

Intumescent Polydopamine Coatings for Fire Protection

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Polydopamine coatings containing additional bioderived flame retardants were used as coatings for polyurethane foam and cardboard. The ability to form intumescent coatings was crucial for achieving good flame protection. Dopamine can effectively intercalate clay to produce well distributed coatings. The amount of polydopamine coating applied to clay platelets and morphology of the aggregates formed was greatly affected by the catalyzing base used. Microcombustion calorimetry, flame spread, and cone calorimetry experiments reveal that aminomethylphosphonic acid and glycine phytate produce intumescent chars that, in combination with montmorillonite, form a protective barrier for both foam and cardboard.

ARTICLE TYPE: research article

KEYWORDS: bioinspired, coatings, dopamine, flammability, morphology, natural materials

Notation

AEHC – average effective heat of combustion (MJ/kg)

AMPA – aminomethylphosphonic acid

DAP – ammonium phosphate, dibasic (diammonium hydrogen phosphate)

FPUF – flexible polyurethane foam

Gly – glycine

His - histidine

HRC – heat release capacity (J/g·K)

Im - imidazole

NaMT – sodium montmorillonite

MCC – microcombustion calorimetry

PA – phytic acid

PDA – polydopamine

PHRR – peak heat release rate

T - taurine

THR – total heat release (kJ/g or MJ/kg)

Tris - 2-amino-2-(hydroxymethyl)-1,3-propanediol

TTI – time to ignition

1. Introduction

Nature inspired design of materials has become a valuable approach for the development of novel and task-specific products. Since there is a limited number of molecules and environmental conditions available in nature, most of the extraordinary properties are due to unique hierarchical microstructures. Replicating these structures in the laboratory can offer a new classes of advanced materials useful to the transportation sector, energy production, military, optics, sensors, and biomedical applications, just to name a few.(1, 2) A reoccurring theme in nature is the use of interdigitated molecules to design materials that are stiff, strong, and tough. For most materials, stiffness and strength are often improved at the expense of flexibility or toughness. In bone and exoskeletons, nature seamlessly incorporates brittle inorganic particles to imbue strength within flexible polymeric structures such as collagen, chitin, and proteins. Scientists have used this knowledge to develop super-tough ceramics and carbon nanotube yarns.(1) Since most of these composites are constructed from dissimilar materials, tailoring the interfaces, whether strengthening or weakening, is paramount. One of the best examples of nature inspired control of interfaces is the use of polydopamine in the marine mussel foot proteins.(3, 4)

Dopamine, (4-(2-aminoethyl)benzene-1,2-diol), is a catecholamine found throughout nature. It is used by plants as an antioxidant, growth regulator, and stress responder;(5) in invertebrates as a neurotransmitter, insect cuticle hardening, and mussel adhesion;(6, 7) and in vertebrates as a neurotransmitter, regulating a variety of brain functions.(8) When dopamine is placed in an alkaline aqueous solution of about pH 8 to about 10, and particularly a pH of about 8.5, it self-polymerizes and adheres to a wide variety of substrates, regardless of polarity, including inorganic materials, such as glass, minerals, etc., synthetic polymers, such as polytetrafluoroethylene (e.g. Teflon), polyethylene glycol (PEG), etc., and natural polymers, such as cellulose, chitosan, etc.(3, 4) The adhesion of dopamine, during the polymerization process, to a substrate, is promoted by the formation of covalent bonds with the substrate, as well as other strong intermolecular interactions, such as hydrogen-bonding, metal chelation, and π - π interactions. There is significant debate over the exact mechanism of dopamine polymerization, but there are two well accepted models.(3, 4, 9, 10) In both cases, the alkaline solution oxidizes the dopamine to a mixture of 5,6-dihydroxyindoline and its diione derivative. In one model, these two oxidation products polymerize and cross-link through the formation of covalent bonds. In the other model, a supramolecular aggregate forms between the two oxidation products through strong intermolecular forces, including charge transfer, π -stacking, and hydrogen bonding. Both mechanisms may actually be occurring. A tris(hydroxymethyl)aminomethane (Tris)-HCl-based buffer system is often used in dopamine polymerization reactions to achieve the desired alkaline condition. The structure of tris(hydroxymethyl)aminomethane (Tris) contains the same end groups that are found in dopamine, -OH and -NH₂ groups. Without being held to a single theory, it is believed that tris(hydroxymethyl)aminomethane participates, or is incorporated, at some level, in the cross-linked structure of poly(dopamine).(11) Whether the polydopamine (PDA) is formed through covalent polymerization or strong physical attraction, it forms a durable layer that can entrap additional molecules for a variety of purposes.

The use of polydopamine in flame retardant coatings was first reported within this decade.(12, 13) Since then, PDA has been combined with a number of fire retardants to improve its efficacy. PDA has been used in combination with graphene oxide to increase the rate of polydopamine loading and add fire protection to the matrix.(14-16) It was used as a binder for mineral based flame retardants to protect natural fibers and fabrics.(17-19) And, traditional phosphorous and/or nitrogen based flame retardants were adhered to open and closed cell foams, or fabrics using polydopamine.(20-24) As noted in these studies, PDA acts in the condensed phase as a char forming flame retardant. The char forming mechanism can be enhanced by choosing compounds that intumesce.(25) Intumescence compounds are insulating, foamed-char forming materials that reduce heat and oxygen transport between the flame and unburned fuel source. Intumescence materials are comprised of (a) an acid source, which dehydrates a carbon source and/or the substrate (b) a carbonization agent or carbon source which chars during decomposition, and (c) a blowing agent, which generates gas during decomposition.

In this study, we examine the use of polydopamine as a flame retardant coating for flexible polyurethane foam and cardboard. Naturally occurring compounds that can be used to form intumescing flame retardants were added to enhance the flame retardancy of the coatings. The effects of base treatment, an expandable clay, and additional flame retardant molecules are explored.

