

## Chapter 6

# A Comparative Study of the Fire Retardant Effect of Several Metal-Based Compounds Added to an Epoxy-Amine Thermoset

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Several metal containing compounds such as layered double hydroxide of cobalt aluminum dodecanoate, cobalt (II, III) oxide, zinc acetate dihydrate, and cobalt acetate tetrahydrate have been evaluated as fire-retardant additives for a standard epoxy-amine thermoset polymer system. A cone calorimeter was used to evaluate the fire behavior properties of the composites at an external heat irradiation of 50 kW/m<sup>2</sup>. The layered double hydroxide and the metal oxide were found to be rather ineffective fire retardant additives for the epoxy-amine thermoset. In contrast, both hydrated salts performed surprisingly well. The efficacies of metal salts of zinc acetate and cobalt acetate were correlated with the formation of a metal oxide inorganic layer that covered the surface of the underlying polymer under fire conditions. This morphology slowed the release of any flammable volatiles and reduced the heat transfer to the degrading polymer.

## Introduction

Epoxy-based resins are commonly used for applications including adhesives, coatings and advanced composites in the aerospace and electronics industries (1–4). However, the poor fire resistance properties of epoxy-based polymers is a crucial technical disadvantage. Consequently, multiple efforts have been undertaken to enhance the fire properties of these polymer systems. Epoxy systems

can be rendered fire retardant either by incorporation of fire retardant additives (e.g. triphenyl phosphate (5), 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO) (6), decabromo diphenylether (7), aluminum ethyl phosphinate (8)) or by copolymerization with reactive fire retardants (e.g. diglycidylether of tetrabromobisphenol A) (9). Due to recent ecological and health concerns, however, a general tendency towards banning halogen based fire-retardants has been observed. This gives rise to extensive research activities that are aimed at replacing these substances.

An analysis of the wealth of relevant scientific publications shows that metal-based compounds have the potential to become the next generation of effective flame retardant additives for polymers (10–12). However, if a substance contains metal atoms, it is impossible to state a priori, whether or not it will exhibit the desired flame retardancy effect in a particular polymer system. Many factors control the effect of these compounds in polymer combustion including the nature of the metal, degree of oxidation, type of compound, manner of introduction into the polymer, concentration level, dispersion state, conditions of combustion and pyrolysis and the nature of the polymer (13). This field is still in its embryonic stage but recent studies have shown that an understanding of the mechanisms of action of these materials will facilitate the production of materials with enhanced fire performance.

Recently, Morgan (10) in his review article summarized the recent findings on fire retardancy effectiveness of metal oxides, metal salts and metal complexes. He highlighted that there appeared to be a lot of promise in this diverse group of flame retardant additives which utilize a wide range of chemistries and solid state structures to induce either char formation or highly effective vapor phase free radical inhibition for the burning plastic. In particular, he pointed out a study by Yang *et al.* (14) that showed that small concentrations of nickel phosphate (2 wt.%) can allow for the replacement of 7 wt.% of the intumescent FR system while maintaining a UL-94 V-0 result. Prior to that study, Lewin and Endo (15) observed that small concentrations of several divalent and multivalent metallic compounds in the range of 0.1–2.5 wt.% catalyzed intumescent flame retardancy of polypropylene. In that study, it was noted that the extent of the observed catalytic effect varied with the metal ion applied.

Another type of metal-based additives, the layered double hydroxides (LDHs), have also been investigated as potentially novel and effective fire retardant additives for polymers (16, 17). The LDH structure is described with the ideal formula  $[M^{II}_{1-x}M^{III}_x(OH)_2]_{\text{intra}}[A^{m-}_{x/m} \cdot nH_2O]_{\text{inter}}$ , where  $M^{II}$  and  $M^{III}$  are metal cations,  $A^{m-}$  is the anion of charge  $m-$ , and intra and inter denote the intralayer domain and the interlayer space, respectively (18). With poly(methyl methacrylate) (PMMA), in which the LDH is well-dispersed, a peak heat release rate (PHRR) reduction of 50% over the pristine polymer was obtained in cone calorimeter studies (19). A correlation between PHRR reduction and the morphology of the char residues was observed. This char formed a compact residue that covered the entire surface of the aluminum foil holding the sample. It is likely that this char layer serves as a barrier for the heat transfer and slows the transport of combustible volatiles thus leading to considerable enhancement of the fire resistance.

