

E. In Situ Polymerization of Cyclic Butylene Terephthalate(CBT) Oligomers with Conductive fillers for Thermal Management:

Key issues:

Thermal management

Macrocyclic oligomers with ultra-low melt viscosity

PBT copolymers with

Thermal conductivity

Composites

This research is funded by Honeywell Corporation and the Florida High Tech Corridor.

NOTE:

Honeywell and Julie Harmon have signed an agreement with Cyclics Corp. in Schenectady, NY., and as a result, we are able to purchase and use Cyclics's macrocyclic butylene terephthalate (CBT) oligomers for thermal management. We also acknowledge the support of Cool Polymers in Warwick, RI. For the generous assistance in measuring thermal conductivities of our composites.

The original purpose of this endeavor was to develop polymeric composites used as underfills in fiber optic gyros. Encouraging results greatly broadened the applications for these materials. The composites must exhibit high thermal conductivity (TC), cure with a minimal or, no exotherm, resist dissolution and function at temperature extremes. Boron nitride is a typical filler for these systems, as it has excellent thermal conductivity, 250-300 W/mK (49). We have found that inexpensive diamond material is available; this filler has a thermal conductivity $> 1,500$ W/mK (50). We are also investigating the use of carbon fibers and weavings; these materials exhibit an intrinsic fiber TC as high as 913 W/mK (51).

Earlier work with Honeywell focused on the development of boron nitride/epoxy composites. We produced some moderately effective systems and this broadened our insight into the problems encountered with thermal management materials. As a result, we turned our attention to systems that are more effective and more easily processed. We are developing novel underfills based polymerization cyclic butylene terephthalate monomers (52). We are the only group that we are aware of that is using these materials for underfills. The cyclic PBT monomers, unlike commonly used epoxies, do not exotherm upon polymerization. This eliminates a significant problem encountered with epoxy systems, since, high polymerization exotherms destroy solder joints on the circuit board. The polymerization scheme is given in fig. 14.

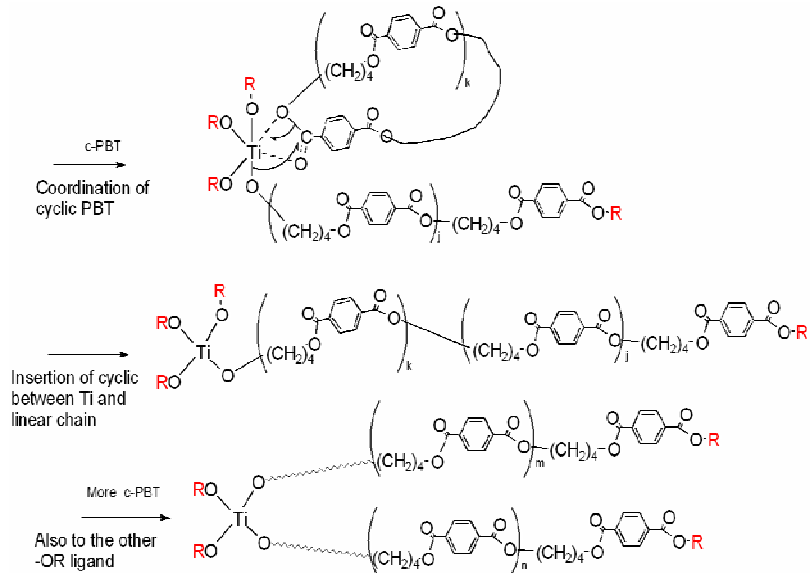


Figure 1

Another group examined the use of PBT in underfills, but the fillers were compounded into the polymer base (53). Since compounding breaks the filler particles TC's were quite low. The cyclic monomers that we used exhibit ultra-low viscosity when melted. This means that high amounts of fillers can be added to the system without processing problems.

