Closed-Loop Recyclable, Self-Catalytic Transesterification Vitrimer Coatings with Superior Adhesive Strength, Fire Retardancy and Environmental Stability

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ABSTRACT: The non-degradability, non-reusability, and flammability of epoxy coatings have brought serious environmental and safety issues. Herein, a multifunctional, fire-retardant epoxy vitrimer coating (DCNC/45PETO) was prepared *via* curing bis(2,3-epoxypropyl) cyclohex-4-ene-1,2-dicarboxylate (DCNC) with a well-designed phosphaphenanthrene-containing polyethylenimine (PETO) at room temperature. DCNC/45PETO exhibits excellent adhesion to different substrates, with a high adhesive strength of 7.9 MPa on wood, outperforming previous wood coatings/adhesives. The DCNC/45PETO coating endows wood with excellent fire retardancy, including a high limiting oxygen index of 34.0% and a vertical burning (UL-94) V-0 rating. DCNC/45PETO demonstrates durable adhesion and fire-retardant performances in harsh environments. The self-catalytic transesterification within DCNC/45PETO network effectively avoids the application of extra toxic catalysts, and this coating can be reused for at least 5 times in mild conditions without compromising its performances. This study provides an innovative design strategy for creating multifunctional vitrimer coatings, showing great application potential in construction field.

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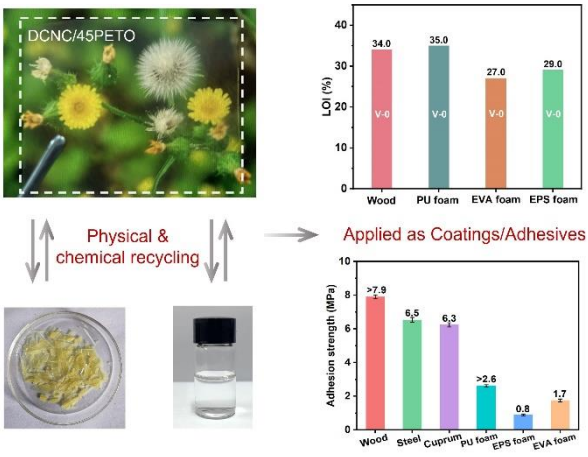

A multifunctional, transparent epoxy vitrimer coating combines room-temperature curing ability, closed-loop self-catalytic recyclability, exceptional adhesion and superior fire retardancy.

As environmental problems become increasingly serious, researchers are committed to promoting carbon neutrality and circular economies [1]. As important thermosets, epoxy resins (EPs) are widely used as coatings and adhesives in industry due to their high adhesion strength and great chemical resistance [2-4]. However, the permanently cross-linked network of EP makes it non-degradable/repairable [5-7], and its wide applications also bring about serious plastic pollution and waste of resources [8, 9]. Based on the circular economy strategies, there is an urgent need to develop practical and sustainable epoxy coatings and adhesives.

Endowing EPs with recyclability and reusability is a promising approach to address the plastic pollution issue and have been widely explored in academia and industry [10-12]. With the development of dynamic chemistry, a new kind of polymeric material (vitrimer) with covalent adaptive network (CAN) has been developed in recent years, which combines the advantages of thermoset and thermoplastic[13-15]. Due to the existence of dynamic covalent bonds, the vitrimer can be reprocessed and remolded under external stimulus, *e.g.*, temperature and light, by topological rearrangement [16, 17]. The first epoxy vitrimer was reported by Leibler's group in 2011, which could be reprocessed in the presence of metal catalysts [18]. Since then, different dynamic covalent bonds, e.g., β-hydroxy ester [19, 20], disulfide bond [13, 21], Schiff-base (imine) linkage [22, 23], and siloxane equilibration [24, 25], have been applied to produce epoxy vitrimers. The development of epoxy vitrimers offers a meaningful guideline for the preparation of sustainable coatings and adhesives [26-28]. However, these EP vitrimers usually need high curing temperatures and harsh recycling conditions, which prevents them from being used as reusable coatings and adhesives. Therefore, it is necessary to develop epoxy vitrimer coatings/adhesives that can be cured at room temperature and recycled under mild conditions.

Transesterification is the most applied dynamic chemistry for preparing epoxy vitrimer [29, 30], but the additional catalysts, such as zinc acetate and triazabicyclodecene, are needed to accelerate the reaction [31, 32]. However, the external catalyst usually tends to leach out from the

matrix in long-term usage and are expensive and toxic. Thus, it is necessary to develop self-catalytic transesterification epoxy vitrimers to meet the requirements of practical applications. EP/polyethyleneimine (EP/PEI) systems have been widely applied in the coating and adhesive fields because of their room-temperature curing and good comprehensive performances [33-35]. After curing, abundant secondary/tertiary amine groups will be generated within the cross-linked network of EP/PEI systems, which have been shown to effectively catalyze the transesterification [2, 8, 36]. Thus, introducing the β-hydroxy ester groups into the EP/PEI network may be a promising strategy to develop room temperature-curable epoxy vitrimer coatings.

The inherent flammability of EP/PEI systems (LOI < 19%, and no rating in UL-94 testing) is another major defect that limits their further application in protective coatings [37-39]. Based on previous works [40-42], developing phosphorus (P)-containing curing/co-curing agents can effectively impart intrinsic flame retardancy to EPs. Integrating additional flame-retardant elements, such as silicon (Si), boron (B), and nitrogen (N), into P-based curing/co-curing agents can strengthen fire-retardant performances *via* synergistic effects [43-45]. For instance, Shao *et al.* [46] synthesized a P-containing PEI curing agent (PTDP) for EPs. The EP material with 30 wt% PTDP exhibited a UL-94 V-0 rating with an LOI of 30.4%, indicating self-extinguishing properties. Although fire-safe EP/PEI systems had been prepared by introducing P element, they could not be reused and recycled [47], which did not conform to sustainable development. Based on the above analyses, introducing β-hydroxy ester and flame-retardant elements, e.g., phosphorus, into EP/PEI systems may be able to create recyclable, fire-retardant coatings.

