Research Article

Unprecedented Nonflammable Organic Adhesives Leading to Fireproof Wood Products

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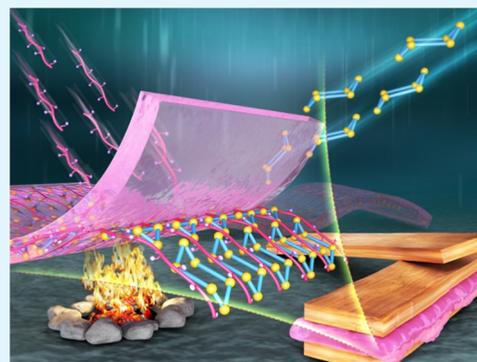
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ABSTRACT: We report an excellent water-based inflammable organic wood adhesive that is able to protect wood products from burning by generating inflammable gases, a porous thick char layer, and radicals that consume the oxygen and hydrogen radicals required in the burning process. The organic adhesive is obtained by the formation of hard supramolecular phases composed of high-density flame-retardant N and P elements through hydrogen bonding and acid−base interaction between the phytic acid and branched polyethylenimine (b-PEI). The phytic acid molecules are packed densely in the framework of the flexible b-PEI so that a porous char layer that would reduce heat conduction can be formed as the adhesive is heated. Together with the formation of inflammable NH_3 gas to dilute the oxygen concentration and a $PO^{\bullet}$ radical to capture the $H^{\bullet}$ and $O^{\bullet}$ radicals, the adhesive-treated wood product displays an extremely high limited oxygen index of 100% and a negligible heat release rate, total heat release, and total smoke release. The current flame-retardant water-based organic adhesive is so far the best adhesive for green and safe wood products from burning.

KEYWORDS: phytic acid, adhesive, flame retardant, coacervate, assembly

1. INTRODUCTION

Wood is used worldwide as a residential building and furniture material in indoor environments. However, the combustible nature of wood has resulted in enormous losses of life and property every year.[1−3] Endowing wood and wood products with flame retardancy has become a significantly important issue in the wood and building industries. Currently, impregnation (dipping)[4] or surface coating is being extensively employed to reduce the burning ability of wood products.[1,5−8] However, surface coatings are usually not durable and the thin coating layer has a limited flame retardant ability.[9,10]

Bulk adhesives are extensively used in the wood industry, not only in the fabrication of plywood, particleboard, and medium-density fiberboard[11,12] but also in fixing the joints of different parts. People therefore envision that if we are able to endow adhesives with flame retardant ability, all the concerns arising in extra flame-retardant technology can be ignored, which is thus very promising for the future development of flame retardant techniques. It has been known that materials rich in phosphors,[13−15] nitrogen, borate,[16] and silicone elements, and a hybrid of inorganic components display excellent flame retardancy.[11,17−24] For this reason, the current fire-retardant adhesives are often based on molecules with the aforementioned elements. For example, Shi et al. exploited borate chemistry to crosslink soy protein (SP), sodium borate, and hyperbranched polyester (HBPE) into a flame-retardant wood adhesive.[11] Zhang et al. introduced calcium sulfoalumi-nate into an adhesive mixture of SP and acrylic acid to induce the in situ polymerization of acrylic acid to endow the adhesive gel with excellent flame retardancy.[17]

Although these strategies achieve a considerable flame retarding effect, few materials display satisfactory comprehensive performance, mainly due to the compromise between the flame-retardant ability and adhesive strength. Usually, adding a large proportion of inorganic materials, such as ammonium polyphosphate, magnesium hydroxide, or aluminum hydroxide, is necessary to achieve the corresponding flame retardant effect at the expense of mechanical performance.[7,8,25,26] As a result, a significant challenge still remains to develop adhesives that simultaneously have excellent flame retardant and adhesive performance.

