

THERMAL RESISTANT COATINGS USING PBI RESIN

^aGreg S. Copeland, ^aMike Gruender, ^bJared M. Pettit, and ^bJohn C. Moore

^aPBI Performance Products, Inc.
9800 Southern Pine Blvd., Suite D, Charlotte, NC 28273 USA
704-554-3036, greg.copeland@pbiproducts.com

^bDaetec, LLC
1227 Flynn Rd., Unit 310, Camarillo, CA 93012 USA
805-484-5546, jmoore@daetec.com

ABSTRACT

Polybenzimidazole (PBI) provides coatings of high thermal resistance for a wide range of applications. The polymer offers thermal properties that exceed other engineering materials ($T_g = 427\text{ }^{\circ}\text{C}$, thermal degradation $>550\text{ }^{\circ}\text{C}$). Unlike many common high MW engineering polymers, PBI resin can be dissolved in an organic solvent system to produce stable noncorrosive solutions. Coatings are produced by simple casting methods. This paper will demonstrate how simple PBI coatings are applied to substrates from carbon-steel to copper, achieving desirable protection and high thermal stability.

1. INTRODUCTION

Engineering coatings continue to be in demand to support electronics, aerospace, and industrial needs, growing at 20% per year, and approaching a \$1b market.[1-2] The growing interest for alternative energy and the prevalence of sensors in automotive performance are examples which require thermal resistant coatings which increase material life in aggressive environments.

PBI was first synthesized in the late '50s by Hoechst Celanese Corporation, in an initiative to produce thermally stable products. More recently, the polymer is primarily used to support flame retardant products in aerospace and as a fabric in fire protection [3-4]. Coatings of PBI have been investigated and reported [5], however, the majority of work focuses on overcoming challenges in producing a quality coating [6-7]. This report presents several methods to coat PBI on a range of substrates, at a range of thicknesses, and achieving desirable properties.

1.1 Thermal Resistance

The aromatic bi-benzimidazole structure of PBI provides superior chemical and thermal resistance due to the strength of its internal molecular bonds (Fig. 1).

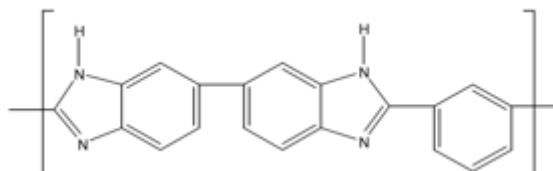


Fig. 1. Chemical structure of PBI polymer.

As compared to other engineering substances, PBI polymer is represented at the top of the maximum temperature index of the polymer performance triangle. The triangle is split in half with amorphous materials on the left, crystalline or semi-crystalline on the right. The performance of PBI, relative to the other materials, exceeds the thermal resistance properties of unfilled substances used for solving industry's most complex challenges (Fig. 2).

