Solid Wastes Toward Flame Retardants for Polymeric Materials: A Review

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It has been significant yet challenging to recycle and reuse different kinds of wastes because of their mass production within society. Many efforts have been conducted to reuse wastes in different fields. Interestingly, some wastes have been employed to replace traditional petroleum-based flame retardants for polymeric materials. This review focuses on the recent development of waste flame retardants and their impacts on thermal stability, flame retardancy, and smoke suppression of polymers, followed by representative flame-retardant mechanisms. Finally, the key challenges associated with waste flame retardants are presented, and some future perspectives are proposed.

INTRODUCTION

With the development of our society, abundant wastes have been continuously generated in daily life and industrial production, which have led to serious environmental deterioration problems, for example, marine microplastics and global warming. Such issues have driven scientists and engineers to explore how to effectively change waste into wealth. Hence, recent years have witnessed the recycle and reuse of different kinds of wastes in various industrial areas (Kabirifar et al., 2020; Zhang et al., 2020).

The superior chemical resistance, and thermal and mechanical properties of polymeric materials have meant they have ubiquitous applications in modern society (Chen et al., 2017; Liu and Wang, 2018; Wang et al., 2020b). However, most of them are highly flammable and produce abundant smoke during combustion, which severely threatens humans and the environment; thus, it is necessary to enhance the fire safety of polymers *via* adding flame retardants (Huo et al., 2020; Xue et al., 2020; Yang et al., 2021a). In the past, flame retardants are mainly derived from petroleum resources, which worsen the depletion of fossil resources (Wang et al., 2019). Based on the sustainable development strategy, many wastes have been reused to replace traditional flame retardants recently, and many important outcomes have been reported, demonstrating that the application of some wastes is an effective way to prepare flame-retardant polymeric materials (Li et al., 2019). For instance, Qian et al. (2015) used Bayer red mud to synthesize Mg/Al/Fe-layered double hydroxides (Mg/Al/Fe-LDHs), which were applied in the preparation of flame-retardant ethylene-vinyl acetate (EVA). Their results showed that the limiting oxygen index of the as-prepared EVA can be up to 26.8%. Das et al. (2016) reported a flame-retardant polypropylene (PP) with ammonium polyphosphate (APP), waste-based biochar, and wool. The results showed that both biochar and wool not only improved the flame retardancy of PP but also retained the mechanical properties. Hence, many waste-based flame retardants exhibit obvious flame retardant function towards polymeric materials.

