

McNair Scholars Journal

Volume 10, Issue 1

2006

Article 10

Advanced High Temperature Semiconductor Packaging Material Based on PBO Foam Technologies

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Brandi Murrell

Abstract

The lack of qualified packing systems above +250°C is a major obstacle in fully realizing the potential of advanced high performance semiconductor materials in military and commercial systems. It is therefore necessary to produce a packaging material able to withstand higher operating temperatures and increased thermomechanical capability with the semiconductor substrate. In attempt to do this, a novel foam material produced via the synthesis of PBO (poly(p-phenylene- 2,6-benzobisoxazole)) was developed. Examination of the resulting foam demonstrates lightweight, non-flammable, non-toxic, shock resistant foam with thermal stability from -260°C to +600°C.

KEYWORDS: Semiconductor, PBO, Polybenzoxazoles, Polymeric Foam

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ABSTRACT

The lack of qualified packing systems above +250°C is a major obstacle in fully realizing the potential of advanced high performance semiconductor materials in military and commercial systems. It is therefore necessary to produce a packaging material able to withstand higher operating temperatures and increased thermomechanical capability with the semiconductor substrate. In attempt to do this, a novel foam material produced via the synthesis of PBO (poly(p-phenylene-2,6-benzobisoxazole)) was developed. Examination of the resulting foam demonstrates lightweight, non-flammable, non-toxic, shock resistant foam with thermal stability from -260°C to +600°C.

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Introduction

Semiconductors are materials with an electrical conductivity that increases with increasing temperature. Also, their conductivity is an intermediate between that of an insulator and a metal. Semiconductors are found in a variety of places and are at the core of electronics. Any device that is computerized or uses radio waves depends greatly on semiconductors. The most common material used in semiconductors is silicon.

The use of silicon and other current technologies in semiconductors are relatively effective; however, critical obstacles have prevented the full realization of advanced high performance semiconductor materials in military and commercial systems. The most significant obstacle that has limited this full realization is the lack of qualified packaging materials above +250°C. This study attempts to address the issue of increasing operating temperatures by concentrating on two main tasks: (1) alleviating thermal stressor thus allowing packaging material to withstand higher operating temperatures and (2) increasing thermomechanical capability with the semiconductor substrate, for example thermal shock resistance.

A semiconductor works as a complete system and is only as effective as its weakest component.¹ Currently the weakest component in the semiconductor system is the packaging material which leads to the purpose of this particular study. This study attempted to produce a low density porous material to address the limitations facing current semiconductor technology. Low density porous materials, otherwise known as foams, were first developed in the United States in the mid 1930's. Despite the outstanding properties of polymeric foams, such as excellent thermal and acoustic properties, high



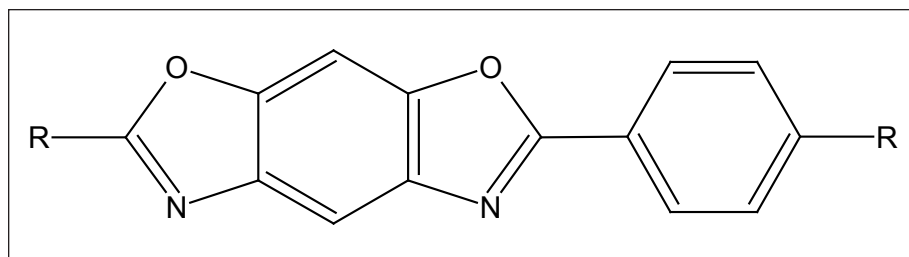
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weight-to-strength ratios, and cost effectiveness, these materials suffer from certain disadvantages. Early polymeric foams have been limited in their use by temperature constraints, poor fire resistance, toxic fume generation, thermal aging and degradation, friability, and susceptibility to thermal cycling and ultra violet light.²

Ultimately this study attempted to produce an advanced high temperature semiconductor packaging material based on PBO technologies. Polybenzoxazoles (PBOs) are rod-like polymers with extended chain conformations. These polymers, like aromatic polyimides, have excellent thermal and oxidative stability as well as good hydrolytic and solvent resistance.^{3, 5-8} PBOs are widely used as high performance polymers and molecular composites due to their superior stability and mechanical properties.⁴ The origin of PBO is rooted in the pursuit to develop a novel plastic material with the same performance as metals while maintaining the ductility of non-metallic materials by the scientist at the Polymers Branch of the US Air Force Materials Directorate Laboratories in Dayton, Ohio. This new material was designed to be an alternative to graphite fiber in the areas of low weight-to-strength ratio, stiffness, environmental resistance, and better elongation and radar transparency. After many years of basic research, it was found that rigid rod polymers had the desired physical and chemical parameters. Thus, PBO was successfully synthesized.^{4,14}