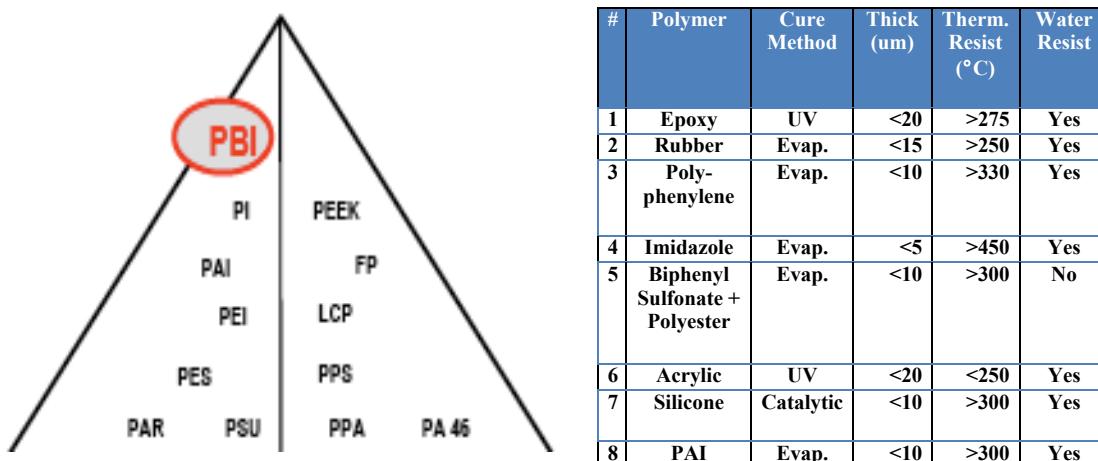


Fig. 2. Top of performance triangle, products of >150 °C temperature index, amorphous (left) and partial crystalline (right). The table to the right indicates a list of polymers used as coatings, many are engineering types. PBI is shown as item #4.

Thermal resistance in polymers can be achieved by a number of ways. This may include blending with other higher Tg polymers or through the addition of fillers. Blending can occur in both amorphous and thermosetting polymers. PBI is attractive polymer for blending due to its very high thermal resistance, as shown in its TGA and other properties in the table (Fig. 3).

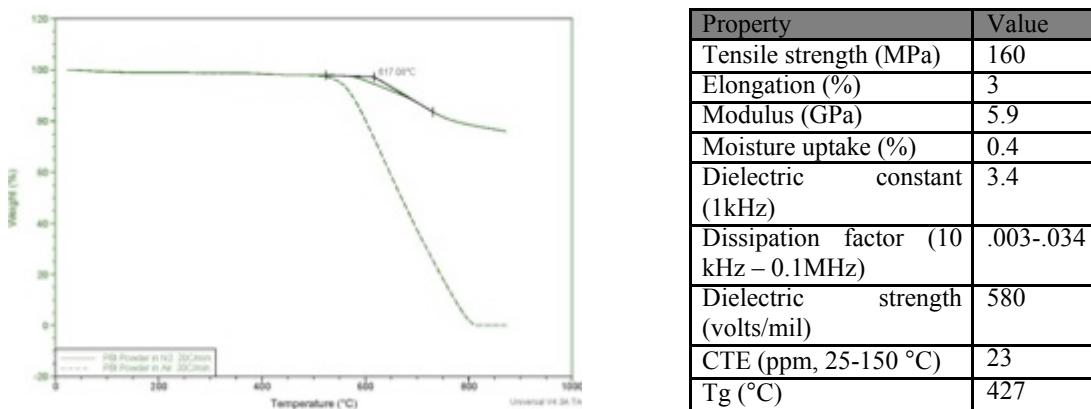


Fig. 3. TGA curve of PBI polymer showing thermal resistance >500 °C in air and >600 °C in N₂. The properties of pure PBI polymer are shown in the table to the right. These values represent the "bulk" properties of the polymer. For coatings, the properties may vary, depending upon thickness and substrate.

Examples of PBI blends are shown in Fig. 4 where PBI is blended with polyetherketoneketone (PEKK) [8]. The findings of these blends suggest that the Tg of the mixtures represent the major component. In a 60:40 PBI:PEKK blend, the Tg is close to that of the pure PBI polymer. For thermal resistance, both PBI and PEKK exhibit good thermal resistance >500 C. A slight improvement is noted for PBI:PEKK mixtures where the PBI content is >80% (Fig. 4).