The common theme in the relevant literature reports on the fire retardancy properties of polymeric systems modified with metal-based compounds is the lack of complete understanding of the mechanisms of actions of these additives. However, all authors recognize the great deal of potential associated with the use of metallic compounds due to the numerous chemical compounds commercially available or obtainable through chemical synthesis. The goal of this study was to evaluate a potential use of several metal-containing compounds such as cobalt oxide, cobalt aluminum layered double hydroxide, and hydrated metal salts of zinc and cobalt as fire retardant additives for a standard epoxy-amine thermoset polymer.

## Experimental

Zinc acetate dihydrate [ $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ ] (ZnAc), cobalt acetate tetrahydrate [ $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$ ] (CoAc) and cobalt (II,III) oxide nanopowder (CoOnano) with a reported characteristic particle size smaller than 50 nm, were purchased from Aldrich Chemical Company and used as received. Layered double hydroxide of cobalt aluminum dodecanoate (CoAl) was synthesized via coprecipitation as reported elsewhere (20). The ratio of the metals, cobalt to aluminum, was maintained at 2 to 1. The structure and composition of the synthesized CoAl was confirmed by powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA).

EPON 826, a low viscosity liquid epoxy resin often used in coatings and composite applications with an epoxy equivalent weight of 178-186 grams was supplied by Hexion and used as received. The hardener, Jeffamine D230, with an amine equivalent weight of 60 grams, was supplied by the Huntsman Corporation and also used as received.

The composites were prepared as follows: the additives were mixed directly in bisphenol A epoxy resin for several minutes at 60 °C. The additives were dispersed with a mechanical stirrer. The hardener was added to the mixture in a stoichiometric amount and stirring continued for an additional 30 minutes at room temperature before the contents were poured into a mold. The samples were cured at 80 °C for 12 hours and post cured at 135 °C for an additional 3 hours. Prior to curing, the mold containing the mixed reactants was degassed in vacuum to remove any trapped air. The prepared compositions are listed in Table 1.

The glass transition temperature values for various epoxy/amine composites were obtained using a TA instruments Q1000 DSC at a heating rate of 10 °C/min. The sample size was maintained between 7 and 10 mg. Tg value was taken as the midpoints of the inflection from DSC scans. The additives exhibited no effect on the extent curing as confirmed by the fact that the glass transition of the composites was the same as of the epoxy-amine control. In addition, the consecutive DSC runs of the composites showed no difference in Tg from scan to scan. A TA instruments Q500 thermogravimetric analyzer (TGA) was used to evaluate the thermal stability of the networks and the additives. The samples (~10 mg) were tested in air or nitrogen environments at a heating ramp rate of 10 °C/min from 25 to 600 °C.

Cone calorimeter measurements were performed with the Govmark cone instrument according to ASTM E 1354 using a cone shaped heater with an incident flux set at 50 kW/m<sup>2</sup>. The exhaust flow was set at 24 L/s and the spark was turned on continuously until the sample was ignited. Typically the data generated by a cone are quite reproducible with an uncertainty which does not exceed  $\pm 10\%$  (21). A set of fire-relevant parameters can be obtained using the cone calorimeter including the peak heat release rate (PHRR), average mass loss rate (AMLR), average specific extinction area (ASEA), time to ignition ( $t_{ig}$ ), carbon monoxide yield, and specific heat of combustion.