SCHEME 1 | Schematic of industrial, domestic, and plant wastes for flame-retardant polymers.
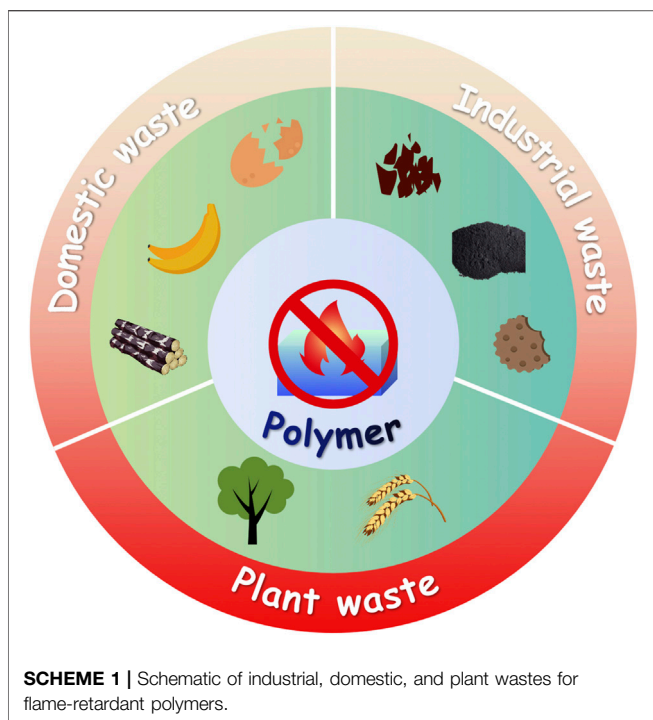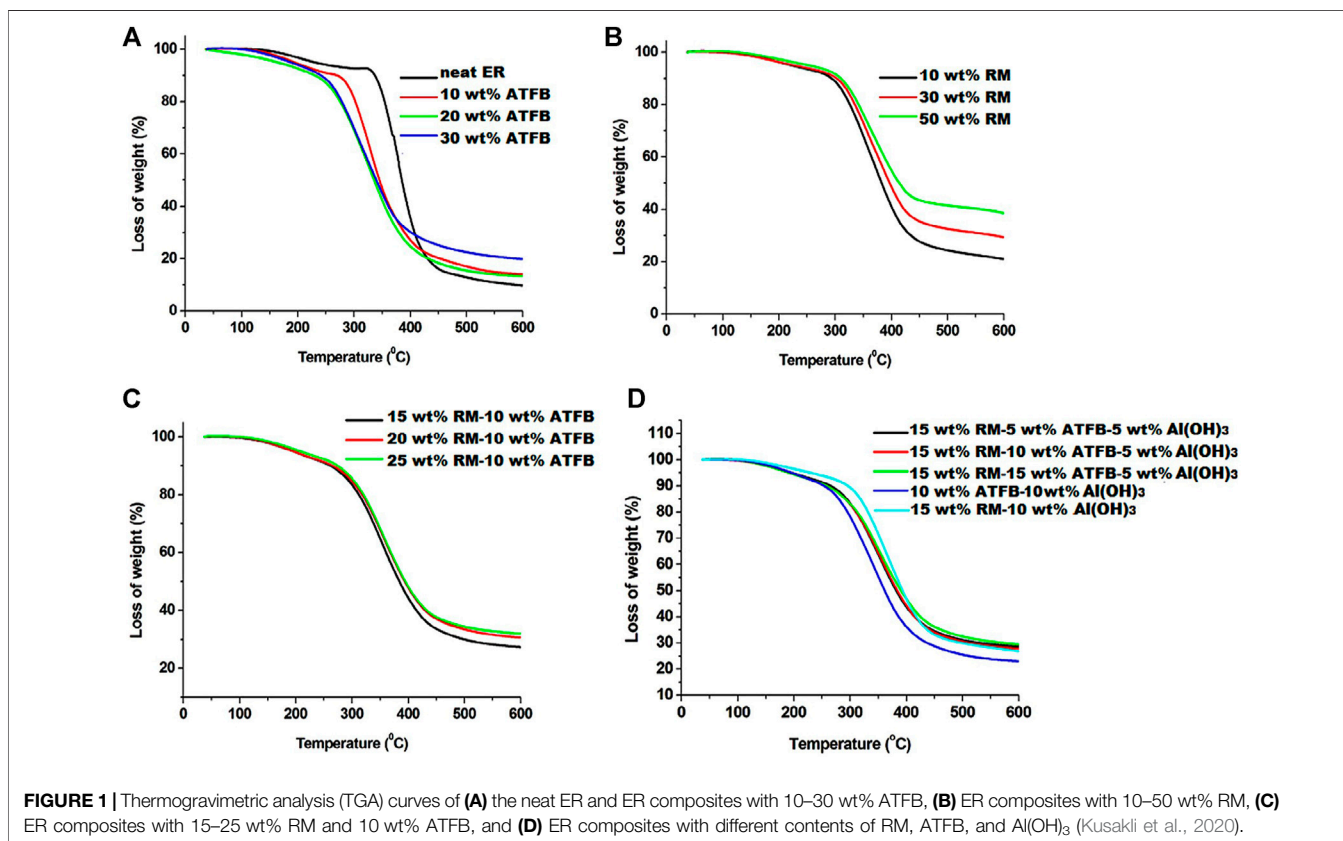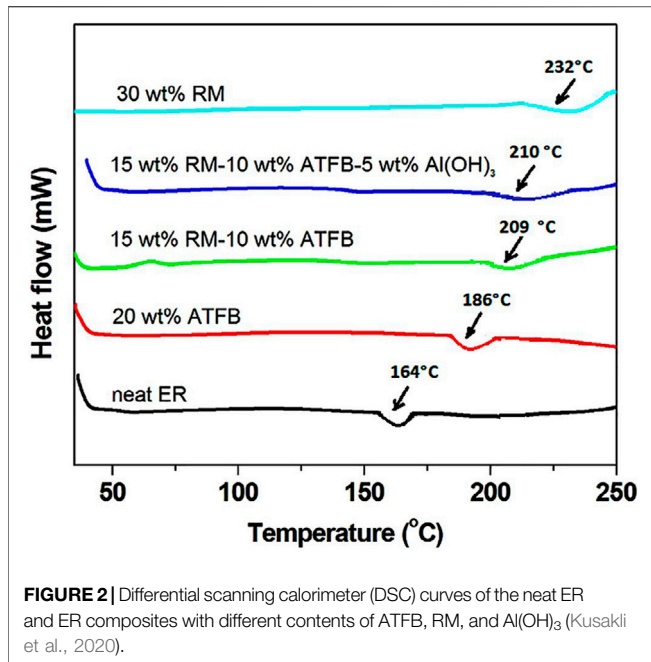
Herein, this review focuses on the recent development of three kinds of common wastes (industrial, domestic, and plant; see **Scheme 1**) and highlights their influences on the thermal stability, flame retardancy, and smoke suppression of polymeric materials. Additionally, the flame-retardant mechanism of different wastes will be analyzed. Finally, their key challenges and future perspectives will also be indicated.