Herein, a multifunctional self-catalytic transesterification epoxy vitrimer coating (DCNC/45PETO) was prepared by the curing reaction of DCNC (an epoxy monomer) and PETO (a bio-based, P-containing PEI) at room temperature. The abundant hydrogen bonding sites in DCNC/45PETO vitrimer endows it with excellent adhesion performances. Especially, the shear strength of DCNC/45PETO on wood can be up to ~7.9 MPa. The DCNC/45PETO

coating shows high pencil hardness and superior fire retardancy on wood. Even after different aging treatments, DCNC/45PETO maintains excellent fire-retardant and adhesive properties, indicative of superior environmental resistance. DCNC/45PETO can be fully recycled and reused for many times in mild physical/chemical conditions. The DCNC/45PETO coating possesses both multifunctionality and practicability, which can find ubiquitous applications in construction and outdoor facility.

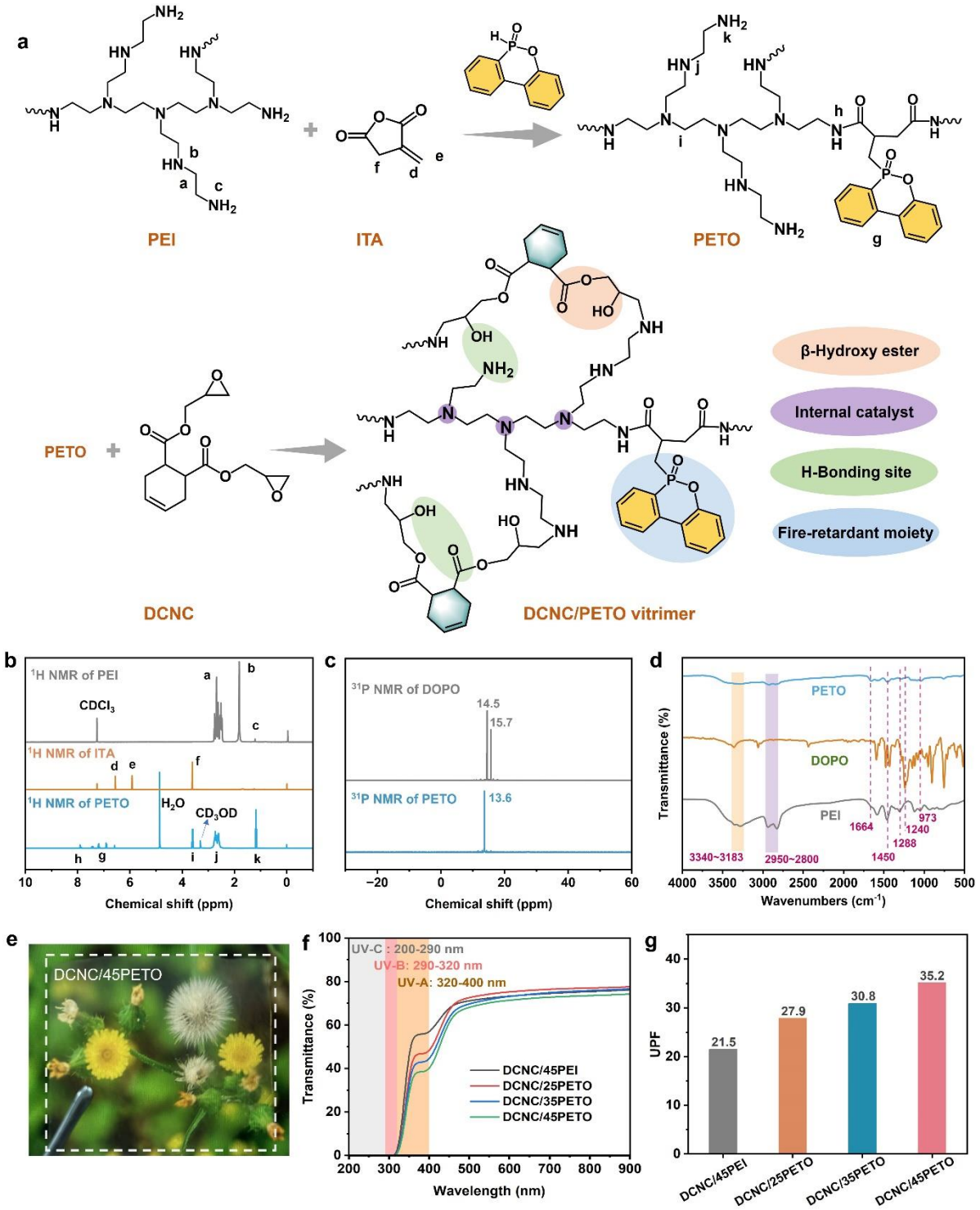

Figure 1. (a) Schematic illustration for the preparation of DCNC/PETO vitrimers, (b) ^{1}H NMR of PEI, ITA, and PETO, (c) ^{31}P NMR of PETO, (e) FTIR spectra of PEI, ITA, and PETO, (e) digital photo of DCNC/45PETO film (thickness: 500-600 μm), and (f) UV-Visible transmission spectra and (g) ultraviolet protection factor (UPF) values of DCNC/45PEI and DCNC/PETO vitrimers.

The closed-loop recyclable, self-catalytic transesterification DCNC/PETO vitrimers were fabricated by solvent-free polymerization of DCNC and PETO at room temperature (Figure 1a). The cross-linked network with abundant β-hydroxy esters, tertiary amines, and hydrogen bonding sites endows DCNC/PETO with high adhesive properties and closed-loop recyclability (Figure 1a). In detail, the bio-based, P-containing polyethylenimine (PETO) was synthesized using PEI, itaconic anhydride (ITA) and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) as raw materials (Figure 1a). The chemical structure of PETO was characterized by nuclear magnetic resonance (NMR), Fourier transform infrared (FTIR) spectroscopy and gel permeation chromatography (GPC) with the spectra presented in Figure 1 and S1. For the ^{1}H NMR of PEI, the chemical shifts of -NH_2, -NH-, and -CH_2- appeared at 1.10, 1.80, and 2.47-2.76 ppm (Figure 1b) [48]. After the reaction of PEI with ITA and DOPO, signal belonging to the aromatic ring can be observed at 6.5~7.4 ppm in the ^{1}H NMR of PETO, and another signal appeared at 7.9 ppm attributed to the amide group. Besides, only one peak appeared at 13.6 ppm in the ^{31}P NMR of PETO (Figure 1c), which was different from that of DOPO, further proving that PETO was successfully synthesized. In the FTIR spectrum of PEI (Figure 1d), the characteristic peaks at 3183-3340 and 2800-2950 cm^{-1} are attributed to the -NH- and -CH- groups, respectively [47]. For PETO, the peaks at 1240, 1450, and 973 cm^{-1} are ascribed to the P-O, P-C, and P-O-C structures of its DOPO moiety, proving the existence of DOPO groups [43, 49]. The peaks at 1664 and 1288 cm^{-1} belong to the oxygenated amino and acyl groups in the amide structures, respectively. The number average molecular weight (M_n) and polydispersity (D) of PETO are 26950 and 3.19, which are much higher than those of PEI (Figure S1). The above results confirm the successful synthesis of PETO.