**Table 1. Studied Compositions**

<i>Formulation</i>	<i>Additive (wt.%)</i>
Epoxy/amine control	0
Epoxy/amine/a% CoAl	a = 4 , 7
Epoxy/amine/b% CoOnano	b = 4 , 7
Epoxy/amine/c% CoAc	b = 4 , 7
Epoxy/amine/d% ZnAc	c = 4 , 7 , 13 , 18 , 27

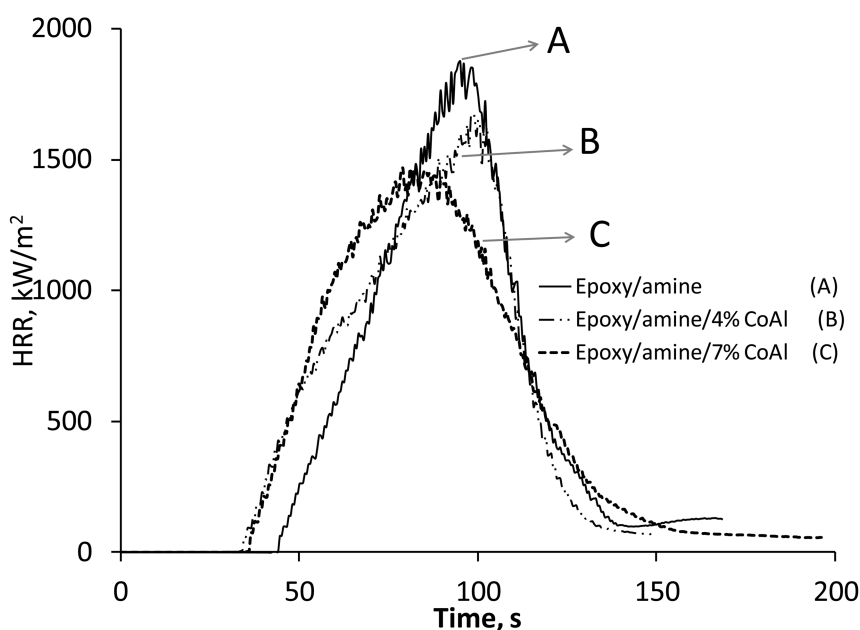
## Results and Discussion

This section begins with a report on the flame retardant potential of a layered double hydroxide and a metal oxide additive in an epoxy/amine thermoset polymer. The efficacy of hydrated metal salts of zinc acetate and cobalt acetate dispersed in the same polymer is discussed next. This work enables a comparative study on the flame retardant potential of the different metal-containing additives in an epoxy/amine system.

### Layered Double Hydroxide and Metal Oxide

Cobalt–aluminum dodecanoate LDH (CoAl) was added to an epoxy/amine thermoset, as described in the experimental section, and the samples were tested in the cone. Figure 1 shows the heat release rate curves for the pristine epoxy/amine and its LDH composites containing 4% and 7% wt/wt of the mineral phase. The reduction in the PHRR, as compared to the pure polymer, was only 22% with 7% wt/wt of LDH. Figure 2 shows the char remaining after epoxy/amine and epoxy/amine/7%CoAl samples were burned in the cone. Adding LDH apparently did not enhance the char formation. The virgin epoxy/amine sample yielded a rather small amount of residue accounting for only 1 wt.% of the original sample mass. In addition to the carbonaceous residue, one can also clearly see traces of an inorganic phase, the residue of the LDH. Very modest enhancement of the fire retardant properties of the epoxy/amine/CoAl systems was attributed to the rather

poor LDH dispersion in the polymer matrix. The epoxy/amine composites of CoAl were opaque even at low concentration while the pure epoxy/amine control sample was transparent. LDH exhibited a pronounced sedimentation caused by gravity leading to a rather heterogeneous dispersion state when top and bottom of samples are compared. The samples though were consistently tested with the same side oriented towards the heat flow. Poor LDH phase dispersion was related to low viscosity of the original epoxy resin which prevented the dispersion of the layered stacks beyond the primarily particle size. It is clear based upon these observations that one can anticipate further enhancement in fire properties once the improvement in the dispersion state of the LDH additive in this polymer can be achieved.