INDUSTRIAL WASTE

With the development of modern production, a constant stream of industrial waste is discharged into the environment, which has been harming the ecosystem and even human health severely. Thus, the reuse of industrial waste has become a hot topic in both academia and industry (Huo et al., 2021). Fortunately, many types of industrial wastes, for example, fly ash, oil sludge, and red mud, contain different valuable flame-retardant ingredients, such as thermally stable SiO_2, Al_2O_3, and Fe_2O_3, thus exhibiting huge potential in the fabrication of flame-retardant polymers (Cao et al., 2017; Zhang et al., 2019; Liu et al., 2020). For instance, Kusakli et al. (2020) fabricated a flame-retardant epoxy resin (ER), which contained ammonium tetrafluoroborate (ATFB), aluminum hydroxide ($Al(OH)_3$), and red mud (RM). Obviously, the introduction of ATFB, $Al(OH)_3$, and RM improves the charring capacity of ER (see **Figure 1**). During the burning process, RM effectively retards the combustion of epoxy matrix due to its abundant Fe, Al, and Si elements. Additionally, the combination of ATFB, $Al(OH)_3$, and RM endows epoxy resin with improved flame retardancy, mechanical properties, and thermal stability (see **Figure 2**), for example, a limited oxygen index (LOI) of 29.0%, a tensile strength of 112 MPa, and a glass transition temperature (T_g) of 210°C. Jia

FIGURE 1 | Thermogravimetric analysis (TGA) curves of **(A)** the neat ER and ER composites with 10–30 wt% ATFB, **(B)** ER composites with 10–50 wt% RM, **(C)** ER composites with 15–25 wt% RM and 10 wt% ATFB, and **(D)** ER composites with different contents of RM, ATFB, and $Al(OH)_3$ (Kusakli et al., 2020).

FIGURE 2 | Differential scanning calorimeter (DSC) curves of the neat ER and ER composites with different contents of ATFB, RM, and Al(OH)₃ (Kusakli et al., 2020).

et al. (2014) synthesized an Mg-Al-Fe ternary-layered double hydroxide (LDH) using red mud as a raw material, and the corresponding flame-retardant and thermally stable ethylene-vinyl acetate/layered double hydroxide/graphite powder (EVA/LDH/GP) composites were fabricated. The results show that the as-prepared

EVA/LDH/GP exhibits 81.1 and 54.2% reductions in the peak of the heat release rate (PHRR) and the average of the heat release rate (AHRR), respectively, relative to the neat EVA, indicating significantly improved flame retardancy. The combination of LDH and GP contributes to the formation of compact char layers due to their condensed-phase effect, thus leading to the significantly reduced heat release and improved fire safety of EVA composites. Such results further verify that waste-based RM can be used to prepare flame-retardant LDH because of its abundant metallic elements, for example, Al, Ca, and Fe. Fly ash rich in Si/Al oxides is also recognized as one class of effective waste flame retardants. Nguyen (2020) reported the synthesis of stearic acid–modified fly ash and the preparation of the corresponding flame-retardant epoxy resins with various fly ash contents (see **Figure 3**). Twenty wt% of fly ash decreases the burning rate of epoxy thermoset to 16.78 mm/min and increases the LOI to 23.2% (see **Figure 4**), demonstrating the flame-retardant characteristic. In addition, Wang et al. (2020a) employed magnesium alloy scrap to enhance the fire resistance of intumescent fire-retardant polyacrylate-based coatings applicable to structural steel. Magnesium alloy scrap is capable of significantly increasing the char expansion degree and suppressing the heat transfer of intumescent coatings when exposed to high-temperature flame (see **Figure 5**). In detail, introducing 0.48 wt% scrap reduces the backside temperature of the coating from 310 to 171°C by 44.8%, with a 100.8% increase in char expansion degree. The highly intumescent char effectively suppresses the heat transfer and protects the underlying steel during combustion. Hence, the waste-based magnesium alloy scrap can be used as a synergist for

