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Tannic acid-based prepolymer systems for enhanced intumescence in epoxy thermosets

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Tannic acid (TA) is a bio-based high-molecular-weight organic molecule. Although biologically sourced, TA is a pollutant in industrial wastewater streams, and there is desire to find applications in which to downcycle this molecule. Many flame retardants (FRs) used in epoxy are synthesized from petroleum-based monomers. Various bio-based modifiers have been developed, but increasing the flame retardancy of the system without trade-offs with other properties has proved challenging. In this work, TA is incorporated into the thermoset. The molecular behavior of the system was dependent on the TA loading, with low concentrations causing the molecule to be surface-functionalized, while at higher concentrations the molecule was cross-linked into the network. The material was further characterized for its cross-link density, thermal stability, mechanical and thermomechanical properties and FR ability. In this work, TA was found to work well as an intumescent agent but did not reduce the heat release rate. The results of this study suggest that the external (hydrophilic surface-phenol groups) and internal (D-glucose and attached phenyl groups) structural regions of the TA molecule impact the FR ability of the molecule in epoxy separately. Maintaining the structural integrity of both regions is critical to the synergistic FR behavior of the molecule.

Notation

S_e	standard error
T_d	temperature of thermal degradation
T_g	glass transition temperature
ϕ_c	weight fraction cross-linked
ϕ_f	weight fraction surface functionalized

1. Introduction

After the initiation of a fire, it is estimated that in a modern home, an individual has 3 min to evacuate, an amount of time that has significantly decreased since the mid-twentieth century.[1,2] The reduction in fire escape times is largely due to the change in household materials from more natural, plant-based wood and fibers to more flammable materials such as plastics and synthetic fibers and foams that are used currently in many domestic consumer products.[3] There are two main types of plastics in use in the modern home: (*a*) thermoplastics, such as nylon, polyethylene and polystyrene, which are used in many applications such as insulation, packaging and casings, and (*b*) thermosets, such as polyurethane, polyurea and epoxy, which are used in many other applications, including floor coatings, pipe linings, upholstered furniture and electronics.[4–8] In 2015, the global demand for plastic exceeded 300 Mt, and this value is growing steadily at an average rate of 3·4%, with US plastic companies employing over 1 million workers and providing nearly US$400 billion in annual shipments.[9,10] The vast majority of plastics are synthesized from precursor chemicals that are industrially sourced from petroleum during the refining process.[11,12] For this reason, it is unsurprising that these chemicals would cause concern with flammability in domestic applications and decrease the time to evacuate.

Although the adoption of flame retardants (FRs) in the industry has led to a significantly increased time to evacuate, there are significant concerns with the toxicity of these chemicals, particularly at the end of the life of the material.[13,14] Although it is expected that in most materials the resulting composite would be inert and benign, this is in fact not the case. Research shows that these FR additives, other additives and unreacted monomer or precursor units in plastics leach out during the lifetime of the consumer product and then after the product is put into the waste stream, resulting in many of these compounds entering the potable water supply.[15–17] This is particularly concerning, as in most plastics, FR additives are loaded between 2 and 60 wt% into the system, making them often a considerable amount of the weight of the polymer.[18,19] More recent research has shown that bioaccumulation of select FRs in humans can lead to delayed growth, thyroid alterations, attention deficit hyperactivity disorder, poor social complexity symptoms and even cancer.[20] Furthermore, the health impacts of some FRs are felt more strongly in less wealthy regions of the world, where individuals are found to have elevated concentrations of FRs in breast milk and water.[21] In response to this, researchers have developed synthetic, non-brominated, alternative FR compounds, but many of these compounds still bioaccumulate, require similar loading levels if not higher than their counterparts and have high persistence and toxicity in the environment and human health.[14] Ongoing research

shows that there is a significant need for non-toxic, non-synthetic alternative FRs to minimize toxicity at the end of life of products. For this, most researchers have turned to biologically sourced compounds to minimize the effects to humans and the environment downstream when leaching inevitably occurs.

There is currently ongoing research on biologically based and eco-friendly FR additives in the literature, including molecules such as cellulose, deoxyribonucleic acid, lignins, phytic acid, isosorbide, diphenolic acid, cyclodextrin, condensed tannins and tannic acid (TA). These compounds are often limited in application by solubility mismatches between compounds and hydrophobic polymer systems.[22–28] There is currently a wealth of literature on eco-friendly FR alternatives, including phosphorus-doped silica,[29] zinc-based smoke suppressants[30] and alumina-coated silica and silica,[31] and processing methods for making hybrid inorganic–organic coatings, including layer-by-layer deposition by spray and dip coating[27] and sol–gels for thermoplastic materials and even fabrics,[27] but many of these hybrid solutions are limited by their durability to washing and the processes are difficult to scale up for industrial application.[27] There are very few biologically and/or eco-friendly FR additives currently in use for thermoset materials, particularly for epoxy. One example is inorganic hydroxides, which are relatively non-toxic and smokeless; however, polymer composites of metal hydroxides do not always meet the demand for epoxy.[28] Epoxy is a thermoset material that is formed by the reaction of a diglycidylated compound, often the diglycidyl ether of bisphenol A (DGEBA), and a multifunctional hardening agent that can be aminated, sulfonated, acid-based or even phenol-based among other functionalities. Epoxy materials are used in a variety of domestic applications, including electronics, floor coatings and domestic potable water pipe linings.[8,32,33] The addition of epoxy into domestic applications is at least partially responsible for the decrease in domestic evacuation times described in the literature, and the use of FRs in this material, particularly in electronic circuit boards and domestic coatings, is a well-known method to decrease its flammability.[13,34,35]