*Figure 1. Heat release rate curves for the pristine epoxy/amine thermoset and the resin modified with different amounts of CoAl layered double hydroxide conducted at an external irradiation 50 kW/m<sup>2</sup>.*

Cobalt oxide has also been added to the epoxy/amine system and the fire behavior properties of the corresponding composites evaluated in the cone. Figure 3 displays the corresponding heat release rate curves for epoxy/amine control and also the resins containing different amounts of CoOnano. From the cone data, one can see only a minimal, less than 10% at best, improvement of PHRR. Thermal degradation studies are required to further understand how this additive interacts with the polymer matrix and help explain the poor performance observed for this set of samples.

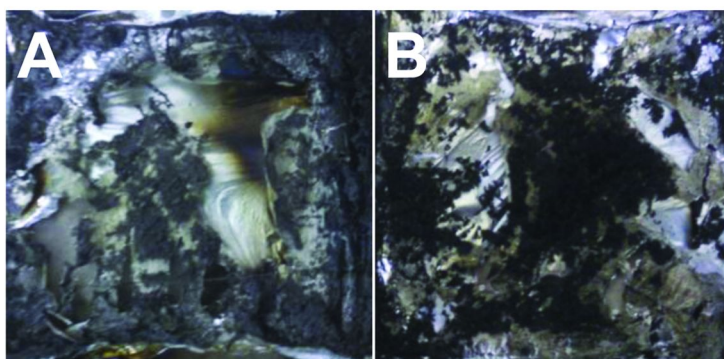


Figure 2. Images of the residues for (A) epoxy/amine and (B) epoxy/amine/7%CoAl samples after cone testing.

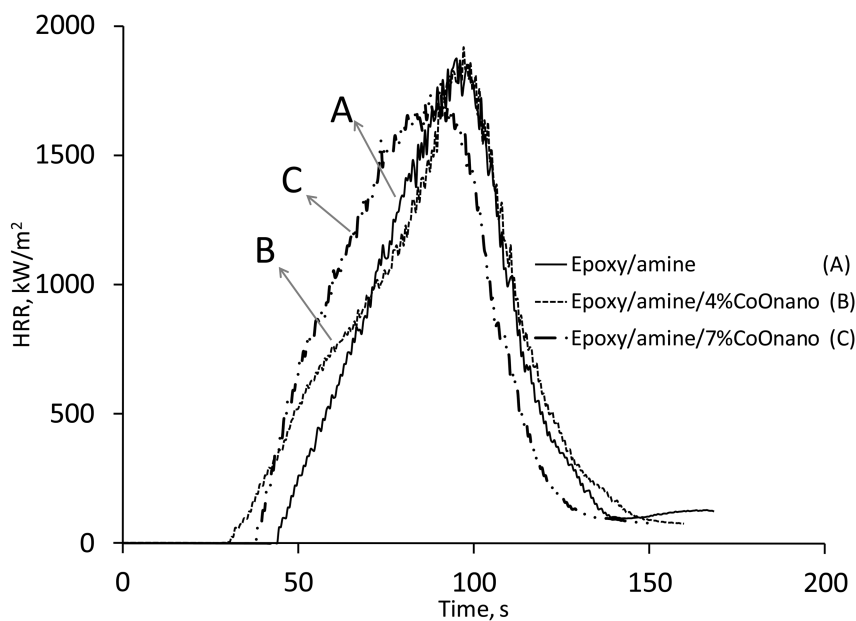


Figure 3. Heat release rate curves for epoxy/amine control and resins modified with CoO nanopowder conducted at an external irradiation of 50 kW/m<sup>2</sup>.

**Table 2. Cone data summary for epoxy/amine systems containing ZnAc**

<i>Matrix</i>	<i>t<sub>ig</sub></i> [s] ± 4	<i>PHRR</i> [kW/m <sup>2</sup> ] ± 70	<i>THR</i> [MJ/kg] ± 1	<i>AMLR</i> [g/m <sup>2</sup> .s] ± 1.6	<i>EHC</i> [MJ/kg] ± 0.5	<i>Residue</i> [%] ± 0.7	<i>ASEA</i> [m <sup>2</sup> /kg] ± 23
Epoxy/amine	42	1861	93	45.5	31.0	1.2	759
Epoxy/amine/7 %ZnAc	38	1015	81	28.2	29.9	11.3	635
Epoxy/amine/13%ZnAc	36	846	77	24.3	30.1	14.4	631
Epoxy/amine/18%ZnAc	29	853	73	24.8	29.3	15.9	623
Epoxy/amine/27%ZnAc	20	607	73	17.0	29.5	17.9	608

**Note:** *t<sub>ig</sub>*, time to sustained ignition; PHRR, peak heat release rate; THR, total heat released; AMLR, average mass loss rate; EHC, Average effective heat of combustion; ASEA, average specific extension area.