FIGURE 3 | Schematic diagram of fly ash–containing epoxy networks after curing (Nguyen, 2020).
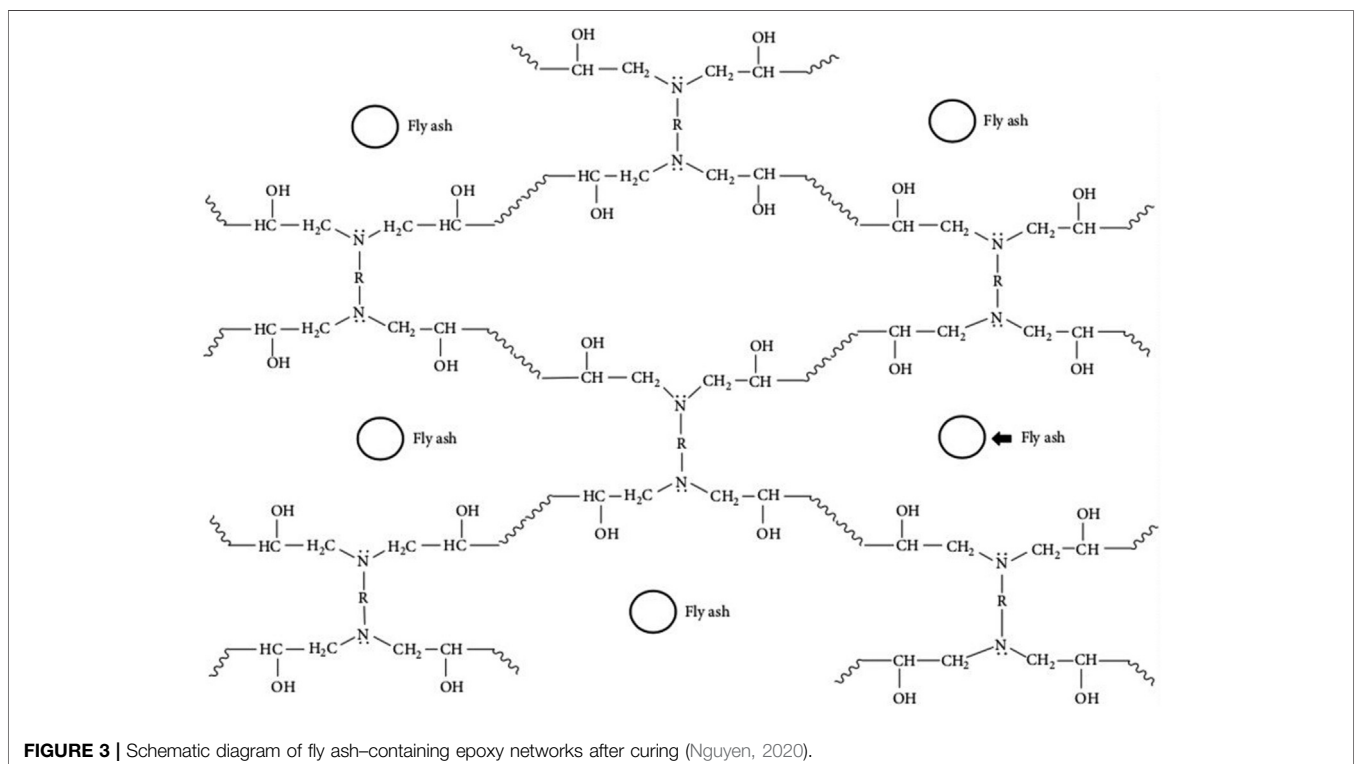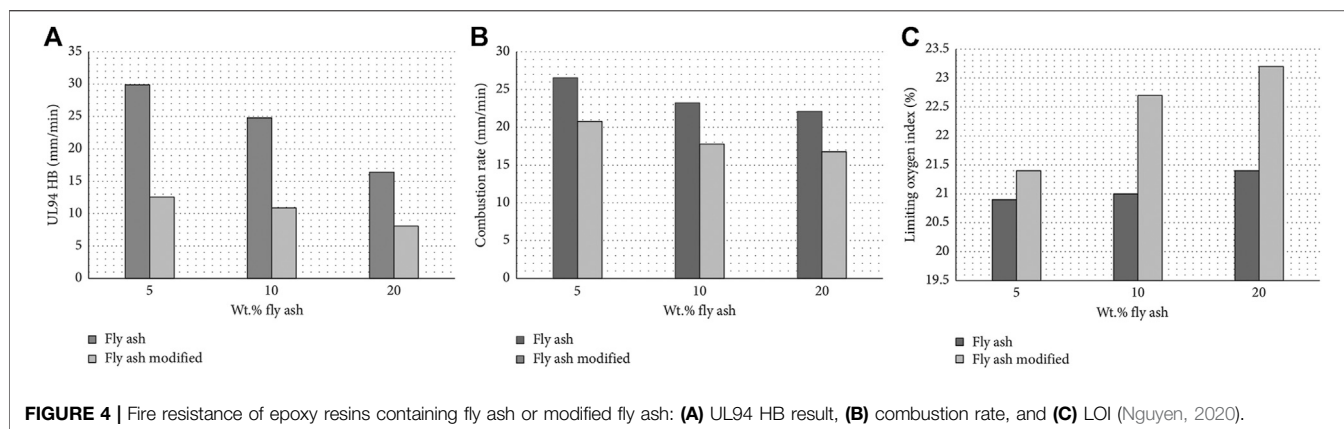
FIGURE 4 | Fire resistance of epoxy