2. Materials and Methods[†]

2.1 Materials

2-(3,4-Dihydroxyphenyl)ethylamine hydrochloride (Dopamine-HCl, 99 %) and imidazole (Im, 99 %) were obtained from Acros Organics. Ammonium hydroxide (30 mass %), taurine (T, 97 %), phytic acid (PA, 50 % aqueous solution), and histidine (His, 99 %) were acquired from Sigma Aldrich. Diammonium hydrogen phosphate (DAP, 98.0 %) was acquired from Alfa Aesar. 2-Amino-2-(hydroxymethyl)-1,3-propanediol (Tris, ultra pure grade) was obtained from Amresco. Glycine (Gly, ACS grade) was acquired from Fisher Scientific. Aminomethyl phosphonic acid (AMPA, Rhodaphos) was obtained from Rhodia, Inc. Sodium montmorillonite clay (NaMT, Na+Cloisite) with a cationic exchange capacity of 0.92 meqv/g was acquired from BYK, Inc. Deionized water (18.2 MΩ) was obtained from a Millipore Essential Elix 3 – Advantage system. Triple wall, Kraft cardboard was acquired from Box USA. A flexible, open cell, reticulated, polyester, polyurethane foam containing carbon black, type T50 (FPUF) was acquired from Crest Foam (Troy, MI).

2.2 Methods

2.2.1. Polydopamine and Polydopamine Coated Clay

Exchanged montmorillonites were prepared by adding 110 % of the cation exchange capacity of ammonium acetate, hydrochloric acid, or dopamine-HCl to a 1.5 % by mass aqueous slurry of NaMT. After stirring for 5 days at room temperature, the clays were filtered and washed with 20 volume % ethanol/80 volume % water using Soxhlet extraction for 2 days. The clays were air-dried, finely ground, and dried at 110 °C in air for 1 h prior to use.

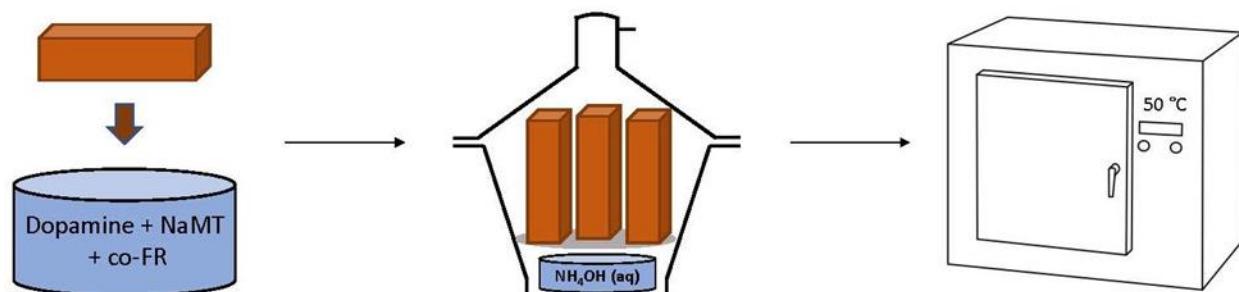
To prepare polydopamine (PDA) coatings, a 4 % mass fraction dopamine-HCl (in deionized water) was prepared. When additional compounds were used, the amount of water was adjusted to maintain a 4 % dopamine-HCl solution. Taurine, AMPA, and glycine were added as solids and mechanically stirred until completely dissolved. Phytic acid was added as a 50 % mass fraction aqueous solution. The phytic acid solution was thoroughly mixed just prior to use. NaMT was added last as a 2.25 % mass fraction aqueous slurry. The clay solution was prepared at least 24 h prior to use to aid in the exfoliation of the platelets. In a few instances, a NH₄MT or a HMT solution was added instead of NaMT. To form polydopamine coatings, 10 g of dopamine solution was added to a small petri dish for no base and NH₃ polymerized samples and 9 g of dopamine solution was added for Tris or DAP polymerized samples. For the NH₃ polymerized sample, the Petri dish was placed in a closed desiccator over concentrated NH₄OH for 1 hour. For Tris and DAP polymerized samples, 1 g of a 1.8 M base solution was added. The solution was allowed to evaporate 5 d under a fume hood. Some coatings were then heated in a conventional oven to 80 °C for 1 h.

PDA was characterized using powder x-ray diffraction (XRD), thermogravimetric analysis (TGA), microcombustion calorimetry (MCC), and scanning electron microscopy (SEM). XRD experiments were performed on a Rigaku Miniflex II powder x-ray diffractometer. The d-spacing was calculated from peak positions using Cu K α radiation ($\lambda = 0.15418$ nm) and Bragg's Law. Clay samples were ground into a fine powder and hand pressed into low background sample holders. Standard x-ray measurements were performed over a 2θ range of 1.5° - 12° at a continuous scan rate of 0.5°/min with a scan width of 0.01°. The uncertainty was $\sigma = \pm 0.01$ °. Thermal stabilities were measured using a TA Instruments Q-500 Thermogravimetric Analyzer or a Netzsch STA 449 F1 instrument. Sample masses of 5.0 mg \pm 0.2 mg were placed in open platinum pans and heated at a scan rate of 10 °C/min while purged with 25 mL/min N₂. The temperature of both the onset (5% mass fraction loss) and peak mass loss rate typically have an uncertainty of $\sigma = \pm 2$ °C. MCC samples (7.5 mg \pm 0.5 mg) were tested with a Govmark MCC-2 microcombustion calorimeter at 1 °C/sec heating rate under nitrogen from 200 °C to 600 °C using method A of ASTM D7309 (pyrolysis under nitrogen). Based on polystyrene compliance samples, the total heat release, heat release capacity, and char yield have standard deviations, $\sigma = \pm 10$ %. Morphology was examined using a JEOL JSM-IT100 InTouchScope SEM. Samples were gold sputtered and imaged at 10.0 kV to reduce surface charging.