Considering that high-density flame-retardant elements and multiple interactions are the fundamental requirements for excellent flame retardant ability and adhesive performance, respectively, we decide to conceive an aqueous coacervate-based adhesive with phytic acid (PA) and branched polyethylenimine (b-PEI) since both of them are well-known
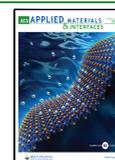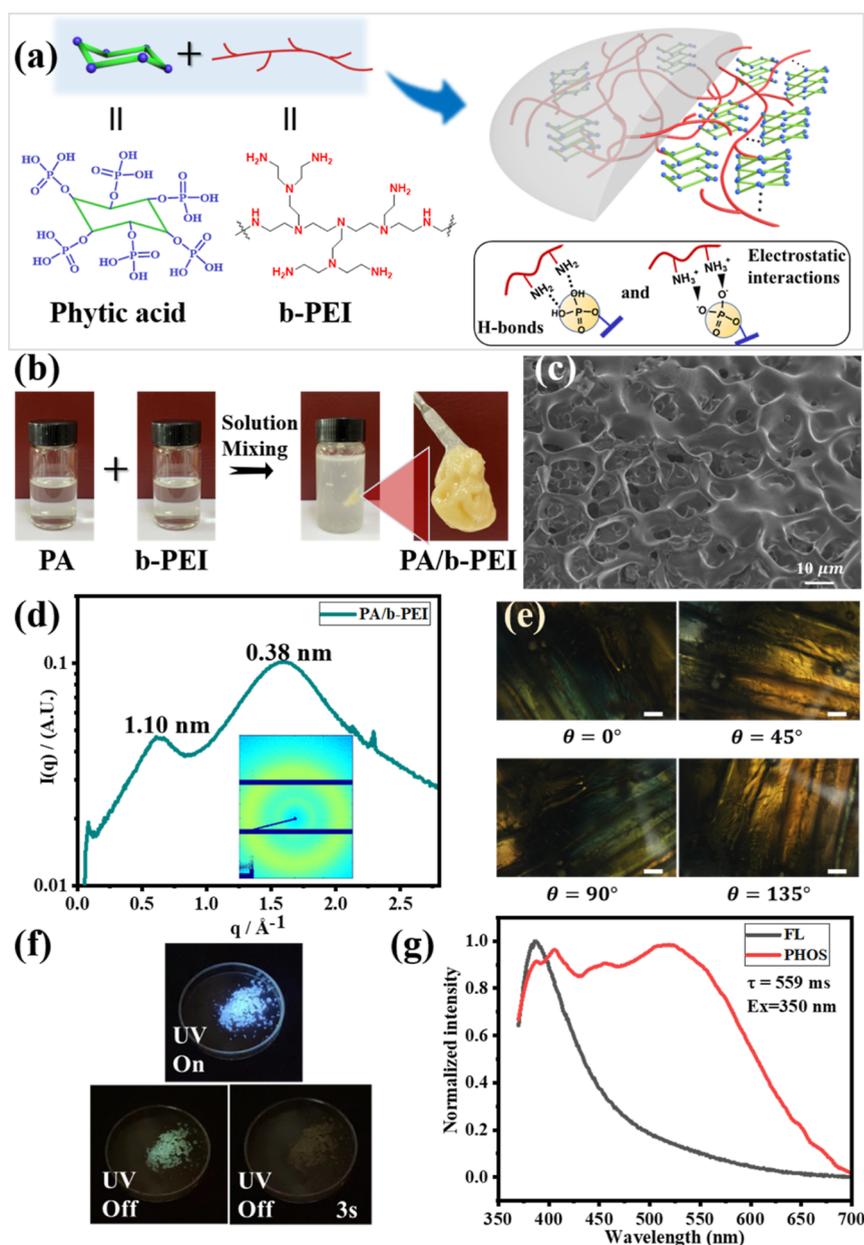
Figure 1. (a) Molecular structures of PA and b-PEI and schematic illustration of the self-assembly of PA/b-PEI, leading to the formation of complex coacervates. (b) Preparation process and the photograph of the PA/b-PEI coacervate. (c) SEM image for the lyophilized coacervate. (d) Wide-angle X-ray scattering (WAXS) profile of the PA/b-PEI sample. The inset shows the two-dimensional WAXS image. (e) POM of the dry coacervate PA/b-PEI. The scale bar is 50 μm. (f) Photos of the dry coacervate under a 365 nm UV light. (g) Normalized FL and PHOS spectra of the dry coacervate.