There is a need for researchers to develop methods for increasing the dispersibility of biologically based FR alternatives in epoxy without the need for chemical modification or solvents. There is very limited research in this topic for several bio-based chemicals earlier mentioned, in particular TA. TA is a biologically sourced antioxidant found in nuts, galls, seeds and tree bark that is Food and Drug Administration approved to be consumed by humans and is generally regarded as safe. TA has been explored as an additive in a variety of polymer matrices, including poly(lactic acid) (PLA), nylons, formaldehyde-based polymers, polyesters and urethane foams.[36–44] It has previously been explored as a functional additive in epoxy, but not for its intumescent ability in this polymer, which is mostly due to the significant compatibility mismatch between TA and epoxy.[35] Previous researchers have combated these compatibility limitations in many polymer systems by use of chemical modification and have been able to achieve high loading levels of TA up to 50% in many polymer systems.[38,43–45] While many researchers have explored the dispersion of TA in different polymer matrices, the success of incorporation of unmodified TA has mixed FR results. Researchers have shown that incorporation of unmodified TA into PLA, polyamide and acrylonitrile–butadiene–styrene and coating on nylon 6,6 did not increase the flame retardancy of the systems unless additional synergistic additives or chemical modification were used.[28,46–49] However, other researchers have shown that chemical incorporation of only 2% TA into an epoxy/clay aerogel system decreased the heat release rate (HRR) by up to 20%.[50] Other researchers have shown that chemical incorporation of tannins to formaldehyde phenolic foams decreases ignitability and the HRR.[49] Previous work has determined methods for dispersing high concentrations of unmodified TA in epoxy while maintaining compatibility without the use of solvents or chemical modification. Little research has been done to explore chemically incorporating TA into epoxy as a prepolymer resin that, on hardening, results in an FR thermoset. Because two-part epoxies are utilized industrially, finding methods to incorporate TA into epoxy resin or the hardeners currently used would increase the likelihood of adoption into the application.

The purpose of this work is to determine the chemical interactions at low loading levels of TA in DGEBA with the hope of developing an ideal prethermoset resin of reacted TA and DGEBA without producing a polymer that is too viscous to be hardened further, as is the case with epoxy samples containing TA at 9 wt% or higher. Further, to meet the knowledge gap in chemically incorporated TA systems in the scientific literature, the flame retardancy of the resulting thermoset was studied. The resulting prepolymer resin shows promise for use in this application, as not only did it produce a material that was less prone to crystallization and could potentially have an increased shelf life, but also it will hopefully reduce the impact of FR intumescent additives on human health and the environment.

2. Methods

2.1 Materials

TA was purchased from Sigma-Aldrich (St Louis, MO, USA). EPON 825 (DGEBA) resin was purchased from Hexion, Inc. (Louisville, KY, USA). Mold Max 60 silicone precursor and initiator (parts A and B) were purchased from Smooth-On, Inc. (Macungie, PA, USA). Industrially, there are many hardeners utilized for epoxy and the hardener depends on the application. For this study, GP2074 novolac resin was chosen as the hardener for this study and was purchased from Georgia Pacific (Atlanta, GA, USA). This hardener was chosen because it is currently industrially utilized in a variety of applications, including molding, laminates, coatings and electrical applications. Additionally, aminated compounds that are commonly used as epoxy hardeners, such as triethylenetetramine, have been found to react with the surface phenol groups on tannins, which could affect the properties of the resulting polymer.[51] Twenty-milliliter

borosilicate scintillation vials were purchased from Thermo Fisher Scientific (Waltham, MA, USA). Poly(tetrafluoroethylene) magnetic stir bars were purchased from Carolina Biological Supply Company (Burlington, NC, USA).

2.2 Composite positive mold preparation for plaques and bars

A three-dimensional design of a composite block was created using the Fusion 360 software program to make the necessary silicone molds. A ramp on the side of each mold was included that serves as a starting point when taking silicone out of the mold to prevent ripping the silicone. About 0·5 inch (12·7 mm) of space on each side of each positive mold was created, and about 0·25 inch (6·35 mm) on top of the mold was designed to create the bottom for the silicone mold to be generated later. A computer-aided manufacturing process in Fusion 360 was used to machine all the corners on the composite using a sheet router. An orbital sander was used to sand down the top surface of each plaque or bar using 220 grit sandpaper. This allowed silicone to separate from the composite positive mold more easily and the epoxy to separate more easily from the silicone negative mold later. The mold was sprayed with air to remove any unwanted composite dust.

2.3 Silicone mold preparation

Mold Max 60 part A (Smooth-On silicone rubber compound) was poured into a large beaker and mixed with part B at a 100A/3B ratio by mass. The solution was mixed thoroughly until it was homogeneous and red colored. The composite positive molds for each batch of epoxy were prepared by spraying with mold release (Stoner E206 silicone mold release), and then the Mold Max 60 mixture was poured into the mold until it was filled to the top edges. The silicone mold was cured for at least 12 h at room temperature on a flat surface.

2.4 TA–DGEBA heating

About 150 g of DGEBA resin (Hexion Epon 825 resin) was poured into a clean and dry beaker, and the mass was measured and recorded. The corresponding mass of TA to mix into the resin based on the desired percentages (0·10, 0·32, 1·00, 3·20, 5·00, 6·00, 7·00 and 8·00%) was calculated and added to the resin in a Nalgene container. The Nalgene container was sealed and placed in a FlackTek SpeedMixer using the 400 Max 100 holder for a 10 min mixing cycle (3 min at 1600 revolutions per min (rpm), 30 s at 0 rpm, 3 min at 1600 rpm, 30 s at 0 rpm, 3 min at 1600 rpm). The mixture was then poured into a 250 ml beaker with a magnetic stir bar and placed in a hot oil bath at 105°C for 3 h with constant stirring. Samples with higher weight percentages than 8 wt% TA were not studied in this procedure, as during this heating step, samples became too viscous to mix, which is consistent with the previous literature.[35] After 3 h, the mixture was removed from the hot oil bath and allowed to cool for approximately 20 min. Once cool, the TA–DGEBA resin mixture was poured into an aluminum foil container and heated in an oven at 150°C for 4 h. After heating, the mixture was allowed to cool to room temperature and stored for future epoxy creation.

