Tannic acid based super-intumescent coatings for prolonged fire protection of cardboard and wood

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1 | INTRODUCTION

Intumescent coatings, defined as coatings that swell into a thick, thermally-insulative foam in a fire situation, have as key ingredients a char-forming carbonaceous material, a mineral acid catalyst, a blowing agent, and a binder resin[1] and have been the subject of more recent reviews.[2]–[5] Such coatings are used in many applications, a principal one being the protection of steel structures to significantly delay the effects of a fire on the weakening of such structures. Intumescent formulations have not witnessed substantial compositional changes in recent years, although there is increasing awareness of environmental impact and a drive toward improved sustainability of intumescent coatings. As an example, boric acid is a popular ingredient due to its ability to form mechanically-robust char ‘glass’ (essentially boron oxide) via an endothermic dehydration mechanism and supplying protons as a catalyst to char-forming reactions. However, boric acid is emerging as a reprotoxin, and its toxicity has resulted in its classification as a “Substance of Very High Concern” by the European Chemical (ECHA), which led us to develop an alternative based on poly(acrylic acid) and partially-neutralized compositions.[6]
The increasing attention toward sustainability and toxicity of intumescent coating components has inspired investigation into bio-sourced ingredients, outlined well in a review by Hobbs.[7] These include tannins, phytic acid, isosorbidies (derivatives of starch), and more. Particularly, this work aims to focus on the use of tannic acid (TA).

Over the last 10 years, it has garnered increased attention for application in fire protection.[8–13] A few notable examples as they pertain to this work are summarized here. First, the work of Kim et al. discusses incorporation of TA in to bisphenol A-based epoxy to create resins with a 46% increase in limiting oxygen index.[14] Second, Shao et al. mixed TA-functionalized graphene with ammonium polyphosphate and pentaerythritol to be coated on expanded polystyrene foam. A 300 μm coating was reported to improve the UL-94 rating from a failing rank to V-0 and decrease peak heat release rate by approximately 54% (435.6–201.4 kW/m²), all while maintaining the insulation utility of expanded polystyrene foams measured by similar thermal conductivities (0.048 W/mK control to 0.053 W/mK sample system).[15]

The third and final example discussed here is that of Silveira et al. in which black wattle tannin was incorporated in to epoxy-based resins alongside various concentrations of boric acid, melamine, and the organophosphorus flame retardant known as 9,10-dihydro-9-oxo-10-phosphaphenanthrene-10-oxide. This mixture was coated on steel plates, cured, and exposed to a blow torch to obtain time-temperature plots up to 30 min. Relative to the no-coating control which reached (and maintained) 450°C within 10 min, the best composition had a max temperature of 147°C after 30 min.[16]

This manuscript aims to build on the existing base of knowledge in two major areas. First, published literature on coatings for substrate protection offer limited comparison to that of fully complete control intumescent system such as one containing pentaerythritol, ammonium polyphosphate, and melamine (char former, acid source, and blowing agent, respectively). In addition, this paper offers substantial char analysis to elucidate composite fire protection mechanisms relative to the aforementioned control intumescent system and the role tannic acid plays in those mechanisms. This char analysis can act as a base by which further composites can be evaluated and compared against to further the field as a whole.

Herein, we report on the use of TA in epoxy resin formulations that also include melamine and ammonium polyphosphate to afford coatings with outstanding intumescence characteristics. Of particular significance is our observation of what we term ‘super-intumescence,’ specifically the creation of copious amounts of low-density (< 4 mg/cc) char, and the ability of such coatings on, for example, cardboard and various types of wood to protect the materials from combustion for over 15 minutes in a propane torch flame. As discussed in detail herein, the TA-based formulation was characterized by quantitative combustion techniques with resulting char studied via Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and surface area measurements. We believe our observations and analytical results are superior as compared to previous reports using TA composites and merit attention toward a variety of potential applications if not limited to the fire protection and safe packaging.

2 | EXPERIMENTAL METHODOLOGY

2.1 | Materials

2.1.1 | Chemicals used

Two-part epoxy resin was used as a binding agent in the intumescent coatings. The BPA-based epoxy (EPON Resin 828) was obtained from Hexion Inc., and the polyamine curing agent (Ancamide 903MAV) was obtained from Evonik without need for further purification. TA, melamine, and pentaerythritol were all obtained from Sigma–Aldrich. Ammonium polyphosphate (Exolit AP 422) was obtained from Clariant Corporation. The cardboard was recycled from used Amazon-brand shipping boxes. The plywood and poplar were obtained from a local lumber store (WoodCraft of Cleveland).

2.2 | Methods

2.2.1 | Additive preparation

All composites were made with 56 wt% additive and 44 wt% epoxy resin binder. Particles were ground using a Hamilton Beach brand coffee grinder and passed through a 75 μm sieve to ensure small particle sizes and optimal compatibilization with the binder. In all sample preparation methods, additives were added to a single vial and mixed on a Fisher brand analogue vortex mixer. The maximum speed was used (3200 rpm) for at least 2 min for optimal powder dispersion.