2.2.2. Polydopamine Coated Foam

Substrates were coated using a simple dip method, followed by exposure to ammonia gas, as shown in Scheme 1. Small pieces of foam, approximately 2 mm x 2 mm x 2 mm, were cut with scissors. Dopamine solutions were immediately transferred to a shallow plastic dish. Foam was soaked in the solution 3 times and manually squeezed to remove excess solution. The last soak was commenced for 2 minutes and the foam was squeezed until there was a 300 % by mass solution pickup. The wet foam was placed in a desiccator over concentrated

ammonium hydroxide for 1 h. The foam was then dried at 50 °C overnight. In some cases, the foam was dried at 50 °C prior to exposing it to ammonia gas in the desiccator. MCC samples (4 mg to 8 mg) were tested with a Govmark MCC-2 microcombustion calorimeter at 1 °C/s heating rate under nitrogen from 200 °C to 600 °C using method A of ASTM D7309 (pyrolysis under nitrogen). Based on polystyrene compliance samples, the total heat release, heat release capacity, and char yield have standard deviations, $\sigma = \pm 10\%$.



Scheme 1. Protocol for applying the flame retardant coating to a solid substrate.

2.2.3. Polydopamine Coated Cardboard

Cardboard was coated using the same basic procedure as described in Scheme 1. Cardboard was cut into 100 mm x 100 mm (for cone calorimetry) and 127 mm x 12.7 mm specimens (for flame spread) using a craft knife. The cardboard was conditioned in a glove bag containing saturated magnesium nitrate to maintain a constant 50 % relative humidity. Dopamine solutions (250 mL) were immediately transferred to a shallow plastic dish. Specimens were soaked in the same solution for 2 min while gently shaking to aid in solution transfer through the corrugated portions of the cardboard. All three cone samples were soaked prior to the flame spread samples. The wet specimens were placed in a dessicator over concentrated ammonium hydroxide for 1 h, then dried at 50 °C overnight.

Flame spread specimens were burned using a flame spread test according to the UL-94 standard in both the vertical and horizontal positions. Although this is not a standard for cardboard specimens, it does provide qualitative assessment of the ability of the coatings to inhibit ignition of the cardboard. Vertical burn was performed once and horizontal burn was conducted in triplicate. Small pieces were cut prior to testing for SEM imaging using a JEOL JSM-IT100 InTouchScope SEM. Samples were gold sputtered and imaged at 10.0 kV to reduce surface charging. Cone Calorimeter experiments were conducted in triplicate on an FTT Dual Cone Calorimeter at a heat flux of 35 kW/m² with an exhaust flow of 24 L/s using the standardized cone calorimeter procedure (ASTM E-1354-07). All samples were conditioned at 23 °C and 50 % relative humidity for at least 48 hours. The back side of the samples was wrapped in aluminum foil prior to placing in the retainer frame (to reduce edge burning) as per suggested ASTM. The frame reduced the exposed surface area to 88.4 mm². If the specimen did not ignite within 5 minutes, the test was terminated. Data collected from all samples is believed to have an error of $\pm 10\%$.

3. Results and Discussion

3.1 Polydopamine Structure and Intumescence

Pure PDA flame resistant coatings typically take too long to form to be practical.(13, 15) To address this, we examined both the effects of the initiating base used and the addition of co-additives to the coating. Clay has often been used in flame retardant coating formulations because it can enhance the formation and durability of char with a very small loading.(26-28) Most formulations examined include the use of montmorillonite, an expandable clay material with exchangeable cations. In acidic environments, dopamine is a cation, and can intercalate into the clay layers. The interlayer distance of the clay, as measured by XRD, expanded from 1.15 nm to 1.38 nm to accommodate the dopamine molecules within the layers (Figure 1a). The dopamine intercalated clay was found to be thermally stable in air up to 320 °C (Figure 1b). From the TGA data, the dopamine mass fraction within the clay was calculated to be 6.2 %.

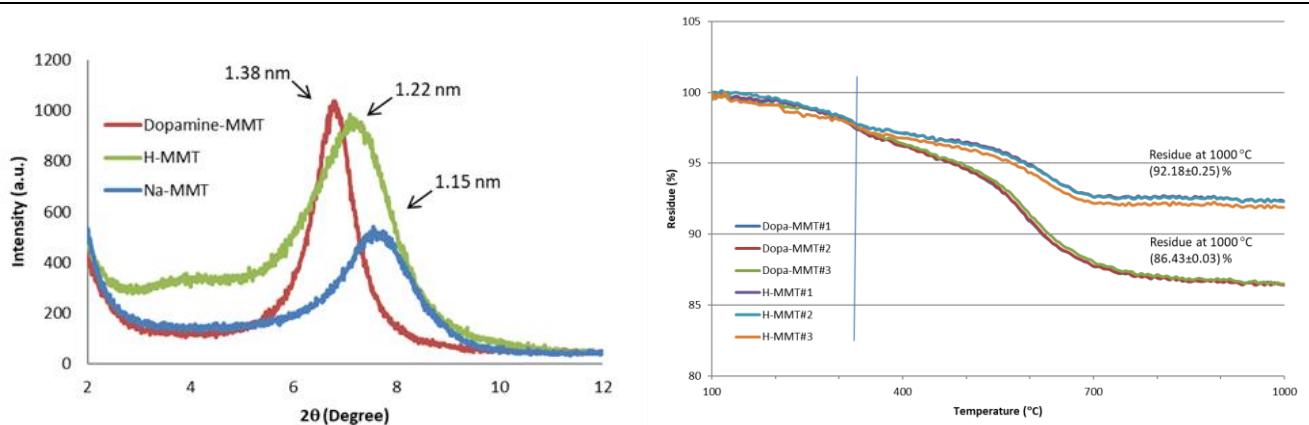


Figure 1. (a) Powder x-ray diffraction and (b) thermogravimetric analysis in air of dopamine intercalated montmorillonite.