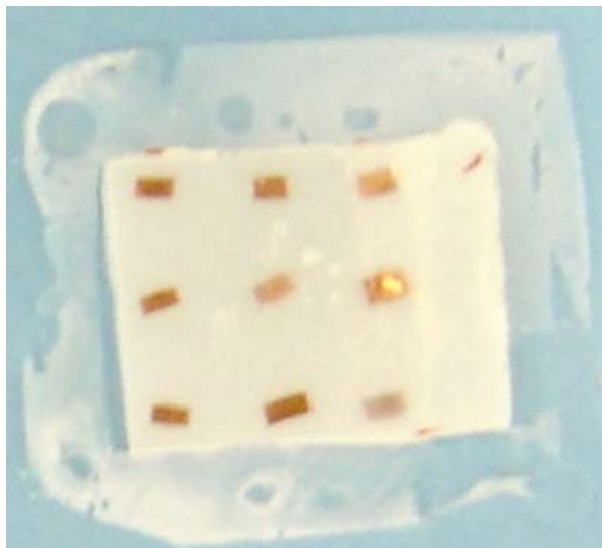


Figure 2 An image of an underfill prototype

The cyclic monomer material was melted and filled with 40 wt % boron nitride. We applied a vacuum under heat and were able to draw the material through 7 mil copper spacers added to simulate the thickness of the solder (Fig. 15). The temperature was increased and curing ensued. Encouraging results prompted Honeywell, Inc to file a patent application with us (54).

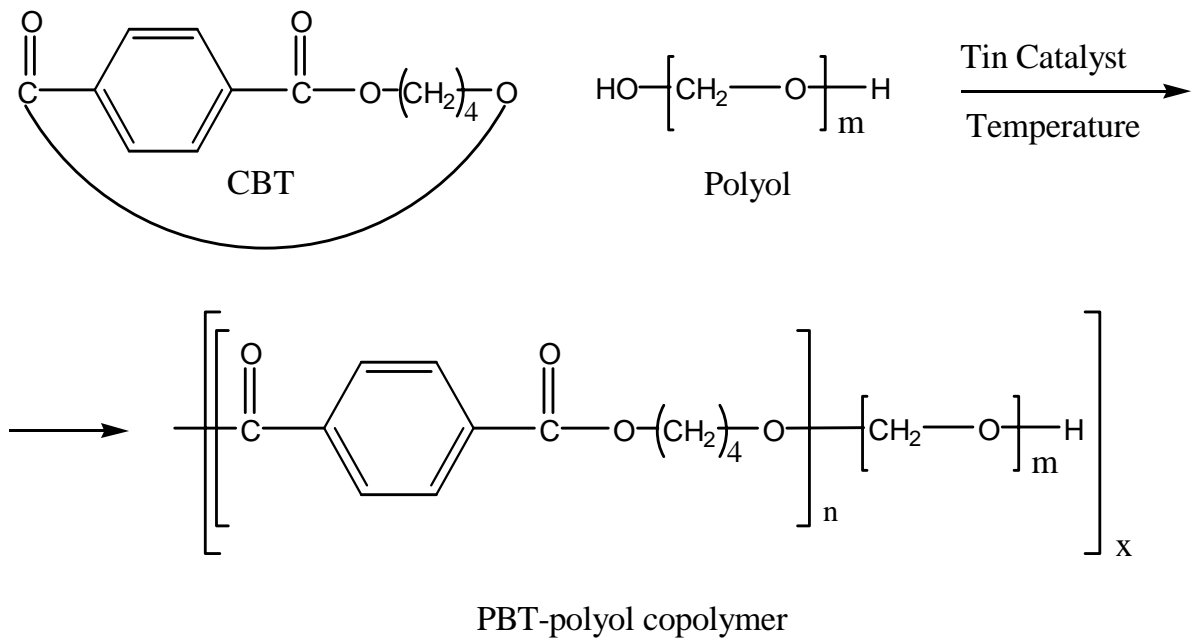
The target thermal conductivity for an efficient underfill is 1.3 to 4 W/mK in the plane of the sample. (55). One of our 40% diamond composites, tested by Cool Polymer, Inc. in

Warwick. Cool Polymers measured a value of 4.21 W/mK in the plane of the specimen; this exceeded our expectations. The highest value that we have seen recorded in the literature, estimated from a plot of thermal conductivity versus filler content, was just under 4 W/mK (56).