2.5 Epoxy sample preparation

The silicone negative molds for each batch of epoxy were prepared by spraying with mold release (Stoner E206 silicone mold release), heating for 5 min at 80°C and then spraying again. The desired TA–DGEBA epoxy resin was prepared for hardening with GP2074 by measuring out approximately 54 g into a Nalgene container, and the mass was recorded precisely. The GP2074 resin was ground up using a mortar and pestle prior to mixing. The Nalgene container was sealed and placed in the FlackTek SpeedMixer without any milling media using the 400 Max 100 holder for the same 10 min mixing cycle as the TA–DGEBA resin synthesis described earlier. The mixture was then poured into a 250 ml beaker with a stir bar and heated in an oil bath at 65°C for 13 min plus an extra 1 min for every percent of TA in the solution, with the stir bar spinning continuously. Every 2 or 3 min, the mixture was monitored, and the stirring speed was increased as the viscosity of the mixture decreased. After removing the beaker from the oil bath, the mixture was poured into the silicone molds using a clean spatula. Next, the epoxies were placed in the oven for a 12 h curing program: warm for 1 h from 80 to 140°C, hold at 140°C for 3 h, warm to 160°C over the course of 1 h, hold at 160°C for 2 h and cool to room temperature over the course of 5 h (Figure 3).

2.6 Epoxy sample characterization

Optical microscopy was performed using a Zeiss optical microscope (Zeiss, Thornwood, NY, USA). Samples prepared for dynamic mechanical analysis (DMA) were analyzed under the microscope to ensure uniform thickness between samples. Image analysis was done using the ImageJ software program (National Institutes of Health, Bethesda, MD, USA).

Ultraviolet–visible (UV–Vis) spectroscopy was performed using a Lambda 950 UV–Vis–near-infrared spectrophotometer (PerkinElmer, Waltham, MA, USA). Three samples at each concentration were prepared in acrylic cuvettes. All absorbance values were normalized to an empty cuvette. Transmission was measured for all wavelengths between 200 and 800 nm to measure the full visible light spectrum. Transmission curves were analyzed using the OriginPro 2019 software program (OriginLab, Northampton, MA, USA). A UV flashlight was also used to help characterize samples. An Optimax 365 UV light-emitting diode (Led) flashlight (Spectroline, Westbury, NY, USA) was pointed at the samples. The photograph was taken using a PowerShot A70 camera (Canon, Woodridge, IL).

Thermogravimetric analysis (TGA) was performed with a Q50 thermogravimetric analyzer (TA Instruments, Newcastle, DE, USA). Samples were prepared for TGA by breaking samples in half and shaving off 15·0 ± 2·3 mg of the sample, as a powder, from the fractured surface of the epoxy. Experiments were performed in nitrogen with a 60 ml/min flow rate using a 20°C/min heating rate

from 30 to 900°C. Three epoxy samples were run at each concentration, and the results were averaged. T_d was determined by finding the peak of the mass loss rate (MLR) curve using the Universal Analysis software program (TA Instruments, Newcastle, DE, USA) and averaging the temperature values at this point. Remaining char values were calculated by measuring the weight fraction of the sample using the Universal Analysis software program (TA Instruments, Newcastle, DE, USA) at the completion of the TGA test (800°C) and then averaging the weight fraction values at this point. Thermal degradation temperatures were calculated by using the peak of the tan (δ) curve. The weight fraction of surface-functionalized TA in the system was estimated by the weight loss before 350°C on the TGA curves using the Universal Analysis software program. The weight fraction of cross-linked TA in the system was estimated by using the weight loss after 350°C on the TGA curves using the Universal Analysis software program.

Differential scanning calorimetry (DSC) was performed on liquid prepolymer samples 1 week after the precuring procedure was followed in order to give samples time to crystallize using a Q2000 differential scanning calorimeter (TA Instruments, Newcastle, DE, USA). Samples of 12·0 ± 1·2 mg were loaded into aluminum pans and run using a heat/cool/heat cycle from −75 to 200°C with a heating and cooling rate of 25°C/min. Three samples were run at each concentration, and the mean glass transition value of the curve was calculated as the midpoint of the incline/decline observed on thermograms and averaged for each concentration using the Universal Analysis software program (TA Instruments, Newcastle, DE, USA). The heat of melting was calculated by integrating the melting peak of the thermogram using the Universal Analysis software program.

DMA was performed on all samples using a Q800 dynamic mechanical analyzer (TA Instruments, Newcastle, DE, USA). Samples were prepared having dimensions of 5·5 cm × 1·2 cm × 0·35 cm by pouring prepared solutions into silicone molds and then curing. Samples were polished to remove remaining silicone from their surfaces. A dual-cantilever mechanical test was performed at a frequency of 1 Hz and displacement of 0·15 µm. The temperature was held constant at 30°C, and the storage modulus was measured for 20 min. Three samples were run at each TA concentration and were averaged. E' values were calculated by averaging the data points for all samples of the same wt% TA using the Universal Analysis software program (TA Instruments, Newcastle, DE, USA). Cross-link densities were calculated by using the equation of state for rubber elasticity, as done by previous researchers.[35,52]

Fourier transform infrared (FTIR) spectroscopy was performed using a PerkinElmer Spectrum 100 FTIR spectrometer (PerkinElmer, Seer Green, Beaconsfield, UK) outfitted using a zinc selenide (ZnSe) crystal. Samples were scanned from 650 to 4000 cm^{-1} in transmissive mode. Control EPON 825 samples were measured at room temperature. TA–DGEBA composite samples were prepared by isolating shavings from the epoxy bars described previously in the form of a powder. Samples were scanned four times and normalized to the phenyl peak at 1605 cm^{-1} using Spectrum (PerkinElmer, Seer Green, Beaconsfield, UK). Absorbance values were calculated using Spectrum (PerkinElmer, Seer Green, Beaconsfield, UK) and were averaged between samples.

Mechanical testing was performed using a compression fixture on a mechanical testing frame (MTS Instruments, Eden Prairie, MN, USA). Cylindrical samples were prepared with dimensions of 24·2 ± 1·3 mm × 30·1 ± 4·8 mm being the diameter and height, respectively. Five samples were run at each concentration, and they were loaded to break, which was determined by observable cracking and fracture on the surface of the part. Toughness values were obtained by integrating the stress/strain curves using the OriginPro 2017 software program (OriginLab Inc., Northampton, MA, USA).

