Characterization of Novel Phosphorus-Based Flame Retardant Mixed Epoxy Resin Systems

Mustafa Mukhtar

Chemical & Materials Engineering Department, University of Dayton

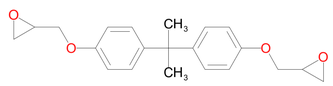
Abstract

This poster summarizes the results of a series of ongoing experimental investigations into the curing reactions between a novel Phosphorus-Diglycidyl Ether of Bisphenol A (P-DGEBA) flame retardant, Diglycidyl Ether of Bisphenol A (DGEBA) epoxy resin, and an aliphatic amine curing agent. The primary motivation for this study was the promising preliminary experimental results obtained recently on a novel organophosphorus flame retardant (P-DGEBA) synthesized by the UD Chemistry Department. This research aims to identify the feasibility of reactive organophosphate compounds that could be integrated into existing epoxy formulations to provide fire-resistant composites with little or no compromise in processing, treatment, and mechanical properties. This required investigating a series of experimental mixing formulations and curing conditions to provide further insight into curing behavior. The cure reaction was characterized with Differential Scanning Calorimetry (DSC), and char yield was evaluated with Thermogravimetric Analysis (TGA). Flammability testing was conducted with the Micro Combustion Calorimeter (MCC) instrument at UDRI. The results indicated good char formation behavior and good reduction in peak heat release rate (HRR) compared to the control sample. The level of gas/fire plume formation was undesirably high, but the smoke release rate was much lower than the control sample.

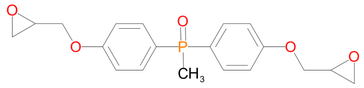
Introduction

Epoxy resin systems are one of the most common thermosetting polymers used in many industrial applications such as adhesives, coatings, and composite matrices. They have been used as high-performance materials because of excellent mechanical properties and chemical resistance, good adhesive strength, low cure shrinkage, and can be formulated with appropriate rheology for surface coatings. However, the flammability of epoxy resins has critically limited their use in many applications such as electronics, aerospace, and transport vehicles. In the recent years, several types of flame retardants have been developed for epoxy resins, although some of these are in the form of separate additives that can phase-separate or leach out over time. Phosphorus compounds are able to form a char layer on the surface when a threshold temperature is reached in a fire situation. The char layer imparts fire resistance by forming a thermal and diffusion barrier at the surface. In this project, the strategy is to incorporate the phosphorus species into an epoxy monomer structure, such that it will become incorporated into the final network and therefore be as non-intrusive as possible. In the current study, curing conditions were characterized by various physical and thermal properties using TGA and DSC. Cured samples were also tested using MCC to investigate the flammability and decomposition characteristics of cured epoxy-amine resin systems.

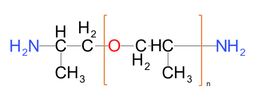
Materials



A. Epoxy resin
EPON 825 (DGEBA) (liquid)



B. Flame Retardant (P-DGEBA)
Phosphorus-Diglycidyl Ether of Bisphenol A
(Synthesized by UD Chemistry Dept. faculty)



C. Curing Agent
Epikure 3274 (liquid)

Experimental Procedure

Step 1: Sample formulation

- EPON825/P-DGEBA: 61 wt%
- Epikure 3274: 39 wt%

This mixture kept the blend of EPON825/P-DGEBA and Epikure in stoichiometric balance and diluted gradually by P-DGEBA from 0% to 75% in the final mixture.

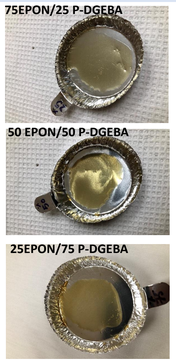
Step2: Mixing

- Heat P-DGEBA to 100 °C and held for 1 hr in a convection oven to remove moisture.
- Add Epikure and Epon, mix manually until it became a uniform solution.

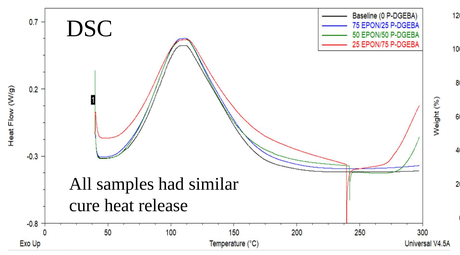
Step 3: Curing

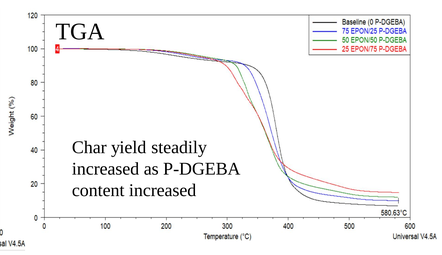
The sample was mixed in an aluminum pan and cured for 2 hour at 170 °C in a convection oven.

Results and Discussion



The samples were successfully produced: the resin cured to a hardened statet with no voids or bubbles.



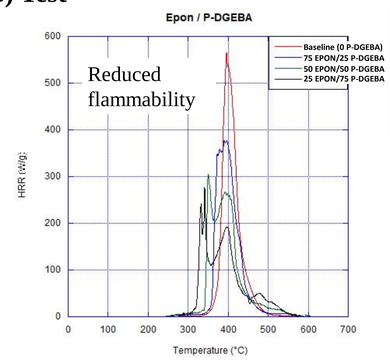


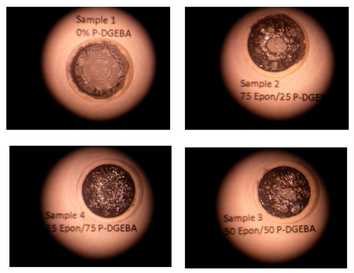
As shown in both DSC and TGA analysis the dilution P-DGEBA by 50% wt. with EPON825 is the best option due to the good balance between both of curing and thermal properties.

Micro combustion calorimeter (MCC) Test

MCC exposes a small sample (5-50 mg) to very fast heating rates to mimic fire type conditions.

Testing was performed at UDRI with 1 °C/sec heating rate under nitrogen from 200 to 650°C using method A of ASTM D7309-19 (pyrolysis under nitrogen).





Char steadily increased from 5.4% (baseline) to 16.0% (25 Epon/75 P-DGEBA)

The samples containing P-DGEBA ignited at lower temperature than the control samples, but they did reduce the peak HRR and the total amount of heat release during combustion. This indicates the flame retardant helped form a higher level of char which lowered total heat release and resulted in a shorter burning time.

Conclusions

- A procedure for preparing high quality flat resin samples containing P-DGEBA was successful.
- As P-DGEBA was added to the epoxy samples in increasing amounts, the total heat release decreased and the char yield increased, strongly suggesting a condensed phase char formation reaction.
- Micro combustion calorimeter results showed good char formation behavior, and there was a good reduction in the average heat of combustion compared to the control.
- Additional research is needed to determine the exact mechanism of flame retardancy, but the results indicate that P-DGEBA is an effective flame retardant for epoxy.

Applications for Flame Retardant Epoxy Matrix Composites

Faculty Advisors / Collaborators. Center for Flame Retardant Materials Science.

Donald Klosterman, Ph.D.
Chemical & Materials Engineering Dept.
University of Dayton

Vladimir Benin, Ph.D.
Chemistry Department
University of Dayton

Alexander Morgan, Ph.D.
Power & Energy Division
University of Dayton Research Institute (UDRI)