The cross-linked networks of DCNC/45PEI (PEI content: 45 wt%) and DCNC/PETO were characterized by equilibrium swelling experiments. As the PETO content increases, the gel fraction of DCNC/PETO gradually increases, and finally that of DCNC/45PETO (PETO

content: 45 wt%) reaches 95.4%, indicative of high cross-linking density (Table S2). As presented in Figure 1e and S2, all DCNC/PETO films (thickness: 500-600 μm) exhibit high transparency, which is mainly attributed to the good compatibility between DCNC and PETO. Moreover, the transmittance of DCNC/45PEI film at 900 nm is 76.2%, while that of DCNC/25PETO, DCNC/35PETO, and DCNC/45PETO films is 77.6%, 76.6%, and 74.2% respectively, indicating that the DOPO group has little impact on transparency (Figure 1f and S2a). Obviously, the amorphous structure of DCNC/PETO is responsible for the high transparency (Figure S2b). The transmittance of DCNC/PETO films in the UV-A, UV-B, and UV-C bands (200-400 nm) is lower than that of DCNC/45PEI film, and the ultraviolet protection factor (UPF) of DCNC/45PETO reaches 35.2, with an increase of 38.9% compared with 21.5 of DCNC/45PEI (Figure 1g). Introducing benzene-rich groups into PEI contributes to enhancing the UV resistance of DCNC/PETO [43]. Therefore, DCNC/PETO films possess high transparency and improved UV resistance, thus it can be applied as transparent coating.