We published a detailed study characterizing the thermal and mechanical properties of these systems (52).

We have also expanded the window between the crystalline melting point(145°C) and polymerization temperature of CBT by blending it with low molecular weight polyols. For example, the addition of poly(tetrahydrofuran):

- 1) This particular low molecular weight polyol has melting point of 15°C and when blended with CBT decreases the melting point. This allows the system to flow at lower temperatures, preventing damage to the circuit board.
- 2) The polyol allows the melting point of the resulting copolymer to be adjusted for individual application where reflow is desired.



The following table illustrates the extent to which the thermal properties of the system can be “dialed in” to produce tailor made copolymers:

	Moles of Polyol	Moles of CBT	T _g Polyol	T _m Polyol	T _g PBT	T _m PBT
Pure PBT	0	1	---	---	---	228
Pure Polyol	1	0	-32.2	15.37	---	---
Pure CBT	0	1	---	---	---	134-144
CFC 01	1.5	1	-66.8	10.1	---	184-198
CPR 01	1.5	1	-63.6	---	35.9	194.9
CFC 02	3.1	1	-67.4	8.3	---	152-170
CPR 02	3.1	1	-67.0	-1.6	66.4	166.6

CFC 03	6.0	1	-66.9	-1.0	28.3	125.8
CPR 03	6.0	1	-68.9	3.52	---	129.1
CBT 02A (no catalyst)	3.1	1	-67.9	17.4		110-128

Our current and future work focuses on the mechanism of heat transport in these materials. Phonons transfer heat in nonmetal materials and any phonon scattering will decrease heat transfer efficiency. Xu et. al. (57) discussed three methods of decreasing phonon scattering, forming conductive filler networks, increasing the size of the filler, and minimizing flaws at the filler-polymer interface. We are pursuing the use of fibrous nanocarbon fillers to form conductive filler networks. Some recent interest in this topic has appeared in a patent application (58).

References:

1. "PMP/CNT Composites", J. P. Harmon and L. Clayton, USF Provisional Patent Application, 04A044PR.
2. "Transparent Polymer Nanotube Composites," J. P. Harmon, L. Clayton, P. Muisener, Utility Patent Application, 10/604,735.
3. "Transparent PMMA/SWNT Composites with Increased Dielectric Constants", L. Clayton, T. Gerasimov, M. Meyyappan and J. P. Harmon, Advanced Functional Materials, Vol. 15, No. 1, 101, (2005).
4. "Processing of Transparent Polymer Nanotube Composites via Heat, UV Radiation and Ionizing (Gamma) Radiation Using Ultrasonication and Solvent Dissolution", L. Clayton, R. Muisener, J. P. Harmon, A. Sikder, A. Kumar, A. Cassell, M. Cinke and M. Meyyappan, Materials Research Society Proceedings, Vol. 773, M 2.4, (2003).
5. "Transparent Polymer-Nanotube Composites Produced Via UV Radiation, Ionizing Radiation and Heat", L. M. Clayton, J. P. Harmon, M. Meyyappan, M. Cinke, A. Cassell, A. Kumar and A. K. Sikder, Materials Research Society Proceedings, Vol. 697, P9.7, (2002).
6. "Gamma Radiation Effects on the Glass Transition Temperature and Mechanical Properties of PMMA/SOOT Nanocomposites", L. Clayton, T. Gerasimov and J. P. Harmon, Polymer Bulletin, Vol. 52, 259-266, (2004).
7. "Probing Multi-walled Nanotube/PMMA Composites with Ionizing Radiation" Shelli R. Tatro, L. Clayton, Patricia A. O'Rourke Muisener, Apparao M. Rao, and J.P. Harmon. Polymer, Vol. 45, No. 6, (2004).
8. "Using Carbon Nanotubes to Detect Polymer Transitions", Q. Zhao, J. R. Wood, Journal of Polymer Science: Part B: Polymer Physics, Vol. 39, 1492, (2001).
9. "Effects of Gamma Radiation on Poly (methyl methacrylate)/ Single-wall Nanotube Composites," O'Rourke Muisener, P., Clayton, L., D'Angelo, J., and Harmon, J. P, Journal of Materials Research, Vol. 17, No. 10, 2507, (2002).
10. "Ionizing Radiation Effects on Interfaces in Carbon Nanotube-Polymer Composites," Julie P., Muisener, P. A. O., Clayton, L., D'Angelo, J., Sikder, A. K., Kumar, A., Meyyappan, M., and Cassell, A. M., Materials Research Society Proceedings, Vol. 697, P9.7, (2002).

