

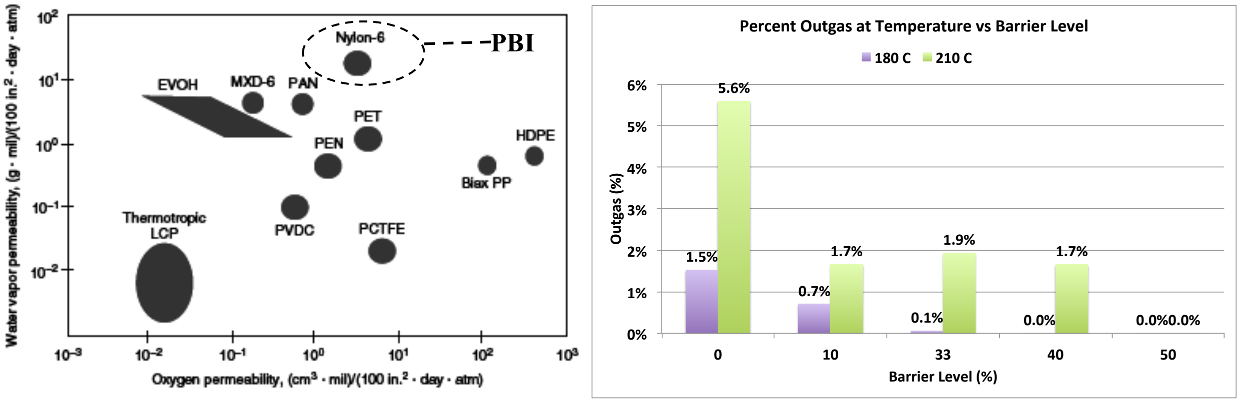


Fig. 6. Barrier polymer permeability of water vapor and O_2 (left), excerpt with permission.[6] Reduced outgassing by formulating with barrier polymer as low as 10% (right).[2]

1.2 Applications

Most polymer systems designed for electronic applications are formulated. They include additives designed to tune the final properties towards a desired outcome. That may include any of the properties discussed here with the applied needs as coating thickness and shelf life. This paper presents a short list of applications requiring a minimum thermal resistance of 300°C.

1.2.1 Protective Coatings – 3DIC

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. In 3DIC processes, topography and exotic metals will interact with the adhesive or coating to produce residue. A washable coating, DaeCoat^{TM} 515,[7] planarizes the wafer surface and protects the features over 100um until carrier demount and cleaning. The DaeCoat^{TM} 515 is available in different viscosities for thin and thick coatings, cures to a rigid-hard condition, and offers thermal and mechanical stability to fragile thin wafers until handling is completed (Fig. 7).

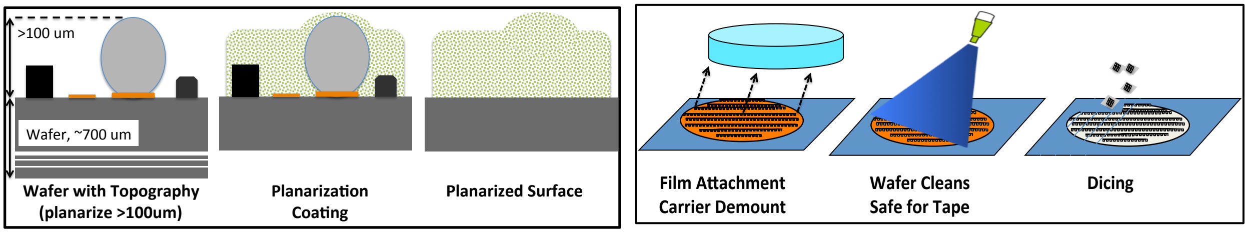


Fig. 7. Applying DaeCoat^{TM} 515, protection during 3DIC processing (left), and cleaning (right).

1.2.2 Protective Coatings – Laser Processing

A proven product for laser processing is DaeCoat^{TM} 515, formulated with thermally stable polyester, eliminates residues seen by common products as polyvinyl alcohol (PVA) and pyrollidone (PVP). The DaeCoat^{TM} 515 is applied, laser processed, and water rinsed to remove debris from the heat activation zone (HAZ, Fig. 8).[3]