2.2.2 | Puck formulation

Sample pucks were formulated by compounded powder additives with an epoxy resin prior to curing. In an example system, 10 g of TA (or PER), APP, and MEL in a 1.3:1:1 mass ratio, respectively, were mixed with 4.7 g of epoxy in a teflon mixing dish. The mixture was blended by hand for 5 min until a viscous uniform paste was formed. After sitting for 5 min, 3.2 g of polyamine curing
agent was added. After 5 more min of mixing, the reaction mixture was cast into a circular teflon puck mold with dimensions of 3.5 mm deep and 56.8 mm in diameter. Excess material was discarded. The cast sample was held under vacuum for an hour to remove any dissolved gases, and then placed into an oven to cure at 60°C for 18 h.

2.2.3 | Cardboard coating formulation

The procedure for cardboard coating was identical to the puck preparation. However, instead of casting into a teflon puck mold, the viscous mixture was brushed evenly onto a 12.7 × 12.7 cm cardboard sheet and cured via the same procedure. Specific concentrations can be found in Table 2.

2.2.4 | Capsule formation

Following the cardboard tests, capsules were created to simulate how the coatings would respond to a package fire. Using an Epilog Pro 48 brand laser cutter, a design (Figure S1) was used to produce samples cut from soft wood such as plywood and hardwood such as poplar. Due to their soft nature, cardboard samples were cut out by hand. Once cut, cardboard samples were assembled and adhered to one another using duct tape, while the wooden samples were adhered using the epoxy and amine binder. The control wooden capsules were held together with duct tape, as epoxy would unnaturally alter the failure time. The back square piece had dimensions of 7.62 × 7.62 cm. Once assembled, the capsule had opening dimensions of 12.7 × 12.7 cm with a diagonal length of 10.2 cm.

2.2.5 | Cone calorimeter sample preparation

Sample plates for cone calorimetry were prepared using the same method as the puck samples, but instead were cast into a 10 × 10 × 0.25 cm mold and cured via the same conditions. These dimensions were chosen to adhere to ASTM E1354.

2.3 | Fire-Testing techniques

2.3.1 | Meker torch testing for circular pucks

Sample pucks were oriented perpendicular to a horizontal-facing meker torch and held 5 cm away (which corresponds to a ~ 515°C incident flame). Additionally, the torch was shifted 1 cm to the right of the center of the puck. For safety, experiments were performed in laboratory hood, whose vacuum pulls the torch’s flame toward the back of the hood. These dimensions were chosen to allow the fire to directly hit the center of the puck (Figure S2). A meker torch was chosen rather than a Bunsen burner to provide more realistic testing conditions. This is because the meker torch’s flame is a turbulent flame, which better simulates real-world fire conditions. Similar changes were made for other meker torch testing as well. The sample puck was then exposed to a turbulent meker torch flame (which uses natural gas at a flow rate of 175 ml/min). When intumescent char covered the torch, excess char was scraped away with forceps to allow intumescence to continue. Sample testing was concluded when no solid composite was left to intumesce.

2.3.2 | Cardboard coating failure test

Cardboard coating failure tests were adapted from procedures used in the Department of Transportation and Federal Aviation Administration joint report on passive protection of lithium battery shipments. The coated cardboard sheets were mounted above a char collection pan via a sidearm in order to obscure as little of the coated surface as possible (Figure S3). A propane torch was positioned 6 cm from the center of the sheet, which translates to an approximately 815°C incident flame. Once the propane blow torch gas valve was opened completely and ignited, the test lasted until the failure, defined as the presence of a flame on the uncoated side, or 10 min if the sheet was not compromised in that time. For thin composites of TA and PER (1.0 mm thick), testing continued until failure to quantify a more definitive difference. In addition, for these two sample sets a thermocouple was fixed to the back of the cardboard to monitor temperature rise in real time. Temperature was monitored on an Oakton Acorn temperature JKT thermometer with attached thermocouple.

2.3.3 | Coated capsule failure test

Capsule failure testing was performed similar to that of the meker torch puck tests, shown in Figure S4. Using the same orientation, the end of the meker torch was situated 8 cm from the back of the capsule, 1 cm above the bottom lip, and 4 cm from the right lip. A typical experiment started by igniting the meker torch (still using a flow rate of 175 ml/min) and continued until a noticeable
failure was observed. A “noticeable failure” was defined as either a hole in through the substrate or ignition of exterior, uncoated substrate.

2.4 | Analytical techniques

2.4.1 | Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed on PER and TA using a TA Instruments brand Q500 TGA. Data were collected by heating 6–10 mg of sample from 20 to 600°C under constant nitrogen flow. Data were analyzed using TA Universal Analysis software and plotted alongside differential thermogravimetry (DTG), which is the derivative of the mass loss plot as a function of temperature. Plotted data were created using Origin software.