## Hydrated Metal Salts

The use of metal salts to enhance the fire retardant properties of polymers has only recently caught researchers' attention. Kashiwagi *et al.* prepared clay-based SAN nanocomposites with zinc chloride as the catalyst (11). They observed a large improvement in the PHRR relative to the control polymer, but their results indicated that the two additives (clay and zinc chloride) were contributing independently. In our work, a question was posed of whether the fire retardancy properties of an epoxy-amine thermoset can be enhanced by only adding a halogen-free metal containing salt.

Therefore, zinc acetate dihydrate (ZnAc) was added to the epoxy/amine thermoset polymer. ZnAc formed a microdispersion in the epoxy-amine thermoset. With a naked eye, small, microscopic inclusions could be observed near the surface. The fire behavior properties of the epoxy/amine composites of ZnAc were evaluated in the cone calorimeter at an external heat flux of 50 kW/m<sup>2</sup>. The cone data are summarized in Table 2. Epoxy/amine resins containing different amounts of ZnAc revealed significant reductions of the PHRR values. The fire retardant effect of ZnAc additives is fairly strong. Adding only 4% wt. of ZnAc led to 36% of PHRR reduction. Adding 7 wt.%, 13 wt.%, 18 wt.% and 27 wt.% resulted in 46%, 55%, 54% and 67% reductions of PHRR values as compared to the unmodified control respectively. The time to ignition however gradually decreased with increasing ZnAc content. The reduction of the time to ignition showed a correlation with the thermal stability data. The TGA experiments revealed that the thermoset polymer containing ZnAc starts decomposing at lower temperature as compared to the pure epoxy-amine control. It should be noted here that ZnAc melts and decomposes at considerably lower temperatures than the polymer in the composites. Somehow ZnAc or the products of its degradation promote earlier degradation of the epoxy-amine polymer.

The heat release rate curves of both the unfilled polymer and the various epoxy/amine composites of ZnAc are provided in Figure 4. The HRR curve for the pure epoxy/amine sample showed a sharp, narrow peak, indicative that the sample was pyrolyzed fairly rapidly. This cone behavior was in accord with the classical patterns typical of weakly charring samples (22). With addition of ZnAc, the shape of HRR curves for the composites changed towards the behavior associated with the formation of a very resistant char barrier layer on the surface of the burning polymer. Figure 5 shows images of the cone test residues for the epoxy-amine control and the sample containing 7% of ZnAc. Adding ZnAc led to the formation of a char layer upon ignition that is enriched on the surface with crystalline ZnO, an inorganic product of the thermal decomposition of ZnAc, making the whitish surface appearance of the composites after burning. Formation of crystalline ZnO was confirmed by WAXD, and it is generally known that zinc oxide is a white substance. With the addition of more ZnAc, the whitish surface layer became much denser, with lesser vent holes observed on the char surface. Apparently this whitish zinc oxide char layer formation on the top of the degrading polymer matrix contributes to the fire resistance as it prevents the entry of flammable gases into the gas phase and insulates the underlying polymer from the flame (23). A question can be posed as to how ZnO micro particulates reach



the surface and concentrate there. Inspecting the char residue bulk morphology suggests the presence of small bubbles which form a cellular structure within the char residues. It is quite possible that these small bubbles formed by the products of degradation or water released upon melting of zinc acetate dihydrate in the cone experiment lead to the convectional flow which carries the zinc oxide particles to the surface of the burning polymer.

