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MODERN PLASTICS: ADVANCES IN SAFE, NON-FLAMMABLE POLYMERIC MATERIALS AND ADHESIVES

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Professional Positions

Director, NSF-sponsored Materials Research Science & Engineering Center (MRSEC) on Polymers at the University of Massachusetts	2009-present
Professor, Polymer Science & Engineering, UMass Amherst	2011-present
Associate Professor, Polymer Science & Engineering, UMass Amherst	2007-2011
Assistant Professor, Polymer Science & Engineering, UMass Amherst	2001-2007

2011 Chair, Macromolecular Materials Gordon Research Conference, Ventura CA

2011 Chair, Polymeric Materials Science & Engineering (PMSE) Division of the ACS

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2011-2006 Polymer Materials Science & Engineering (PMSE) Division of the American Chemical Society; PMSE Chair 2011-2012; PMSE Chair-Elect 2010-2011; PMSE Vice Chair 2009-2010 PMSE Treasurer 2007-2009; PMSE Graduate Travel Award Chair for women and minority applicants 2006-2007.

2010 Milestone Award from the Intellectual Property office at UMass (for >5 awarded patents)

2010 Keynote lecture at Bayer Material Science Innovation Technology Symposium

2008 Featured speaker at Hybrid Materials 2009, Tours, France

2006 Arthur K. Doolittle Award from the Polymer Materials Science & Engineering (PMSE) Division of the American Chemical Society

2005 Juniata College Young Alumni Achievement Award

2004 University of Massachusetts President's Office Technology Development Award

2003 Selected by the NSF as a U.S. delegate to the CERC-3 in Gotenborg, Sweden

2003 National Science Foundation CAREER Award

2002 Exploratory Research Award from the Center for UMass-Industry Research on Polymers

2001 Omnova, Inc. Signature Young Faculty Award

MODERN PLASTICS: TOWARDS SAFE, NON-FLAMMABLE POLYMERIC MATERIALS AND ADHESIVES

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Introduction. Synthetic polymers touch every aspect of modern life, including textiles, transportation vehicles, microelectronics materials, lithographic processes, flexible (plastic) electronics, and *in vivo* implant devices. Despite the widespread societal advances made possible with polymers, one significant drawback associated with most polymer materials is related to their flammability. Burning plastics and foams represent serious issues that impact numerous industries, including housing, insulation, upholstery, and transportation. Blending small molecule fire retardants with polymers leads to a significant reduction in flammability, and enables finished polymer products to satisfy industry-standard flame tests. However, the significant flame-retarding benefits of these small molecule additives are offset by environmental and health concerns, especially for brominated aromatic compounds that are under scrutiny with respect to health and safety implications in the U.S. and Europe.[1,2]

Ideal polymers of the future would possess 1) all of the needed physical/mechanical properties needed to satisfy a given application, and 2) an inherent non-flammability. Such an objective represents a formidable challenge to polymer chemists and engineers, which we address by 1) novel monomer synthesis, 2) polymerization chemistry, and 3) thermal characterization such as pyrolysis combustion flow calorimetry (PCFC) for measuring heat release on very small (milligram) samples. Our research on novel non-flammable polymers has centered on two monomer types, termed bis-hydroxydeoxybenzoin (BHDB) and bisphenoltriazole (BPT). These monomers have been integrated into step-growth polymerization processes to afford new polymers (such as polyesters, polyphosphonates, polyurethanes, epoxy polymers, and cyanate ester resins) [3-10] that exhibit low heat release and thus represent candidates for integration into non-flammable polymer materials. As novel bisphenols for the production of step-growth polymers, both BHDB and BPT have the potential for integration into polymer reactions as substitutes for bisphenol A (BPA), a common monomer for the production of plastics, but one that is questioned both for flammability as well as environment/health concerns as an estrogen mimic.[11] The lecture associated with this document will focus specifically on the diepoxide of BHDB (termed BEDB, or bis-epoxydeoxybenzoin) for the preparation of cross-linked epoxy resins, and the cyanate ester derivative of BPT that produces novel thermoset materials (termed BPTCE).

BEDB Resins. BEDB was prepared by reacting BHDB with epichlorohydrin, and cross-linked resins of BEDB were obtained by its reaction with multi-functional amines, such as 4,4'-diaminodiphenyl sulfone (DDS), 4,4'-diaminodiphenyl methane (DDM), and *meta*-phenylene diamine (*m*-PDA). Pyrolysis combustion flow calorimetry (PCFC) was performed to measure the total heat release (THR [kJ/g]) and heat release capacity (HRC [J/g-K]) (Table 1). Of the diamine resins tested, those mixed with BEDB consistently demonstrated lower HRC and THR values than those mixed with EBPA. Char yields were also increased, from 12% to 30%. Resins formulated with more than one amine were tested, and showed even lower HRC and THR values. A mixture of BEDB and a 1:1 ratio of DDS and DDM reduced the HRC by 24% relative

to a resin mixed only with DDS or DDM. Mechanical properties were examined to determine the lap shear stress, storage modulus, critical stress intensity factor (K_{IC}), and critical strain energy release rate (G_{IC}). Mixtures with BEDB and EBPA with either DDS or DDM were tested. BEDB resins displayed an increase in shear strength from 11MPa to 15.4 MPa and 9.2MPa to 12.8MPa for DDS and DDM mixtures respectively. Storage modulus tests showed that the cross-link densities of BEDB resins were higher than EBPA resins. Critical stress intensity and critical stress energy release were tested with compact tension samples

BPTCE Resins. Bisphenol-1,2,3-triazole cyanate ester (BPTCE) resins were produced and found to have a much higher melting point than the the cyanate ester of BPA (BPACE) (160 °C vs. 82 °C). Four BPACE:BPTCE mixtures were formulated following weight ratios of 9:1, 8:2, 7:3, and 1:1 respectively. The HRC of BPACE was 332 J/g-K, while BPTCE:BPACS mixtures ranged from 200-285 J/g-K [6], and BPTCE cured products (self-cured) had exceptionally low HRC values of ~10 J/g-K. Thermal gravimetric analysis showed that BPTCE and its mixtures with BPACE have higher char yield than BPACE alone [6].

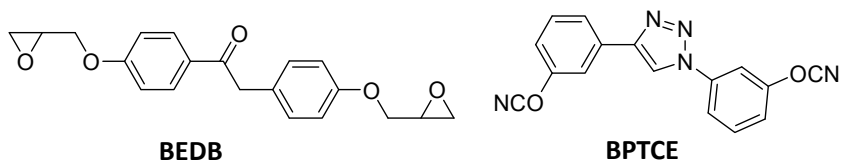


Figure 1. Left: Diglycidyl ether of BHDB, termed BEDB; right: dicyanate ester of bisphenol T, termed BPTCE.

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