2.4.2 | Microscale combustion calorimetry

Microscale combustion calorimetry (MCC) was performed on PER and TA using a Fire Testing Technology microscale combustion calorimeter. Sample testing adhered to ASTM D7309, method A, using a heat rate of 1°C/s to 750°C using a sample mass of 5–10 mg. Samples were tested in triplicate, with plotted data being a representative curve. Data plotting were done using Origin software.

2.4.3 | Cone calorimetry testing

Cone calorimetry (CC) was performed on sample composites with the dimensions of 10 × 10 × 0.25 cm using a Fire Testing Technology brand oxygen-consumption calorimeter. Sample testing adhered to ASTM E1354, with a heat flux of 50 kW/m². Samples were replicated three times to ensure statistical significance. Under the ASTM standard, a grid is recommended. However, based on unpublished data, a grid does not deter expansion but rather increases ‘noise’ in resultant data. As such, grids were not used during testing. Data plots were created using Origin software.

2.4.4 | Nitrogen adsorption–desorption testing

Nitrogen adsorption–desorption isotherms were recorded on a TriStar II 3020 (version 2.00) BET instrument at –196°C. Before BET measurements the samples were calcined overnight at 200°C under continuous nitrogen gas flow. The specific surface area was calculated using adsorption data by the BET method and the pore size distribution was computed from the desorption branches of the isotherm using density functional theory available in the BET software.

2.4.5 | Raman spectroscopy

The Raman spectra were collected by Raman spectroscopy (Renishaw), using 514 nm laser with a 50× air objective and a laser power of 20 mW for an accumulation time of 30 s and averaging over consecutive three scans. The spectra were analyzed by baseline normalization and peak fitting using Origin software.

2.4.6 | X-ray photoelectron spectroscopy

The chemical composition of the char was characterized by XPS on PHI 5000 Versaprobe XPS using a monochromatic Al X-ray source with spot size of 200 μm. The survey scan was performed in the range 0–1200 eV, with pass energy 93.90 eV, energy step 0.400 and time/step 25 ms. For high resolution (HR) XPS scans, pass energy of 11.75 eV, energy step of 0.100 and time/step of 50 ms were used. XPS data analysis was done with the commercially available Casa XPS software (www.casaxps.com), and the HR peaks were deconvoluted into sub-peaks using Gaussian or Gaussian-Lorentzian (GL) functions. The charge correction of the spectra was done by placing the main C 1 s component at 284.5 eV as a reference for graphitic carbon.[18]

3 | RESULTS AND DISCUSSION

3.1 | Thermal investigation via TGA and MCC

Prior to composite formulation, powders of PER and TA were evaluated to understand their degradation properties. Pentaerythritol is a well-known and well-utilized chemical in the realm of intumescent coatings.[19–21] Arguably the most common char-forming agent, PER is a tetra-ol molecule that can readily create char in the presence of an acid-catalyzing species. Alone, it is known to undergo a single stage volatilization without degradation at approximately 200°C, corroborated experimentally in Figure 1(A), (B).[22]
TA, on the other hand, has only gained traction in the area of fire science in recent years, partially inspired by its green origins.\cite{7,23} Much like PER, TA degradation literature exists that corroborates data shown in Figure 1 (A)-(B) and elucidates the specific degradation mechanism. The bimodal peak beginning at approximately 200°C is attributed to release of 1,2,3-benzene triol and carbon dioxide via a decarboxylation mechanism that occurs on TA’s outer rings.\cite{24}

While degradation information is known in literature with respect to TGA analysis, thermal performance via MCC, as shown in Figure 1(C) is novel and insightful, especially when coupled with TGA data. Via ASTM D7309, method A, samples were heated in an inert atmosphere, with degradation volatiles swept up in to a 900°C, oxygen-rich combustor to ensure complete volatile combustion. From the TGA literature, it is known that PER volatilizes rather than degrades, so no heat change should occur. However, a large exothermic event is observed in MCC (Figure 1(C)) in a similar range. This corresponds to the volatile PER degradation in the combustor region. This conclusion is corroborated by the complete lack of PER char yield after the experiments (Table 1).

The information gleaned from tannic acid, on the other hand, is differently in multiple ways. First, the degradation of the volatile components (1,2,3-benzene triol and carbon dioxide) contribute to the degradation events beginning at 200°C. Additionally, TA only releases 43% of the heat PER does with respect to total heat release (THR). THR is obtained as the integration of the peaks in the HRR versus temperature plots. Finally, the char yields vastly differ. Concordant with literature information, TA retains a large percentage of mass at higher temperature via crosslinking of the internal rings.

To establish baseline thermal stability, PER and TA composites were created and analyzed via TGA and DTG (Figure S5A,B). As is expected with epoxy composites, degradation did not begin in earnest until approximately 200°C in both composites. This allows a wide range of operating temperatures for both PER- and TA-based coatings. From there, a complex set of degradation steps

![Figure 1](image-url)
occurred which correspond to the generally-accepted intumescent mechanism (acid-catalyzed formation of char, blowing agent release, and char vitrification) that created the resultant post-test char. The resultant composite char yield of TA at 700°C (32%) relative to that of PER (24%) is corroborated by the TGA shown in Figure 1, showing a better retention of mass by TA composites than that of PER composites.