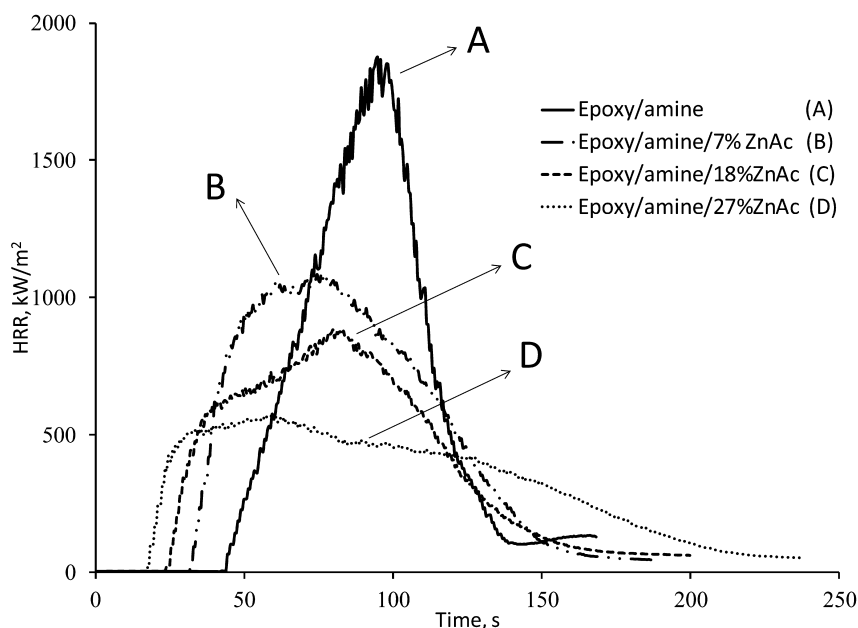


Figure 4. Heat release rate curves of epoxy/amine thermoset containing different amounts of ZnAc.

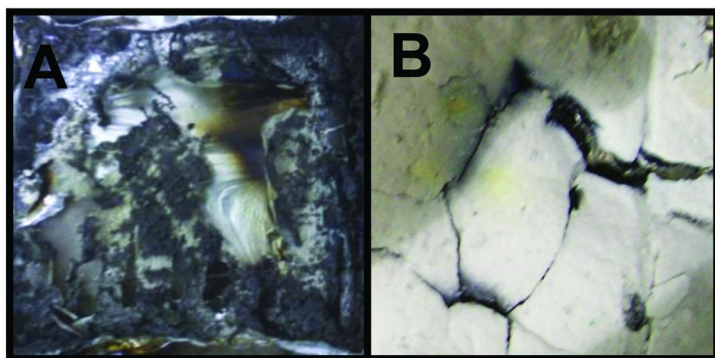


Figure 5. Images of the char residues for: (A) epoxy/amine and (B) epoxy/amine/7%ZnAc.

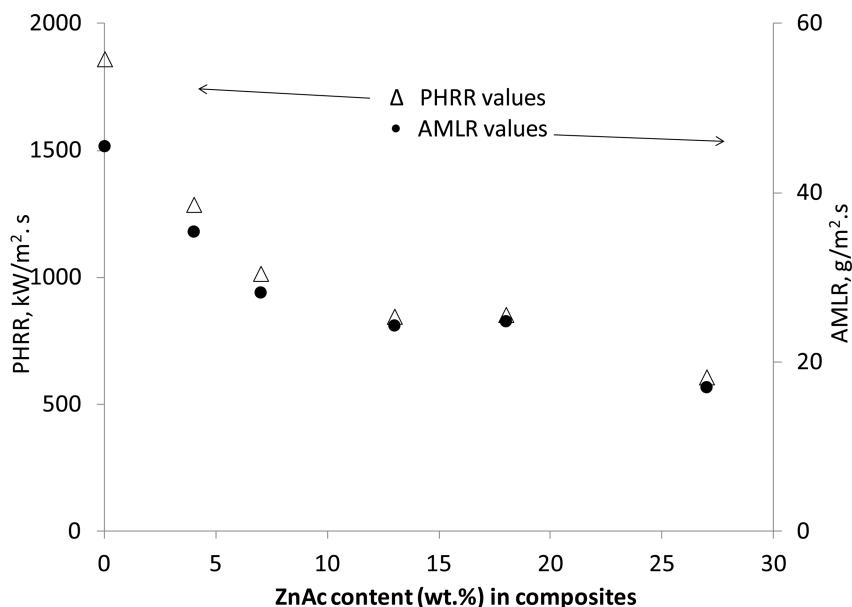


Figure 6. Peak heat release rate (PHRR) and Average mass loss rate (AMLR) values for the composites of ZnAc.