The flammability of PDA coatings was screened using microcombustion calorimetry (MCC). Examination of the samples after the test revealed that many of the coatings were intumescent (Figure 2). In particular, the addition of an amine (AMPA, taurine, or melamine) produced the largest foamed char structures. It was observed that the mass of the polydopamine coating that formed during base treatment was dependent on the base used. Tris and ammonia produced a higher mass of insoluble matter than dopamine used, indicating the base was incorporated within the polymerized structure. This is consistent with previous studies examining the use of Tris to polymerize dopamine.(29) As shown in Table 1, dopamine itself was almost completely consumed during the test and produced a significant amount of heat (total heat released, THR = 14.7 kJ/g). However, the addition of clay resulted in significant charring of the dopamine. (Sum of the averages would predict a THR of 7.3 kJ/g and a char yield of 51 mass-%.) The synergy is not as pronounced when AMPA is added, and without clay, AMPA and dopamine are not synergistic. It was also found that the PDA consists of soluble and insoluble fractions and that the insoluble fractions produced less combustible material than the combined fractions.

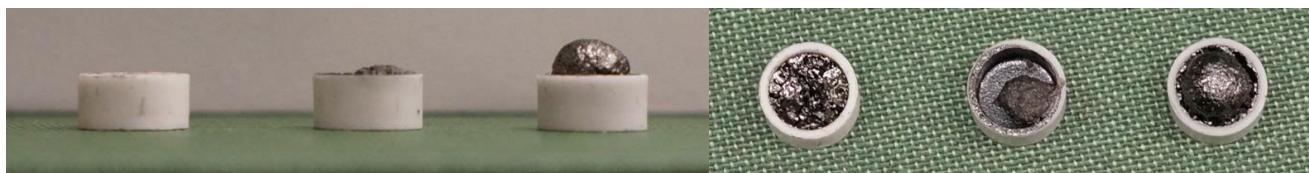


Figure 2. (a) Side view and (b) top view of MCC char residue after tests. Samples shown are pure polydopamine (left), pure AMPA (middle), and polydopamine + AMPA (right).

Table 1. Microcombustion Calorimetry Results for Dopamine Components^a

Coating Formulation	THR (kJ/g)	HRC (J/g·K)	Char (mass %)	Peak 1 ($^{\circ}$ C)	Peak 2 ($^{\circ}$ C)
dopamine	14.7	280	15.3	356	418
NaMT	0.0	0	86.9	---	---
Tris	17.6	403	0	316	---
AMPA	5.1	92	16.8	340	555
(1:1) dopamine:NaMT (by mass)	2.9	39	61.8	323	530
(1:1) dopamine:AMPA (by mass)	9.2	174	39.8	412	474
(1:1:1) dopamine:AMPA:NaMT (by mass)	5.9	89	48.2	417	463

^a Single samples were measured. Based on polystyrene compliance samples, the error in measured values is $\pm 10\%$ for THR, HRC, and Char and $\pm 5\ ^{\circ}$ C for peak temperatures.

To investigate the insoluble forms further, we applied different base treatments to form PDA coated clay. Solutions containing 4.0 mass-% dopamine-HCl and 0.51 mass-% NaMT were treated with different bases to induce polymerization. The initial composition after air drying and after heating at 80 $^{\circ}$ C for 1 h were compared to the theoretical mass based on solution compositions (Table 2). All of the dried solids had a higher mass than the solids added to the initial solution. Most of this mass gain is water, as evidenced by the decrease in mass after heating the air dried sample at 80 $^{\circ}$ C for 1 h. The higher mass gain for air dried Tris and DAP polymerized samples indicates

that these bases are more hydrophilic than dopamine and montmorillonite. The mass gain for NH₃ polymerized samples shows that NH₃ is incorporated into the solid matrix. The most likely mechanisms are through the reaction with HCl to form NH₄Cl and through the incorporation into the polydopamine structure.

Table 2. Composition of Polydopamine Coated Clay

Coating Formulation	Dopamine (g)	HCl (g)	NaMT (g)	Base (g)	Solid mass (g)	Mass gain (mass-%)
No base	0.33	0.08	0.06	0	0.50	7
+ heat	0.31	0.07	0.06	0	0.46	6
Tris polymerized	0.28	0.07	0.05	0.23	0.81	29
+ heat	0.28	0.07	0.05	0.21	0.66	8
NH ₃ polymerized	0.35	0.08	0.06	0	0.64	27
+ heat	0.32	0.08	0.06	0	0.53	14
DAP polymerized	0.28	0.07	0.05	0.26	0.78	18
+ heat	0.28	0.07	0.05	0.25	0.68	4

The base used and heat treatment after evaporation both altered the amount of insoluble material formed (Table 3). A sample of the dried solid was added to water and shaken to dissolve the soluble fractions of each sample. The “insoluble” portions were isolated by centrifugation and the “colloidal” portions were separated by filtering through a 0.2 μm filter. The portion of the solid that penetrated the filter were deemed to be “soluble”. This portion would contain the soluble salts, acids, and bases as well as unpolymerized dopamine and small oligomeric forms of polydopamine. The water content was not accounted for in the calculated percentages, which slightly raises the soluble mass fractions, especially for the samples without heat treatment. The addition of dopamine-HCl leads to flocculation of the NaMT, as evidenced by the significant decrease in colloidal material. The theoretical mass fraction of NaMT in the solid is dependent on the base used. Without base, there is little insoluble polydopamine that forms, since the insoluble mass fraction is about the same as the amount of clay in the initial solid. About 5 % of the dopamine forms an insoluble structure when using DAP. The amount of insoluble coating is significantly increased when using Tris and NH₃ to initiate the polymerization. The observed 4-fold increase over the DAP polymerized sample when using Tris is unlikely due to just polydopamine and is evidence of Tris incorporation into the polydopamine structure. The doubling of insoluble form when using NH₃ may be due to just increased amounts of insoluble polydopamine. However, the hydrogen bonding ability of NH₃ would likely lead to at least some incorporation within the polydopamine structure.