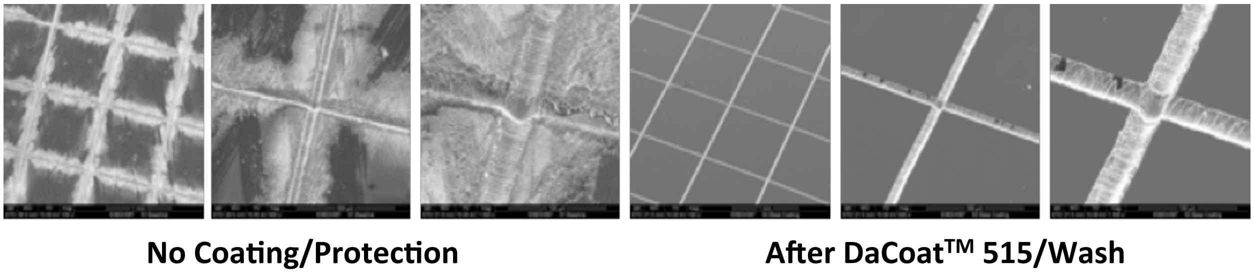
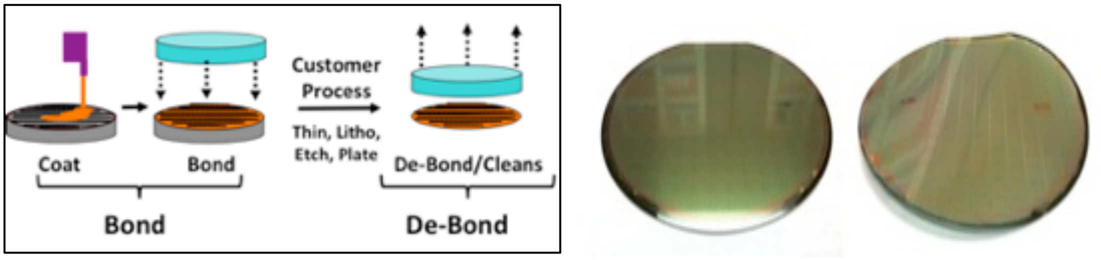


Fig. 8. SEM photos of laser processing without a coating (left) and with DaeCoat^{TM} 515 (right).

1.2.2 Semiconductor Thin Substrates

Many polymer types have been reported as temporary adhesives to support 3DIC processes, including rosin-urethane [8], silicone [9], rubber [10], and acrylic.[11] Temporary support with a carrier is required for wafers thinned to 100um or below is needed to prevent bow/warp and damage when handling. Material is applied to the device wafer, bonded to the carrier, processed, de-bonded, and cleaned (Fig. 9).



Before (~700um) Thinned (~100um)

Fig. 9. 3DIC process (left) and the need to support thinned wafers due to bow/warp (right).

3DIC temporary adhesives must be inert to the customer's process while being exposed to a range of chemicals and heat. The carrier-bonded device wafer offers good surface planarity, low total thickness variation (TTV), and reduced internal stress.[12-15] Thinning uniformity TTV at $\leq$0.5% is maintained throughout processing.[8-9] De-bonding practices vary from chemical solvation, thermal slide, or laser ablation, lasting anywhere from 15min to several hours.

Temporary bonding agents as DaeCoat^{TM} 615, 620, and 625 exhibit thermal resistance in excess of 250°C. These agents use high total acid number (TAN) polymers that allow cleanup in the detergents, DaeClean^{TM} DP-108 & DL-409, which are diluted in water. A silicone system used for temporary bonding, DaeCoat^{TM} 300, offers thermal resistance >300°C and cleans up in a solvent-based bond breaking chemistry, DaeClean^{TM} SL-300. These materials have been demonstrated for 3DIC processes for substrate thinning to below 25um.[8-11]

1.2.3 Flexible Displays

The same miniaturization and weight reduction influences in semiconductor are encouraging the use of flexible substrates made from thin glass and organic substrates. A fundamental part of this evolution is the application of low temperature polysilicon (LTPS), indium tin oxide (ITO), and related exotic materials.[16-17] Many process flows are being investigated involving the temporary adhesion of various films to carrier glass, process them in existing tooling, and de-bond by simple mechanisms (Fig. 10).

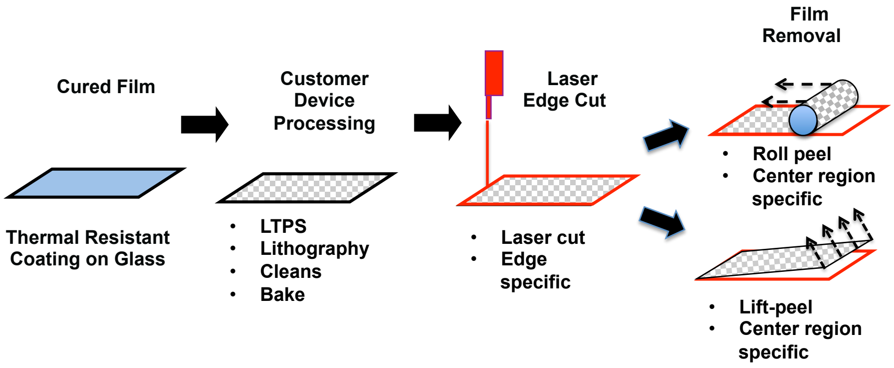


Fig. 10. Example process flow for manufacturing flexible displays.

Mechanisms of removing thin substrates from carrier glass exist.[18] The removal of large-area substrate materials by peeling becomes a physics problem with the different interacting forces represented as vectors and peel force measured by gages (Fig. 11).