### 3.2 Flame testing

Based on TGA and MCC analysis, TA certainly warrants further analysis in composite testing. TA-containing intumescent composites were prepared and analyzed via a variety of qualitative and semi-quantitative flame tests to understand intumescent capabilities.

### 3.2.1 Puck testing

The first qualitative test was chosen to evaluate the overall intumescence of the composite. The sample geometry was chosen to be a circular puck with dimensions of 3.5 mm thick × 56.8 mm diameter (Schematic 1(A),(E)). Interestingly, upon combustion of TA composite pucks via a meker torch, a large volume of char was formed compared to other unpublished intumescent formulations investigated in the Wnek lab. Mass-wise, the 16.4 g puck yielded 6.4 g of char (Schematic 1(B)), giving a char yield of 39%. This contrasts significantly to that of PER composites, shown in Schematic 1(E)-(G). Resultant PER char shows significantly less expansion and marginally less overall char produced (16.1 g puck yielded 5.5 g of char). The chars also showed significantly different structures, shown in Figure 2, with TA showing

| Name       | PHRR (W/g) | THR (MW/g) | Char residue (%) |
|------------|------------|------------|------------------|
| Pentaerythritol | 377 ± 31   | 18.5 ± 0.18 | 0 ± 0            |
| Tannic acid  | 127 ± 12   | 7.92 ± 0.23 | 24.1 ± 2.4       |

Abbreviations: PHRR, peak heat release rate; THR, total heat release.
significantly smaller feature sizes. Furthermore, rectangular portions were isolated from the rest of the char and weighed to calculate apparent density. After analyzing 10 samples to ensure statistical significance, the apparent char density was calculated as $0.00213 \pm 0.00042 \text{ g/cm}^3$. Certainly, the resultant char can be classified as a low-density carbon foam, which can fit in to a number of application spaces. The PER char, on the other hand, could not readily be manipulated to determine apparent density due to its large interior pores (Schematic 1 (F)-(G)).

### 3.2.2 Cardboard coatings

With promising preliminary data on the intumescent capabilities of the TA-containing composites, the next flame test performed was adapted from a DOT/FAA report\(^{17}\) in which coated cardboard samples were exposed to a propane blow torch until failure or 10 min passed. Multiple compositions were investigated with various controls, outlined in Table 2.

Testing of the coated cardboard samples yielded interesting results. Conceivably, the uncoated cardboard samples failed after only 7 s (Figure 3(A)). Both cardboard samples with TA-containing coatings and PER-containing coatings withstood direct exposure to a propane torch for over 10 min without failure (Figure 3(B)). Further experimentation on the thinner coatings was performed to quantify failure time, with the addition of a thermocouple being placed on the back of the cardboard to measure the rise in temperature. Transitioning from 4.4 mm coatings to 1.0 mm coatings provided clear differences between the compositions; the TA-thin coating protected the cardboard from failure for nearly 27 min, unlike the PER coating which compromised after approximately 7 min (Figure 3(C)). This time–temperature data is compared in Table 3 against other time–temperature plots in literature. Since use of cardboard substrate is not significantly studied in literature, coatings with steel

![FIGURE 2](image1.png) Camera images of: Pentaerythritol composite char at (A) 2× magnification and (B) 10× magnification, tannic acid composites at (C) 2× magnification and (D) 10× magnification.

![FIGURE 3](image2.png) Cardboard coatings exposed to a propane blow torch. Uncoated compromised after 7 s (A). 1 mm coated cardboard burned for 27 min (B). Coated sample displayed a final expansion 25 times its original thickness. (C) Plot of time–temperature testing showing uncoated, PER composite, and TA composite.
substrates are reported for comparison. While only the thin coatings (1.0 mm) were compared against literature data, it is hypothesized that thicker TA coatings can be employed to provide protection times longer than the 27 min displayed by the thin coatings.

A notable trait of the tannic acid system was the massive volume of hierarchically porous char formed during combustion (Figure 3(B)). In this particular experiment, the millimeter-thick coating expanded over 25 times its initial thickness, supporting prior puck burning experimental results shown in Schematic 1(B). Not only a large amount of char was formed upon exposure to flame, but this expanded char quantitatively protected the underlying substrate better than control samples, elongating the time to failure $230 \times$ relative to uncoated cardboard and $3.9 \times$ relative to PER composite coated cardboard.

### 3.2.3 Cardboard capsule

Further building on data from the previous qualitative flame testing, an additional layer of complexity was added in the form a multi-wall sample, referred to as a ‘capsule.’ This experiment was designed to replicate a fire inside of a shipping package. Furthermore, it was designed to give insight in to how expanding char fronts intersect with one another upon expansion.