flame-retardant materials endowed by abundant P and N elements in their structure. In particular, there are six phosphate groups around a six-membered ring in PA, which can attract 12 NH/NH$_2$ groups in b-PEI, thus generating a hard region with concentrated nonflammable elements. In previous work, PA and b-PEI have been used either individually or in the form of layer-by-layer assembly to construct flame-retardant coatings on cotton,[27] wool fabrics,[28,29] polylactic acid,[30] polypropylene,[31] and epoxy resins.[32] However, such a coating layer strategy is not applicable to wood adhesives due to the lack of sufficient internal cohesion forces. Herein, we show that the bulk coacervate phase could provide super strong internal cohesion forces required for a strong adhesive. Owing to the hydrogen bonding and acid−

base interaction between the amide and the phosphate groups, the hard region that is rich in nonflammable elements around the six-membered PA ring is packed regularly in the adhesive. Upon heating, the hard phases with rich N−P elements would release inflammable NH$_3$ and a PO$^\bullet$ radical that consumes the H$^\bullet$ and O$^\bullet$ radicals required for burning. Meanwhile, the surrounding carbon is transformed into porous graphite. As such, the PA/b-PEI adhesive displays an ultrahigh limited oxygen index (LOI) of 100% and a strong adhesion force of 5.5 MPa toward the wood substrate, which means that even in pure oxygen, the wood adhered with the PA/b-PEI adhesive is nonflammable. We envision that the current strategy of dense complexation of flame-retardant elements to form crystalline hard phases in a soft polymeric network would offer a safer and
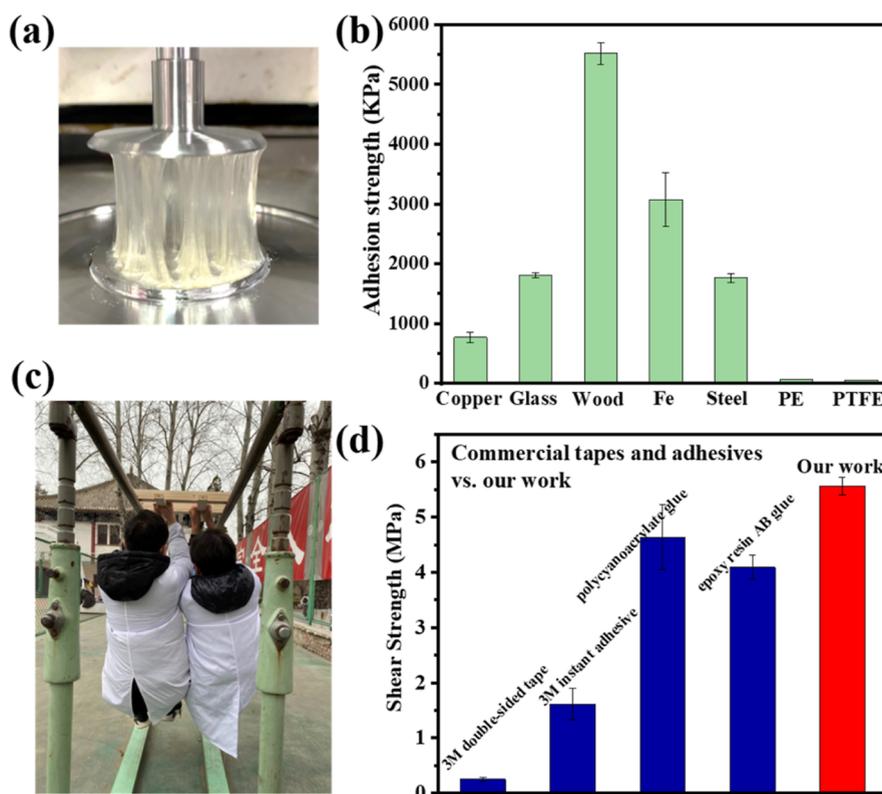
Figure 2. (a) Photograph of the stretchable viscous PA/b-PEI coacervate adhered between the two plates of steel. (b) Adhesion strength of the adhesive on different substrates. (c) Photograph showing the robust adhered wood surfaces (the adhered area is 4.3 × 4.3 cm^2) and the loading experiment of 150 kg weights recorded in a video (Movie S2). (d) Comparison of adhesion strengths of industrial tapes and commercial glues vs the PA/b-PEI wood adhesive.

healthier life for people by providing nonflammable furniture and relevant products.