Statistical analysis was performed using JMP (SAS Institute, Cary, NC, USA). A Student's *t*-test was run to compare samples. A *p*-value <0·05 was used to indicate statistically significant differences between samples. Regression analysis was performed using the OriginPro 2017 software program (OriginLab Inc., Northampton, MA, USA). Results were fit to an exponential decay and linear models, and the reported equations and standard error (S_e) values were output by the software after regression analysis. S_e values <0·05 were determined as appropriate fits for the regression.

Mass loss calorimetry (MLC) was performed using an MLC 2004 mass loss calorimeter (Fire Testing Technology, East Grinstead, UK) that was modified with a chimney and additional thermopiles. The procedure determined by Mendis *et al.*[34] was performed. Poly(methyl methacrylate), polystyrene and ethylene glycol standards were used to calibrate the instrument. The heat source was set at 35 kW/m^2 and remained constant for the duration of the test. A spark igniter was used to ignite the samples. The test was concluded when the MLR was less than 2·5 g/min. Five specimens were analyzed for each composition and were prepared according to ASTM E 2102-15 at average dimensions of 93·67 ± 0·40 length × 93·76 ± 0·40 width × 3·2 ± 0·2 height.[53] A metal frame and aluminum foil backing were used. Mass loss curves were analyzed using the OriginPro software.

3. Results and discussion

3.1 Prepolymer TA–DGEBA systems

TA has been found to react with epoxy groups as well as epoxy resin at elevated temperatures. Verification of chemical modification through FTIR spectroscopy and optical microscopy were performed (Figures S1 and S2 in the online supplementary material). The results from this study were consistent with previous literature that indicated that TA did in fact react with the epoxy resin.

Samples were characterized using UV–Vis spectroscopy to characterize their degree of 'brownness' and to measure quantifiably the dispersion in the samples (Figure 1). This browning effect was expected and is the typical result of using tannins in polymer

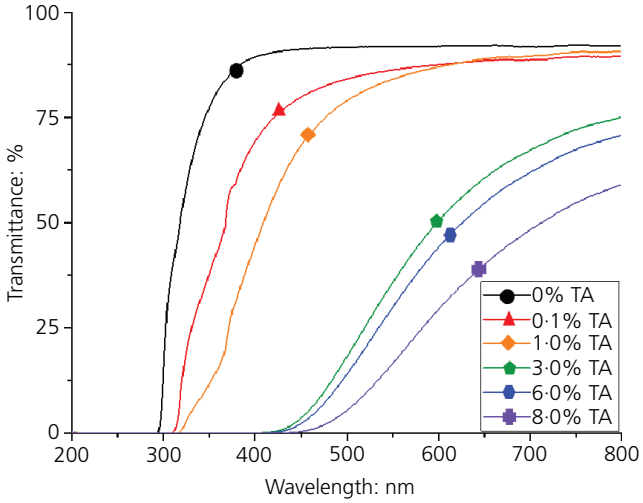


Figure 1. UV–Vis absorbance curves for TA-loaded DGEBA prepolymer resins

matrices.[35,36,39,42,44] Samples of 1 wt% TA or less were found to have transmittance values in the range of 80% or higher for all wavelengths in the visible light spectrum. At loading levels past 3 wt% TA, samples were found to have decreased transmittance at all wavelengths and near 0% transmittance at all values below 410 nm. On average, samples were found to have increased transmittance values at higher wavelengths associated with red, orange and yellow light and absorb more light in the wavelengths associated with green, blue and violet light. This result is to be expected, as samples appeared to 'brown' with increased TA loading, resulting in transmittance of colors that would produce brown. A UV Led flashlight was shone on samples and showed that at least some of the loss in transmittance was due to scattering from aggregated particles (Figure S3 in the online supplementary material).

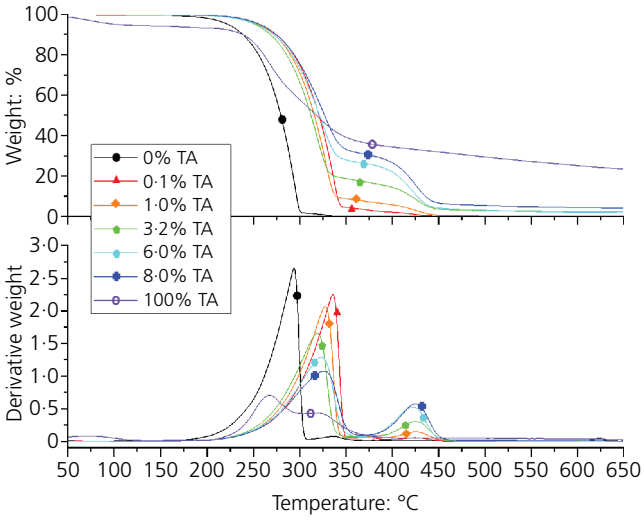


Figure 2. TGA thermograms of TA–DGEBA samples and controls

To understand the samples further, they were analyzed using TGA (Figure 2). The results from TGA show that all samples containing TA and DGEBA have elevated temperatures of thermal degradation (T_d) compared with either control, which could be indicative of the loss of protons in the sample, which are known to catalyze chemical decompositions.[54,55] No significant differences were found between the temperature of degradation in any composite system, but the magnitude of the maximum value of the derivative weight curve decreased as the concentration of TA in the composite system increased. A second degradation was observed in all TA–DGEBA composites at 425°C, and the magnitude of the maximum value of the derivative weight curve increased as the concentration of TA in the composite increased. This second peak did not correspond to TA, which indicates a more chemically stable complex of TA and DGEBA. The thermal degradation of the DGEBA control sample at 280°C has been found in the literature to be associated with degradation of the epoxy rings within the molecule.[35] Similarly, the degradation of TA at 260°C has been found by previous research to be associated with the phenol groups on the molecule.[35] No TA–DGEBA composite samples had thermal degradation peaks at either of these values, and the peak temperatures of thermal degradation associated with these composites were significantly different from the controls, although the derivative weight curves were quite broad.