At present PBO is only found in fiber form where it is used in bulletproof vests, protective suits for firefighters, lightweight armor for military personnel, and rip cords of parachutes. The fiber is classified as "high performance" and is unique in that it has both superior thermal and tensile properties greatly desired in many aerospace and electronic applications.^{4,14} The resonance stabilization allotted by the

Figure 1. Chemical structure of (poly(*p*-phenylene-2,6-benzobisoxazole)).



aromatic structure of PBO lends itself to an increase in bond strength which contributes directly to its heat resistance. Solubility is yet another characteristic where PBO displays superiority. PBO is insoluble in most all solvents and is in fact only soluble in polyphosphoric acids. This feature adds to the overall mechanical strength of PBO; however, it also makes for difficult processing and limits commercial applications.^{4,14} For this reason PBO was produced in situ for this study.

EXPERIMENTAL

Nitration of Bisphenol A

Bisphenol A (10.290g) was dissolved in acetone (50.0mL) at room temperature in a 250mL Erlenmeyer flask with stirring. The mixture was then cooled to 0°C. HNO₃ (8.5mL) was added drop wise over a time period of 30 minutes. The mixture was then allowed to stir and warm to room temperature for one hour while a yellow/orange precipitate formed. Afterward distilled water (25mL) was slowly added to mixture. The resulting solid was collected by vacuum filtration and washed with 3:1 mixture of acetone: DI water. The solid was allowed to air dry for approximately 24 hours. After drying the solid was examined by Infrared (IR) and Nuclear Magnetic Resonance (NMR) spectroscopy (10.883g, 78.04% yield).

¹³C NMR: δ = 30.4, 42.1, 120.3, 121.9, 133.1, 137.0, 141.8, 153.8

¹H NMR: δ = 10.51 (s, 2H), 8.03 (d, J=2.46 Hz, 2H), 7.32 (dd, J=8.79 and 2.49 Hz, 2H), 7.06 (d, J=8.79 Hz, 2H),

1.65 (s, 6H)

IR: R-NO₂ peaks 1530cm⁻¹ and 1322cm⁻¹

Mp: 132.9°C – 133.6°C

Reduction of Bis(o-nitrophenol)

Bis(o-nitrophenol) (7.180g) was dissolved in 5%NaOH (400mL) with stirring in a 1000mL Erlenmeyer flask. Solution was then heated. Once hot Na₂S₂O₄ (45.573g) was added SLOWLY to solution. The solution was then neutralized with glacial acetic acid. Once neutralized the mixture was cooled to room temperature then placed in ice bath. Crystals formed and were filtered by vacuum filtration and washed with cold water. After drying approximately 24 hours the crystals were examined by IR and NMR spectroscopy. This process of nitration and reduction was repeated with various starting products to produce four distinct diamine monomer products (4.878g, 83.70% yield).

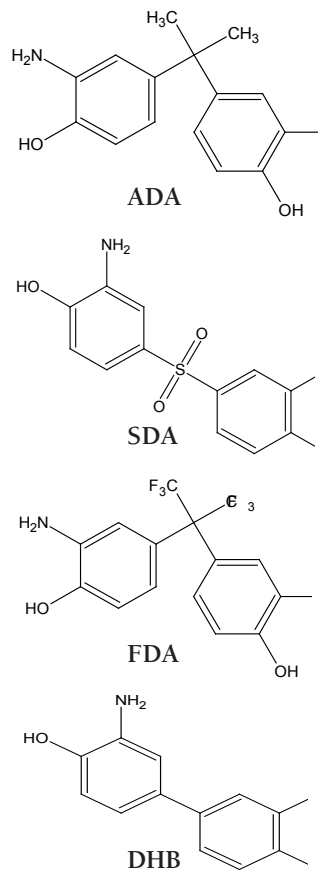
¹³C NMR: 31.6, 41.5, 114.02, 114.05, 114.7, 136.1, 142.2, 148.8

¹H NMR: 8.74 (s, 2H), 6.49 (d, J=7.98 Hz, 2H), 6.39 (d, J=2.46 Hz, 2H), 6.29 (dd, J=8.22 and 2.20 Hz, 2H), 4.33 (s, 4H), 1.44 (s, 6H)