2. RESULTS AND DISCUSSION

2.1. Fabrication and Characterization of the Adhesive. The high-density flame-retardant adhesive was constructed by directly mixing the aqueous solution of PA and branched PEI (Figure 1). Since PA contains six phosphoric acid groups and every one of them is a binary acid, it would offer 12 protonation groups around the small inositol ring. This high-density protonation groups interact with the amines in b-PEI through acid−base neutralization (Figure S1), thus leading to a viscous coacervate (termed as PA/b-PEI) with the molar ratio between PA and b-PEI being 3.8 (Table S1 and Figure S2). The freshly prepared PA/b-PEI adhesive is a viscoelastic fluid with a water content of 36.7%. The initial apparent viscosity for this coacervate is 6000 Pa·s (Figure S3a,b). Scanning electron microscopy (SEM) for the lyophilized PA/b-PEI coacervate reveals an interconnected porous three-dimensional network, indicating a high cohesion performance (Figure 1c).

X-ray scattering measurement (Figure 1d) reveals a sharp peak at $q = 0.57$ Å^{-1}, indicating the formation of hard phases with the average separation of $d = 2\pi/q = 1.10$ nm based on Bragg's law.[33−35] Meanwhile, a broad peak occurs at $q = 1.65$ Å^{-1}, featuring an average distance of 0.38 nm. These data suggest that the polymer chains have regularly folded around the PA molecules.[36−39] In line with this, the coacervate displays birefringence under polarized optical microscopy (POM) (Figure 1e), indicating that the size of the ordered

crystalline region is about several hundred nanometers, which is comparable to the wavelength of the visible light.[40] As shown in Figure 1f and Movie S1, this dry coacervate gives fluorescence (FL) under 365 nm UV irradiation and emits obvious afterglow. Spectral measurements reveal the FL centers at 390 nm and the afterglow [phosphorescence (PHOS)] at about 520 nm with a lifetime of 559 ms (Figure 1g). Since no typical conjugated groups exist in the system, the occurrence of the FL and afterglow indicates the clustering of the electron-rich atoms (O, N, and P atoms) through space conjugation.[41,42] Taken together, it is therefore rational that the coacervate is a supramolecular 3D network of the hard mesophases of clustered PA bridged by the b-PEI chains, leading to a high density of P and N flame retardant elements in the system. This approach is green and allows mass production of PA/b-PEI adhesives. Although currently the prices of PA and b-PEI are not very low, we believe that they would become economic with the improvement of technology and enlargement of market share. In this regard, this advanced adhesive could hold enormous potential to make fireproof furniture, flooring, and wall materials for some special places, such as art museums.

2.2. Adhesive Property. As presented in Figure 2a, the PA/b-PEI coacervate could be stretched into viscous filaments, manifesting its excellent cohesion capacity. Indeed, the coacervate displays strong adhesion ability toward various substrates such as skin, steel, wood, PTFE, glass, and plastic (Figure S4). It is noteworthy that the adhesion strength for wood can be as high as the constant value of 5520 kPa after curing for 7 h in the air, which is the strongest adhesion among

different substrates (Figure 2b). As shown in Figures 2c and S5 and Movie S2, the PA/b-PEI coacervate-bonded wood sticks were able to load two adults with a total weight of 150 kg. The best adhesion of PA/b-PEI on wood was attributed to the existence of multiple hydrogen bonding groups in wood so that they may interact with the phosphate groups in PA and amide groups in b-PEI to form extensive hydrogen bonds (Figure S6). Additionally, the wood surface is coarse, which allows the formation of mechanical interlocking in the presence of viscous PA/b-PEI, as evidenced by the SEM measurement (Figure S7). This mechanical interlocking between the two wood strips also improved the interfacial interactions, thus leading to excellent bonding performance,[43−46] as illustrated in Figure S8.

Moreover, the bonded wood sheets were placed indoors for several months to test the effect of weather changes. During these months, the highest air humidity in Beijing was close to 95%, and the lowest was 3%, but the large-span weather changes had little effect on the adhesive performance (Figure S9) because it is difficult for humidity to penetrate the adhesive between the wood strips. Strikingly, our aqua-based adhesive displays the best adhesion property when compared with the most often used robust commercial adhesives (Figure 2d).