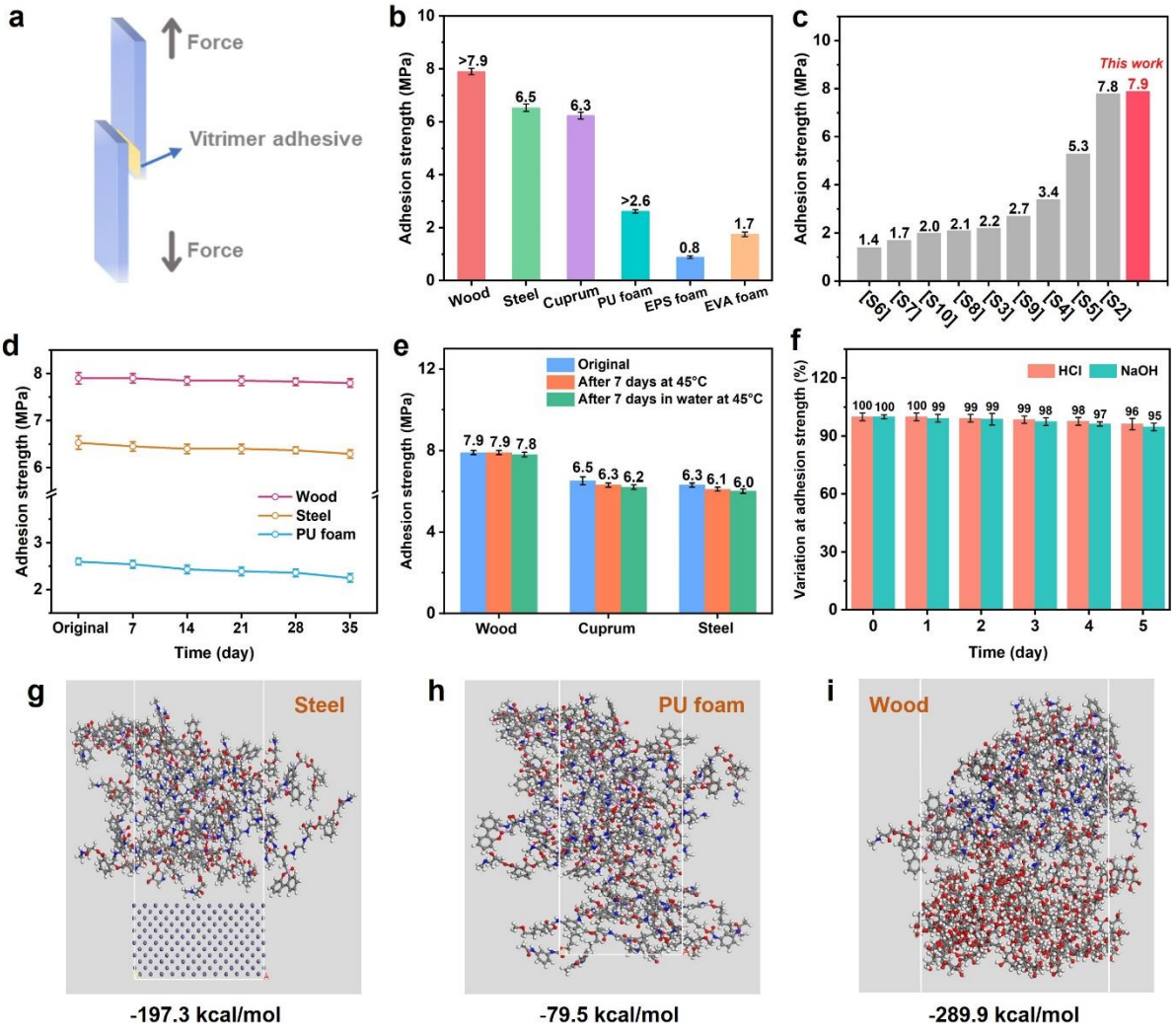

Figure 2. (a) Schematic illustration for the fabrication of lap shear specimen using DCNC/PETO as adhesive, (b) adhesion strength of DCNC/45PETO on different substrates, (c) comparison of the adhesion strength of DCNC/45PETO and previous adhesives on wood, (d) adhesion strength of DCNC/45PETO on wood, steel and PU foam over time, (e) adhesion strength of DCNC/45PETO on wood, steel and cuprum after thermal and hydrothermal aging, (f) variation at adhesion strength of DCNC/45PETO on wood after soaked in NaOH and HCl aqueous solutions for different days, and the energy modeling for molecular dynamics simulations of DCNC/45PETO on (g) steel, (h) PU foam, and (i) wood substrates.

The DCNC/45PETO vitrimer, with the highest cross-linking density and lots of hydrogen bonding sites (esters and amines), exhibits significant potential in the fields of coatings and

adhesives. The adhesive properties of DCNC/45PETO were thoroughly investigated, with the results illustrated in Figure 2. Furthermore, the glass transition temperature (T_g) values of DCNC/45PETO and other samples were investigated by differential scanning calorimetry (DSC), with the results shown in Figure S3. The T_g of DCNC/45PETO is 55.8 °C and higher than 52.5 °C of DCNC/45PEI. Thus, the introduction of rigid P-containing groups elevates the operational temperature of DCNC/45PETO, which can behave as a glassy polymer at room temperature [2]. Additionally, the pencil hardness of DCNC/45PETO impressively reaches 4H (Table S2). Figure 2a demonstrates the fabrication of DCNC/45PETO adhesives on various substrates, including wood, steel, cuprum, polyurethane (PU) foam, expanded polystyrene (EPS) foam, and ethylene vinyl acetate (EVA) foam. The adhesive strength of DCNC/45PETO on wood far exceeds 7.9 MPa since the wood fractures before the adhesive fails (Figure 2b and S4). DCNC/45PETO also exhibits high adhesive strength on other substrates. The adhesive strength of DCNC/45PETO on steel, cuprum, PU, EPS, and EVA foam materials reaches 6.5, 6.3, 2.6, 0.9, and 1.7 MPa, respectively. Compared with previously reported adhesives/coatings for wood (Ref. S2-S10 in Supporting Information), DCNC/45PETO shows much higher adhesive strength, thus outperforming its counterparts (Figure 2c and Table S3). Furthermore, DCNC/45PETO exhibits excellent durability under various harsh conditions. The single lap shear specimens using DCNC/45PETO adhesive and different substrates, including wood, steel, and PU foam, were placed outdoors for 35 d to investigate the environmental stability (Figure 2d). After placing, the adhesive strength of DCNC/45PETO is effectively maintained, demonstrating great environmental stability. The durable adhesion of DCNC/45PETO on various substrates was further confirmed through thermal/hydrothermal aging tests (Figure 2e). After treating for 7 d at 45 °C in an oven and hot water, the shear strength of DCNC/45PETO on wood reaches 7.9 MPa and 7.8 MPa, respectively, and similar results can be obtained on cuprum and steel. The chemical resistance of vitrimer adhesives in practical applications is also

questioned due to their dynamic cross-linking networks. DCNC/45PETO was immersed in 1 mol/L NaOH and 1 mol/L HCl aqueous solutions at room temperature for 5 d to investigate the chemical resistance. After immersion, DCNC/45PETO exhibits no significant weight change (Figure S5), and its adhesion strength on wood still retains 96% and 95% of the original value, respectively. DCNC/45PETO demonstrates robust and durable adhesion, and thus it can be used as a coating and adhesive for various substrates, especially wood.

The adhesive performances are predominantly influenced by the interfacial interaction between the coating and substrate [50]. Hence, molecular dynamics (MD) simulations were employed to analyze the interfacial interaction energy of DCNC/45PETO with various substrates, e.g., wood, polyurethane, and steel. Since the complex cross-linked structure of DCNC/45PETO is not conducive to simulation calculation, its molecular model was optimized by selecting a representative cross-linking fragment (Figure S6). In Figure 2g-i, the interaction energy of DCNC/45PETO with wood is -289.9 kcal/mol, significantly surpassing that with polyurethane (-79.5 kcal/mol) and steel (-197.3 kcal/mol), further verifying the strong adhesion of DCNC/45PETO to wood. The presence of ester, amine, and hydroxyl groups within the DCNC/45PETO network facilitates the formation of abundant hydrogen and coordination bonds with wood, polyurethane, and metal substrates. Additionally, the hyperbranched structure of PETO contributes to effective energy dissipation, enhancing resistance against internal crack propagation under external stress[51]. Thus, the strong adhesion of DCNC/45PETO to diverse substrates is primarily ascribed to its H-bonding/coordinating interaction and hyperbranched architecture.