IR: R-NH₂ peaks 3411cm⁻¹ and 3325cm⁻¹

Mp: ###.°C - ###.°C

Figure 2: Synthesized Diamine Monomers



Production of PBO foam

In an aluminum reactor ADA (42.57g), ODA (33.0g), and ODPA (48.36g) were added. THF (252.0g) and methanol (64.0g) were then added to the mixture and stirred for two hours at 60°C. After two hours ODPA-TA (60.31g) was added to the mixture and the temperature was raised to 85°C in order to concentrate the sample. Mixture was allowed to stir for an additional hour. At the conclusion of this process the resultant dialkylester-diacid diamine salt solid was ground into powder and heated at 125°C for 15 minutes. Powder was then heated again at 126°C to form friable balloons. These balloons were produced from a variety of monomer combinations

and then sifted for uniformity to an average size of 50-300µm. Once sifted balloons were then placed into a mole for further heat treatment. Various reaction times and temperatures were investigated to produce the most thermally stable foam article.

Figure 3: General Reaction Scheme for PBO Production

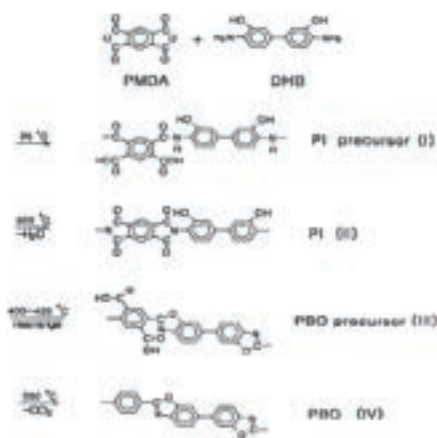


Figure 4: IR Spectroscopy of ADA Foam Sample

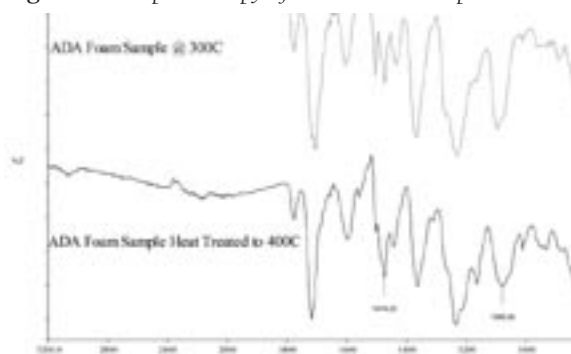


Figure 5: ADA Comparison by Thermogravimetric Analysis (TGA)