After proper sample preparation and orientation, TA-composite coated cardboard capsules were exposed to a meker torch flame and burned until the back-wall failure. The expansion is captured in Figure 4, in which the coating is shown from ignition to peak intumescence at 15 s intervals. Interestingly, the corners in which the expanded coatings collided proceeded to expand outward simultaneously. Ultimately, the system compromised after 15 min, shown in Figure S4. This is a significant increase relative to the 10 s

| Name                      | Composition                                      | Total weight of coating (g) | Time to failure (s) | Coating thickness (mm) |
|---------------------------|--------------------------------------------------|----------------------------|---------------------|------------------------|
| Cardboard                 | N/A                                              | 0                          | 7                   | N/A                    |
| Foil                      | N/A                                              | 0                          | 20                  | N/A                    |
| Epoxy on foil             | 59.5% Epoxy                                      | 15.8                       | 17                  | N/A                    |
| Tannic acid               | 26.2% Epoxy                                      | 35.8                       | >600                | 4.4                    |
|                           | 17.9% Amine                                      |                             |                     |                        |
|                           | 22.3% TA                                         |                             |                     |                        |
|                           | 16.8% MEL                                        |                             |                     |                        |
|                           | 16.8% APP                                        |                             |                     |                        |
| Tannic acid thin          | 26.2% Epoxy                                      | 17.9                       | 1615                | 1.0                    |
|                           | 17.9% Amine                                      |                             |                     |                        |
|                           | 22.3% TA                                         |                             |                     |                        |
|                           | 16.8% MEL                                        |                             |                     |                        |
|                           | 16.8% APP                                        |                             |                     |                        |
| Mel and APP (no char-former) | 26.3% Epoxy                                   | 35.8                       | >600                | 4.4                    |
|                           | 17.9% Amine                                      |                             |                     |                        |
|                           | 27.9% MEL                                        |                             |                     |                        |
|                           | 27.9% APP                                        |                             |                     |                        |
| Mel and APP thin (no char-former) | 26.3% Epoxy                                | 17.9                       | 184                 | 1.0                    |
|                           | 17.9% Amine                                      |                             |                     |                        |
|                           | 27.9% MEL                                        |                             |                     |                        |
|                           | 27.9% APP                                        |                             |                     |                        |
| Pentaerythritol thin      | 26.2% Epoxy                                      | 17.9                       | 415                 | 1.0                    |
|                           | 17.9% Amine                                      |                             |                     |                        |
|                           | 22.3% PER                                        |                             |                     |                        |
|                           | 16.8% MEL                                        |                             |                     |                        |
|                           | 16.8% APP                                        |                             |                     |                        |
| DOT/FAA Intumescent Composition | N/A                                              | N/A                        | 37                  | 25 layers (~0.63 mm)$^a$ |

$^a$Reference does not measure thickness but rather number of coatings. Approximating 25 microns per layer, we approximate a 0.63 mm coating thickness.
furthermore, even when the coating failed and a hole was formed at the back-wall of the cardboard capsule, the exiting flame did not ignite the uncoated cardboard surrounding it. Our current hypothesis proposes a combination of a charred exterior that is less likely to ignite coupled with expanded coating extending over the hole formed, protecting the lightly-charred exterior cardboard from ignition.

3.2.4 | Soft and hardwood capsules

While cardboard is appealing for application in packaging, other substrates were investigated as well to potentially expand the coating’s application space. To that end, soft and hard woods were investigated in the form of plywood and poplar, respectively. This expands application-space significantly, extending into areas such as framing, pallets, furniture components, and more.

Testing procedure was identical to that of cardboard. Shown in Figures S6 and S7 are images of the plywood and poplar samples before ignition, at peak intumescence, and at failure time. Much like the cardboard coatings, the multiple char fronts expanded into one another and protected the corners. Ultimately, the expanded char retarded failure for a significant amount of time relative to the uncoated capsule, outlined in Table 4.

3.3 | Quantitative testing via CC

To introduce quantitative data to complement the flame testing of TA-containing coatings, CC was performed to evaluate various thermal characteristics of the composite.
Important properties obtained from this experiment include heat release rate (HRR), peak heat release rate (PHRR), total heat release (THR), mass loss, and time to ignition (TTI).

The CC experiment was performed using a 50 kW/m² heat flux, and three sets of composites were analyzed: the epoxy resin control, the PER-composite standard, and the TA-composite samples.

### 3.3.1 HRR curve analysis

Before consideration of numerical values, the curvature of the HRR curves can provide insight into the composite properties. Explained in the work of Schartel and Hull,[29] composite characteristics, such as whether or not a composite is char-forming, is described. Starting with the epoxy curve in Figure 5(A), there is a relatively sharp slope that begins at 29 s that corresponds to the intense, non-charring epoxy burning. Based on the complete absence of residual mass, it makes sense that the experimental data relates to curves described in literature as thin and non-charring.