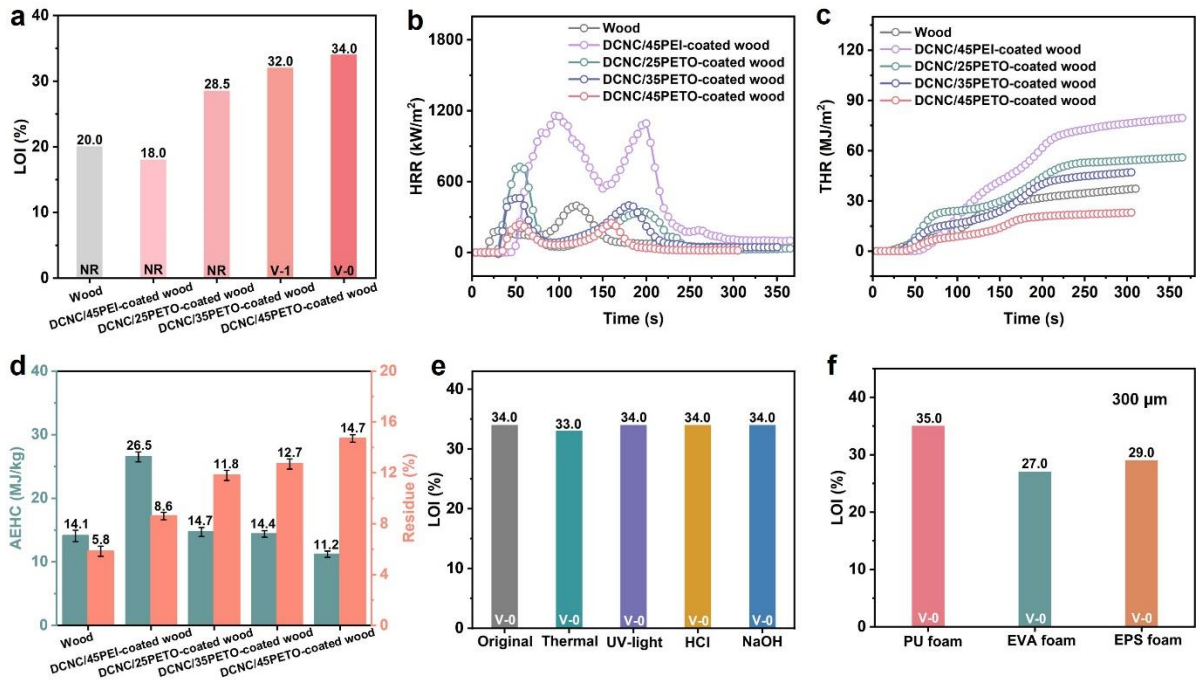

Figure 3. (a) LOI and UL-94 results of DCNC/PEI- and DCNC/PETO-coated woods (coating thickness: 80 μm), (b) heat release rate curves, (c) total heat release plots, and (d) average effective heat of combustion (AEHC) and residue values of DCNC/PEI- and DCNC/PETO-coated woods, (e) LOI and UL-94 results of DCNC/45PETO-coated wood after different durability measurements, and (f) LOI and UL-94 results of DCNC/45PETO-coated PU, EVA, and EPS foams (coating thickness: 300 μm).

Wood has been widely applied in architecture and construction due to its renewability, carbon neutrality, and high specific strength. However, wood is subject to the inevitable fire hazards, and thus it must be undergone fire-retardant treatment. The transparent DCNC/45PETO with impressive pencil hardness and adhesion is an ideal fire-retardant wood coating. The thermal stability of coatings is closely related to their fire retardancy. Due to the enhanced charring ability of PETO, the *CY* values of DCNC/PETO are obviously increased relative to DCNC/45PEI (Figure S7 and Table S4). The significantly enhanced carbonization performances of DCNC/45PETO indicate its fire retardancy to some extents.

Figure S8 shows the scanning electron microscopy (SEM) image of DCNC/45PETO coating on wood surface, demonstrating that the coating thickness is 80 μm. The other coatings also maintain the same thickness when applied to wood. In Figure 3a, the LOI of wood is only 21.0%, and it fails the UL-94 test, indicating high flammability. In contrast, the DCNC/45PETO coating significantly increases the LOI and UL-94 rating of wood to 34.0% and V-0. Hence, the DCNC/45PETO-coated wood is a self-extinguishing material.

The uncoated wood shows a time to ignition (TTI) of 16 s, with a peak heat release rate (PHRR) of 397 kW/m^2, a total heat release (THR) of 39.2 MJ/m^2, and a residue of 5.8% at flameout (Figure 3b-d and Table S5). The TTI of the DCNC/PETO-coated wood is obviously extended due to the enhanced thermal oxidative stability caused by DCNC/PETO. Furthermore, the PHRR and THR of the DCNC/45PETO-treated wood are reduced to 251 kW/m^2 and 23.0 MJ/m^2, with decreases of 36.7% and 41.3% compared to wood (Figure 3b, c, and Table S5). These results demonstrate that the DCNC/45PETO coating effectively enhances the flame retardancy of wood by suppressing its heat release. Additionally, the residue of the DCNC/45PETO-coated wood significantly increases and is 154% higher than that of wood (Figure 3d and Table S5), indicating that DCNC/45PETO facilitates the carbonization of wood during combustion. The average effective heat of combustion (AEHC) is an important parameter for evaluating the combustion degree of gaseous volatiles (Figure 3d and Table S5) [27, 44]. Coating with DCNC/45PETO reduces the AEHC of wood from 14.0 MJ/kg to 11.2 MJ/kg. Obviously, the pyrolysis products of DCNC/45PETO inhibit the combustion of gaseous volatiles, leading to incomplete combustion. This gas-phase flame-retardant effect is primarily attributed to the radical quenching action of P-containing groups in the coatings. The enhanced carbonization capacity also contributes to reducing the gas-phase combustion.

The DCNC/45PETO coating maintains excellent flame-retardant properties in various harsh environments. The DCNC/45PETO-coated wood was respectively exposed to 1 mol/L HCl, 1

mol/L NaOH, 45 °C and UV-light to investigate the fire-retardant durability of DCNC/45PETO. After different aging tests, the DCNC/45PETO-coated wood still achieves a UL-94 V-0 rating and high LOI values (>33.0%), confirming durable fire retardancy (Figure 3e). Besides wood, DCNC/45PETO also exhibits excellent flame retardancy on various polymer foams. The PU with DCNC/45PETO coating (thickness: 300 μm) can achieve a UL-94 V-0 rating and an LOI of 35.0%. High LOI values of 27.0% and 29.0% can be achieved for the DCNC/45PETO-coated EVA and EPS foams, respectively. These further demonstrate the wide application of DCNC/45PETO coating in construction.