11. "Ionizing Radiation Resistant Carbon Nanotube/Polymer Composites," J. P. Harmon, P. Muisener, L. Clayton and J. D'Angelo, Patent filed. USF Ref No: 01B090P.
12. Background information in NASA Research Announcement: NRA 03-OBPR-07, p. A-1.
13. "Synthesis and Magnetic Properties of Polymer Nanocomposites with Embedded Iron Nanoparticles", J. L. Wilson, P. Poddar, N. A. Frey, H. Srikanth, K. Mohomed, J. P. Harmon, S. Kotha, and J. Wachsmuth, Journal of Applied Physics, Vol. 95(3), 1439-1443, (2004).
14. "In-Situ Synthesis and Magnetic Properties of Polystyrene/Polypyrrole Nanocomposite Materials With Uniformly Dispersed Nanoparticles", H. Srikanth, P. Poddar, J. L. Wilson, K. Mohomed and J. P. Harmon, Materials Research Society Proceedings, Fall 2003, Vol. 788, 1.3.42.1, (2004).
15. "In-Situ Syntheses and Performance of Titanium Oxide/Poly (Methyl Methacrylate) Nanocomposites", U. C. Bandugula, L. M. Clayton, J. P. Harmon and A. Kumar, Journal of Nanoscience and Nanotechnology , Vol. 5(5), 814, (2005).
16. "Future Nanotechnology Developments for Automotive Applications", H. Prestling and U. Konig, Materials Science and Engineering, C 23, 737 (2003).
17. "Polymer-TiO₂ Nanocomposites: A route Towards Visually Transparent Broadband UV filters and High Refractive Index Materials", Macromolecular Materials Engineering, 288, 44 (2003).
18. "Preparation and Optical Absorption of Dispersions of Nano-TiO₂/MMA (Methacrylate) and Nano-TiO₂/PMMA", Materials Research Bulletin, 34, 701 (1999).
19. <http://www.jewellerycatalogue.co.uk/diamonds/simulants.htm>.
20. "Electric and Optical Properties of the 90° Ferroelectric Domain Wall in Tetragonal Barium Titanate", H. Chaib, F. Schlaphof, T. Otto and L. M. Eng, Journal of Physics, Condensed Matter, Vol. 15, 8927 (2003).
21. "Highly Nonlinear Bismuth-Oxide Fiber for Smooth Supercontinuum Generation at 1.5 μm", J. T. Gopinath, H. F. Shen, H. Sotobayashi and E. P. Ippen, Optics Express, Vol. 12(23), 5697 (2004).
22. "Comparative Study of Lead Borate and Bismuth Lead Borate Glass Systems as Radiation shielding Materials", Nuclear Instruments and Methods in Physics Research B, 225, 305 (2004).
23. "Polyamide Pseudorotaxanes, and Catenanes Based on Bis (50carboxy-1, 3-phenylene)-(3x+2) Crown-x Ethers", H. W. Gibson, D. S. Nagvelar, N. Yamaguchi, S. Bhattacharjee, H. Wang, M. J. Vergne and D. M. Hercules, Macromolecules, Vol. 37, 7514 (2004).
24. "Transition-Metal-Templated Synthesis of Rotaxanes and Catenanes: From Small Molecules to Polymers", J-M. Kern, J-P. Sauvage, G. Bidan, and B. Divisia-blohorn, Journal of Polymer Science Part A: Polymer Chemistry, Vol. 41, 3470 (2003).
25. "Metal-Organic Rotaxane Frameworks: MORFs", S. J. Loeb, Chemical Communications, (Cambridge, United Kingdom), Vol. 12, 1511 (2005).
26. "Transition Metal-Complexed Catenanes and Rotaxanes as Molecular Machine Prototypes", J-P. Sauvage, Chemical Communication (Cambridge, United Kingdom), 1507 (2005).