Analyzing the PER and TA systems is slightly less trivial, but can be adequately ‘fit’ nonetheless. Shown in the inset of the HRR plot, the PER and TA composites show 2 and 3 peaks, respectively. For PER composites, the two peaks likely correspond to a combination of deformation and char-cracking, followed by a slow decay of HRR indicative of a thickly charring system. TA is hypothesized to act similarly, with the exception of an additional peak at approximately 150 s hypothesized as corresponding to additional char-cracking via char deformation.

| Coated substrate | Failure time (uncoated) | Failure time (coated) | Coating thickness (mm) |
|------------------|-------------------------|-----------------------|-----------------------|
| Cardboard        | 10 s                    | 15 min                | 1 mm                  |
| Plywood          | 1 min, 15 s             | 16 min                | 1 mm                  |
| Poplar           | 2 min, 15 s             | 16 min                | 1 mm                  |
3.3.2 | Quantitative flammability results

CC provides an abundance of quantitative data to describe material flammability, such as that shown in Figure 5(A),(B) and Table 5. Starting with PHRR and THR, TA samples shown markedly lower values, which is advantageous in a fire situation. This is because the lower values of PHRR and THR correspond to less intense and smaller total amounts of heat released from the burning composite. Additionally, the fire growth rate (FIGRA) term is lower (which is preferential) for TA composites than PER and epoxy control systems. Defined as the PHRR divided by the time to reach PHRR (TTPHRR), FIGRA is a preliminary indicator of the ability of a fire to spread.[30] The lower PHRR and slightly longer TTPHRR is credited for TA’s ability to better protect underlying composite from heat and degradation.[31] Further investigation will occur in the char analysis section. Finally, one term that the authors believe can show insight into the composites is the THR/mass loss term. Inspired by CC data analysis in the work of Cheng et al.,[32] composite heat release per unit of mass lost during combustion is obtained by simply dividing total heat release by mass loss. This dynamic term shows a very similar value for PER and TA, both of which are noticeably lower than that of epoxy control. While TA may provide lower PHRR and THR alongside higher char yields, similar amounts of heat are released per unit mass. This indicates that the difference in performance between the PER and TA composites likely does not originate from the chemical degradation of the materials.

Also shown in Table 5 are 10 literature systems that utilize tannic acid in their compositions for flame retardant applications. These materials are used in a wide range of application spaces, but each perform cone calorimetry that provides flammability data to compare against. These TA-containing literature composites show powerful flammability reduction in their respective

| Sample                        | TTI (s) | PHRR (kW/m²) | TTPHRR (s) | FIGRA (kW/m² s⁻¹) | THR (MJ/m²) | THR/mass loss (MJ/m² g⁻¹) | Mass loss (g) |
|-------------------------------|---------|--------------|------------|-------------------|-------------|--------------------------|---------------|
| Epoxy control                 | 29 ± 0.8| 1560 ± 180   | 71 ± 6     | 22.6 ± 1.7        | 74.0 ± 4.4  | 3.06 ± 0.02               | 24.2 ± 1.3    |
| PER control                   | 14 ± 0.8| 211 ± 45     | 77 ± 8     | 2.43 ± 0.51       | 37.2 ± 1.5  | 1.91 ± 0.17               | 19.7 ± 1.7    |
| TA Composite                  | 14 ± 0.9| 108 ± 6.7    | 86 ± 6     | 1.27 ± 0.07       | 24.4 ± 0.57 | 1.92 ± 0.22               | 12.8 ± 1.2    |
| PVC/MH@PASn[33]               | 16      | 233.6        | 65         | 3.59              | 45.4        | N/A                       | N/A           |
| Coated E20CT3[31]             | 3 ± 0.6 | 319 ± 10     | 185 ± 7    | 1.7 ± 0.3         | 62 ± 2      | N/A                       | N/A           |
| EPS/ATG20[15]                 | 80.0 ± 8.8| 704.0 ± 63.4 | N/A        | N/A               | 75.0 ± 6.7  | N/A                       | N/A           |
| ABS/SS35[35]                  | 33 ± 5  | 368 ± 7      | N/A        | N/A               | 96          | N/A                       | N/A           |
| NR@AGT60[10]                  | 58      | 436.8        | 160.7      | 2.76              | 94.8        | 5.33                      | 17.8          |
| 2 wt% TA-MoS2/PAN[56]          | 2.9     | 332.8        | N/A        | N/A               | 12.1        | N/A                       | N/A           |
| BPC/SFR@SHNT[37]              | 30.8    | 723.0        | N/A        | N/A               | 136.6       | N/A                       | N/A           |
| PU-TA@RG05[38]                | N/A     | 235.23 ± 3.78| N/A        | N/A               | 21.72 ± 0.42| N/A                       | N/A           |
| P5/T2/S[32]                   | 7       | 166          | 37         | 4.5               | 7.5         | N/A                       | N/A           |
systems. However, when compared to one another, no one system completely outperforms our TA composites, with few even getting close.