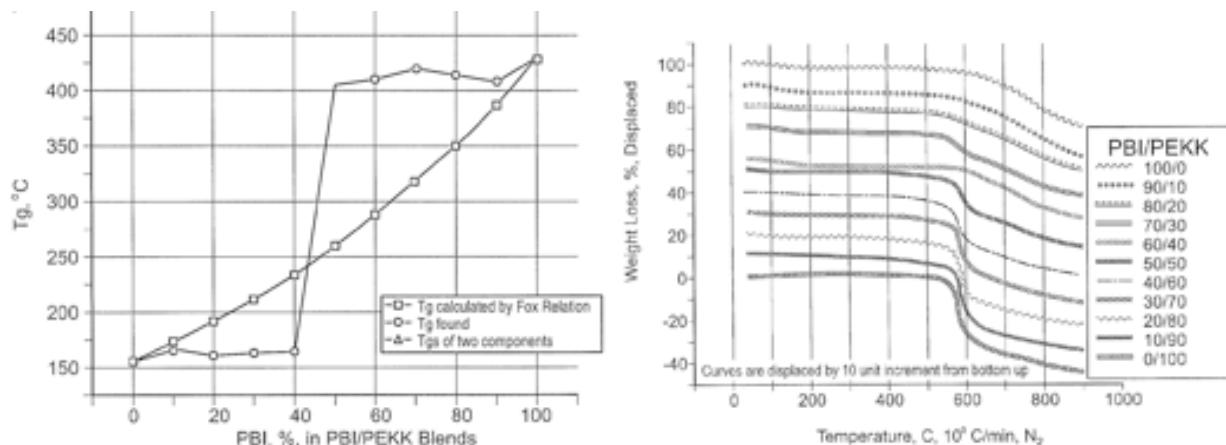


Fig. 4. Thermal resistance properties represented on curves of PBI polymer blends with PEKK. Curve on left is the change in Tg vs. PBI content in blends of PBI:PEKK. Curve on right shows the inflection in weight loss from TGA testing on PBI:PEKK blends [8].

From the properties observed from mixtures, it is possible to achieve increased Tg and reduced weight loss at high temperatures. By preferentially shifting the weight percent in a manner that reflects a majority of PBI, the final mixture begins to reflect the same properties.

1.2 Solutions

PBI polymer is an amorphous thermoplastic that may be easily dissolved into aprotic solvents such as n,n-dimethylacetamide (DMAC), dimethylsulfoxide (DMSO), and n-methylpyrrolidone (NMP). PBI polymer is produced in a coarse powder form, classified as 0.8 IV (intrinsic viscosity). Solvent mixtures of PBI may be prepared by adding to the chosen solvent, heating, and mixing. The solution requires ionic stabilization by the addition of lithium chloride (LiCl) or similar. Non-corrosive applications may consider the use of lithium nitrate (LiNO₃). Typical concentrations of ionic materials are <2% LiCl, or <0.5M. PBI polymer solutions are available as 26% in DMAC with LiCl and 10% in DMAC without LiCl [4].

1.3 Coatings

Coatings of PBI polymer are applied to various substrates to offer protection from aggressive conditions. Solutions of PBI use room temperature casting methods followed by a cure. Solutions are composed of PBI polymer dissolved in an organic solvent. The coating is applied and then evaporated during a rapid post cure process.

It is well known that the observed properties of a coating do not always represent the bulk properties of a particular substance. This is especially true for thin coatings of a few microns or less where the chemistry of the substrate may be reflected in the final material. Nevertheless, it is

possible to prepare thin coatings that perform as protective barriers. Coatings produced with PBI provide high thermal resistance and protect from the combination of heat, moisture, and chemicals. PBI has also been proven useful in high vacuum plasma chambers where it is especially resistant to oxidative and thermal aggressive conditions. Coatings of PBI and the combinations with other polymers have been shown to reduce friction on steel. Coatings that are applied in a planarization manner will reduce the R_q value of roughness and coefficient of friction (COF).

PBI has been proven useful in high vacuum plasma chambers to increase the life of seals, gaskets, and other wearable components. PBI materials are especially resistant to oxidative and thermal aggressive conditions found in plasma equipment. Coatings of PBI polymer on chambers and tooling are an especially good means to extend equipment wear.

