

# SUSTAINABLE FLAME RETARDANTS: BIO-DERIVED PRODUCTS AS INTUMESCING MATERIALS

Mauro Zammarano<sup>\*</sup>, Douglas M. Fox<sup>\*</sup>

Department of Chemistry, American University, Washington DC, 20016, USA

Sbazolcs Matko, Takashi Kashiwagi, Jeffrey W. Gilman, Rick D. Davis

National Institute of Standards and Technology (NIST), 100 Bureau Drive, Gaithersburg, MD 20899-8665, USA.

<sup>\*</sup> Guest researcher at NIST.

## ABSTRACT

Scientists are shifting their attention towards technology sustainability and sustainable materials, specifically in terms of energy and environmental impacts. The flame retardant community is also more concerned about these aspects. The recent banning of some brominated flame retardants in Europe and USA points out that environment impact in terms of persistency and bio-accumulation is becoming a key factor for public perception. Intumescent systems based on phosphorous compounds have been suggested as highly efficient alternative to halogenated flame retardants. Lately, not only halogen based flame retardants but also phosphorous based flame retardants are under scrutiny for their environmental and health safety (EHS) issues. It appears that there is a need for sustainable flame retardants with low EHS impact. In this work we show how natural derived products, like modified lignin, can be used for preparing sustainable intumescent systems with high efficiency. Lignin is the second most abundant organic substance on earth after cellulose and is increasingly available as by-product of cellulose production. Its price (20¢/lb) is significantly lower than commodity polymers, thus lignin is commonly used as polymer filler. Here, we show that modified lignin is also an effective flame retardant. Epoxy resin is used as a case study. The mass loss rate of the epoxy-lignin composites is investigated by means of gasification apparatus. Preliminary results show that lignin-based products produce a continuous protective char capable to protect the underlying polymer throughout the combustion process and, thus, decrease the heat release rate.

## MATERIALS<sup>\*</sup>

Three different grades of kraft lignin were kindly provided by MeadWestvaco Corporation: (1) unsulfonated lignin (Indulin AT), (2) sulfonated lignin (REAX 907) and (3) sulfonated ethoxylated lignin (REAX 825E). Talc (Polyststormor, Mallinckrodt) was used as control filler. Ammonium tartrate (Aldrich) and melamine (Melamine 003 fine, DSM) were used as blowing agents. An epoxy monomer (DER331) was obtained from Dow Plastics. Jeffamine D230 (Huntsman Corp.), a diamine terminated polypropylene glycol, was used as curing agent. The samples were prepared by: drying the fillers (12h at 80 °C) and dispersing them in the epoxy monomer with a mechanical stirrer; cooling the mixture to room temperature; adding the curing agent in a stoichiometric amount and stirring for 5 min; curing (room temperature for 24h, 80 °C for 2h, 125 °C for 3h). The total amount of

---

<sup>\*</sup> This work was carried out by the National Institute of Standards and Technology (NIST), an agency of the US government and by statute is not subject to copyright in USA. The identification of any commercial product or trade name does not imply endorsement or recommendation by NIST.

filler was kept constant at 10 %<sup>†</sup> in each formulation. Type and amount of filler for each formulation are reported in Table 1.

**Table 1.** Formulations and gasification apparatus data.

Formulation ID	Filler	PMLR (g·s·m <sup>-2</sup> )	ΔPMLR (%)	t <sub>p</sub> (s)	Residue (%)
Neat epoxy	None	56.5	-	200	8.6
Talc	10 % Talc	51.9	8.1	173	18.0
UL	10 % unsulfonated lignin	40.1	29.0	157	15.1
SL	10 % sulfonated lignin	28.5	49.6	234	16.5
SEL	10 % sulfonated ethoxylated lignin	25.2	55.4	179	17.7
AT+SEL	3 % ammonium tartrate + 7 % sulfonated ethoxylated lignin	39.8	29.6	285	18.1
ML+SEL	3 % melamine + 7 % sulfonated ethoxylated lignin	34.5	38.9	273	17.4