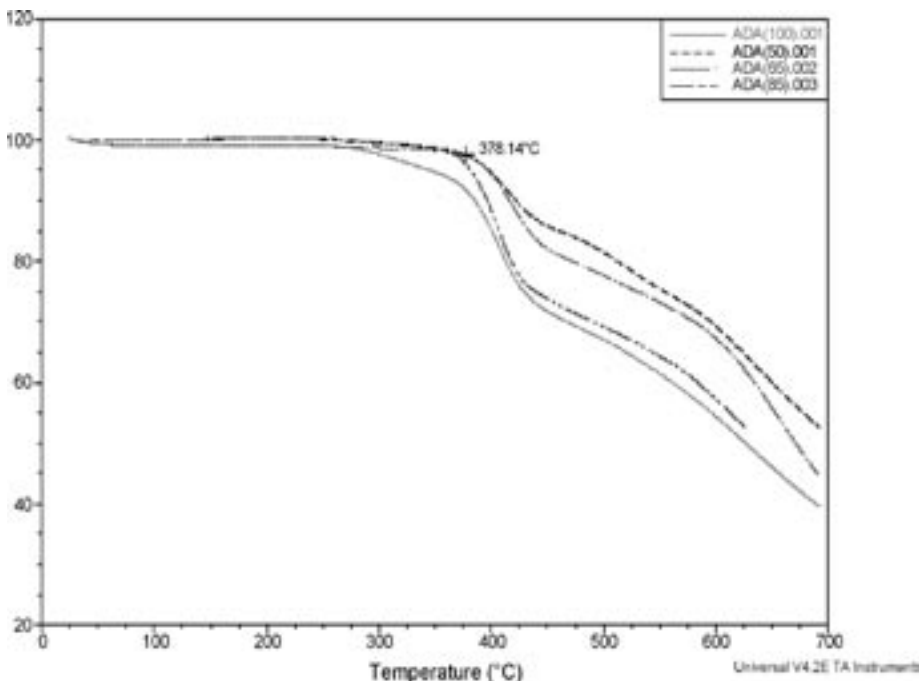
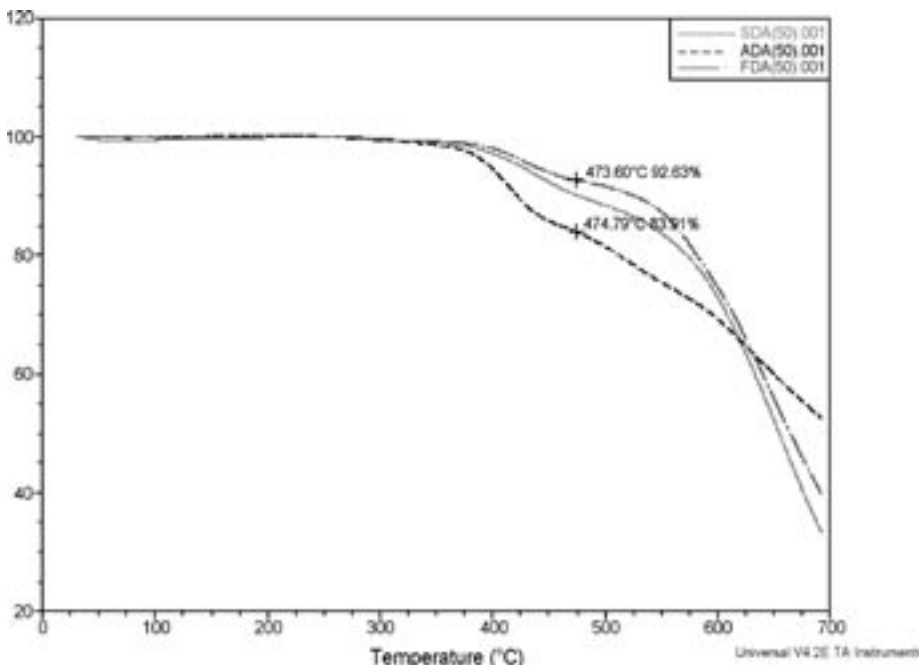


Figure 6: TGA Monomer Comparison of FDA, SDA, and ADA



Results and Discussion

The thermal conversion from PBO precursor to PBO by way of polyhydroxyimide was confirmed by IR spectroscopy. By examining the foam product in its polyhydroxyimide stage and then in its suspected polybenzoxazole stage, we were able to see the difference that takes place due to thermal conversion at 400°C. The results of the polybenzoxazole stage showed clear peaks at ~1470cm⁻¹ and ~1080cm⁻¹, which is consistent with previous literature values of PBO formation.

Further testing was administered to analyze weight percent composition and temperature using Thermogravimetric Analysis (TGA). Using various combinations of ADA we expected a decrease in weight composition at ~400°C due to the thermal conversion to PBO which is marked by the loss of CO₂. Results were consistent with expectations, showing thermal rearrangement at 378.14°C. However, all ratios of ADA showed further weight decomposition beyond 400°C.

With the continued weight decomposition beyond 400°C in all ADA samples further investigation of alternate synthesized diamine monomer products was warranted. Using Thermogravimetric Analysis samples of FDA, SDA, and ADA were analyzed to compare thermal stability. As in previous TGA analysis weight percent composition was measured as a function of temperature. The results showed a thermal rearrangement to PBO at ~400°C; however, SDA and FDA continued to be thermally stable more so than the ADA samples. FDA displayed the greatest thermal stability, possessing 92.63% composition at a temperature of 473.60°C.

Conclusion

This study, in accordance with previous research, confirms that PBO forms at approximately 400°C ± 20°C. However, unlike our predecessors

we were able to successfully produce PBO as a foam article. Using various monomer combinations it was concluded that ADA showed thermal decomposition over 400°C. Also SDA and FDA showed thermal stability at 500°C with FDA being the most thermally stable overall. This finding has inspired further investigation of the FDA monomer as a possible starting material for PBO production.

This study was supported by the National Science Foundation, Dreyfus Foundation, Spacecraft Component Technologies Branch Space Vehicles Directorate, Air Force Research Laboratory, and the McNair Scholars Program.

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