resins containing fly ash or modified fly ash: **(A)** UL94 HB result, **(B)** combustion rate, and **(C)** LOI (Nguyen, 2020).
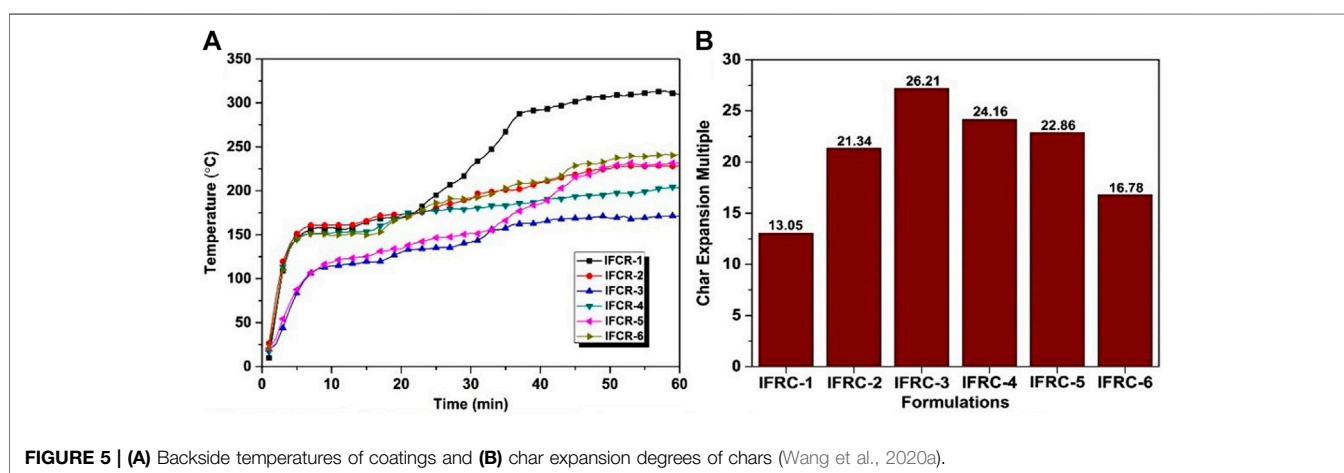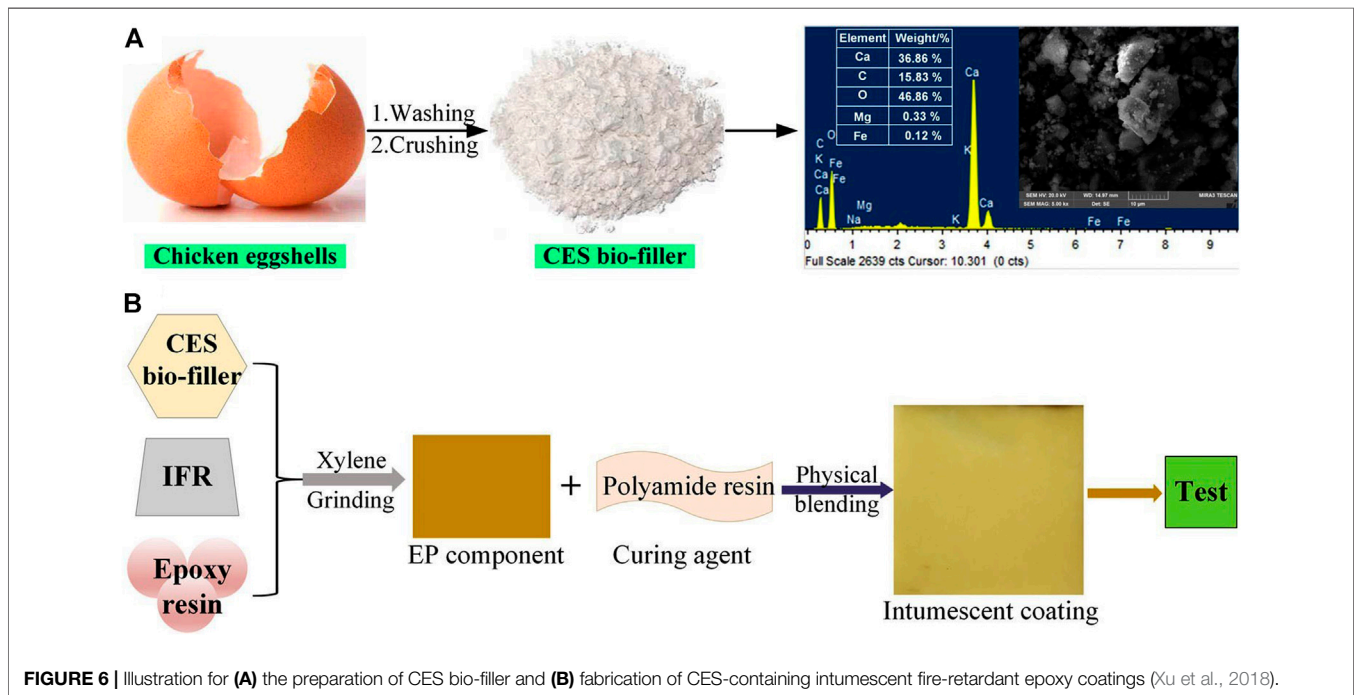