1.3.1 Step-Wise Process

PBI coatings can be applied to a wide range of substrates, including steel, aluminum, glass, Si, quartz, and other ceramics and metal alloys. In general, successful PBI coatings are achieved using a three (3) step process:

1. **Substrate preparation** – cleaning and passivating the substrate to ensure good adhesion with minimal chemical interaction.
2. **Coating** – solution identification and adjustment, where necessary, depending upon the choice of application method. Mixture condition is important to ensure the achievement of substrate wetting, desired thickness, and uniformity.
3. **Curing** – proper fixing and condensing of the coating onto the surface to conform or planarize the surface.

The success of any coating process depends upon the substrate preparation. This includes the removal of surface contamination, debris, particles, and surface passivation. In the case of metals, this will enhance chemical interaction between the PBI polymer and the substrate, while reducing oxidative interaction with the substrate while curing in air (Table 1).

Table 1. Substrate preparation (cleaning, left) and cure schedule (right).

Substrate	Cleaning	Passivation	Step	Temp (°C)	Time (min)
Copper	Acid/Aalkali	Triazole	1	90-110	<5
Steel (high carbon, etc.)	Alkaline	Phosphate, Borate	2	175-250	<5
Aluminum	Neutral or mild alkali	-none-	3*	250-325	<5
Stainless (304, 316, etc.)	Alkaline	Phosphate, Borate			

* high temperature for outgas requirements

Ceramics and oxide forming metals (i.e. aluminum, silicon, titanium, etc.), commonly require only a washing step (no passivation). PBI coatings are cured by evaporative means to drive off remaining solvent, leaving the condensed polymer (Table 1). The cure conditions noted here do not apply to UV cure practices.

1.3.2 Inspection

Several practices are recommended to ensure that the PBI polymer coating is uniform with high adhesion. Values of thickness, adhesion, and thermal resistance may be different for every industry and application.

Many approaches exist for measuring thickness, including a simple spot micrometer or a more accurate scanning profilometer. Adhesion tests are performed on coated parts using a modified tape-pull test (ASTM 3359). The modification may use a variation of crosshatch dimension and/or tooling. The general approach to rapid adhesion tests is shown below.

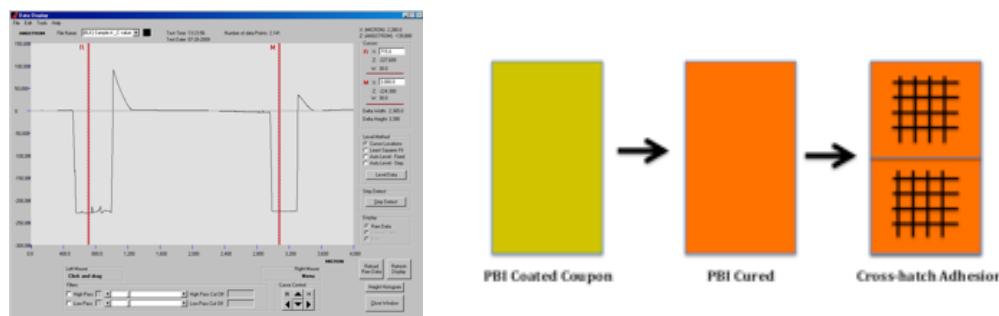


Fig. 5. Profilometer test using a trench scan of a coating on glass or similar hard substrate.

2. EXPERIMENTAL

2.1. Materials

For subsequent analytical testing, quartz substrates as are chosen and prepared at Daetec along with 100-200 mm (4-8") silicon wafers (1-0-0, ~525 μm) re-manufactured from Wollemi Technical, Inc. (Taiwan, www.wollemi.com.tw). Materials used include commercially available spin-coated adhesives and other developmental products produced at Daetec [9]. UV-cure applications are conducted with n,n-dimethylacrylamide (DMAA) available from San-Esters and various photoinitiators under the tradename *Irgacure*, available from BASF. Solvents and other chemicals considered to be common to a development laboratory are available.