27. "Persistent Interactions Between Hydroxylated Nanoballs and Atactic Poly (2-Hydroxyethyl Methacrylate (PHEMA)), K. Mohomed, H. Abourahma, M. J. Zaworotko and J. P. Harmon, Chemical Communications, 3277 (2005).
28. "Nanostructure Matrix Interactions in Methacrylate Composites", K. Mohomed, T. Gerasimov, H. Abourahma, M. Zaworotko and J. P. Harmon, Accepted for Publication in Materials Science and Engineering, March, (2005).
29. "Hydroxylated Nanoballs: Synthesis, Crystal Structure, Solubility and Crystallization on Surfaces", H. Abourahma, A. Coleman, B. Moulton, B. Rather, P. Shahgaldian, M. M. J. Zaworotko, Chemical Communications, (Cambridge, United Kingdom) 22, 2380 (2001).
30. "Water Structure in Hydroxyethyl-Co-Glycerol Methacrylate Materials", G. Gates, J. P. Harmon, J. Ors and P. Benz, ANTEC 59th Vol. 2, 1898 (2001).
31. "Intra and Intermolecular Relaxations in 2,3-Dihydroxypropyl and 2-Hydroxyethyl Methacrylate Hydrogels", Polymer, Vol. 44, 207 (2003).
32. "2,3-Dihydroxypropyl Methacrylate and 2-Hydroxyethyl Methacrylate Hydrogels: Gel Structure and Transport Properties", Polymer, Vol. 44, 215 (2003).
33. "Interaction Between Water and Hydrophilic Polymers", H. Hatakeyama and T. Hatakeyama, Thermochemica ACTA, 308, 3 (1998).
34. "Water in Hydrogels. 1. A Study of Water in Poly(N-vinyl-2-pyrrolidone/methyl methacrylate) Copolymer", F. Quinn, E. Kampff, G. Smyth, and V. J. McBrierty, Macromolecules, Vol. 21, 3191 (1988).
35. "Mechanical Behavior of Hydroxyalkyl Methacrylate Polymers and Copolymers", J. Janacek, Reviews in Macromolecular Chemistry, Vol. 10, 1, (1973).
36. "Molecular Origin of relaxations in Polymers", J. Heijboer, In Molecular Basis of Transitions and Relaxations, New York: Gordon and Breach Science Publishers Press, 75 (1978).
37. "A Broad Spectrum Analysis of the Dielectric Properties of Poly (2-hydroxyethyl methacrylate)", K. Mohomed, T. G. Gerasimov, F. Moussy and J. P. Harmon, Polymer, Vol. 46, 3847 (2005).
38. "Conductivity Relaxation in a Concentrated Aqueous Electrolyte Solution", J.H. Ambrus, C.T. Moynihan, P.B. Macedo, Journal of Physical Chemistry, Vol. 76(22), 3287-3295 (1972).
39. Anelastic and Dielectric Effects in Polymeric Solids, N.G. McCrum, B.E. Read, G. Williams, and New York: Dover, (1967).
40. "The Dipolar and Conductivity Relaxations in Ionic Conductors" G.P. Johari, K. Pathmanathan, Physical Chemistry of Glasses, Vol. 29(6), 219-224 (1988).
41. "The Merging of the Dielectric α - and β -relaxations in Poly-(Methyl Methacrylate)", R. Bergman, F. Alvarez, A. Alegria, J. Colmenero, Journal of Chemical Physics, 109(17), 7546 (1998).
42. "Dielectric Analysis of Polymers" P. Avakian, H.W. Starkweather, Jr., W.G. Kampert, S.Z.D. Cheng, editor. Handbook of Thermal Analysis and Calorimetry, New York: Elsevier, Vol. 3, pp. 147-164 (2002).
43. "Electrical Conductivity Studies in Hydrogels" P. Pissis, A. Kyritsis, Solid State Ionics, Vol. 97, 105-113 (1997).