Samples were also analyzed using DSC (Figure 3). After cross-linking, all samples showed a glass transition temperature near −18°C regardless of TA loading into solution, although the value was found to increase significantly in highly loaded TA samples (≥3 wt% TA) (Table 1). The control and samples containing ≤1 wt% TA are shown on the heat curve to have a melting temperature at 34°C, and no significant changes in melting temperature were observed from the control samples. The magnitude of the melting peak was increased for both the 0·1 and 1 wt% TA samples compared with that of the control. Conversely, samples containing 3·2 wt% or more TA were found to have no melting peak during the heating cycle. There were no observed crystallization peaks on the cooling curve, although glass transition was observed in all samples regardless of TA loading. For samples loaded at or below 1 wt% TA, there was no statistically significant increase in T_g. For samples loaded at 3 wt% TA or higher, there was an observed significant increase in the T_g of samples compared with that of the control.

Previous researchers have found that TA and epoxy resin react at elevated temperatures.[35,56,57] The results from this study further indicate and elaborate on the molecular behaviors between TA and DGEBA previously unexplored in the literature. At low loading levels, DGEBA reacts with TA to functionalize its surface, but the odds of DGEBA-functionalized TA molecules finding additional phenol groups in solution are rare – due to the extreme excess of epoxy groups in the solution. At loading levels at or above 1% TA, the molecules in the solution are present in high enough amounts to find each other and react, forming a cross-linked network (Scheme 1). DSC results corroborate this claim, as surface-modified TA molecules in concentrations below

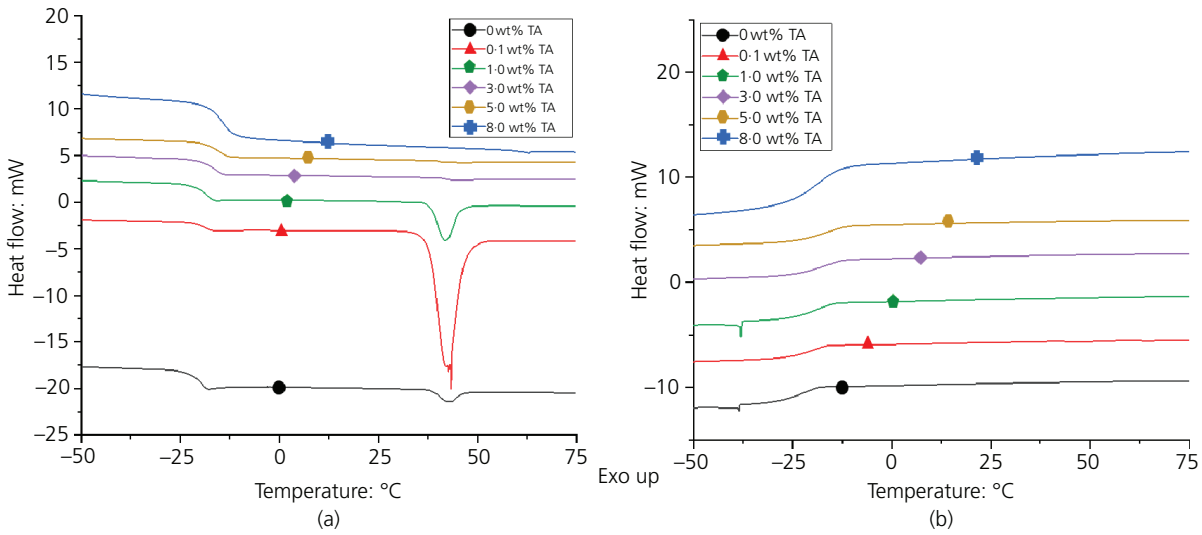
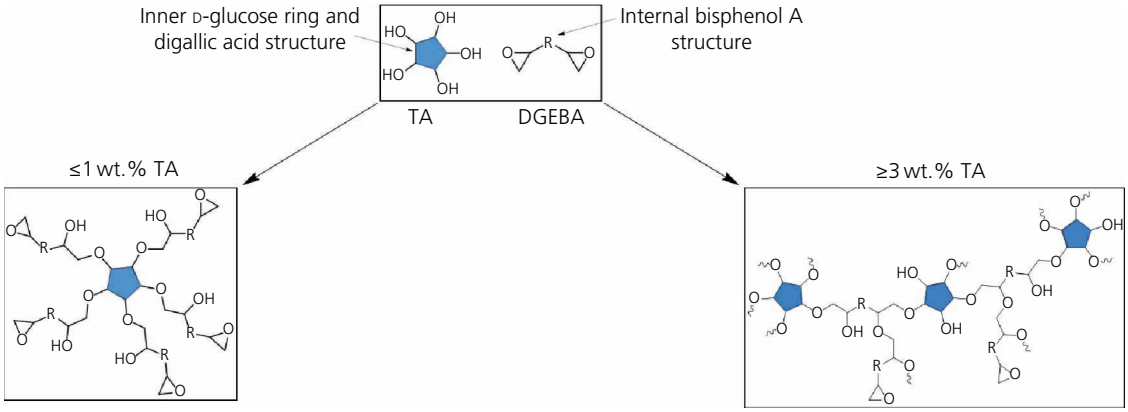


Figure 3. Differential scanning calorimetry of TA–DGEBA composites: (a) heating and (b) cooling



Scheme 1. Reaction scheme for the concentration dependence of the molecular interactions of TA and DGEBA in solution