FIGURE 5 | **(A)** Backside temperatures of coatings and **(B)** char expansion degrees of chars (Wang et al., 2020a).

the intumescent fire-retardant systems that comprise ammonium polyphosphate (APP), pentaerythritol (PER), and melamine (MEL). Similar reuse of waste for the fabrication of fire-resistant polymers had also been reported by Saba et al. (2019). Obviously, the flame-retardant element (e.g., Al, Mg, and Si)-rich industrial wastes can be applied in the preparation of flame-retardant polymeric materials. However, the compatibility between industrial wastes and polymeric materials is an unavoidable issue, which impacts the comprehensive properties of polymers, and thus significantly restricts the practical applications of industrial wastes. In addition, the efficiency of the industrial waste–based flame retardants is not high enough, and needs to be further increased.
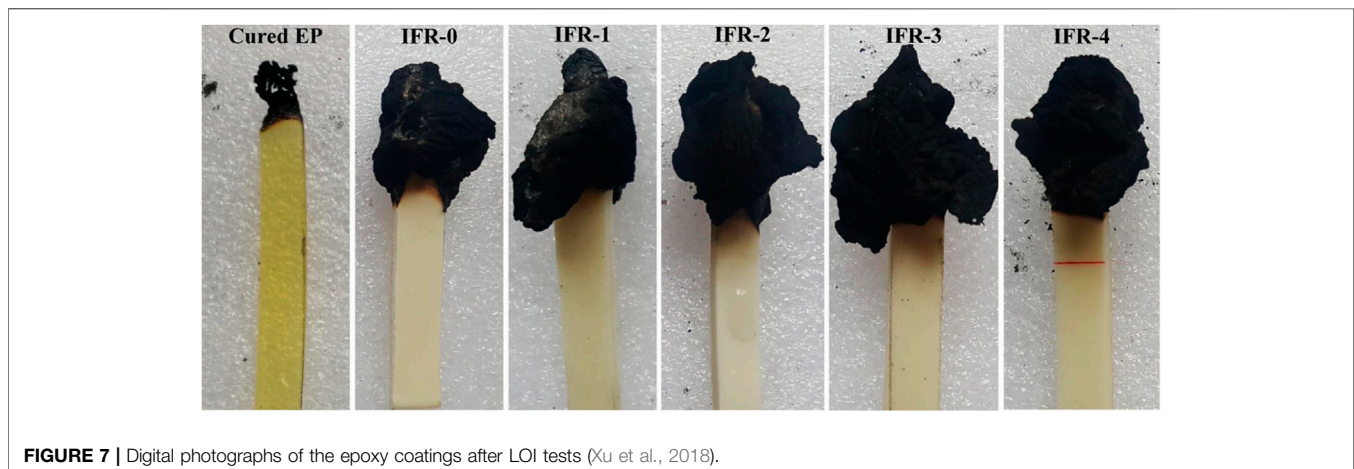
DOMESTIC WASTE