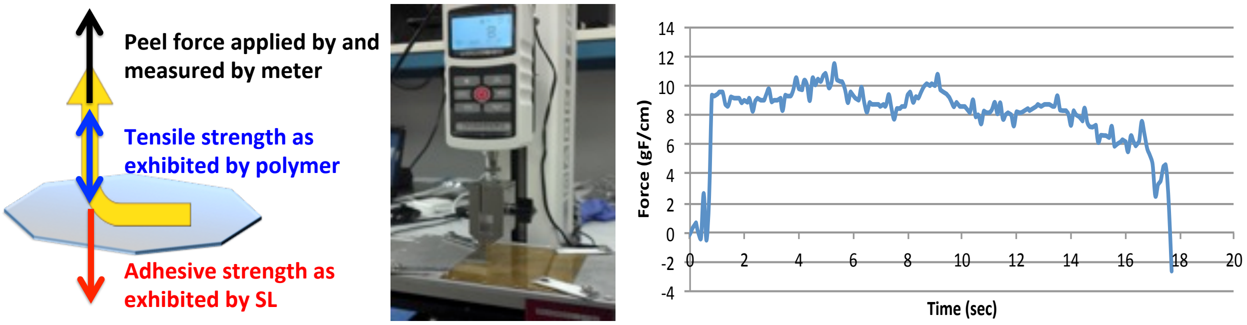


Fig. 11. Peel mechanism model (left) with graph of peel force (right).

Investigations of new materials for the manufacture of displays are continuing, beginning with a material's thermal resistance and transparency. Thin film substrates which are applied by casting methods include DaeCoat^{TM} 200 (sulfone), DaeCoat^{TM} 250 (polyimide), and adhesives for thin substrates as DaeCoat^{TM} 300 & 350 (silicones).[7] These products have specific processing requirements. 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 µm, Wollemi Technical, Inc.), and glass (10cm X 10cm X 0.5mm, Fitek Industrial, Inc.). Several polymers were procured for this work: polyimides include U-varnish (UBE Industries, Ltd., www.ube-ind.co.jp), and U-Varnish (Unitika, Ltd., http://www.unitika.co.jp/e/). Soluble inorganic silicates with different SiO_2 loadings are available from PQ Corporation. Aqueous thickening agents used in inorganic coating formulations are hydroxypropylcellulose under the trade name *Klucel*, and Polyvinylpyrrolidone Polymers (PVP), both available from Ashland, Inc.. Several inorganic nano-sized fillers were procured for this work: Aerosil silica and alumina (Evonik Industries, Corp.), Polyhedral Oligomeric Silsesquioxane (POSS) (Hybrid Plastics, Inc.), Pyrograf III Carbon nanofibers (Pyrograf Products, Inc.), Graphene powder (Angstron Materials, Inc.), and Nexsil aqueous colloidal silica (Nyacol Nano Technologies, Inc.). Formulated and proprietary materials as silanols, DaeCoatTM 200s, 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 trade name *Irgacure*, available from BASF, as Irgacure 2022 (BAPO/∝-hydroxykeone). Solvents as DMAC, DMSO, NMP, n-ethylpyrrolidone (NEP), 1,3-dioxolane, and gamma-butyrolactone (BLO), Xylene 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), 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). Furnace support uses box type #ST-1200C-121216 with microprocessor programming, nitrogen purge, and dispersion fan for chamber uniformity (www.sentrotech.com). FTIR Spectrum 100 and UATR Ir coating accessory (www.perkinelmer.com) and UV/VIS spectrometer Cary 50 (www.varian.com). Force gage M5-series with 90 degree sled and stand ESM301, fixtures, and software (www.mark-10.com).

3. RESULTS

Five polymer samples, including three polyimide varnishes, a silicone and a sulfone are prepared. Three (3) of these systems are represented by DaeCoat^{TM} products: DaeCoat^{TM} 200 (sulfone), DaeCoat^{TM} 250 (PI #3), and DaeCoat^{TM} 300 (silicone). Thermal stability is measured by a modified TGA by coating approximately 1 gram of liquid on the glass slides, measured after each temperature interval isothermal (15min) from 350 to 500°C in 50-degree-increments with appearance observations. Thermal exposures of samples are performed in a N_2 purged furnace (8% O_2). Each exposure is followed by a 15min-cooling step (Figs.11-12).

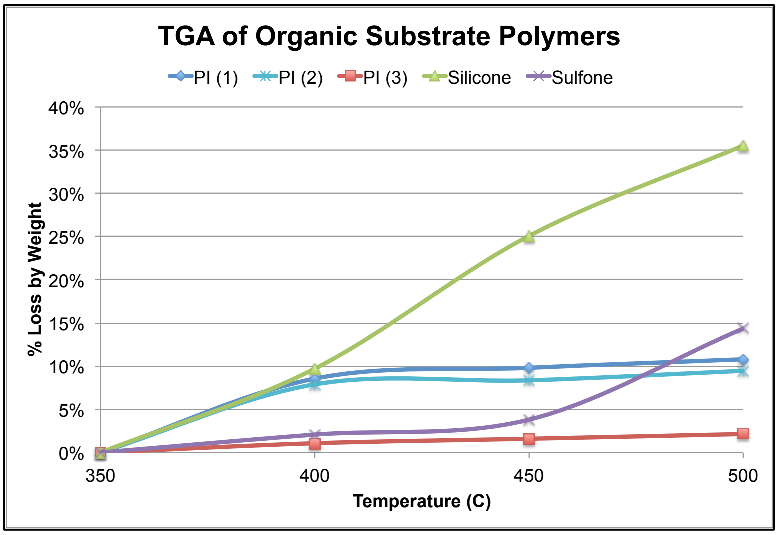


Figure 11. TGA of thermal resistant polymers in purged N_2 system (~8% O_2) to 500°C.