## METHODS

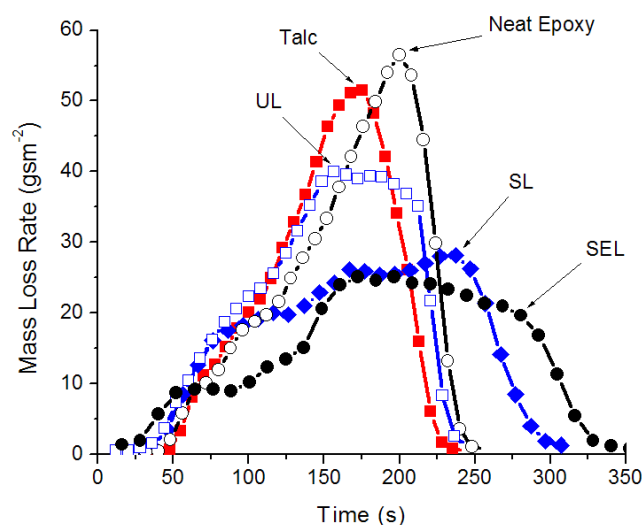
A radiative gasification apparatus<sup>1</sup> was used to measure the mass loss rate of specimens exposed in a nitrogen environment to a 50 kW/m<sup>2</sup> radiant heat flux from a cone-shaped heater. These non-flaming conditions allow the condensed-phase gasification processes to be de-coupled from complicating gas-phase processes; permit a better estimate of the actual incident heat flux that is producing the fuel gas; and provide a much better view of surface phenomena (*e.g.*, bubbling, charring, intumescence) during degradation. The standard uncertainty is ±2% for the measured mass loss (and residue) and ±10% for the mass loss rate. The peak mass loss rate (**PMLR**) and the time to PMLR (**t<sub>p</sub>**) are related to the peak heat release rate and time to peak measured by cone calorimetry, which are key flammability measures. The standard uncertainty for the measured t<sub>p</sub> is ±15%. The samples were disks with a diameter of 75 mm and a mass of 25 g. All samples were conditioned at (25±1) °C and (50±5) % relative humidity.

## RESULTS AND DISCUSSION

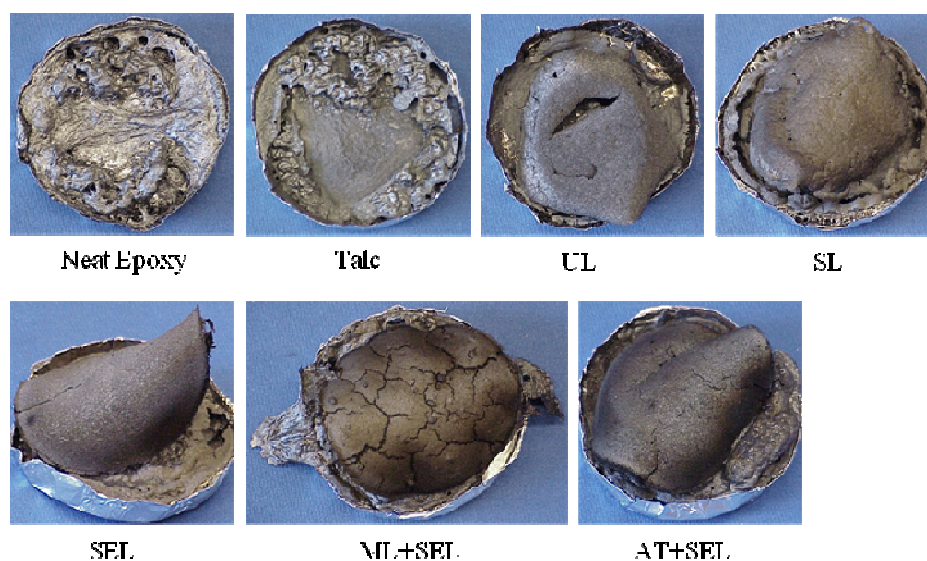
The mass loss rate measured by gasification apparatus for the neat epoxy and the samples containing 10 % talc, unsulfonated lignin, sulfonated lignin or sulfonated ethoxylated lignin are shown in Figure 1. All fillers reduce the PMLR of neat epoxy. The reduction achieved with inert fillers like talc is minor and is due to a decrease in the organic combustible fraction. Table 1 reports the decrease in PMLR (ΔPMLR) as compared to the neat epoxy and the residue produced after the test. Talc has a ΔPMLR of 8.1 % and does not increase the amount of char. UL shows a more pronounced decrease in PMLR (ΔPMLR = 29.0 %) but no significant charring. SL and SEL show a strong decrease in PMLR (ΔPMLR is 49.6 % and 55.4 % for SL and SEL, respectively) and also an increase in residue due to epoxy charring (see Table 1). This is most likely an effect of lignin sulfonated groups, in fact, the charring agent precursor is usually a phosphorous compound, but sulphur compounds can also be used. When heated, sulfonates decompose to form strong mineral

<sup>†</sup> %, meaning mass fraction percent, is used as such throughout this paper.

acids that catalyze dehydration reactions and promote charring<sup>2</sup>. According to the technical data sheets, SEL contains about 1.7 times more sulfonated groups than SL. Thus, difference in charring performance between SL and SEL can be explained by a different degree of sulfonation. The ethoxylation of lignin in SEL can also improve the dispersion of the filler and, therefore, the mechanical properties of the composite.<sup>3</sup> A comparison between the residues generated after the gasification apparatus test is shown in Figure 2. A compact protective char was produced during the first 100 s by SEL. After that this protective shell debonded and exposed the underlying polymer. UL and SL have a similar behaviour but charring is less pronounced. Talc and SL have a similar behaviour but charring is less pronounced.