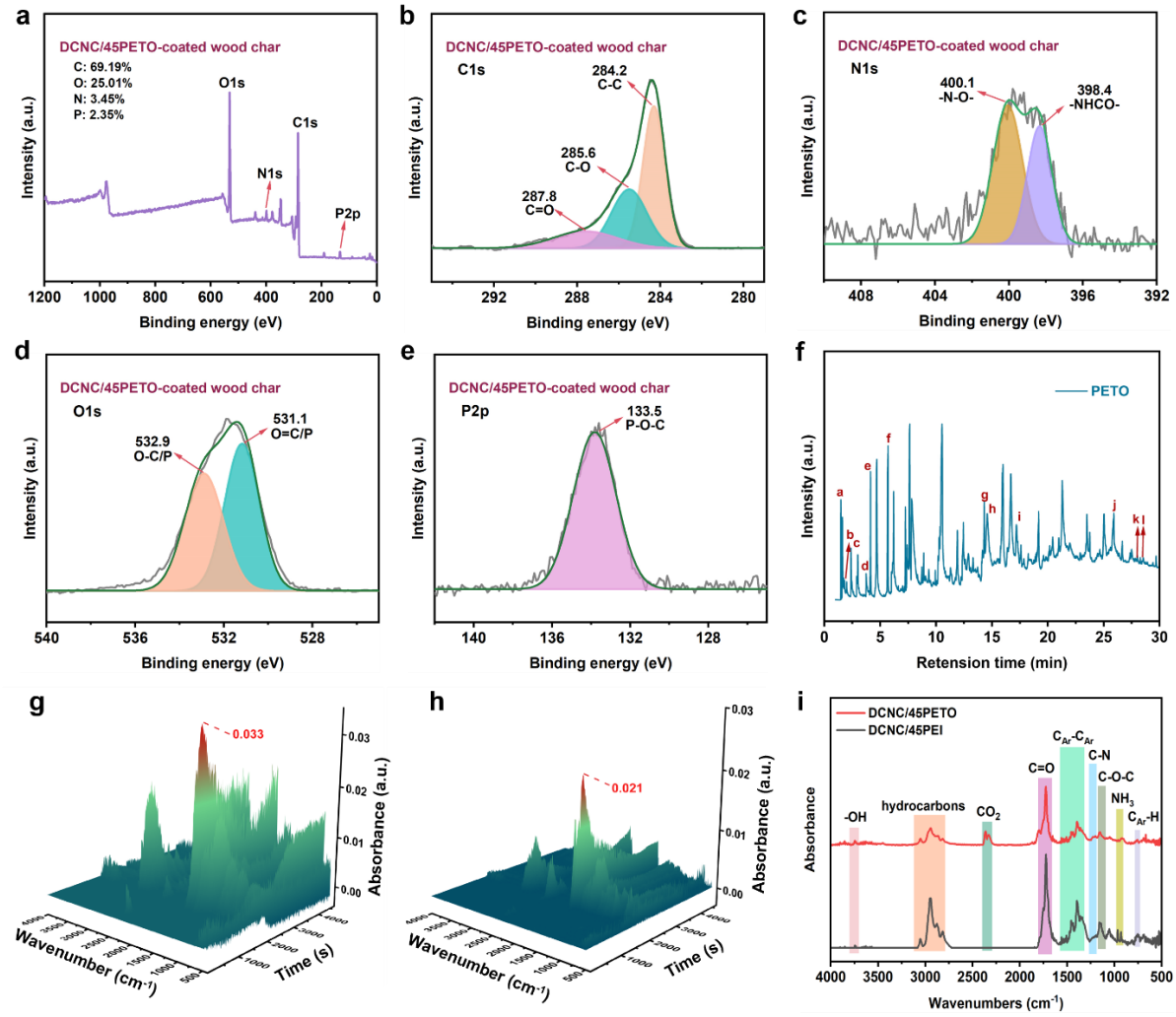

Figure 4. (a) XPS full-scan, and high-resolution (b) C1s, (c) N1s, (d) O1s, (e) P2p XPS spectra of the DCNC/45PETO-coated wood char after cone calorimetry test, (f) total ion chromatogram

of PETO, (g) 3D TG-IR spectra of pyrolysis products for (g) DCNC/45PEI and (h) DCNC/45PETO, and (i) FTIR spectra of pyrolysis products for DCNC/45PEI and DCNC/45PETO at T_{max1}.

It is valuable to investigate the flame-retardant mode-of-action of DCNC/45PETO coating on wood. Hence, Raman and X-ray photoelectron spectroscopy (XPS) techniques were employed to explore the action of DCNC/45PETO in the condensed phase. The Raman spectra of all samples present D and G peaks at 1364 and 1592 cm^{-1}, respectively, in Figure S9. The D band belongs to the vibration of amorphous carbon, and the G band belongs to the tensile vibration of graphitized carbon on the sp^2 hybridization surface. The integral area ratio (I_D/I_G) of the D to G bands is inversely proportional to the graphitization degree of carbonaceous materials [37]. The wood char exhibits the highest I_D/I_G, whereas that of the DCNC/PETO-coated wood char decreases gradually with increasing PETO content. The I_D/I_G value of the DCNC/45PETO-treated wood char is lower than that of the DCNC/45PEI-treated one, further demonstrating that PETO is effective in improving the graphitization of wood char. Such results further confirm the flame-retardant condensed-phase effect of DCNC/45PETO. The XPS spectra of the DCNC/45PEI- and DCNC/45PETO-coated wood chars are shown in Figure 4a-e and S10. In Figure S10, the main elements of the DCNC/45PEI-coated wood char are carbon, nitrogen, and oxygen. Apart from these elements, the DCNC/45PETO-coated wood char also contains phosphorus, further indicating that the DCNC/45PETO coating contributes to the carbonization during combustion (Figure 4a). Meanwhile, the high-resolution C1s, N1s, and O1s spectra are similar for both samples (Figure 4b-d and S10). The C1s spectra have three peaks at 284.2, 285.6, and 287.8 eV belonging to C-C, C-O, and C-O bonds, respectively [43] (Figure 4b and S10b). The peaks at 400.1 and 398.4 eV in both N1s spectra correspond to -N-O- and -NHCO- bonds (Figure 4c and S10c). In the O1s spectrum of the DCNC/45PETO-

coated wood residue, the peaks at 532.9 and 531.1 eV are attributed to O-C/P and O=C/P structures (Figure 4d). A P-O-C peak at 133.5 eV appears in the P2p spectrum (Figure 4e). This further demonstrates that some phosphorus-based fragments produced from PETO are involved in the formation of highly graphitized char during combustion. Thus, the condensed-phase flame retardancy of DCNC/45PETO mainly originates from the catalytic carbonization effect of its DOPO groups.