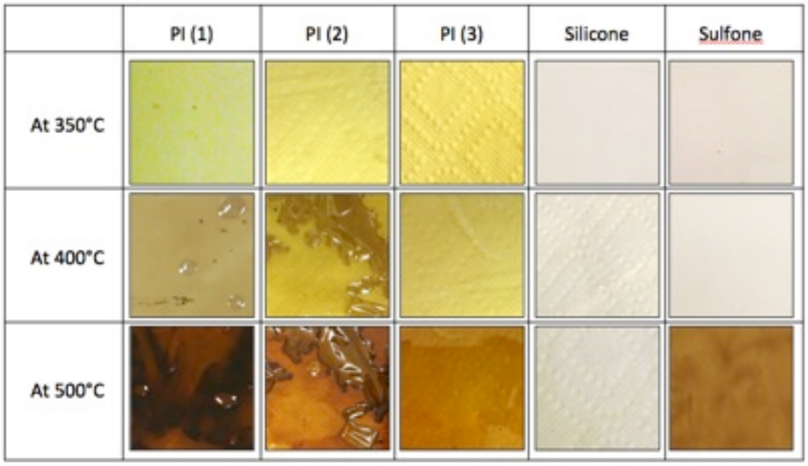


Figure 12. Appearance of thermal resistant polymers in purged N_2 system (~8% O_2) to 500°C.

Polyimide (1) and (2) experience significant mass loss at 400°C, and coating delamination is observed (Fig. 12). The lowest mass loss of the three polyimide systems is PI #3 (DaeCoat^{TM} 250), with appearance as smooth and unchanged to 450°C, while 500°C is discolored. The silicone (DaeCoat^{TM} 300) retains transparency but experiences high weight loss throughout the process. The sulfone (DaeCoat^{TM} 200) is transparent to 400°C discolored at 500°C.

Transparency and thermal stability are of highest interest for display applications, so the sulfone sample is selected for further study at 400°C. Various nanoparticles mixed with the sulfone to observe their effect on mass loss at 400 and 450°C. Nanoparticles chosen for the experiment includes alumina (AluC), trisilanol POSS (SO 1430), carbon nanofibers (PR-19-OX and PR-24OX) and graphene (N008-P40). Low loading and matching refractive index are preferred to maintain the transparency of the sulfone coating system. The same modified TGA approach described earlier. The results from Fig. 11 suggest a post-baking step is necessary before deposition. Improvements in outgas reduction are observed with nanomaterials to near a 60% reduction with carbon nanofibers and grapheme at <0.01% (Fig. 13).

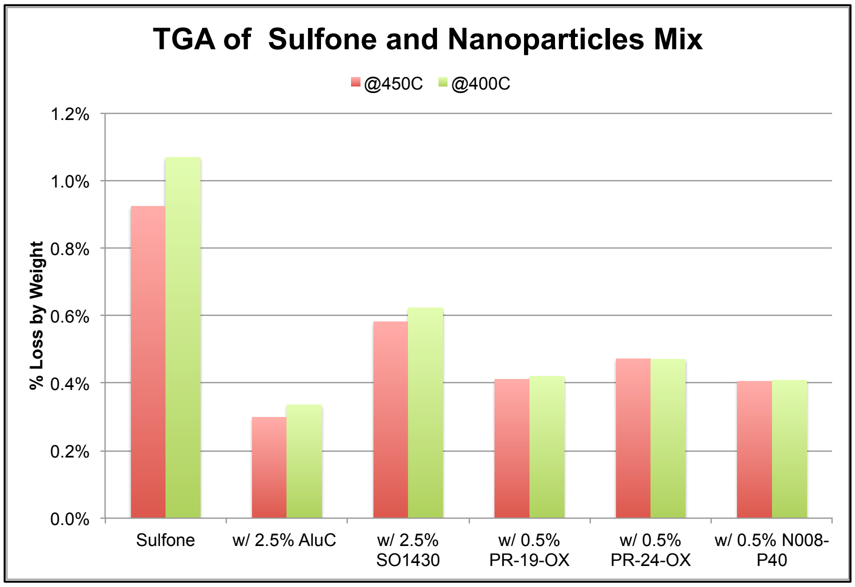


Figure 13. TGA of sulfone with various nanoparticles in purged N_2 system (~8% O_2), to 450°C.