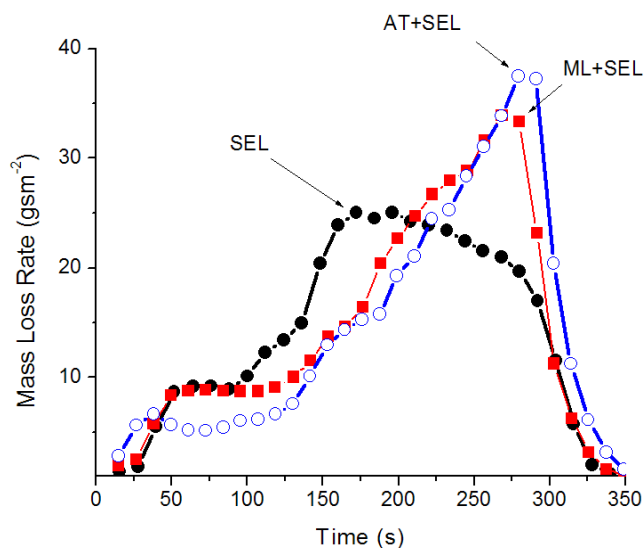


**Figure 1.** Mass loss rate measured by gasification apparatus for the neat epoxy and the samples containing 10 % talc, unsulfonated lignin (UL), sulfonated lignin (SL) or sulfonated ethoxylated lignin (SEL). A reduction of 55 % in PMLR is achieved for SEL.



**Figure 2.** Comparison between the residues generated after the gasification apparatus test.

Flame retardant systems where a char source (*e.g.*, epoxy or a polyol) is combined with a charring agent (*e.g.*, phosphates or sulfonates) and a blowing agent (*e.g.*, melamine) are called *intumescent systems*. They produce a viscous swollen char on the surface of the burning polymer which protects the underlying polymer by thermal shielding. This is one of the most effective mechanisms of flame retardancy.<sup>4</sup> We prepared intumescent systems by combining sulfonated ethoxylated lignin with a conventional blowing agent, *i.e.*, melamine (ML+SEL), or an alternative bio-derived blowing agent, *i.e.*, ammonium tartrate (AT+SEL). Figure 3 shows that the mass loss rate of ML+SEL and AT+SEL is significantly reduced in an early stage as compared to SEL. However, according to video analysis, there is no significant swelling at this point, so the early reduction of MLR is not induced by intumescence. The presence of ML or AT seemed to enhance the quality of the char. The extent of intumescence obtained is limited by a highly crosslinked and rigid protective shell; in fact, a fine tuning of viscosity is required for effective intumescence.<sup>5</sup> In a later stage, the pressure generated in the underlying liquid material induced cracks and, finally, the protective char debonded from the substrate and exposed the underlying polymer. In the case of ML+SEL, the PMLR was reached when the products of decomposition leaked out from the aluminum catch pan promoting a further increase in MLR. The residue produced by ML+SEL (Figure 3) shows cracks that affect the thermal insulation especially at a late stage, whereas a more continuous protective layer is observed in AT+SEL.



**Figure 3.** Mass loss rate measured by gasification apparatus for the formulation containing sulfonated ethoxylated lignin only (SEL), and the formulations containing a combination of sulfonated ethoxylated lignin with ammonium tartrate (AT+SEL) or melamine (ML+SEL). Ammonium tartrate can be used as a bio-derived replacement for melamine.

## CONCLUSIONS

These preliminary results show that sulfonated ethoxylated lignin is a promising flame retardant for applications, like one-time short-period-use products, where biodegradability and sustainability is a priority. Ammonium tartrate, in combination with sulfonated ethoxylated lignin, can be used as a blowing agent for the preparation of fully bio-derived intumescent flame-retardant

systems. A fine tuning of viscosity and extent of cross-linking is still required to optimize the swelling in intumescent epoxy systems.

## REFERENCES

- 
- <sup>1</sup> Austin, P. J.; Buch, R. R.; Kashiwagi, T. *Fire Mater.* 1998, 22, p221.
  - <sup>2</sup> Lewin, M; Brozek, J; Marvin, M.M. *Polym. Adv. Technol.* 2002, 13, p1091.
  - <sup>3</sup> Thielemans, W.; Can, E.; Morye, S.S.; Wool, R.P. *J. Appl. Polym. Sc.* 2002, 83, p323.
  - <sup>4</sup> Camino, G.; Lomakin, S. Intumescent materials, in: A.R.Horrocks and D. Price. Eds. *Fire Retardant Materials*, Woodhead Publishing, Cambridge, UK, 2001, p318.
  - <sup>5</sup> Bourbigot, S.; Le Bras, M; Duquesne, S; Rochery, M. Recent advances for intumescent polymers. *Macromol. Mater. Eng.* 2004, 289, p499.