### 3.3.3 Total heat evolved versus mass loss

Another analysis technique shown in the Schartel and Hull paper is that of plotting total heat evolved (THE), which is defined as the final THR value, against mass loss. By plotting points from each test and fitting a line to the average value relative to the origin, insight into certain aspects of the flame retardant mechanism can be elucidated. From data presented in Figure 6, two changes are apparent between the epoxy control and the other two systems. First, there is a decrease in the slope of the line. This is indicative of a gas-phase mechanism that reduces the amount of heat released per unit mass loss. Since the PER and TA composites release inert gases as byproducts of intumescence that dilute the concentration of combustible materials in the local combustion area, this change is to be expected. Second, less mass loss is shown in the PER and TA composite systems, indicative of a condensed-phase flame retardant mechanism.[29] This most certainly refers to the protective char formed by the two composite systems. However, as seen in the figure, the data points for the TA char show less mass loss than the PER composites. This translates to better retention of TA char relative to PER char.

### 3.4 Char analysis

Transitioning from combustion analysis to char analysis, nitrogen adsorption–desorption testing using BET analysis to evaluate the pore distribution along with the specific surface area, and Raman and XPS studies were performed to estimate the structural and chemical characteristics.

#### 3.4.1 Nitrogen adsorption testing

Nitrogen adsorption–desorption testing was performed on both the PER and TA char post-combustion and post-calcination. Shown in Figure 7 are the resultant pore size distribution plots with their associated specific surface area.
areas listed on the plot. From the calculated specific surface area, we can see that the TA char value is approximately 11 times greater than that of PER char. This correlates well with the reduced pore widths of PER char, shown by the reduced incremental volume values. Clearly the TA char is hierarchically porous and contains higher specific surface area which imply that this char provides more air-filled porous compartments against the fire as compared to the PER char. Such air-filled compartments might be helpful in blocking the radiative and convective heat transport from the torch toward the target and hence the improved fire-protection capability of TA char was observed. In terms of heat protection, there is little published data relating fire protection to the microstructural details of the material. Here we have made a correlation between the fire protection capability of the composite and/or char to the porous structural characteristics of the char which could guide us toward further developments in this field.

### 3.4.2 Raman spectroscopy

In addition to pore analysis, Raman spectroscopy was performed on the post-combustion char. Within the purview of this manuscript, the region of interest lied within 1300–1660 cm\(^{-1}\). Taking inspiration from graphitic structures, such as carbon nanotubes, it is known that two peaks are of great importance, the D peak shown at approximately 1360 cm\(^{-1}\) (≈1357 and 1370 cm\(^{-1}\) for PER and TA char, respectively). This peak corresponds to disordered sp\(^2\) hybridized, and/or amorphous content in carbon material. The G peak, shown at approximately 1580 cm\(^{-1}\) (≈1581 and 1586 cm\(^{-1}\) for PER and TA char, respectively), corresponds to vibrations within the hexagonal carbon rings present within the material. Such hexagonal carbon rings consist sp\(^2\) hybridized carbon atoms.\(^{[39,40]}\) Furthermore, the ratio of the two peak intensities (I\(_D\)/I\(_G\)), provides insight into the relative sp\(^2\)/sp\(^3\) carbon content, varying differently in amorphous, crystalline and semi-crystalline carbon materials.\(^{[41]}\) Based on the integrations of the fitted peaks for the PER and TA char, shown in Figure 8, the I\(_D\)/I\(_G\) ratios were calculated as 1.15 and 1.06, respectively. This implies that the TA char may contain slightly more sp\(^2\)-C than the PER char which can be well explained from Schematic 1. However, relative to other flame retardant literature that utilize Raman analysis, these values are noticeably lower which might be helpful for fire protection.\(^{[42,43]}\)

### 3.4.3 XPS analysis

The final analysis of the char residues was via XPS with the purpose of understanding the chemical structure within the char. XPS survey spectra and high resolution regional spectra for different elements have been shown in Figure 9(A)-(I). Both the TA and PER chars consist of C, N, P and O in different relative amounts as presented in Table 6. TA char is more carbonaceous while the PER char is more oxygen-rich. Detailed analysis of the XPS spectra for different elements reveals that the PER char has more P content (16.15 at%) than TA char (P: 12.38 at%) and a higher proportion of P atoms in PER char is bonded with O atoms.\(^{[44,45]}\) This explains the presence of higher O content (42.66 at%) in PER char than that in TA char (O: 29.29 at%). Moreover, the N content is higher in TA char (N: 3.63 at%) than that in PER char (N: 1.56 at%). TA char possesses about 31.80 at% sp\(^2\) hybridized C content which is much lower (25.88 at%) in PER char, and this observation supports the lower I\(_D\)/I\(_G\) ratio for TA char as observed in Raman analysis (Figure 8). It is evident that the TA char is more carbonaceous and contains higher proportion of sp\(^2\)-C atoms and lower proportion of O atoms as compared to PER char. Furthermore, the relative sp\(^3\)-C content in TA char is about 9.53 at% which is higher than in PER char (5.51 at%) which might have helped in formation of three dimensional and mesoporous morphology of TA char. It is also observed that more proportions of C atoms are bonded to the N and/or P heteroatoms in TA char (13.12 at% C-N + C-P) as compared to that in PER char (C-N + C-P: 7.87 at%). In terms of fire protection, this concentration difference between O and C atoms and the observed higher proportion of C-heteroatoms bonding environment may have implied a robust internal bonding
networks formation in the TA char and hence the improved fire resilience is observed.