Polyimide #3 from previous testing is selected to test the effect of oxygen on organic polymers properties. UV/VIS %T at 500nm, tensile strength, and adhesion force is tested in (a) N_2 purged (~8% O_2) and (b) Vacuum-sealed system (<0.1% O_2, Ar purge). Thickness of the PI #3 is measured as 10 ±0.5 µm characterized by contact profilometery. PI is cured to 350°C and exposed to 500°C isothermally for 15 minutes and observed after each exposure (Fig. 14). Tensile and adhesion is measured by Mark-10 peel tester at 90° configuration (Fig. 15).

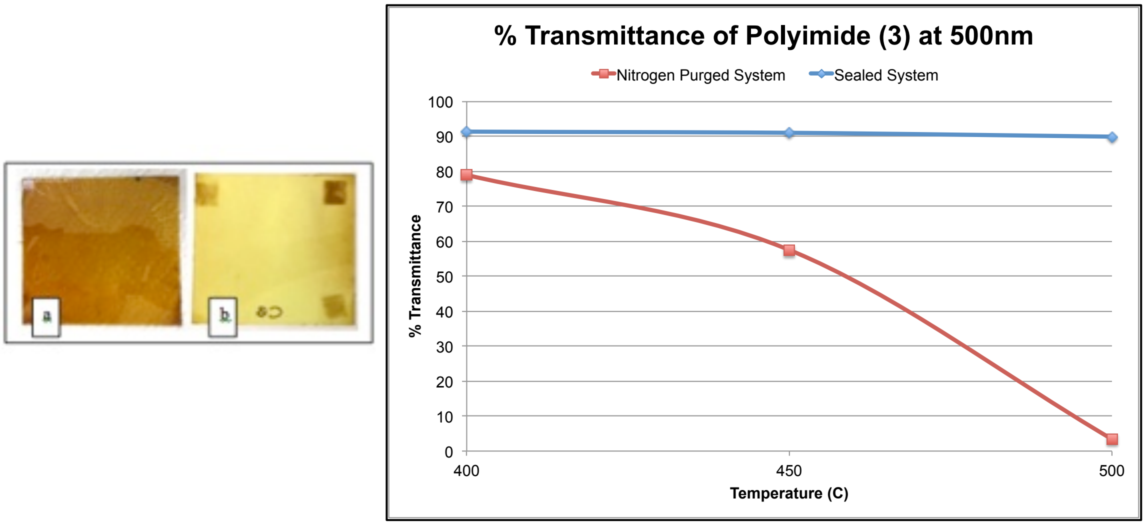


Figure 14. Observations of PI #3 taken to 500 °C in (a) N_2 purged (~8% O_2) (b) Vacuum-sealed system (<0.1% O_2) with %T measurements.

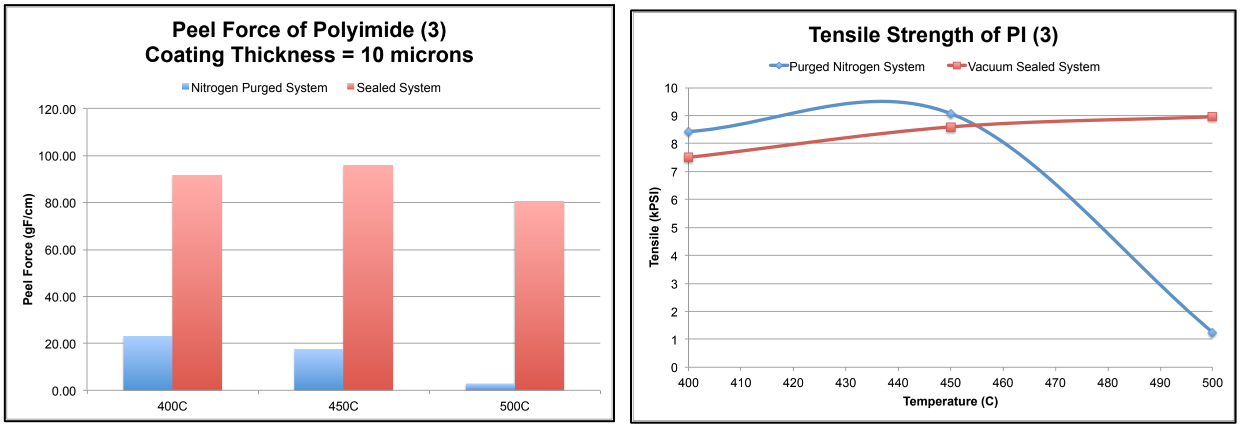


Fig. 15. Adhesion & tensile of PI #3 taken to 500 °C in (a) N_2 purged (~8% O_2) (b) Vacuum-sealed system (<0.1% O_2).

Inorganic polymers are tested for thermal resistance in oxygen environment. Metal silicates are used as the binder material and are mixed with silica nanoparticles to create nano-composite coatings for testing. Nano-composites with different porosity were prepared by varying the binder: filler ratio. A blend is defined as porous for this test when %binder is less than 50% and defined as non-porous if %binder is higher than 50%. Sulfone is used as a baseline comparison.