Table 3. Soluble Fractions of Polydopamine Coated Clay

Coating Formulation	NaMT (mass %)	No heat treatment			80 °C, 1h		
		Insoluble (mass %)	Colloidal (mass %)	Soluble (mass %)	Insoluble (mass %)	Colloidal (mass %)	Soluble (mass %)
None (pure clay)	100	0.0	98.0	2.0	0.0	97.0	3.0
No base	12.9	12.7	0.9	86.4	13.8	1.5	84.7
Tris polymerized	8.2	54.3	1.4	44.3	42.7	2.0	55.2
NH ₃ polymerized	12.9	20.5	2.4	77.0	24.4	3.3	72.3
DAP polymerized	7.9	12.2	0.7	87.1	12.7	1.2	86.1

The morphology of the coated clay was examined using SEM (Figure 3). The base used was found to have an enormous effect on the morphology of the PDA coatings. Without treating with base, the dopamine solution darkened significantly, which may indicate that polymerization or oxidation still occurred. It is likely that the slight alkalinity of the clay solution resulted in polymerization initiation. The dopamine formed a thin, even film on the clay platelets, such that the SEM images did not appear any different than the dried, pure clay solution. (See Supplemental Material for images of the pure additives.) Tris induced a 3-dimensional globule network over individual clay platelets. Ammonium hydroxide also formed a 3-dimensional network, but the structure was more porous and sheet-like. DAP changed the polydopamine structure to a 2-dimensional coating over the clay platelets, which were still visible after the polydopamine formed. With heating the base treated coatings to 80 °C induced significant changes to the polydopamine structure. The structures became less porous and more uniform, almost char-like in appearance. Crystals were observed in the DAP treated sample, which were identified as the DAP salt. The differences in buffers on the morphology of polydopamine confirms previous studies.(11, 29)

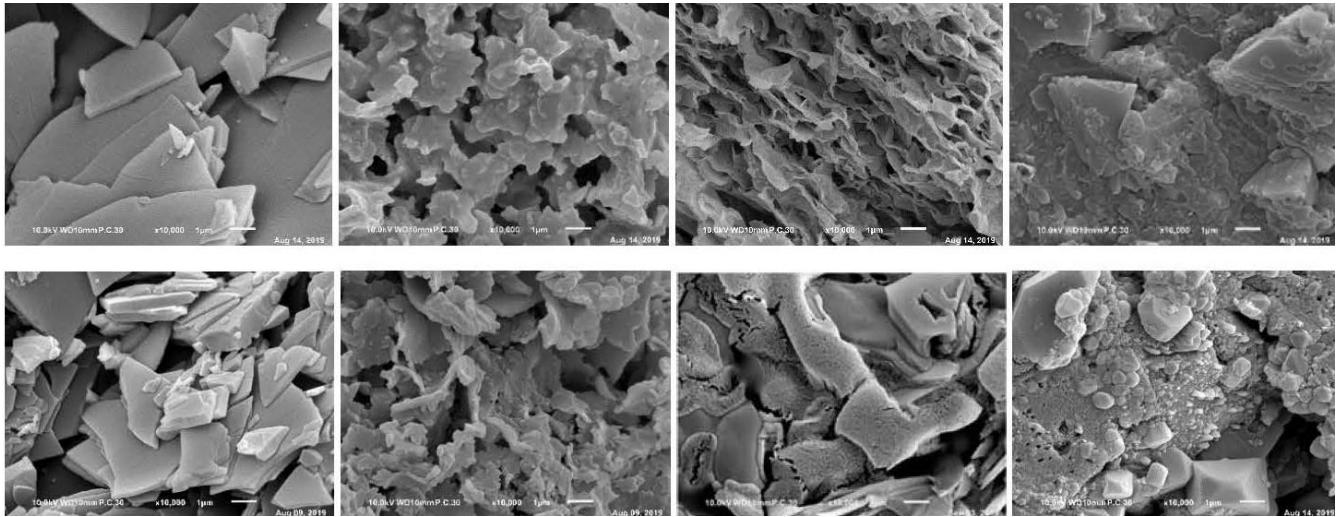


Figure 3. SEM images of air dried (top row) and heat treated (bottom row) polydopamine coated montmorillonite at 10,000x magnification. Morphology differences are observed between no base treatment (far left), Tris polymerized (left center), ammonium hydroxide polymerized (right center), and diammonium phosphate treatment (far right).

3.2 MCC of Foam coated samples

The ability for the dopamine coatings to protect a matrix was first investigated using flexible polyurethane foam (FPUF) (Table 4). FPUF was chosen as a matrix because there is a need for new methods to reduce the flammability of residential upholstery while minimizing the migration or leaching of potentially toxic compounds (30-32) and polydopamine has been used previously to reduce the flammability of foam, allowing for a comparison of the efficacy of flame retardant compositions.(13, 33) Composition codes for the different coatings in are given in molar ratios relative to dopamine, with the exception of montmorillonite, which is given in mass ratios. For a composition code labeled PDA-0.17PA-0.17Gly-0.12NaMT, the soaking solution is comprised of 4 % by mass dopamine-HCl, 1:6 molar ratio of phytic acid to dopamine (2.88 % by mass phytic acid), 1:6 molar ratio of glycine (1.96 % by mass glycine), and 1:8 mass ratio of sodium montmorillonite (0.50 % by mass NaMT). PDA coatings resulted in minimal changes in the total heat release (THR) and heating rate normalized peak heat release (otherwise known as heat release capacity, HRC). However, the addition of montmorillonite significantly reduced the THR and often prevented the foam from melting or collapsing. The flame resistance of the coating was further improved by the addition of intumescence components, especially with organic acids and amine containing compounds. In particular, AMPA, phytic acid, and amino acid neutralized phytic acid had the lowest THR and HRC. Generally, the char yield increased as the THR was reduced.