Table 1. DSC and TGA quantitative analysis for TA–DGEBA composites

TA: wt%	Glass transition temperature: °C	Melting temperature: °C	Heat of melting: J/g	Thermal decomposition temperatures: °C	Weight fraction surface-functionalized, ϕ_f	Weight fraction cross-linked, ϕ_c
0	−20·0 ± 1·5	42·40 ± 0·03	3·80 ± 0·80	293·0 ± 8·5 N/A	3·10 ± 0·23	—
0·1	−18·6 ± 1·6	42·50 ± 0·80	26·80 ± 3·50	331·0 ± 6·2* 425·0 ± 0·8	7·20 ± 0·24*	0·10 ± 0·02
1·0	−19·7 ± 0·5	40·10 ± 1·70	7·36 ± 1·80	324·0 ± 5·4* 426·0 ± 2·1	16·80 ± 0·88*	0·20 ± 0·01*
3·0	−16·3 ± 1·9*	—	—	323·0 ± 9·6* 428·0 ± 3·4	25·90 ± 0·24*	3·00 ± 0·01*
5·0	−15·7 ± 2·1*	—	—	321·0 ± 10·8* 421·0 ± 4·0	30·40 ± 0·11*	3·10 ± 0·03*
8·0	−14·6 ± 1·9*	—	—	335·0 ± 13·2* 427·0 ± 2·2	—	5·50 ± 0·02*

Note: samples labeled with "*" denote a significant difference from control ($p < 0·05$)

1 wt% TA act as nucleation sites in the solution, resulting in higher crystallinity and a larger magnitude of the crystallization peak in the heat curve. Further, samples that are simply surface-modified show a T_g similar to that of control samples, whereas samples that are not only surface-modified but are also cross-linked show significant increases in T_g compared with the control on DSC. The cross-linked networks largely formed in samples with concentrations of TA at or above 3 wt% TA are more thermally stable than the DGEBA-functionalized TA molecules in solution and degrade at a higher temperature – 425°C. The weight fraction of surface-modified TA and cross-linked TA in the solution was calculated from the thermogram using the residual mass fractions during the plateau and after the second thermal degradation temperature (Table 1). Calculation of the weight fraction of surface-functionalized TA in the system and cross-linked TA by the method described in this study has a limitation, which is that the presence of oxygen in the cross-linked matrix could lead to mass loss during pyrolysis. These values could underestimate the weight fraction of cross-links in the system. Due to the broad nature of the degradation peak at 425°C, there is evidenced a broad distribution of cross-link densities throughout the system, with some cross-links being less dense and degrading below 400°C, while others are denser and degrade near 450°C.

This result is also consistent with UV–Vis data, which indicate a fundamental solubility change between samples loaded at or below 1 wt% TA and those loaded at or above 3 wt%. The increase in the presence of agglomerations in the higher-TA-loaded samples suggests a non-uniformly reacted composite, with regions that are less reacted and more reacted being incompatible with each other, resulting in microphase separation, something not visible to the naked eye but more easily observed under UV light, which is scattered more easily by these agglomerates. Such results have not been seen before in the literature.

3.2 Cross-linked epoxy thermosets

After hardening the TA–DGEBA prepolymers using GP2074, the epoxy samples were characterized to determine their mechanical properties (Figure 4). At low TA loading levels (≤1 wt% TA), observable decreases in ultimate strength, stiffness and work of fracture were seen. At higher TA loading levels (≥3 wt% TA), the samples were not found to be significantly different from the control sample. The preliminary explanation for this behavior is that surface-functionalized TA–DGEBA molecules in small concentrations decreased the overall cross-link density of the sample, resulting in a less strong, stiff and tough thermoset. In order to corroborate these claims, the cross-link density of the samples was calculated using

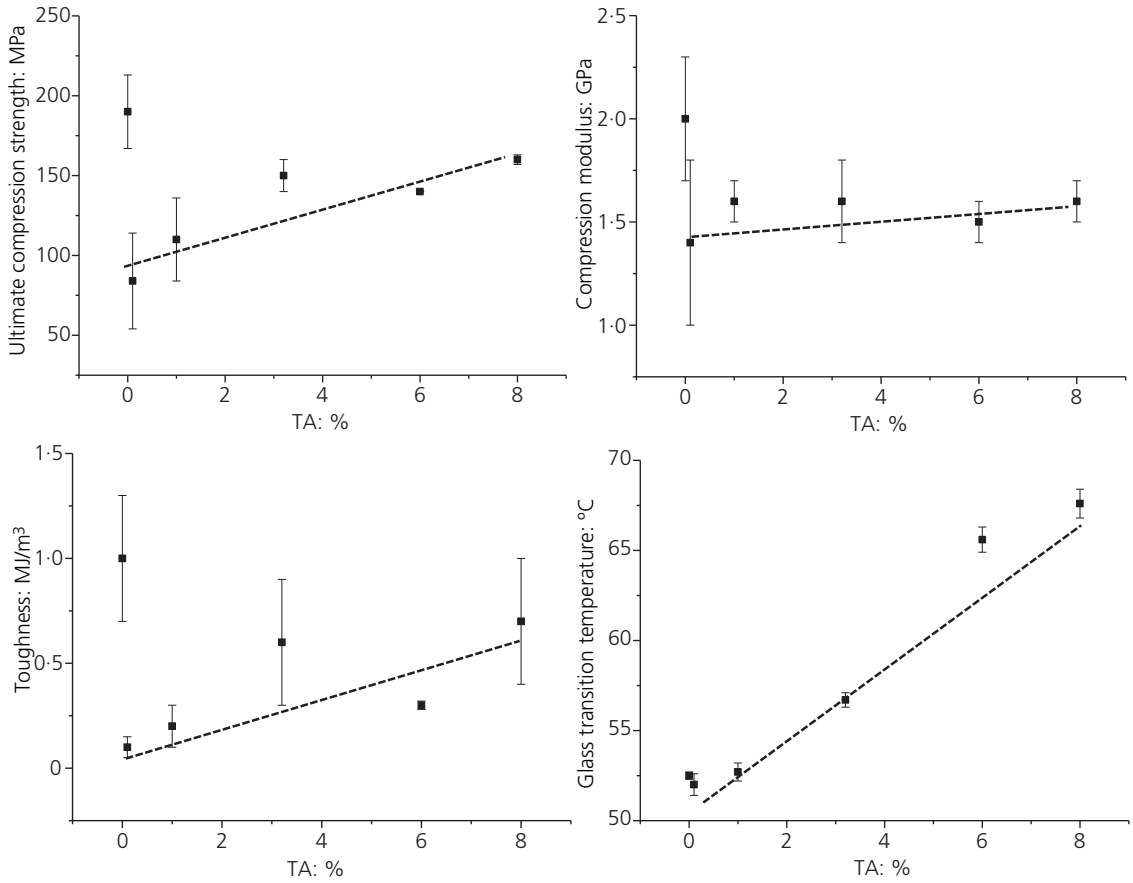


Figure 4. Mechanical and thermal testing results of TA–DGEBA-GP2074 composites. Dashed lines are added to aid the eye

DMA (Table S1 in the online supplementary material). Cross-link density was found to change significantly with TA loading. Samples containing low amounts of TA (<1 wt% TA) were found to significantly decrease the cross-link density of the system compared with the control. However, loading levels of 3 wt% TA or above significantly increased the cross-link density. Significant differences were found between all samples ($p < 0{\cdot}05$), with values significantly increasing as TA loading was increased.