A TGA screen is conducted on inorganic nano-composite coatings using a hard-bake temperature of 350°C followed by a thermal program to 600°C. Thermal exposure of samples are performed in furnace with a N_2 purge (~8% O_2). Weight loss %T is reported normalizing for thickness of the coating based on Beer-Lambert's law (Figs. 16 & 17).

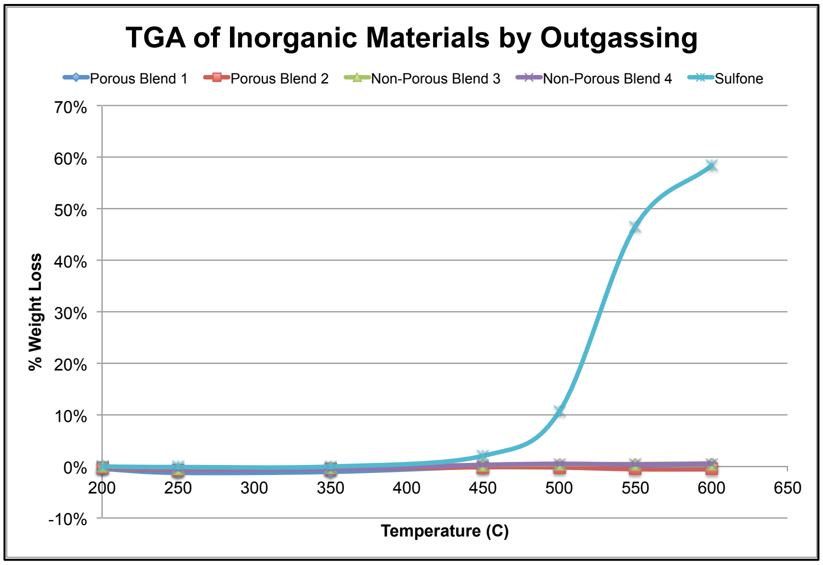


Fig. 16. TGA of inorganic nanocomposites in a N_2 purged (~8% O_2) vs. sulfone to 600°C.

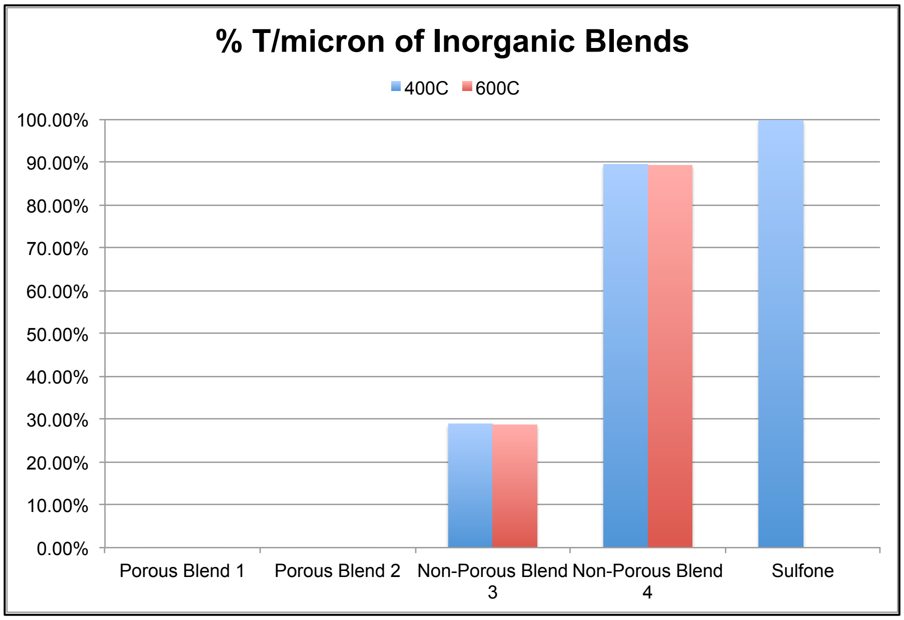


Fig. 17. %T/um (380nm) inorganic nanocomposites, N_2 purged (~8% O_2) vs. sulfone to 600°C.

The same set of samples used for thermogravimetric analysis are subjected to microelectronic processing using silicon nitride deposition at 400°C. Surface roughness and peeling of inorganic nano-composites are tested before and after deposition, and again after annealing at 500°C for 30 minutes. Roughness is reported as Rq values (nm). Peeling is used as a release mechanism for flexible electronics manufacturing. Sample is configured with tape in a 90° arrangement. Peel results are reported as pass/fail, before deposition, after deposition, and after annealing. Pass results reflect release layer operates without damage observed under optical microscope.

Table 1. Pass/fail peel testing of inorganic nano-composites before and after thin film deposition.