A correlation was found between the reduction in the average mass loss rate (AMLR) and the PHRR values which are graphically shown in Figure 6. Slow release of the fuel or a delay in mass loss has been typically correlated to a combination of physical and chemical phenomena (24, 25). Three possible reasons are put forward to explain the fire retardant action of ZnAc in the epoxy-amine thermoset. Perhaps the primary cause is that under fire conditions most of the ZnAc additive is converted into zinc oxide. Crystalline zinc oxide forms an inorganic layer that covers the surface of the underlying polymer and thus slows the release of any flammable fragments from the burning polymer and also reduces the heat transfer to the degrading polymer. Also ZnAc may participate in the pyrolysis reactions within the condensed phase by promoting a carbonization process which reduces the yield of volatile and combustible products. Finally ZnAc may also act as a heat sink since when it is heated to higher temperatures it releases water molecules that may cool the flame.

An interesting feature of the fire retardant effect of ZnAc discovered here is that in addition to a considerable reduction of PHRR, the epoxy/amine composites of ZnAc do not produce extra smoke upon ignition. In fact smoke generation was even slightly suppressed in the presence of this metal salt as compared to the epoxy-amine control as one can see from the comparison of average specific extension areas shown in Table 2.

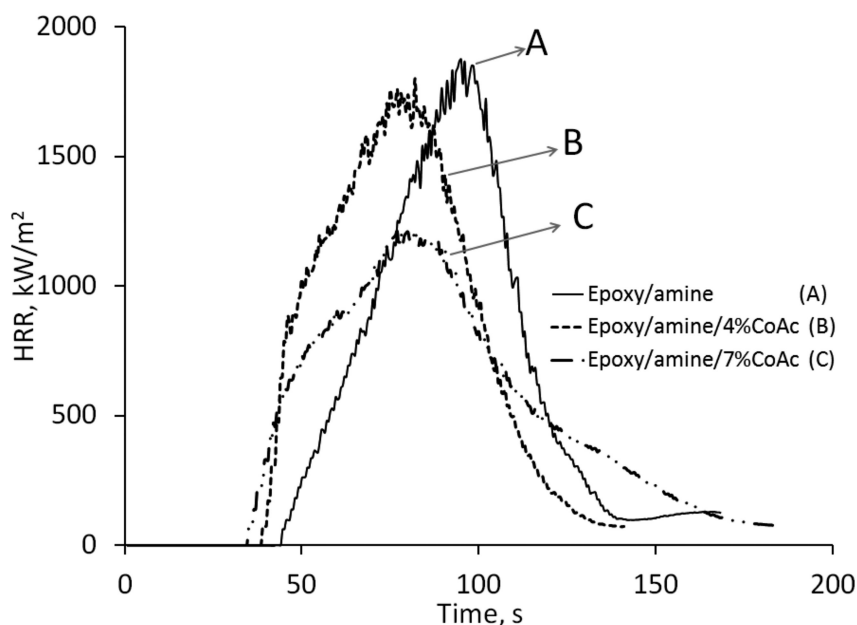


Figure 7. Heat release rate curves conducted at an external irradiation of 50 kW/m<sup>2</sup> for the pristine epoxy/amine thermoset and the resin modified with different amounts of CoAc.