2.3. Combustion Properties of the Dry Adhesive.
Before testing the flame retardant ability of the coacervate, the combustion properties of the dry PA/b-PEI adhesive were examined. Upon exposure to the direct flame of a candle (∼600 °C) and a butane torch (∼1400 °C), the samples cannot be ignited but undergo a self-intumescent process immediately with no flaming molten drops (Figures 3a and S10 and Movies S3 and S4). Moreover, a char layer grows during burning, and the char layer is firmly integrated within the adhesive matrix without falling off, thus playing a long-lasting role in thermal insulation. TGA measurement (Figures

3b and S11) revealed that the coacervate keeps releasing water and volatile gas at temperatures below 500 °C, and the weight of the final char residue can be as high as 40.1% as the temperature is raised to 700 °C, suggesting excellent char forming ability during the thermal oxidation process.

2.4. Flame Retardant Property of the Adhesive-Treated Wood Material.
Next, the flame retardant ability of the adhesive on wood with different adhesive application states was examined. First of all, two pieces of wood adhered with the coacervate were examined. Upon exposure to the direct flame of a butane torch (∼1400 °C), the original wood without adhesives ignited immediately and the flame spread quickly. However, as the fire reached the adhered interface of the two wood pieces, it self-extinguished immediately (Figure S12b−d and Movies S5 and S6). If the adhesive was spread on the surface of a wood (the thickness of 3 mm), the backside of the wood still maintained the original state after being exposed to high-temperature heat radiation for 150 s (Figure 3c and Movie S7). Thermal IR imaging reveals that the temperature on the backside of the wood was below 100 °C when the coating (thickness of 0.25 mm) was exposed to an open flame at around 1400 °C (Figure 3d). Moreover, it is observed that the fire performances are dependent on the thickness. The thicker the coating layer, the better the fire protection performance (Figure S13).

The LOI test indicated that while the original wood gives a low LOI of 22.3%, the adhesive-bonded wood substrates with a four-layer structure show a higher LOI of 28%, and the burned wood products can be endowed with good structural integrity (Figure S14) due to the flame retardant property of the adhesive. Notably, the wood coated with the adhesive exhibits an ultrahigh LOI value of up to 100% (Figure 4a), which means that the adhesive-coated wood cannot be ignited even in a pure-oxygen environment. Indeed, the vertical burning tests (UL-94, inset in Figure 4a) verified that the burning rate of the adhesive-coated wood is zero (Movie S8). In line with this, the cone calorimetry tests (CCTs) show that at a heat flux of 35 kW/m², the adhesive-treated 10 × 10 cm poplar veneer could not be ignited, which is evidenced by the negligible heat release rate (HRR) (Figure 4b), total heat release (THR) (Figure 4c), and total smoke release (TSR) (Figure 4d). The time to ignition (TTI) of pure wood plates was 17 s, while the TTI of the adhesive-coated wood significantly increased by 5200%, up to 884 s. This means that the chance for people to escape from uncontrolled fires can be enhanced 52-fold, and firemen have more chances to extinguish the fire before it causes significant damage.

2.5. Flame Retardancy Mechanism.
Since both the released gases and the remaining char layer are critical for flame retardants,[47] the released gaseous products and the structure of the char layer were analyzed. TG-FTIR measurements (Figure 5a) indicate the start of the release of H_2O (3400−4000 cm⁻¹), CO (2000−2200 cm⁻¹), and CO_2 (2250−2382 cm⁻¹) at temperatures below 460 °C.[48−50] Above 460 °C, the nonflammable gas NH_3 from the thermal decomposition of the nitrogen-containing structures of b-PEI could be also detected at 930 and 964 cm⁻¹.[51] All these nonflammable gases can take effect in the gas phase to dilute the concentration of oxygen in the flame-region combustible gases. Moreover, the peak at 1108 cm⁻¹ characterizing the P−O• started to appear at a low temperature of 100 °C,[52] which can act as a free radical scavenger to remove the H• and OH•
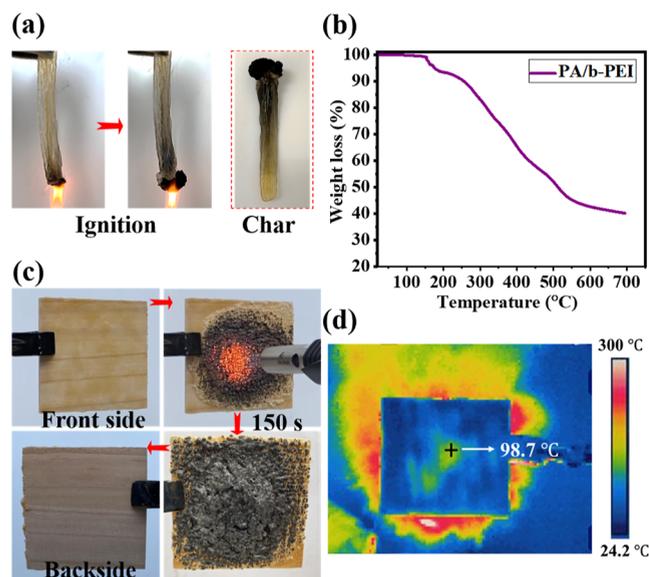