		Before Deposition	After Deposition	After Annealing (500°C)
Sample ID	**Rq (nm)**	**Peel?**	**Peel?**	**Peel?**
Porous Blend 1	177	Yes	Yes	Yes
Porous Blend 2	150	Yes	Yes	Yes
Non-porous Blend 3	41	Yes	Yes	Yes
Non-porous Blend 4	58	Yes	No	No
Sulfone	21	Yes	Yes	No

Inorganic blends from previous test is modified to make create a thick porous structure that can withstand temperatures to 600°C. Larger particle size was selected to increase pore diameter to enhance sorbtivity. Varying materials philicity and phobicity are chosen for absorptivity in a scale from philic to phobic. Such materials are important for thin substrate temporary bonding where chemical exclusion is important. Samples are: 1) metal silicate, 2) PBI composite, 3) vinyl silicone, and 4) silicone composite. Surface roughness (left) and DIW absorptivity within a blue dye is reported (Fig. 18).

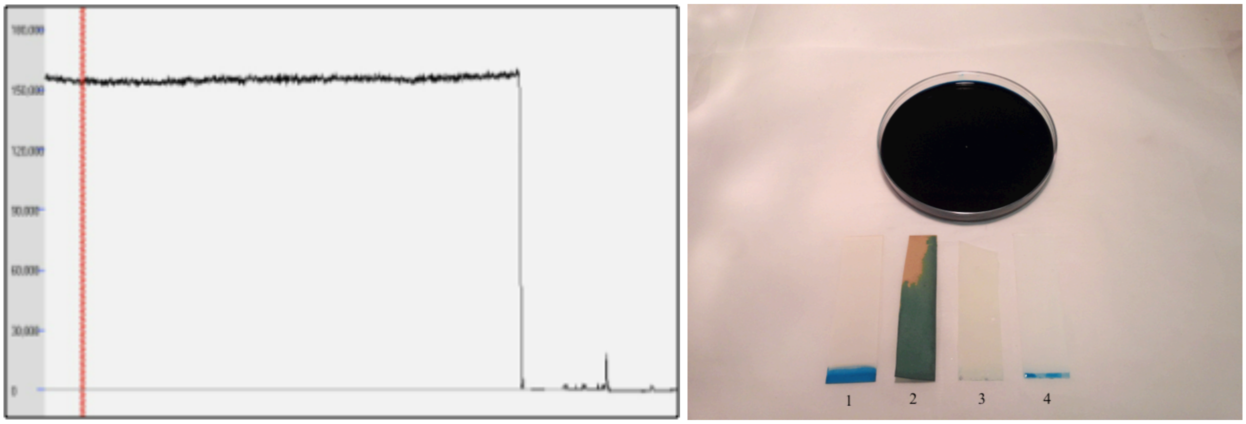


Fig. 18. Surface profile of porous coating (left) and DIW absorption w/blue dye (right).

TGA is performed on various UV curable acrylic composites and taken to 400°C. All systems are cured using a UVA dose of approximately 450mJ/cm^2 and a post bake of 200°C. Samples are described as: a) acrylic (1), b) (a) with 20% PBI, and c) (a) with 20% ionomer (acrylic (2)) showing TGA results and the chemical conditions that are required to effect cleans after thermal exposure (Fig. 19, Table 2).

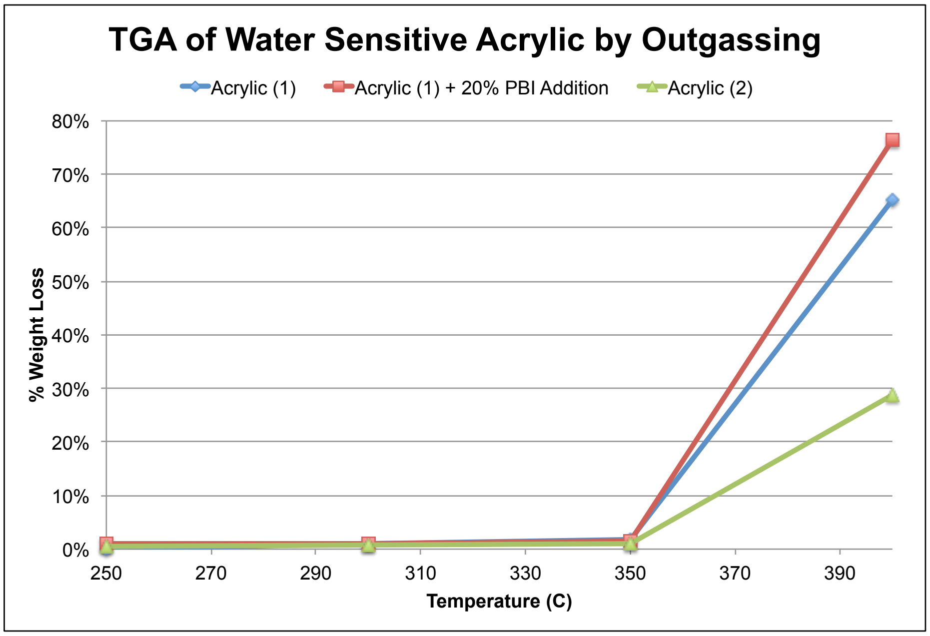


Fig. 19. TGA of water sensitive acrylic systems from 250°C to 400°C.

Table 2. Minimum chemistry conditions to achieve complete cleaning.

