Epoxy-Organoclay Nanocomposites: a Fire Retardant, Bromine Free Plastic

Key words: *Polymer-clay nanocomposite, brominated flame retardants, sustainability*

Introduction: As a consumer, you hope that the products you use are safe, sustainable, and non-toxic - but that is not guaranteed. Many chemicals in everyday products have unknown or concerning impacts on human health and the environment. At the same time, a growing number of people use electronic products on a daily basis and are exposed to the chemicals contained in them, like brominated flame retardants (BFRs). BFRs are used in electronics because they are extremely effective at reducing the inherent flammability of polymeric materials. However, there is a desire in the flame retardant community to move away from brominated chemicals because of increasing concerns about the impact they may have on human health and the environment, especially during e-waste disposal[1]. BFRs are heavily used in high performance applications like epoxy based printed circuit boards. Over 90% of boards contain tetrabromobisphenol A (TBBPA) reacted with the epoxy matrix [2].

A promising new sustainable flame retardant is montmorillonite or "nanoclay" (flame retardant mechanism is shown in Fig. 1)[3] . Montmorillonite is attractive because just a few weight percent of it in a polymer composite improves the flame retardant characteristics, it is abundant in many different countries, and it is a low cost additive. But to date, nanoclay has not been demonstrated to be an effective flame retardant on its own, instead being included in a mix of flame retardants used to achieve the desired properties. These mixes include BFRs in lower concentrations than when used without nanoclay and so still pose sustainability problems.

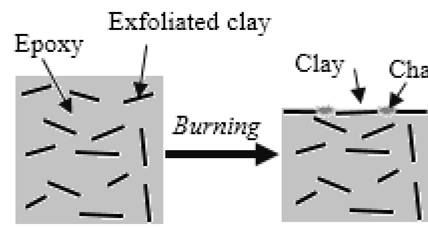

Fig. 1. A layer of clay and char builds during burning, protecting the polymer underneath from further degradation.

Hypothesis: Even dispersion of clay layers and an epoxy-tailored clay surface will improve thermal, mechanical, and fire retardant properties of the epoxy-clay nanocomposite. This material will therefore be suitable for use as a flame retardant, bromine-free plastic.

Research Plan: There are four main challenges in literature regarding the use of nanoclay as a sustainable flame retardant in epoxies, stated below with proposed solutions[4].

1) *Weak bonding between the clay and epoxy leads to poor composite properties*
In order to achieve strong bonding between the two nanocomposite constituents, organically modified montmorillonite (organoclays) will be made. Organoclays have been used to increase the dispersion in polymeric matrices, but the proposed surfactants will also be used to strengthen the interaction between the two phases. Novel surfactants will be grafted onto montmorillonite through well-established methods[4]. Aminosilane and epoxysilane surfactants were chosen because they will bond strongly to the epoxy network and to silica in montmorillonite (Fig. 2). Grafting and bonding strength in the nanocomposite will be determined by Fourier transform infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA) differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA).

2) *Even dispersion of individual clay layers in the epoxy matrix is hard to achieve*
Montmorillonite consists of ~1nm thick by 50-100μm diameter sheets stacked together with weak charges and Van der Waals forces bonding them together. Processing conditions such as grafting reaction temperature/time, intercalation procedure, and the kinetics of the epoxy curing

inside and outside the clay layers will be factors that affect the dispersion of clay layers and will be optimized for this system. Conditions will be assessed by their potential for implementation in large scale manufacturing. Dispersion will be determined by x-ray diffraction (XRD) and transmission electron microscopy (TEM).

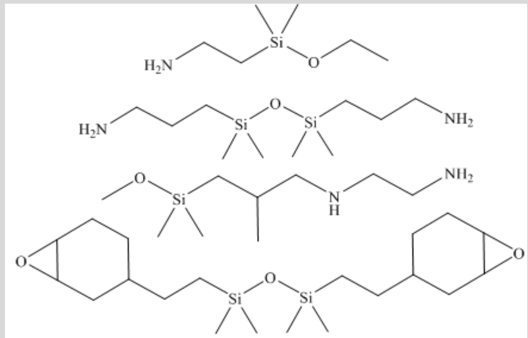

Fig. 2. Selected structures of proposed novel surfactants. Silane groups will bonds to montmorillonite and the amine/epoxy groups will bond into the epoxy network.

3) *Nanoclay has not been shown to meet the UL94 standard when used as a flame retardant by itself*
Flame retardancy of the final nanocomposites will be tested at the Forest Products Lab in Madison, WI, due to the lack of equipment at Purdue University. All nanocomposites are not expected to be promising, but once a final epoxy-organoclay composition is settled on it will be sent to the Underwriters Laboratory (UL) to receive a rating for the UL94 standard "the Standard for Safety of Flammability of Plastic Materials for Parts in Devices and Appliances testing." Flammability will be determined by cone calorimetry and limiting oxygen index (LOI).

4) *There is no standard assessment of sustainability for flame retardants*
In order to determine whether our nanocomposite is more sustainable than what is currently used, a comparative Life Cycle Analysis (LCA) will be conducted focusing on energy & water usage and pollutants produced from cradle to grave. Sustainability will be determined through OpenLCA software used with the EPA's TRACI impact assessments (Tool for the Reduction and Assessment of Chemical and other environmental Impacts).

Expected Results: One or more of the surfactants tested will create an epoxy-organoclay nanocomposite with desired thermal, mechanical, and flame retardant properties when made under specific processing conditions. Higher mechanical and thermal properties are also expected from a fully dispersed nanocomposite. A fundamental understanding of silane modifier structure/properties relationships on epoxy-organoclay nanocomposites will be contributed to scientific knowledge. Four papers will be published on: organoclay and nanocomposite manufacturing and properties, nanocomposite fire retardancy, sustainability assessment of nanocomposites, and reaction scheme of silanes bonding to montmorillonite. Conferences will be attended to present these findings including the American Chemical Society National Meeting and the International Symposium of Sustainable Systems and Technologies.

Broader Impacts: This nanocomposite can be used in current epoxy applications, replacing the need for BFRs. Due to improved properties of the nanocomposite less material will be needed to achieve the same strength, reducing the environmental impact of a potential epoxy product. These findings will also be shared through outreach programs such as Project Interchange and Innovation to Reality to inform and inspire the next generation of scientists and engineers.

[**1.]** Sjödin, A., Carlsson, H., Thuresson, K., Sjölin, S., Bergman, A., and Ostman, C. "**Flame Retardants in Indoor Air at an Electronics Recycling Plant and at Other Work Environments.**" *Environmental Science & Technology* (2001) [**2.]** EPA. "**Flame Retardants in Printed Circuit Boards**" *Design for the Environment* (2008) [**3.]** Morgan, A. B. and Gilman, J. W. "**An Overview of Flame Retardancy of Polymeric Materials : Application, Technology, and Future Directions**" *Fire Materials* (2012) [**4.]** He, H., Tao, Q., Zhu, J., Yuan, P., Shen, W., and Yang, S. "**Silylation of Clay Mineral Surfaces**" *Applied Clay Science* (2013)

Statement of originality: I certify that this proposal is my independent and original work.