### 3.5 Mechanistic details

Based on the various analyses performed in this paper, a mechanism is proposed to explain why quantitative cone calorimetry data (and qualitative flame testing data) show that TA composites are less flammable and act as better protective intumescent coatings than PER composites. The authors propose that the TA structure largely contributes to the overall composite properties. Its polyfunctional, phenolic structure contributes to the rapid formation of char upon exposure to the acid source in the melt. This rapid formation of char is corroborated qualitatively by the rapid formation of char in the burn tests and quantitatively via inspection of the HRR curves in which TA composites showed a longer TTPHRR. With respect to the THE versus mass loss plot, the TA composites had noticeably lower mass losses, although they released comparable amounts of heat per unit burnt. The rapid formation of char deters further mass loss and instead contributes to increased char yield. Additionally,

### TABLE 6 XPS atomic concentrations

| Material  | C% (at.) | N% (at.) | P% (at.) | O% (at.) |
|-----------|---------|---------|---------|---------|
| TA char   | 54.71   | 3.63    | 12.38   | 29.29   |
| PER char  | 39.63   | 1.56    | 16.15   | 42.66   |

Abbreviations: PER, pentaerythritol; TA, tannic acid.
BET analysis presented significantly more porous char in polyfunctional TA composites relative to that of the tetrafunctional PER systems. Reaction of two TA molecules in the presence of an acid source also deters typical decarboxylation degradation on a large portion of the newly formed dimers and also results in a molecule of significantly higher molecular weight than that of a PER dimer. The TA char is more hierarchically porous and contains about 11 times higher specific surface area as compared to PER char, which might have been helpful in dissipating and blocking fire and heat propagation through the TA char. Furthermore, the Raman analysis displayed higher graphitic-carbon content in TA char and specifically, the $I_D/I_G$ ratio of TA was lower than that of PER char, referring to a more graphitic-like structure. This is also corroborated in XPS by a higher relative carbon concentration in TA char relative to that of PER char. The higher carbon content in its hierarchical porous microstructural form and the formation of C–N/P bonding networks in higher proportion are proposed to have helped the TA char readily dissipate heat transfer across the char thickness and provide improved fire protection than that of PER char which can be insightful for advanced technological applications.

To summarize, a proposed intumescent process containing TA as the char former is as follows. First, upon degradation of the epoxy and formation of poly(phosphoric acid) from the degraded ammonium polyphosphate, a ‘melt’ begins to form. This allows acid-catalyzed reactions to begin between the largely polyfunctional (relative to PER) TA molecules. The relatively high molecular weight of TA allows rapid formation of macromolecular char. This is important because the plethora of inert gas released by the subsequent degradation of the melamine blowing agent allows large degrees of expansion of the rapidly forming TA char. These high degrees of expansion facilitate the creation of extraordinarily low density char with distinct hierarchical structure containing pore sizes on the low-nanometer scale. As the expansion process proceeds, carbon–carbon networks are formed in the char, creating carbonaceous, ordered (via Raman spectroscopy) char that acts as an effective thermal barrier (relative to PER).

4 | CONCLUSION

We presented experimental data showing the efficacy of TA-containing intumescent composites in addition to analytical analyses of the resultant char to better glean mechanistic details of fire protection. From the model system of the PER and TA molecules, preliminary heating studies were performed via TGA and MCC, showing that TA releases less heat and retained more char relative to the sublimation that occurs with PER. Subsequently, composites were created incorporating the common intumescent additives APP and MEL, and were evaluated qualitatively in a number of flame resistance tests. In addition to creating a plethora of char, TA composites effectively protected underlying substrates of cardboard, soft wood, and hard wood for up to 27 min of direct flame exposure. To quantify the flammability parameters of the composite materials, cone calorimetry was performed on these coatings relative to epoxy and PER controls. In nearly every parameter, TA composites performed better with respect to fire protection, with the exception of the THR/mass loss, which showed that the TA and PER released roughly the same amount of heat per unit of mass lost. This investigation was curtailed with char analysis via BET testing, Raman spectroscopy, and XPS. From the BET analysis, it was shown that the TA char was significantly more porous than the PER char. The Raman analysis revealed that the TA char contained higher proportion of sp$^2$ hybridized carbon than sp$^3$-C which was also supported by XPS analysis. The XPS results revealed that the TA char contained 54.71 at% carbon within which about 13.12 at% C atoms formed bonding with N and/or P atoms which are much higher as compared to those in PER char. Moreover, the PER char has a larger oxygen-content (42.66 at%). Mechanistically, it is proposed that the large, polyphenolic structure of the TA is the primary contributor to the superior intumescent properties relative to intumescent PER control composites. It should be acknowledged that fire is heavily dependent on scale, with the proposed data occurring primarily on the material and bench-top scale. From the resultant data, however, TA-containing composites certainly warrant further attention and investigation, particularly regarding the performance of the intumescent coatings on a larger and more realistic scale.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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