Exposure (15min)	Acrylic (1)	20% PBI in Base	20% Ionomer
250°C	25°C DIW, 10 Min	25°C DIW, 5 Min	25°C DIW, 2 Min
300°C	70°C, pH 10, 10 Min	25°C DIW, 5 Min	25°C DIW, 2 Min
350°C	No Cleans	70°C DIW, 5 Min	25°C, pH 10, 5 min
400°C	No Cleans	No Cleans	No Cleans

Tests to determine peel force on Al foil, PI, PEN and PET films bonded by silicone adhesive and the ability to tune that adhesive force is reported. Values of tuned silicone adhesive is exposed to 350°C prior to peeling as an attempt to model thermal exposure in a fabrication facility (Fig. 20), and finally the TGA values for the tuned silicones at such temperatures reported (Fig. 21).

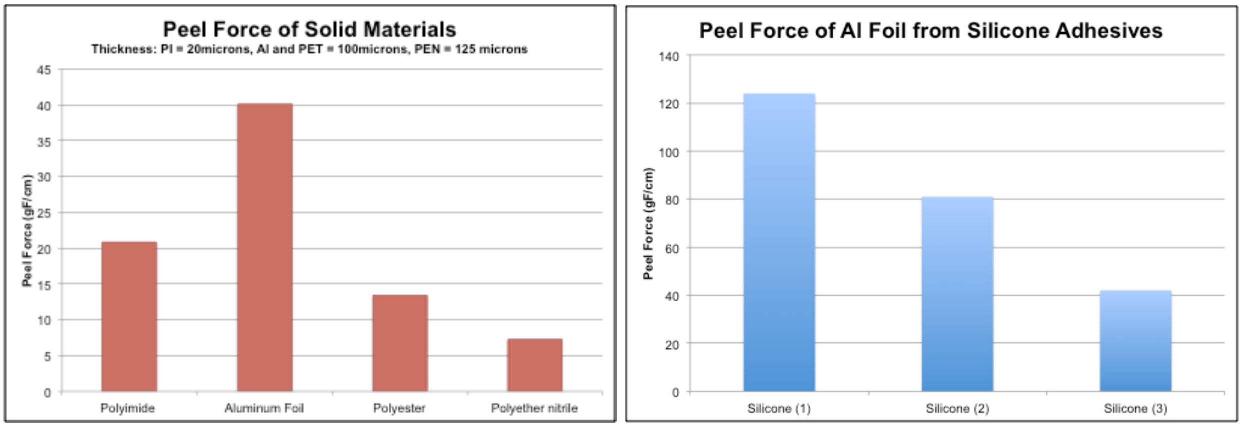


Figure 20. Peel force of films using silicone (left) and tunable silicone (right).

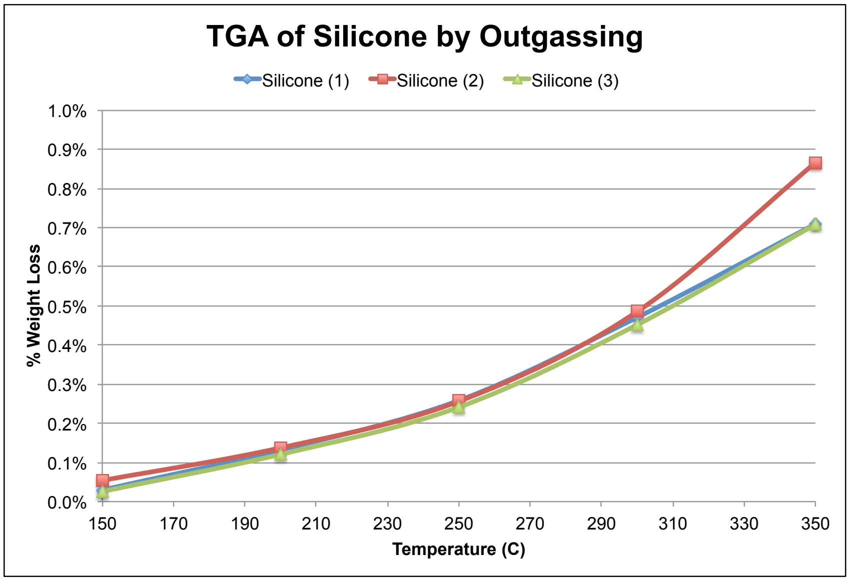


Figure 21. TGA of pressure sensitive silicone adhesives taken to 350°C.

4. CONCLUSION

This paper introduces several polymers subjected to thermal resistance and able to be qualified for microelectronic manufacturing. We observe that these polymers (polyimides and silicones) can be improved as electronic materials by nanomaterial addition. Such improvements include reduced TGA by outgassing, transparency, adhesion force and tensile properties. These are important properties critical in the manufacture of semiconductors and displays. The properties of porous composite coatings may provide benefit for high temperature coatings in electronics. Also shown in our work is the use of nanocomposites to push temperature resistance to >600°C. These developments are very promising for thin adhesive supported films for use as release layers and related practices in electronics manufacturing. 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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