The flame-retardant effect of DCNC/45PETO in the gas phase was also investigated. The pyrolysis behaviors of PETO were studied utilizing pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) technique, with the total ion chromatogram depicted in Figure 4f and the main pyrolysis products summarized in Table S6. The pyrolytic products of PETO include aliphatic amines, nitriles, nitrogen-containing heterocyclic compounds, aromatic organics, and DOPO derivatives. The aliphatic amines, nitriles and N-containing heterocyclic compounds are produced by the pyrolysis of aliphatic amine chain segments. The aromatic substance stems from DOPO moieties, accompanied by the release of phosphorus-based fragments. Notably, the nitrogen- and phosphorus-containing pyrolytic products of PETO contribute to the gas-phase flame retardancy, primarily by dilution and quenching effects. Furthermore, the thermogravimetric analysis/infrared spectroscopy (TG-IR) analysis was performed on DCNC/45PEI and DCNC/45PETO under nitrogen atmosphere to investigate the gas-phase effect of PETO, with the spectra exhibited in Figure 4g-i. Both DCNC/45PEI and DCNC/45PETO decompose to release water/phenol (3651 cm^{-1}), hydrocarbons (2818-3162 cm^{-1}), carbon dioxide (2285 cm^{-1}), carbonyl compounds (1765 cm^{-1}), aromatics (1450, 1610, and 830 cm^{-1}), C-N-based organics (1257 cm^{-1}), and ester derivatives (1176 cm^{-1}) under heating [2]. Crucially, the peak intensities of aromatic compounds, ester derivatives, and C-N-containing fragments for DCNC/45PETO are lower than those for DCNC/45PEI, indicating that the

phosphorus-containing degradation products from PETO suppress the release of pyrolytic gases by facilitating the carbonization (Figure S11).

The possible roles of PETO during combustion are illustrated in Figure S12: (i) its N- and P-group fragments dilute and trap the high-energy radicals originating from coating matrix and wood during combustion, thus inhibiting the combustion chain reaction in the gas phase; and (ii) its P- and N-containing decomposition products cooperatively promote the formation of a compact and expanded char layer on wood surface, effectively hindering the transfer of heat and oxygen in the condensed phase. Therefore, the PETO parts in DCNC/PETO function in both gas and condensed phases to retard the combustion of wood.

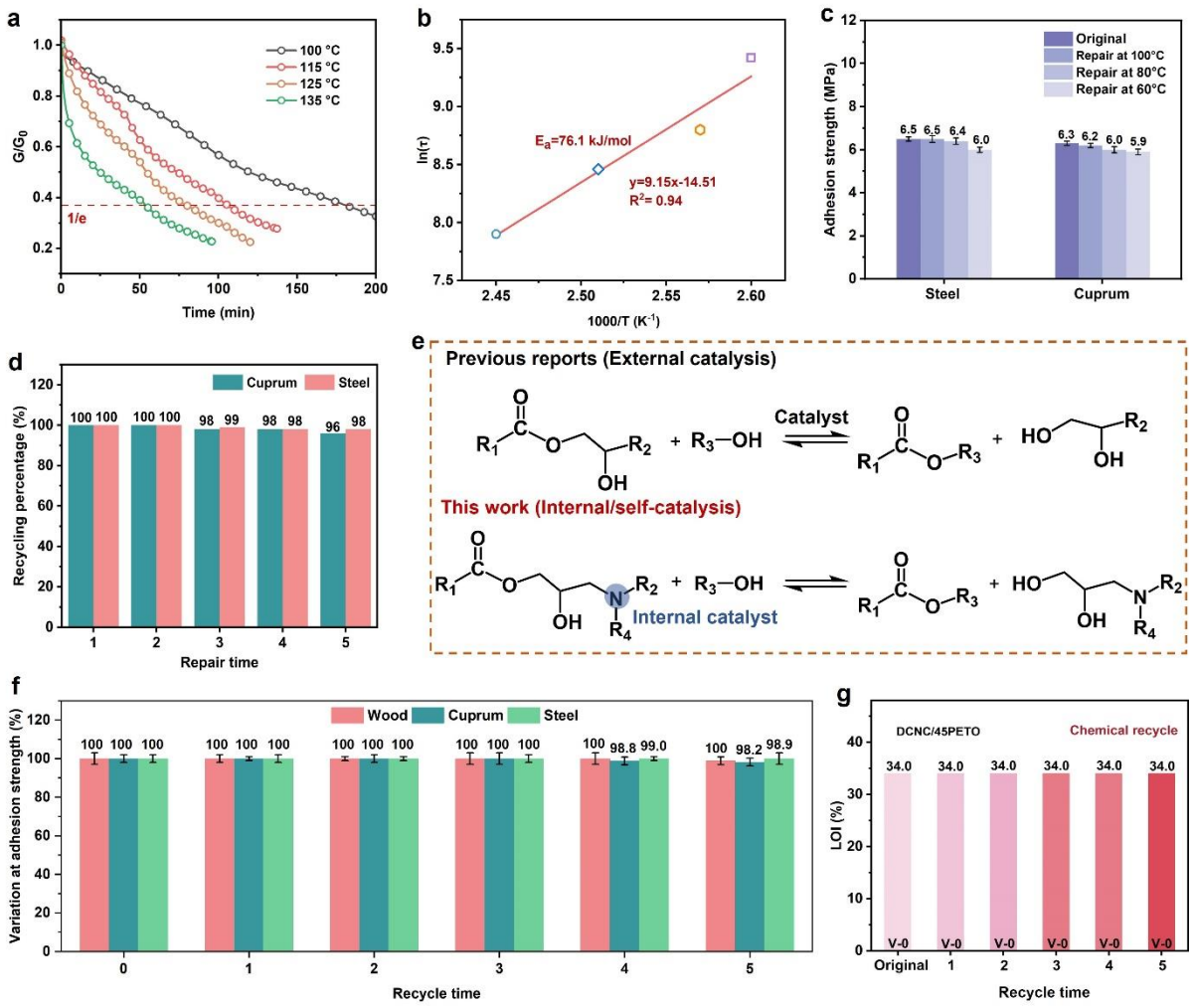

Figure 5. (a) Stress relaxation curves of DCNC/45PETO at different temperatures, (b) the relaxation activation energy (E_a) of DCNC/45PETO obtained from Arrhenius analysis, (c)

adhesion strength of DCNC/45PETO on steel and cuprum after hot-pressing for 30 min at different temperatures, (d) recovery percentage of adhesive strength for DCNC/45PETO after different times of physical recycling (recycling method: hot-pressing at 70 °C for 3 h), (e) transesterification reaction under external or internal catalyst, (f) variations in adhesion strength of DCNC/45PETO on different substrates after different chemical recycling cycles, and (g) LOI and UL-94 results of the DCNC/45PETO-coated wood after different times of chemical recycling.