Figure 3. (a) Digital photos of the dry PA/b-PEI coacervate exposed to the flame of a candle. (b) TGA curve of the dry coacervate. (c) When burning the front wood substrate for 150 s, the adhered layer (the thickness of 0.25 mm) can effectively isolate heat transfer and protect the backside wood substrates. (d) After igniting using the butane torch flame (∼1400 °C) in front of the PA/b-PEI adhesive-coated wood sample, the backside temperature was determined using the IR camera.
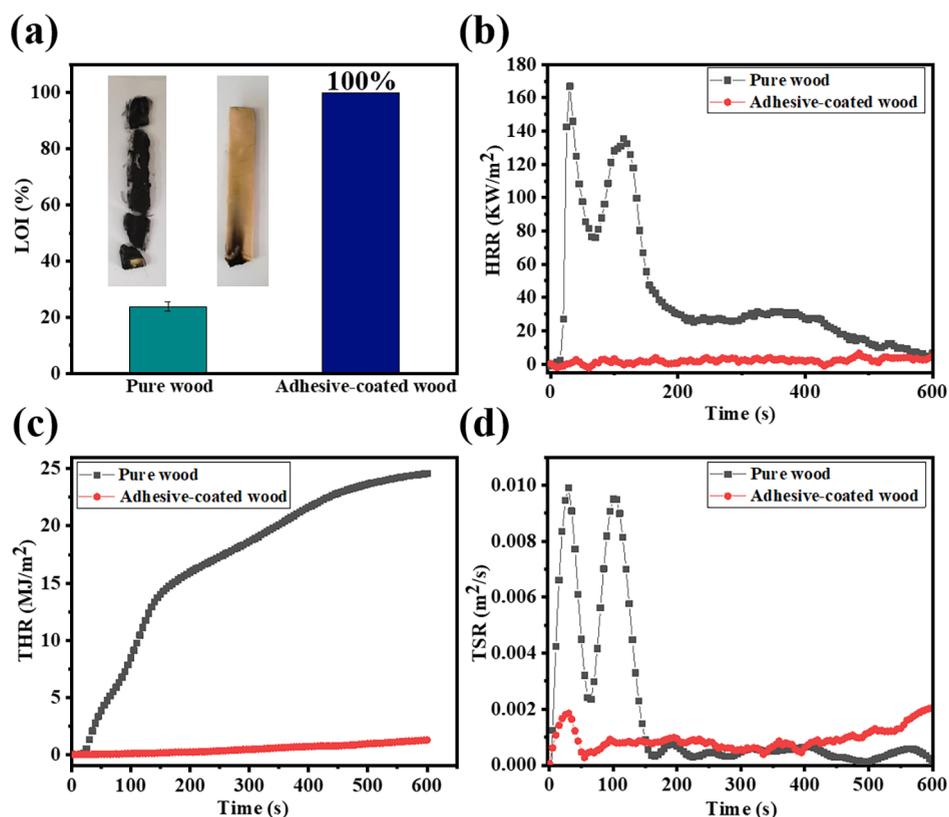
Figure 4. (a) LOI of pure wood and the adhesive-coated wood composite. The inset shows digital photos of pure wood and adhesive-coated wood (from left to right) after the vertical burning test. Cone calorimetric curves showing the (b) HRR, (c) THR, and (d) TSR.
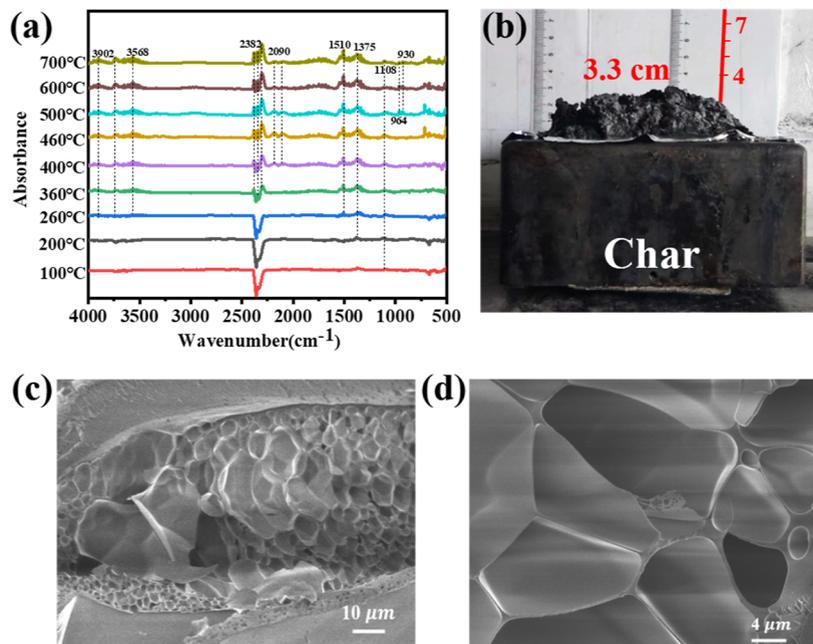