3.3 Cardboard Flammability

The MCC test results for coated foams showed that dopamine coatings containing both montmorillonite and molecules that form an intumescence flame retardant have great potential for protecting a substrate from fire. However, there were some irregularities that were difficult to control due to the nature of FPUF. First, the large surface area and high vapor permeability results in very rapid ignition, structure collapse, and combustion of the foam when exposed to a heat flux or open flame. The rapid consumption of material makes it very challenging to acquire consistent flammability data, reduce the flammability of the foam, and effectively compare the differences between flame retardant formulations. Second, the high flammability of foam led to significant flame spread when montmorillonite was present in the coating. Finally, the coating increased the foam stiffness, which would diminish the value of the coating for commercial applications. To further study the effectiveness of the coatings, the substrate was switched to triple walled cardboard. Cardboard is a flammable material with relatively high surface area, but with a longer combustion time than FPUF. This had the additional advantage of more readily controlling the amount of solution applied to the substrate, because the repeatability of uptake was rather poor for the foam. As a result, it was easier to compare the relative efficacies of the various flame retardant formulations used in this study.

Table 4. Microcombustion Calorimetry Results for Polydopamine Coated Foams^b

Coating Formulation	Coating (mass %)	THR (kJ/g)	HRC (J/g·K)	Char (mass %)	Peak 1 (°C)	Peak 2 (°C)
None	---	25.2	513	0.1	290	400
PDA	11	23.9	585	1.6	287	413
PDA-AMPA	18	22.2	547	7.0	288	401
PDA-AMPA-0.12HMT	26	20.6	386	10.6	296	388
PDA-T-0.12NaMT	47	19.5	319	12.8	291	398
PDA-AMPA-0.25HMT	23	20.7	352	10.0	278	359
PDA-0.17PA-0.25HMT	24	20.5	431	10.6	289	371
PDA-0.17PA-0.25NaMT	37	18.6	343	15.1	307	392
PDA-0.17PA-0.17Im-0.25NaMT	31	19.9	347	12.7	292	389
PDA-0.17PA-0.17Gly-0.25NaMT	36	17.8	297	16.5	307	389
PDA-0.17PA-0.17His-0.25HMT	39	17.8	345	15.8	299	400

^b Uncoated, PDA, PDA-AMPA-0.25HMT and PDA-0.17PA-0.25HMT were performed in triplicate, with measurement errors, σ , of coating mass \pm 5 mass %, THR \pm 0.5 kJ/g, HRC \pm 50 J/g·K, char \pm 1.1 mass %, peak 1 temperature \pm 22 °C, and peak 2 temperature \pm 43 °C

The molecular intumescent formulation that was added to the dopamine – montmorillonite solution had an effect on the morphology of the polydopamine that formed on the cardboard. Pure PDA coatings were not distinguishable from the cardboard surface, indicating a very thin, even coating. The montmorillonite was heterogeneously distributed on the cardboard, with a small number of particles evenly distributed along the individual paper fibers and a number of polydopamine – montmorillonite globules, similar in morphology to the ammonium treated PDA coated clay (Figure 4). The addition of taurine did not significantly affect the morphology, except that needle-like crystallized taurine was present within the polydopamine – clay aggregates. The addition of AMPA or glycine neutralized phytic acid, resulted in an even coating over the cardboard surface. The majority of the fiber morphology was hidden by the coating that formed.