44. "Structure-property Relationships in Proton Conductors Based on Polyurethanes", P. Pissis, A. Kyritsis, G. Georgoussis, V.V. Shilov, V.V. Shevchenko, Solid State Ionics, Vol. 136-137, 255-260 (2000).
45. "A New Generation of Ultra-soft, Non-blocking Polyurethanes with Superior Mechanical Properties for Biomedical Applications", K. Kull, T. Gerasimov and J. P. Harmon, submitted to TOPCON 2005 Bounce Back with TPE's Proceedings, Akron Ohio, (2005).
46. "Molecular Relaxations in Ester-Terminated, Amide-Based Dendrimers", S. K. Emran, G. R. Newkome, C. D. Weis and J. P. Harmon, Journal of Polymer Science, Part B: Polymer Physics, Vol. 37, 2025 (1999).
47. "Viscoelastic Properties and Phase Behavior of 12-tert-Butyl Ester Dendrimer/Poly(methyl methacrylate) Blends", Journal of Polymer Science, Part B: Polymer Physics, Vol. 39, 1381 (2001).
48. "Relaxation Processes in Hyperbranched Polyesters", E. Malmstrom, F. Liu, R. Boyd, A. Hult and U. W. Gedde, Polymer Bulletin, Vol. 32, 679 (1994).
49. http://www.advceramics.com/acc/products/polartherm_follers/
50. "Thermal Conductivity Measurements on CVD Diamond", D.J. Twitchen, C. S. Pickles, S. E. Coe, R. S. Sussmann, and C. E. Hall, De Beers Industrial Diamonds (UK) Ltd., Ascot, Berkshire, UK. Diamond and Related Materials, Vol. 10(3-7), 731-735 (2001).
51. The Aerospace Corporation, El Segundo, CA.
52. "Thermal Analysis of Novel Underfill Materials with Optimum Processing Characteristics", Y. Liu, Yi-Feng Wang, T. G. Gerasimov, K. H. Heffner and J. P. Harmon, Journal of Applied Polymer Science, 98, 1300 (2005).
53. "Thermal Conductivity, Thermo-Mechanical and Rheological Studies of Boron Nitride-Filled Polybutylene Terephthalate", H. Y. Hg, S. K. Lau and X. Lu, Materials Science Forum, Vol. 437-438, 239 (2003).
54. "Reprocessable Electrically-Insulating Thermal Management Composite For Electronic Applications," J. P. Harmon, Y. Liu, K. H. Heffner, W. Dalzel and S. Fleischman, Disclosure H0006075, October, (2003).
55. "Predicting, Measuring, and Tailoring the Transverse Thermal Conductivity of Composites from Polymer Matrix and Metal Filler", International Journal of Thermophysics, F. Danes, B. Garnier, and T. Dupuis, Vol. 24, 771 (2003).
56. "Very High Thermal Conductivity Obtained by Boron Nitride-Filled Polybenzoxazine", H. Ishida and S. Rimdusit, Thermochimica ACTA, Vol. 320, 177 (1998).
57. "Thermally Conducting Aluminum Nitride Polymer-Matrix Composites, Y. Xu, D. D. L. Chung and C. Mroz, Composites Part A, Vol. 32, 1749 (2001).
58. "Thermal Conductive Material Utilizing Electrically Conductive Nanoparticles", S. S. Tonapi, H. Zhong, D. L. Simone, R. A. Fillion, . U.S. Pat. Appl. Publ. (2005), 12 pp.