DSC was used to characterize the undercure and the glass transition of the GP2074-hardened samples (Table S1 and Figure S4 in the online supplementary material). DSC curves show residual undercure in all samples during the heating, which disappeared during the cooling. DSC also showed that samples cured with 3 wt% TA or more had significantly increased glass transition temperatures compared with the control sample. Further, the glass transition temperature was dependent on TA loading into the sample, increasing with TA loading past 1 wt% TA ($p < 0{\cdot}05$). At low concentrations, the glass transition temperature did not significantly change with the addition of TA to the system.

At low TA concentrations, the TA molecules are more modified on average per molecule, as evidenced by FTIR spectroscopy. As listed by the manufacturer, GP2074 has a hydroxyl equivalent weight of 104 g/equivalent (eq), whereas TA has a theoretical hydroxyl equivalent weight of 68·04 g/eq. For this reason, it was surprising that the addition of TA to the system would initially decrease the cross-link density of the system and then increase it. However, the proximity of the three phenol groups that form the galloyl group on the arm makes achieving full surface functionalization impossible. Therefore, after the addition of GP2074 and additional heating, TA molecules in the solution cannot react to increase the cross-link density of the system, resulting in no net change in the cross-link density observed by DMA. At higher concentrations of TA (≥3 wt% TA), the molecules randomly cross-link into the system prior to cross-linking with GP2074, thereby providing additional steric limitations to the chemical functionalization of the molecules. It was expected that for this reason, TA would increase the cross-link density of the system. The results of this experiment show that the proximity of the phenol groups on the surface of TA hinders the reactivity of the individual phenol groups due to steric limitations. Further, at lower loading levels, it actually lessens the cross-link density but does not result in a significant change in T_g. At higher loading levels, it increases the cross-link density and significantly increases T_g.

The GP2074-hardened samples were also characterized using TGA in nitrogen to obtain a preliminary measurement of the FR ability of the composites containing TA (Figure 5). Preliminary results show that there is a significant increase in the temperature of thermal degradation of samples loaded at 1 wt% TA or above. Each sample shows two peaks of thermal degradation, one at 300°C, consistent with the degradation temperature of the surface-modified TA molecules as well as both the control TA and DGEBA curves, and a second at 425°C, consistent with the cross-linked TA–DGEBA degradation peak. The magnitude of the derivative weight curve does not correlate with the amount of TA added to the solution at 425°C. Samples of 1 wt% or higher TA were found to have significantly increased T_d compared with control samples, while 0·1 wt% samples did not significantly change compared with the control samples.

Unhardened TA–DGEBA composites show increased thermal stability, compared with either control alone. When these composites are hardened with GP2074, the thermal stability of the resulting epoxy is increased only in samples at 1 wt% TA or higher. Samples containing TA showed a degradation peak at 300°C that decreased as the TA content increased. This peak could suggest that the smaller monomeric species are less thermally stable than the complex. Surprisingly, samples were not found to have significantly changed remaining char at 600°C compared with the control samples. The preliminary explanation for this behavior is that adding TA to DGEBA in small amounts increased the thermal stability of the resin because it had reacted into the DGEBA networks or that there was a decrease in protons in the sample. The data likely indicate that the surface-modified TA molecules, which did not cross-link in the unhardened samples, are now able to cross-link with GP2074. The resulting TA–DGEBA–GP2074 network could be more thermally stable than just DGEBA–GP2074 networks, resulting in an increased thermal stability. However, GP2074 would be unable to cross-link fully the solution using this procedure, resulting in residual, unreacted, surface-modified TA–DGEBA remaining in the cross-linked thermoset, which degrades at lower temperature.

3.3 Flame retardancy analysis

To determine the flame retardancy of the GP2074-hardened TA–DGEBA thermosets, epoxy samples were analyzed using MLC (Figure 6). Results indicate that at low TA loading levels in DGEBA that have been hardened with GP2074, there was no

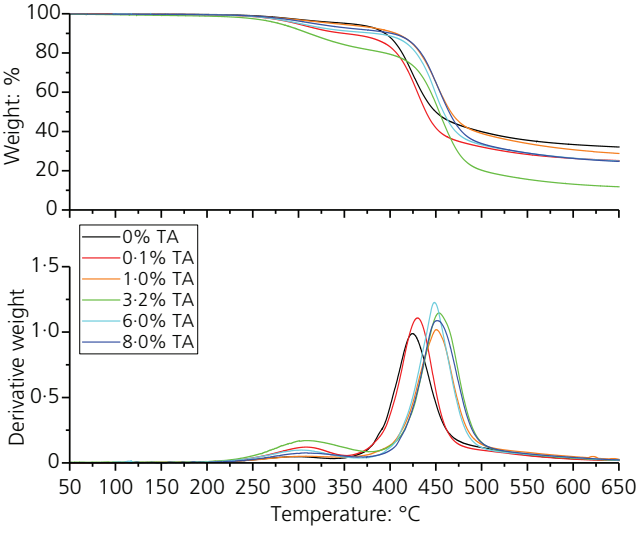


Figure 5. TGA of GP2074-hardened TA–DGEBA prepolymer systems

0% TA top and side views | 3·2% TA top and side views | 8% TA top and side views

Figure 6. Intumescent behavior of GP2074-hardened TA–DGEBA composites after flame testing

significant change in the peak HRR (Table 2). Surprisingly, in samples containing TA in 3·2 wt% or higher, the peak HRR actually increased and did not correlate with greater TA loading. The time to ignition did not significantly change from sample to sample, and in some cases decreased with TA loading. The MLR behavior was the same regardless of TA loading. Past a 1% TA loading level, the peak of the MLR curve increased significantly compared with the control but not relative to the amount of TA present in the sample. These results indicate that TA that is surface-functionalized with DGEBA is unable to function as an FR once hardened with GP2074. The total mass loss was consistent between all samples; the TA did not increase the amount of the sample remaining after MLC analysis. Samples containing TA showed slightly decreased mass loss during the duration of the test, which indicates that in the fire itself, TA can form small amounts of char, but the mass loss was most decreased in the highly TA-loaded samples.