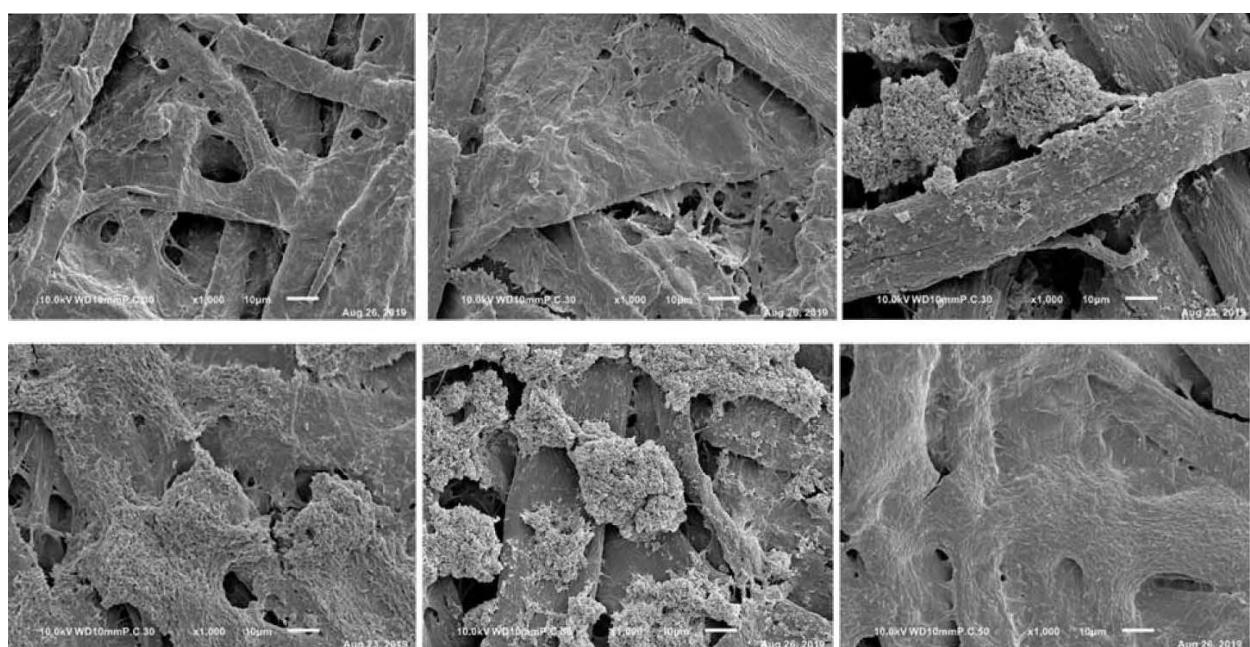


Figure 4. SEM images of polydopamine coated cardboard at 1000x magnification. Images depict (a) uncoated cardboard, (b) PDA coated cardboard, (c) PDA-0.25NaMT coated cardboard, (d) PDA-AMPA-0.25NaMT coated cardboard, (e) PDA-T-0.25NaMT coated cardboard, and (f) PDA-0.17PA-0.17Gly-0.25NaMT coated cardboard.

The flammability of coated cardboard was assessed using flame spread tests and cone calorimetry. Flame spread was conducted in both the horizontal and vertical positions (Table 5). Polydopamine eliminated flame spread in the horizontal position, but the extinguished material continued to smolder until the entire specimen was consumed. The addition of clay slowed the smoldering spread in the horizontal position. In the vertical position, the presence of clay resulted in rapid burning of the surface paper, but the underlying layers remained intact. Smoldering in the vertical position extinguished prior to consuming the entire specimen and slowed the smoldering in the horizontal position. The addition of taurine further slowed the progression of smoldering, but did not eliminate it. The addition of AMPA or Gly neutralized PA resulted in self-extinguished samples with no afterglow in both configurations. Although not as relevant for non-dripping samples, such as cardboard, we did assign a rating to each sample based on the flame spread behavior to readily compare the effectiveness between the different formulations. The addition of a co-flame retardant was necessary to obtain a rating. The use of taurine resulted in an HB rating, while the use of AMPA or glycine phytate resulted in a V-0 rating. The effective reduction in fuel load was assessed using cone calorimetry.

Table 5. Flame Spread of Polydopamine Coated Cardboard

Coating Formulation	Coating (mass %)	HB rate (mm/min)	HB length (mm)	VB flame (s)	VB smolder (s)	VB length (mm)	Rating ^e
uncoated	---	83 ± 6	75 ± 0	40	244	125	NR
PDA	5.9 ± 0.5	6.9 ± 0.6 ^c	75 ± 0	38	254	125	NR
PDA-0.25NaMT	6.7 ± 0.5	6.7 ± 0.1 ^c	75 ± 0	6	108	125 ^d	NR
PDA-AMPA-0.25NaMT	13.0 ± 0.5	0	0	0	2	0	V-0
PDA-T-0.25NaMT	9.9 ± 0.4	3.3 ± 0.6 ^c	22 ± 7	5	110	60 ^d	HB
PDA-0.17PA-0.17Gly-0.25NaMT	13.5 ± 0.6	0	0	0	2	0	V-0

^c - sample flamed out immediately, but continued to smolder; ^d - only the surface layer burned; ^e - there are no drips with cardboard, so ratings are confined to NR (not rated), HB (passes only horizontal burn), V-1, or V-0

Coated cardboard samples were burned in a cone calorimeter. Typical results from the calorimeter are shown in Figure 5. Samples were tested in triplicate, and the results are provided in Table 6. The cardboard substrate is characterized by two primary heat release peaks, a large initial peak at ignition and one that is about 80 % as high during the late stages of combustion. None of the coatings altered the time to ignition (TTI). Polydopamine reduced the peak heat release rate (PHRR) by 10 % and the total heat released (THR) by 5 %. The average effective heat of combustion (AEHC), which is the ratio of the average heat release rate to the average mass loss rate, reflects the degree of burning of volatile gases during combustion. The AEHC was decreased by 25 % when a polydopamine coating was applied. The addition of clay did not significantly alter the overall combustion characteristics of the material, but was effective at reducing the late stage heat release peak. This is an effect of the ability of montmorillonite to form an insulating char layer. The addition of an acid/blowing agent, however, further reduced the heat release properties of the coated cardboard. The addition of AMPA, taurine, or glycine phytate all reduced the peak heat release rate by 33 %. When the cardboard substrate completely burned, the total heat release for all these samples were approximately 20 MJ/m² to 23 MJ/m², which is a 25 % reduction from the uncoated substrate. One of the taurine containing samples and one of the glycine phytate containing samples extinguished prior to complete combustion, which further lowered the total heat release average. Glycine phytate appeared to be the most effective additive, as it also significantly lowered the late stage peak heat release rate.