Domestic waste comprises disposable materials generated by households in daily activities. Nowadays, only some domestic waste can be recycled, and the rest will go to landfills. However, the landfills will be completely filled if the level of waste continues to grow rapidly. To help ease this issue, the reuse of domestic waste has been a high priority in recent years. Interestingly, many kinds of domestic wastes
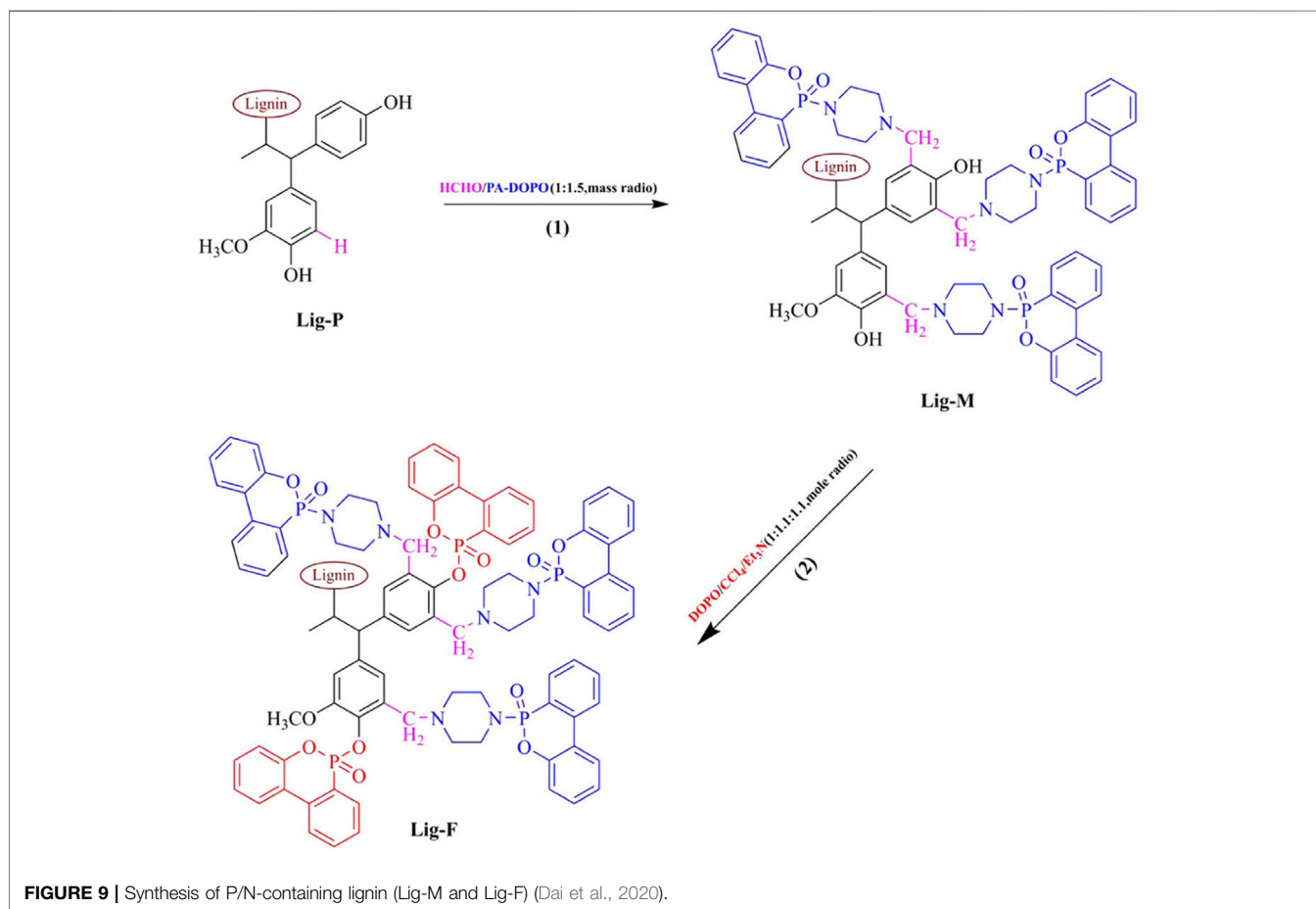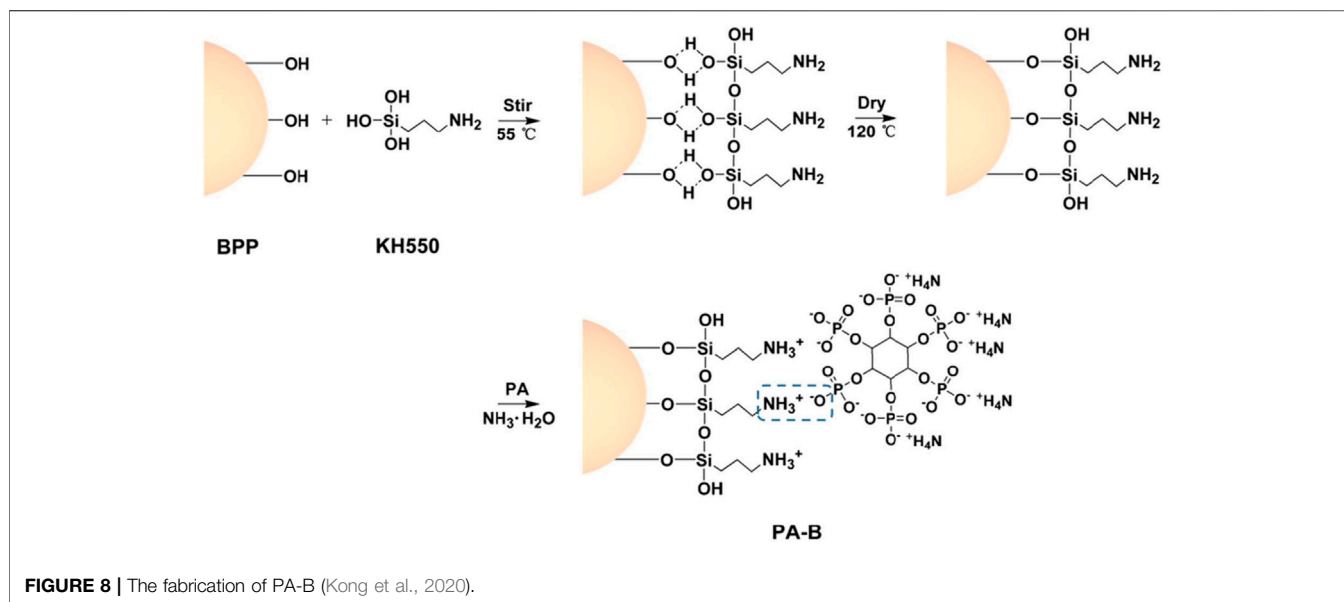
have been explored to create flame-retardant polymers. For example, Xu et al. (2018) employed chicken eggshell (CES) to enhance the flame-retardant and smoke-suppressive performances of APP/PER/MEL-containing epoxy coatings (see **Figure 6**). The main component of CES is $CaCO_3$, which is able to react with APP to generate calcium metaphosphate and calcium phosphate, and release inert gases, thus increasing the compactness and intumescent degree of residual char and diluting the combustible fragments and toxic smoke (see **Figure 7**). In detail, 3 wt% of CES decreases the peak heat release rate (PHRR) and total smoke release (TSR) by 42.2 and 15.0% in comparison to those of the APP/PER/MEL-containing epoxy system. Similarly, chicken eggshell has also been used as a flame-retardant synergist in poly (lactic acid) (PLA), ethylene-vinyl acetate copolymer (EVA), and acrylic resin (Yew et al., 2015; Oualha et al., 2019; Urtekin et al., 2020). Besides, Kong et al. (2020) intentionally collected banana peel powder that can serve as a char-forming agent, and then modified it with phytic acid to improve the flame-retardant performances (PA, see **Figure 8**). The resultant PA-modified powder (PA-B) imparts superior flame retardancy to PLA composite, of which the LOI value and UL-94 rating can reach up to 37.5% and V-0, respectively. Additionally, PA-B obviously reduces the heat release rate of PLA composite during combustion due to its condensed-phase flame-