Figure 5. (a) In situ FT-IR spectra for the degradation process of the coacervate at different temperatures. (b) Digital photo of the residue char after the CCT. The side view of the adhesive-coated wood composite. (c) SEM morphologies of the burned PA/b-PEI coacervate char residue. (d) Enlarged SEM image.

radicals to interrupt the combustion. All these gas species contribute synergistically to improve the flame retardant effect.

Furthermore, the structure and composition of the char residues were characterized. As mentioned in the previous text, the weight of the char residue can be 40% of the original

adhesive. FT-IR, XPS, and Raman scattering measurements indicate that the char residues are composed of graphitic carbon, aromatic hybrid fused rings, and self-condensed PA (Figures S15-S17). For a thin adhesive coating of about 0.25 mm, the height of the char residues is as high as 3.3 cm (Figure

5b), which is so firm that it can support a weight of 500 g (Figure S18). The SEM observation reveals the generation of honeycomb-like structures, which consist of microscale polyhedron cells with shared walls inside the char residue (Figure 5c,d). This special char structure can hinder heat transfer via skeletal network conduction and air convection,[53] which increases the tortuosity and resistance of the through-air flow, thus giving a satisfactory thermal insulation performance. The proposed excellent flame retardancy mechanism for the PA/b-PEI aqua-based adhesive is illustrated in Figure 6a.
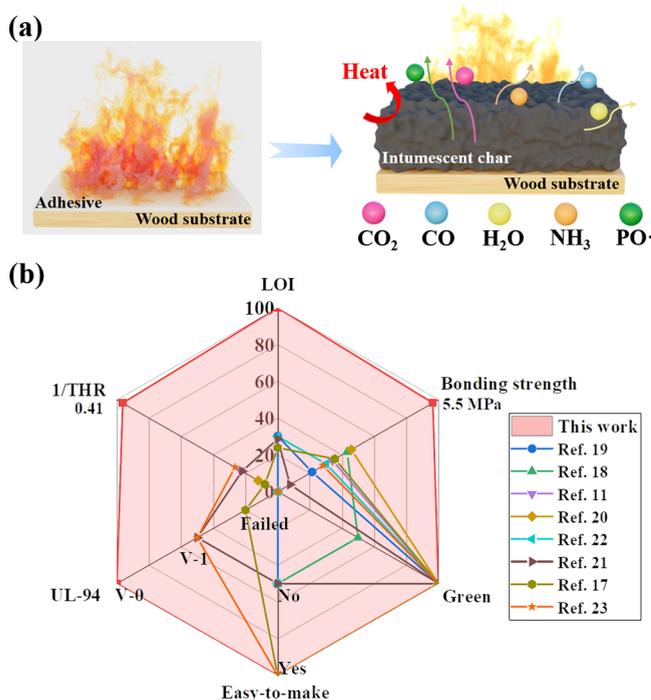

Figure 6. (a) Flame-retardancy mechanism schematic diagram of the PA/b-PEI aqua-based adhesive. (b) Rough comparison between this work and previously reported fireproof wood adhesives in terms of bonding strength, green or toxic, easy-to-make or involves a complex process, LOI, the level of UL-94, and THR.