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 [10]. Where applicable, equipment settings include a 5 mg stylus load, minimum 4 mm distance, and speed of 0.5 mm/sec. For cleaning tests, a Hg probe using a dot and ring contact, model 802B-150, an HP 4140B picoammeter source supported by an MDC measurement system with an I-V plotting program @ 10 mv steps from 0-1V [11]. Typical I-V plots are produced to compare trends and to study breakdown voltage of the protective film. Analytical equipment used in material characterization includes SEM (Hitachi 4700), Energy dispersive X-ray Spectroscopy (EDS), FTIR with ATR (Spectrum 100, DGTS detector, ZnSe coating accessory, Perkin-Elmer www.perkinelmer.com). 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 (Uvitron International, www.uvitron.com).

3. RESULTS

PBI polymer is prepared in DMAC (6-13%) and spin-coated onto silicon wafers cured according to Table 4 and measured for thickness. A second set samples containing a reconstituted form of PBI polymer is prepared as a fine powder. The “recon” powder form of PBI is used for non-DMAC solvents or when performing UV curing, using the process indicated in Fig. 6.

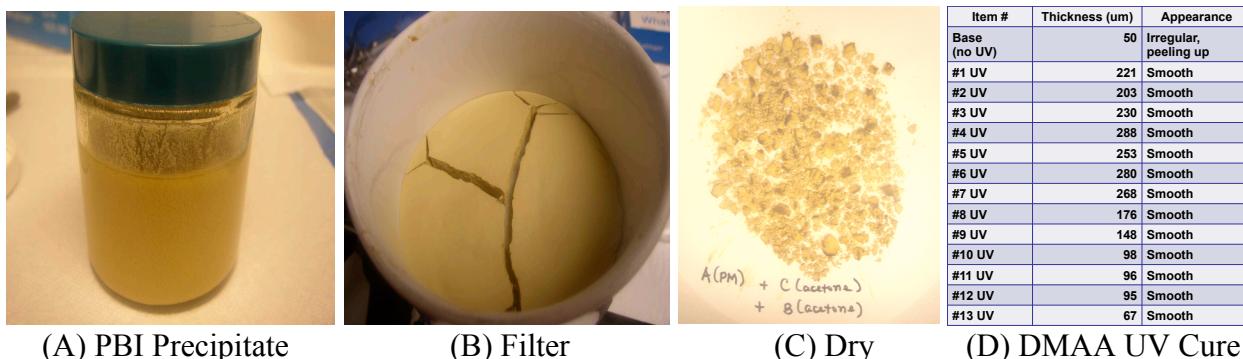


Fig. 6. Process of preparation of PBI “recon”, a reconstituted version of PBI for use in UV applications. PBI dope (26% in DMAC) is mixed with a non-solvent to begin precipitation (A). The precipitate is filtered and washed with additional non-solvent (B), removed and dried (C), and worked-up into DMAA ~10% and UV cured (D). PBI cured on glass is >250um thick.

As described in Fig. 6, PBI is UV cured by using “recon” diluted into n-n-dimethylacrylamide (DMAA) ~10% solids with 5% Irgacure 2022 relative PBI polymer, coated onto glass, and cured by UV at 60sec, followed by thermal outgas 250C, 5min. DMAA is used with applications where UV cure followed by thermal is conducted for thick coatings. UV initiators include common free-radical based systems as Irgacure 2022 (BAPO/ α -hydroxykeone). Thickness of evaporative coated substrates are shown next to the thermal stability of UV cured coatings (Figs.7&8)