Although the quantifiable data obtained by MLC show no statistically significant changes in the peak HRR and MLR of samples containing TA, it is also noteworthy to mention that samples containing TA did not show significantly increased char formation by mass but did show an increase in char volume at the completion of the test (Figure 6). However, the surface of the residual char was visibly cracked. This result indicates that the presence of TA does not noticeably increase or decrease the ignitability of the samples, which matches the data for the time to ignition measured by MLC. However, this result indicates that TA could serve as an intumescent additive in epoxy thermosets.

To circumvent compatibility limitations that have been found to impact significantly the mechanical properties of the resultant polymers, the surface of TA molecules was modified to match better the epoxy resin and therefore increase dispersibility. The results of this study suggest that the ability of TA to retard the spread of a fire is linked to the phenol groups on the surface of the molecule – the very thing limiting compatibility. Limiting the availability of the FR –OH groups from the surface of the molecule did not allow for the TA molecules to retard the spread of the fire significantly.

Table 2. MLC results

TA: wt%	Time to ignition: s	Total heat release: MJ	Peak HRR: kW/m^2	Peak MLR: g/min	Total smoke release: m^2	Weight loss: %
0	96·0 ± 14·4	63·0 ± 5·7	670·0 ± 93·8	0·38 ± 0·04	2600 ± 416	80·0 ± 9·7
0·1	105·0 ± 13·7	64·0 ± 9·6	639·0 ± 70·3	0·33 ± 0·02	2470 ± 272	78·0 ± 10·2
1·0	80·0 ± 8·8	75·0 ± 6·7	704·0 ± 63·4	0·32 ± 0·02	2530 ± 354	80·0 ± 6·8
3·0	114·0 ± 9·1	80·0 ± 9·6	705·0 ± 84·5	0·33 ± 0·04	2850 ± 342	79·0 ± 5·6
5·0	84·0 ± 6·9	74·0 ± 8·1	727·0 ± 83·6	0·34 ± 0·03	2520 ± 378	72·0 ± 4·5
8·0	116·0 ± 12·8	83·0 ± 11·7	744·0 ± 78·1	0·34 ± 0·03	2790 ± 363	77·0 ± 7·3

What are believed to be highly surface-functionalized molecules that were not pre-reacted into the system (≤1 wt% TA) showed no significant differences in the resulting flame retardancy nor the resulting intumescent behavior compared with control samples. This result was expected, as TA was loaded in very small amounts, so little resulting material changes should be observed. However, as TA was loaded in higher amounts (3 wt% or higher), the resulting HRR was not found to change significantly. This indicated that even residual phenol groups in the higher wt% TA systems were not readily available to slow the propagation of the fire at the flame front within the pre-reacted thermoset. The initial explanation for this behavior is that although phenol degradation happens at a lower temperature in the TGA, the flame front is likely at a temperature at which oxidation, cross-linking and phenol degradation are occurring simultaneously. Perhaps cross-linking at the flame front in higher-TA-loaded samples is hiding unreacted phenol groups in the sample. TGA results indicated that cross-linked samples had less readily available residual phenol groups. This was evidenced by the increased temperature of thermal degradation in samples containing 3 wt% or more TA. As cross-linking occurs and pushes the flame front up and away from the bottom of the fixture, less readily available phenol groups could be left behind the flame front and thus be unable to retard the spread of the fire where it will be most impactful. Additionally, the char that was formed showed visible evidence of pores and cracks on the surface. Perhaps there are too many gaseous products released as a result of the degradation of the system, which prevented the highly cross-linked char that was expected from forming.

These results also suggest that it could be that the internal structure (D-glucose ring, phenyl rings of the gallic acid groups) of the molecule alone is what results in the intumescent behavior, as results indicate that –OH groups on TA were less readily available for thermal degradation. On thermal degradation, TA becomes oxidized and cross-links into the polymer network. Simultaneously, previous research suggests that the thermal degradation of TA releases carbon dioxide (CO_2), carbon monoxide (CO) and water (H_2O) into the atmosphere.[25] The present work corroborates these claims. The combination of cross-linking and release of gas causes the intumescent behavior seen in this work. Using this knowledge, a more FR and intumescent TA-based additive for epoxy systems may be engineered. It is important to understand that the compatibility limitations of TA in epoxy causes decreased mechanical properties in the resulting solubility. However, simply surface-modifying the molecule to circumvent these compatibility limitations will result in a purely intumescent material with no significant changes to the HRR and MLR.

4. Conclusion

Currently used industrial FR additives have unintended impacts on both the environment and human health, and there is significant industrial demand for biologically sourced additives to replace these more toxic compounds. Currently, one of the major limitations to many of these biologically sourced compounds is poor compatibility between the additive and the polymer matrix, and this is particularly the case for TA in epoxy. Using high-temperature processing techniques, up to 8 wt% TA was dispersed in epoxy resin with good compatibility, and its intumescent behavior was studied. The results from this study indicate that adding TA to a DGEBA epoxy resin can not only serve to improve the intumescent behavior of the polymer without significantly impacting the mechanical properties of the polymer but can also decrease the propensity for epoxy resin to crystallize in transit. Both results indicate that TA has the potential to serve as a biologically sourced, economical replacement to currently available intumescent epoxy additives.

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