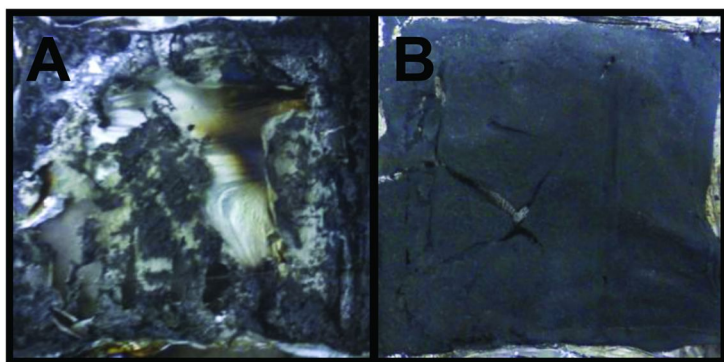


Figure 8. Images of the char residues for: (A) epoxy/amine and (B) epoxy/amine/7%CoAc.

A question was posed if the nature of the metal in the salt plays any role. To explore this fact, cobalt acetate (CoAc) was also added to the epoxy-amine thermoset and the fire properties of its composites were evaluated using a cone calorimeter at an external heat flux of 50 kW/m<sup>2</sup>. The HHR curves for epoxy-amine control and also those containing 4% and 7% (wt/wt) CoAc are shown in

Figure 7. Qualitatively, the HRR behavior of epoxy-amine thermoset containing CoAc was comparable to that with ZnAc. Quantitatively, the fire retardant effect of adding cobalt based salt was found to be slightly smaller than that of adding zinc salt as preliminary measurements showed. When 7 wt.% of CoAc was added, the reduction in PHRR was 38% as compared to 46% with the addition of ZnAc.

The photographs of the char residues after completion of the cone tests for the epoxy-amine control and the 7% wt of CoAc composite are shown in Figure 8. As compared to the ZnAc containing epoxy-amine thermosets, adding CoAc did not lead to the whitish surface appearance. The surface was greenish-black. It should be noted that cobalt oxide color may vary broadly depending on the valence of the Co atom but a green-blackish color is rather common. Therefore, we believe that the mechanism of CoAc action is similar to that of ZnAc. A protective layer of cobalt oxide forms on the surface of the burning polymer which helps with improving the fire retardant properties. Interestingly, adding pure cobalt oxide to an epoxy-amine thermoset as described previously did not lead to a considerable improvement of fire retardant properties. At the same time, the oxide protective surface layer did not form in this case upon burning. We speculate here that the melting of crystalline  $[\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}]$  and subsequent release of water plays a predominant role in the formation of bubbles which carry the oxide to the surface of the burning polymer. Naturally the same idea can be applied for ZnAc  $[\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}]$  salt. New experiments will focus on investigating the efficacy of anhydrous forms of zinc and cobalt acetate as well as the salts with longer organic tails, which are not hydrates, to investigate whether water release plays such an important role.

## Conclusions

When fire retardant nano-additives LDH of cobalt aluminum dodecanoate and cobalt oxide were added to an epoxy/amine thermoset polymer, only modest improvement of fire properties was discovered. The poor dispersion of these nano-additives achieved at the primary microparticle level was suggested to be the main reason why these fire retardant additives did not perform well in the epoxy-amine thermoset polymer as compared to many other polymers. However, if the dispersion state of these additives is improved and reaches a nano-level, greater enhancement of the fire retardancy properties for these systems can be anticipated.

In contrast, metal salt hydrates of zinc acetate and cobalt acetate have been found to be very effective in imparting flame retardancy of epoxy/amine thermoset despite the micro-dispersion state for these additives as well. PHRR values have been reduced by almost a factor two as compared to the epoxy-amine thermoset control when only 7% wt. of metal salts was added. ZnAc was found to be slightly more effective than CoAc. The morphological analysis of the char residues suggested that the main reason for the fire retardant action was the formation of a metal oxide inorganic layer that covered the surface of the underlying polymer. This char residue slowed down the release of any flammable fragments from the burning polymer and also reduced the heat transfer to the degrading polymer. An

interesting additional feature of the metal salts composites discovered here was that in addition to a considerable reduction of PHRR, there was no generation of extra smoke. In fact, generated smoke was even slightly suppressed as compared to the epoxy-amine thermoset control.

## Acknowledgments

The authors thank the Office of Naval Research, award number N00014-07-1-1057, for the financial support of this project.

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