There are very few polydopamine coating studies with quantified flammability data for comparison. Ellison and co-workers dip-coated FPUF in an alkaline dopamine solution over three days.(13) Similar to our pure PDA coated results, they found minimal changes in the heat release profile after 1 d of polymerization and the development of 5 % by mass coating. The PHRR decreased about 50 % after 2 d of polymerization (10 % by mass coating) and 70 % after 3 d of polymerization (16 % by mass coating). The THR did not change much. In a later study,(15) the group used a layer by layer approach to form graphene oxide (GO) / polydopamine coatings on FPUF. A coating containing 2.5 % by mass GO and 2.5 % by mass PDA reduced the PHRR by 65 % and the THR by 12 %, though most of this effect is probably due to the GO, which reduced the PHRR by nearly 50 % on its own. Flame spread tests in the vertical position revealed that the flame spread through most of the sample. The coating, however, did eliminate melting / dripping, prevented foam collapse, was limited to surface burning, and arrested the flame spread before the entire surface was consumed. We observed similar flame spread behavior on our foams (data not shown) and found that additional intumescing agents could further reduce flammability in our cardboard samples. Wang and co-workers grafted polyethylene imine to cotton, and coated the fabric first with ammonium polyphosphate, then with polydopamine.(24) Their coated fabric exhibited an improvement in limiting oxygen index (LOI), a 60 % decrease in PHRR and a 26 %

decrease in THR. It was difficult to ascertain the role of the polydopamine in flammability reduction, however, as the cone calorimetry experiments lacked data on the individual components. Based on the LOI measurements, it appears that much of the reduction in flammability was due to the ammonium polyphosphate and that the PDA was predominantly used as a low flammability binder in this study. And, Zhang and co-workers assembled polydopamine and reduced graphene oxide (rGO) coatings onto FPUF using a layer by layer approach.(33) PDA-rGO-based coating with three tri-layer deposition effectively reduced the PHRR by 49 % and the THR by 5 % compared to the neat FPUF. Higher loadings of bi-layers led to a significant increase in the THR and very little change in the PHRR. Considering the single dip process and lower loadings used in our process, the reductions in flame spread, PHRR, and THR, especially when using glycine phytate, are encouraging.

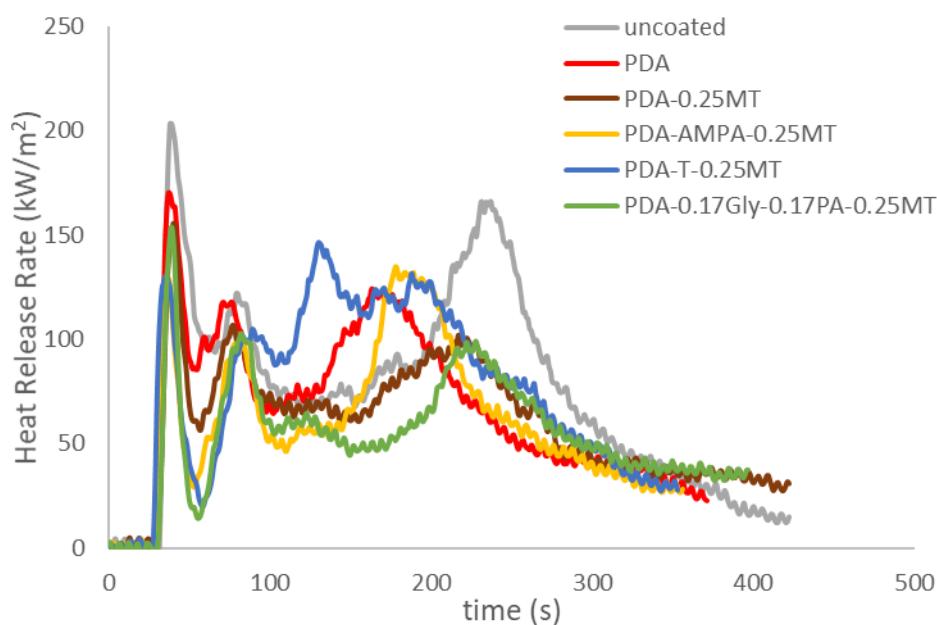


Figure 5. Typical cone calorimeter results for polydopamine coated cardboard.

Table 6. Microcombustion Calorimetry Results for Polydopamine Coated Foams*

Coating Formulation	Coating (mass %)	TTI (s)	PHRR (kW/m ²)	THR (MJ/m ²)	AEHC (MJ/kg)	Residue (mass %)
uncoated	---	15 ± 2	211 ± 14	27 ± 2	11.8 ± 0.6	11 ± 2
PDA	3.1 ± 0.2	15 ± 0	188 ± 20	26 ± 1	8.6 ± 0.4	21 ± 2
PDA-0.25NaMT	4.1 ± 0.2	15 ± 1	176 ± 45	25 ± 0	7.7 ± 0.1	24 ± 3
PDA-AMPA-0.25NaMT	8.7 ± 0.8	15 ± 1	139 ± 13	23 ± 1	6.4 ± 0.1	30 ± 1
PDA-T-0.25NaMT	7.1 ± 0.3	14 ± 1	137 ± 5	17 ± 10	7.7 ± 0.1	49 ± 32
PDA-0.17PA-0.17Gly-0.25NaMT	9.3 ± 0.3	15 ± 2	138 ± 23	16 ± 7	4.4 ± 2.0	47 ± 21

4. Conclusions

Dopamine intercalates into the galleries of montmorillonite layered clay and can produce well dispersed clay platelets when the dopamine is polymerized. Polydopamine coatings are strongly influenced by the base used to catalyze the polymerization. Three dimensional structures containing some of the base is formed when using Tris or NH₃, but not when using DAP. Heating the formed polydopamine, even briefly, reduces the porosity of the coatings and increases the insoluble mass. Although polydopamine and polydopamine –

montmorillonite can reduce the flammability of a protected substrate, the inclusion of other compounds that form an intumescing flame retardant was crucial for significant fire protection. AMPA, amine neutralized phytic acid, and taurine were effective at producing intumescing char, preventing foam collapse, and reducing heat released when pyrolyzing foam. AMPA and glycine phytate were both found to be effective at reducing flame spread of cardboard. The coatings reduce peak heat release rate by 33 % and total heat release rate by 20 %. In some of the taurine and glycine phytate containing replicate samples, the combustion extinguished prior to complete combustion of the cardboard, further reducing the total heat released.

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Acknowledgments

This work was supported in part by NSF Grant No. CHE-1625977.

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