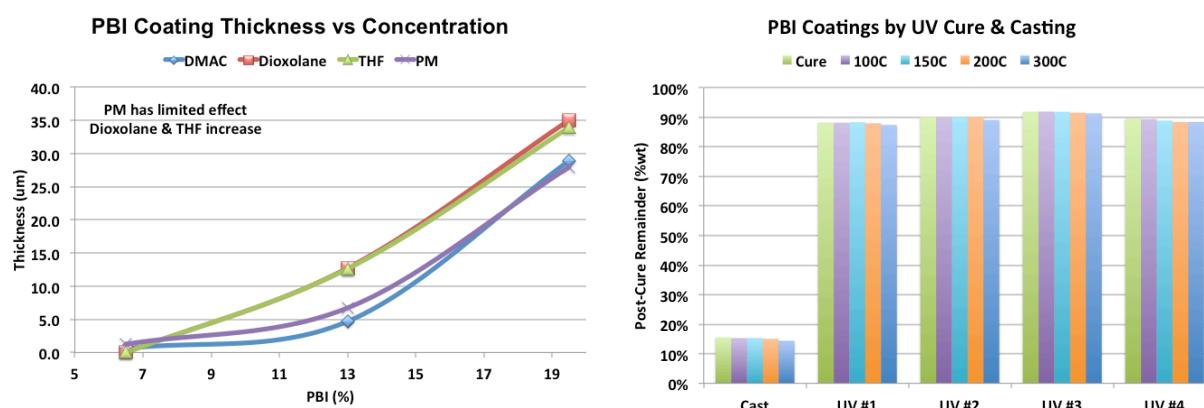


Figure 7. Spin-coating curves showing relationship to PBI % (i.e. 13-19%) and thickness to 35um. UV-coating bar chart indicating PBI polymer mixture stability to 300 °C of similar thickness >30um.

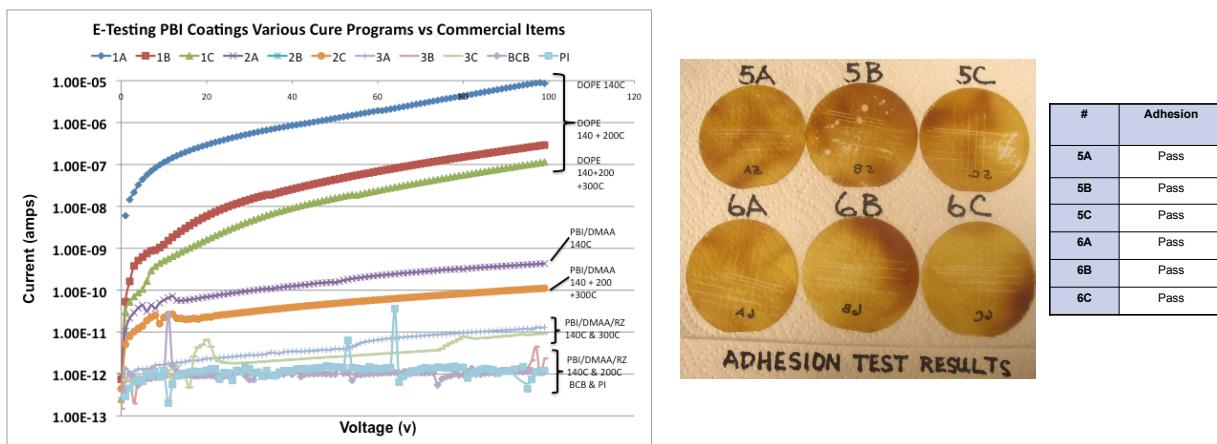


Fig. 8. UV-cured PBI coatings showing electrical properties (left) and adhesion tests (right). Electrical results suggest a very low current (high dielectric value) for curves in lower region of the I-V plots. The adhesion tests all pass the modified ASTM method, a common observation for UV-cured PBI coatings.

The addition of barrier materials are used to stop migration of gaseous by-products in any coating. Non-outgas coatings are desired for sensitive applications such as electronics or aerospace. Barrier substances exhibit low permeability as expressed as the measured gas passing through a specific polymer film of given thickness per day at 1 atm pressure ($\text{cm}^3\text{-ml/day-atm}$). Barrier polymers are macromolecules, which exhibit the ability to significantly restrict the passage of gases, vapors, and liquids [12]. They are widely used in the packaging industry for food preservation and other protection. Literature graph of permeabilities to different gases and an experiment with PBI coatings with the addition of barrier polymers (Fig. 9).