To clearly illustrate the unique design and excellent properties of our fireproof adhesive, a brief comparison of our material with eight representative wood adhesives from recent literature is presented in Figure 6b. In particular, in terms of six key parameters including bonding strength, green or toxic, easy-to-make or involves a complex process, LOI, the level of UL-94, and THR, our material shows a unique combination of advantages. Considering the green fabrication procedure and non-formaldehyde, we envision that the current PA/b-PEI adhesive resulting from high-density complexation of flame-retardant elements would guard people for a safer and healthier life by offering nonflammable furniture and relevant products.

3. CONCLUSIONS

In conclusion, a nonflammable organic adhesive with hard phases of high-density fire-retardant elements based on the coassembly of PA and b-PEI was constructed in this work, which has been proven to be so far the best flame-retardant water-based adhesive for green and safe wood products. Thanks to the high density of the flame-retardant element in

the hard phases, the adhesive displays an ultrahigh LOI of 100% and a strong adhesion force of 5.5 MPa toward the wood substrate, which means that even in pure oxygen, the wood adhered with the PA/b-PEI adhesive is nonflammable. The flame retardancy mechanism is attributed to the generation of nonflammable gases and $PO^{\bullet}$ radicals in the gas phase to break the combustion process and the formation of a porous graphite carbon char layer that prohibits heat transition. This work provides a facile and effective strategy to develop an aqua-based adhesive that simultaneously exhibits excellent flame retardant and adhesive performance, presenting a green and promising concept of fire retardancy in wooden construction.

4. EXPERIMENTAL PROCEDURES

4.1. Materials. PA (70% water solution, Adamas) was supplied by Beijing InnoChem Science & Technology Co., Ltd. Branched poly(ethylene imine) (30 wt % in water, M_w = 100 000) was obtained commercially from Beijing Hwrkchemical Co., Ltd. and used without further purification. Cyanoacrylate (JSENB) glue was purchased from Beijing Dehang Wuzhou Technology Co., Limited. Epoxy resin AB glue (Araldite 2012) was purchased from Beijing Tiannuo Tiancheng Biotechnology Co., Ltd. Water used in all experiments was purified using a Milli-Q Advantage A10 ultrapure water system.

4.2. Preparation of the Wet Adhesive. First, an 8 wt % aqueous solution of phytic acid was prepared by dissolving 4 g of PA into 50 mL of deionized water. Similarly, a 4 wt % aqueous solution of b-PEI was prepared. Then, an equal volume of b-PEI solution was added slowly into the PA solution. Turbidity was observed once the solutions were mixed, and a fluidic wet adhesive was obtained upon shaking, termed PA/b-PEI. After rinsing with deionized water three times, the adhesive could be directly used for application.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.2c19072.

> Video recordings showing experimental results (ZIP)
>
> Characterizations; FT-IR spectra of PA, b-PEI, and the dry coacervate; phase diagram of the PA/b-PEI mixture at pH = 0.8; rheological behavior of the wet coacervate; viscosity of the wet adhesive; SEM image of the glued area; proposed bonding mechanism; digital photos of the dry PA/b-PEI coacervate exposed to the flame of a butane torch; DTG curve of the dry coacervate PA/b-PEI; fire behavior of the bonded wood substrates; FT-IR spectra of the unburn coacervate and char residue; C 1s and O 1s spectra of the unburn coacervate and char residue; Raman spectroscopy of the char residue; and element analysis results of the dry coacervate(PDF)

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Author Contributions

Y.Y. and S.T.G. conceived the idea and designed the experiments. Y.Y. and B.Z. supervised the project. S.T.G., J.W.Q., and R.S.X. carried out the synthetic experiments and analysis. P.Q. contributed to the LOI and vertical burning tests. T.Y.W. carried out the WAXS measurement. S.T.G., B.Z., J.B.H., and Y.Y. wrote the paper, and all authors discussed the results and commented on the manuscript.

Notes

The authors declare no competing financial interest.

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