Transesterification epoxy vitrimer can be reprocessed and recycled [30, 52, 53]. Typically, an external catalyst is always required to trigger transesterification owing to its low exchange rate [54]. The catalyst usually has issues such as poor miscibility with the matrix, high toxicity, and easy leaching [6, 55]. To verify whether the tertiary/secondary amines can catalyze the dynamic transesterification reaction, the dynamic response of DCNC/45PETO was characterized by measuring the stress relaxation with time at a constant strain of 1%. In Figure 5a, the characteristic relaxation time (τ) is defined as the time for the normalized stress to decrease to 1/e. The τ of DCNC/45PETO decreases with increasing temperature, and finally to 48 min at 135 °C, indicating effective stress relaxation without external catalyst. The stress relaxation is closely related to temperature, verifying the dynamic characteristic of DCNC/45PETO. Furthermore, the linear correlation between ln(τ) and 1000/T reveals the Arrhenius flow properties of the DCNC/45PETO network. Based on the curve slope, the activation energy of transesterification reaction within DCNC/45PETO is calculated to be 76.1 kJ/mol (Figure 5b), which is in high agreement with the results reported in previous works (69-150 kJ/mol) [56, 57], demonstrating that DCNC/45PETO is a transesterification vitrimer. To investigate the covalent adaptive network of DCNC/45PETO, it was immersed in *N*-Methyl-2-pyrrolidone (NMP) and NMP/ethylene glycol (NMP/EG, volume ratio: 4:1), respectively, at 120 °C for 3 h (Figure S13). After 3 h, DCNC/45PETO remains partially undissolved in NMP but fully dissolves in

NMP/EG, demonstrating that the presence of EG expedites the ester exchange within the DCNC/45PETO network. Therefore, DCNC/45PETO is a self-catalytic, transesterification vitrimer because the secondary/tertiary amines near β-hydroxy esters within the DCNC/45PETO network accelerates the ester-exchange process (Figure 5e).

The autocatalytic transesterification endows DCNC/45PETO with diverse and closed-loop recyclability, with the recycling process in Figure S14. Clearly, DCNC/45PETO is a reusable coating, thus its adhesive strength towards cuprum and steel after hot-pressing repair method was investigated since the damage occurs only on the substrate rather than the adhesive when using wood and PU foam as substrates. The hot-pressing repair of damaged single lap shear specimens was conducted at different temperatures, with the results shown in Figure 5c. The adhesive strength of the reproduced DCNC/45PETO on cuprum and steel is as high as 6.5 and 6.2 MPa, respectively, after hot-pressing at 100 °C for 4 h. Even when the hot-pressing temperature is reduced to 60 °C, the adhesive strength of DCNC/45PETO reaches 6.0 and 5.9 MPa, suggesting that great adhesive performances can be regenerated quickly by this simple method. Furthermore, the reproduced DCNC/45PETO retains 98% and 96% of its adhesive strength on steel and cuprum after 5 repair cycles (Figure 5d). Thus, the DCNC/45PETO vitrimer can be recycled for many times by a simple hot-pressing method.

The chemical recycling of DCNC/45PETO was also investigated. DCNC/45PETO could be completely degraded within 1 h at 80 °C in 1 mol/L NaOH solution (Figure S14). The degradation products were obtained by neutralizing the solution with 1 M HCl and extracting with ethanol and could be reused as coatings (Figure S14). The adhesion strength of the chemically recycled DCNC/45PETO coating on different substrates is very close to the original value after five chemical recycling cycles (Figure 5f). After five recycling cycles, DCNC/45PETO retains 98.9%, 98.2%, and 100% of its bond strength on wood, cuprum, and steel, respectively. The wood coated with the 5^{th} chemically recycled DCNC/45PETO still

displays an LOI of 34.0% and a UL-94 V-0 rating (Figure 5g). Hence, DCNC/45PETO features closed-loop chemical recyclability.

A flame-retardant, self-catalytic and fully-recyclable epoxy vitrimer with room-temperature curing ability was developed in this work. The DCNC/45PETO vitrimer contains abundant ester, amine, and hydroxyl groups, allowing it to form strong interactions with different substrates as a coating/adhesive. The adhesion strength of DCNC/45PETO towards wood reaches 7.9 MPa, and its pencil hardness reaches 4H. The wood coated with DCNC/45PETO (thickness: 80 μm) achieves a high LOI of 34.0% and a UL-94 V-0 rating, with 36.7% and 41.3% reductions in PHRR and THR compared to uncoated wood. The superior fire retardancy of DCNC/45PETO are mainly due to the gas/condensed-phase flame-retardant effects of PETO. DCNC/45PETO features superior weather resistance, and it can be completely recycled and reused for many times in mild physical or chemical conditions due to its autocatalytic transesterification. This study offers an integrated method to create room temperature-curable, multifunctional epoxy vitrimer coatings for various construction materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at

Experimental Section, Supporting Tables and Figures, References

Author Contributions

Cheng Wang: Data curation, Investigation, Visualization, Writing - original draft. **Guofeng Ye:** Data curation. **Qi Zhang:** Supervision. **Hao Wang:** Supervision. **Siqi Huo:** Conceptualization, Project administration, Supervision, Writing - review & editing, Funding acquisition. **Zhitian Liu:** Supervision.

Declaration of Competing Interest

The authors declare no conflict of interest.

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