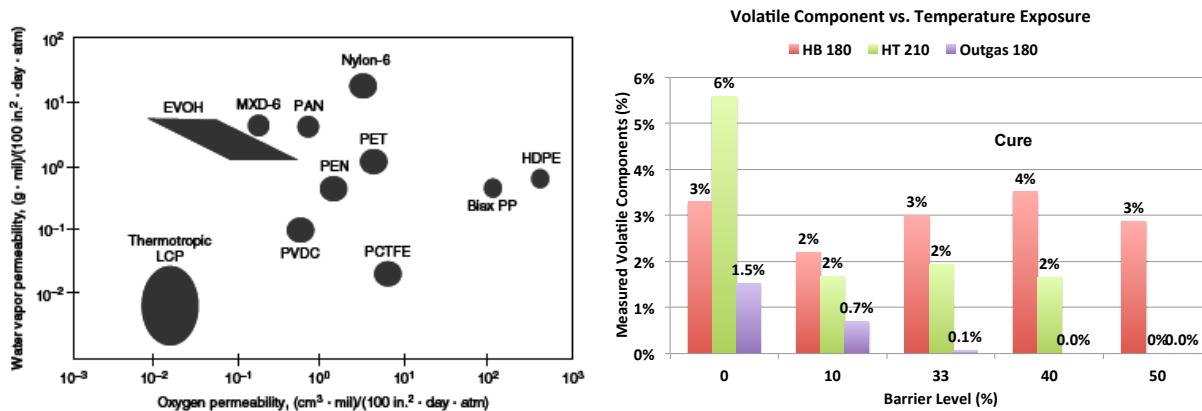


Fig. 9. Barrier polymer data indicating which water vapor and O₂ permeabilities are preferred over others (lower left is preferred), excerpt with permission [12]. The graph (right) represents low outgas as the concentration of barrier polymer exceeds 10% in a PBI mixture.

4. CONCLUSION

This paper presents data and information for achieving PBI-based coatings. This information

includes formulating, processing, and inspection. PBI is a versatile polymer chosen for its thermal resistance and other properties, including adhesion, electrical insulation, and barrier properties. The data in this paper suggest that many coating thicknesses can be achieved, even >300um within 60sec under a UV curing lamp. Using a new formulating practice with the “recon” form of the PBI, the system can be worked up into DMAA and become photoactive. Combining thermal resistance with rapid curing will encourage more use of PBI in coatings.

5. REFERENCES

1. U.S. Paint and Coatings Industry Market Analysis 2006-2011.
2. Specialty coatings for semiconductor applications, SEMI, Global Materials Market Survey, July 2011.
3. E.J. Powers and G.A. Serad, History and Development of Polybenzimidazole, Symposium Proceedings of the American Chemical Society, NY, 1986.
4. PBI is a trade name for polybenzimidazole, PBI Performance Products, Inc., www.pbiproducts.com.
5. J.Moore and J. Pettit, Extreme Temporary Coatings and Adhesives for High-Thermal, Low-Pressure, and Low-Stress 3D-Processing, *Proc. Of Internat. Microelectronics and Packaging Society (IMAPS)*, Long Beach, 2011.
6. U.S. Patent No. 5,066,697, Sandor et. al., Nov. 19, 1991.
7. U.S. Patent No. 5,674,614, Onishi et. al., Oct. 7, 1997.
8. U.S. Patent No. 7,915,351 B2, Dawkins et. al., March 29, 2011.
9. Spin coatings, adhesives, encapsulants, cleaners, equipment, and processing designs utilizing a wide range of cure approaches including evaporative, photo, and thermal are from Daetec, LLC, www.daetec.com.
10. Series XP, AFP, and Xi, are contact and non-contact profilometers as produced by Ambios Technology, Inc., www.ambiostech.com.
11. Model 802B-150 Hg-Probe is produced by Materials Development Corporation, www.mdc4cv.com.
12. S. Dhoot, B. Freeman, and M. Stewart, *Barrier Polymers*, Ency. Poly. Sci. Tech., March (2002).