Characterization of Novel Phosphorus-Based Flame Retardants in Epoxy Resins

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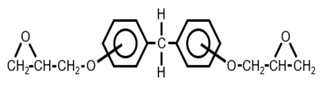
Abstract

This poster summarizes the results of a series of ongoing experimental investigations into the curing reactions between a novel phosphorus flame retardant (FR) and epoxy resin. The novel flame retardant "FR5" was synthesized and provided by UD Chemistry Department faculty. The FR includes secondary amine functional groups which allow it to potentially react with the epoxy resin through covalent bonding. In this work, we successfully scaled up the sample preparation procedures to make 4 in. x 4 in. cured resin plaques for flammability testing. This required investigating a series of experimental mixing formulations and curing conditions to provide further insight into curing behavior. The cure reaction and FR reaction were characterized with Differential Scanning Calorimetry (DSC). Flammability testing was conducted with a cone calorimeter 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.

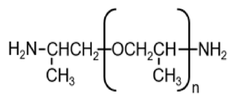
Introduction

Epoxy resin systems are one of the most common thermosetting polymers used in several industrial fields 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 they can be formulated with appropriate rheology for surface coatings. However, the flammability of epoxy resins has critically limited their uses in many applications such as electronics, aircraft interiors, and transport vehicles. In 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 study, the reaction of the flame retardant (FR5) with an epoxy resin system was investigated by Differential Scanning Calorimetry (DSC), and flammability testing was done with a cone calorimeter.

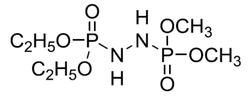
Materials



A. Epoxy resin
EPON 862 (liquid)



B. Curing Agent
Epikure 3274 (liquid)



C. Flame Retardant (FR5)
Phosphoryl hydrazide flame retardant (synthesized by UD Chemistry Dept. faculty) (2P_Et_Me) P = 22.4 wt%

Experimental Procedure

Step 1: Sample formulation

- EPON 862 61 wt%
- Epikure 3274 28 wt%
- FR5 11 wt%

This mixture contained Epon and Epikure in stoichiometric balance, and P in the final mixture at 2.5 wt%

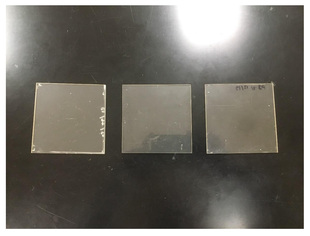
Step2: Mixing

- Heated FR5 at 100 °C for 1hr in a convection oven to remove absorbed water
- Added Epikure and Epon, mixed manually until it became a uniform solution.
- Vacuum degassed the solution in beaker for 10 minutes at room temperature

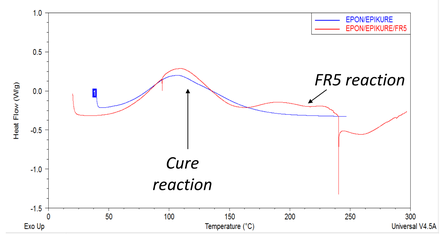
Step 3: Curing

The sample was poured into a square mold and cured at 100 °C for 1 hour in a convection oven.

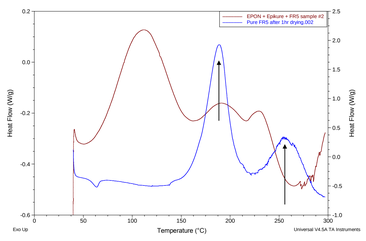
Results and Discussion



Three resin plaques were successfully produced: no voids or bubbles



FR5 did not appear to participate in cure reaction between Epon and Epikure

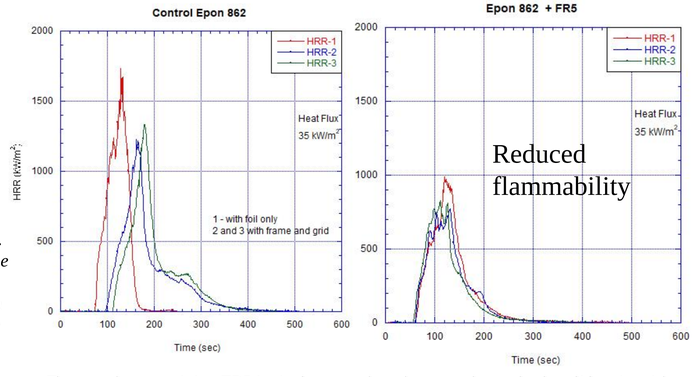


There was a significant difference in the FR5 reaction when cured into the mixture: the 2nd exothermic peak shifted to a lower temperature. This may indicate an interaction between FR5 and the network, possibly related to char formation

Testing was performed at UDRI with a heat flux of 35 kW/m² (acknowledge: Mary Galaska)

Cone calorimeter testing

Samples in holder (post test). Smoke and drips came out the bottom on the frame during testing. The final chars from this sample were more sticky than the control chars, suggesting that some of the epoxy was thermally degraded, but not fully decomposed / charred.

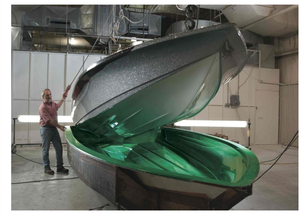


The samples containing FR5 ignited sooner than the control samples but did extinguish a little faster. This indicates the flame retardant helped form a higher level of char which lowered total heat release and resulted in a shorter burning time.

Conclusions

- A procedure for preparing high quality flat resin plaques containing FR5 was successfully developed.
- Although FR5 did not co-cure with the Epon / Epikure resin system, its behavior at high temperature was changed when it was cured into the network compared to in pure form. This indicates an interaction between FR5 and the network, possibly related to char formation.
- Cone calorimeter results showed good char formation behavior but it was highly erratic, as was gas/fire plume formation. Overall there was a good reduction in the average heat of combustion compared to the control.
- By itself this FR is not a promising candidate, but it could be combined with another type that does not have good char formation behavior for synergy.

Applications for Flame Retardant Epoxy Matrix Composites



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