FIGURE 6 | Illustration for **(A)** the preparation of CES bio-filler and **(B)** fabrication of CES-containing intumescent fire-retardant epoxy coatings (Xu et al., 2018).

retardant effect. Thus, this work provides a scalable method to reuse the fruit peel in the fabrication of flame-retardant polymers. Recently, Chen et al. (2020) deposited six chitosan/APP bilayers on the surface of bagasse (BF) to prepare an environmentally benign flame retardant (6BL@BF) for epoxy resin. 6BL@BF reduces the PHRR and total heat release (THR) of epoxy thermoset by 64.6 and 13.2%, respectively, relative to those of the neat epoxy thermoset. Additionally, the incorporation of expandable graphite (EG) can further improve the fire safety of 6BL@BF-containing epoxy thermoset due to the cooperation of 6BL@BF and EG in the condensed phase. Shen et al. (2020) prepared a triglycidylisocyanurate (TGIC)/9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO)–containing bagasse flame retardant (bagasse@TGIC@ DOPO) for epoxy resins. It was found that the char yield of epoxy
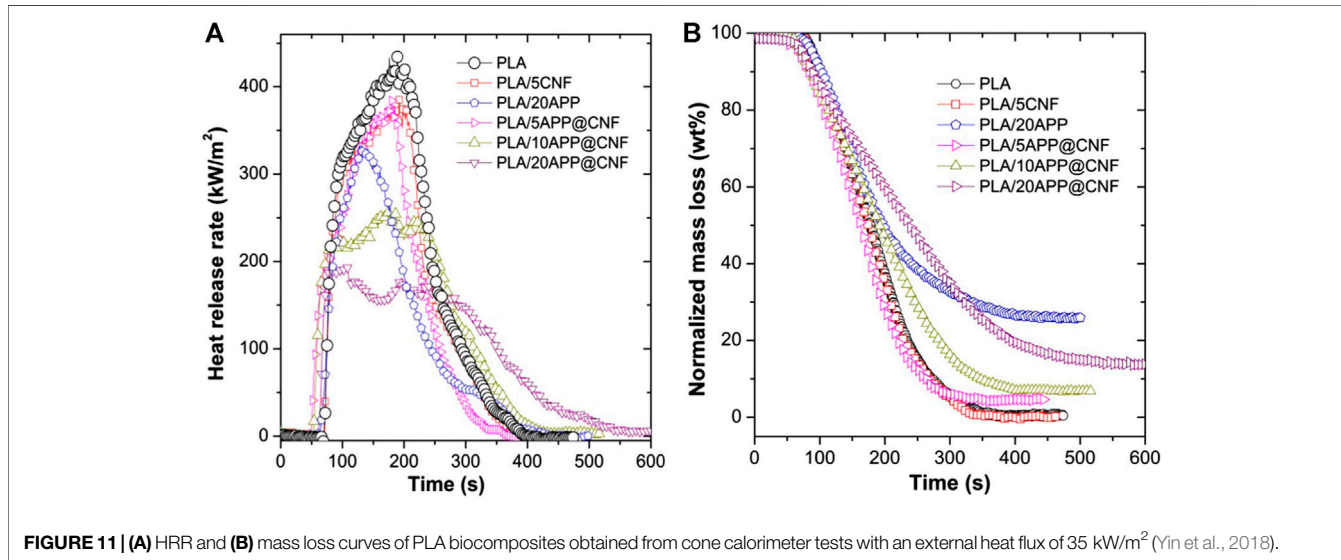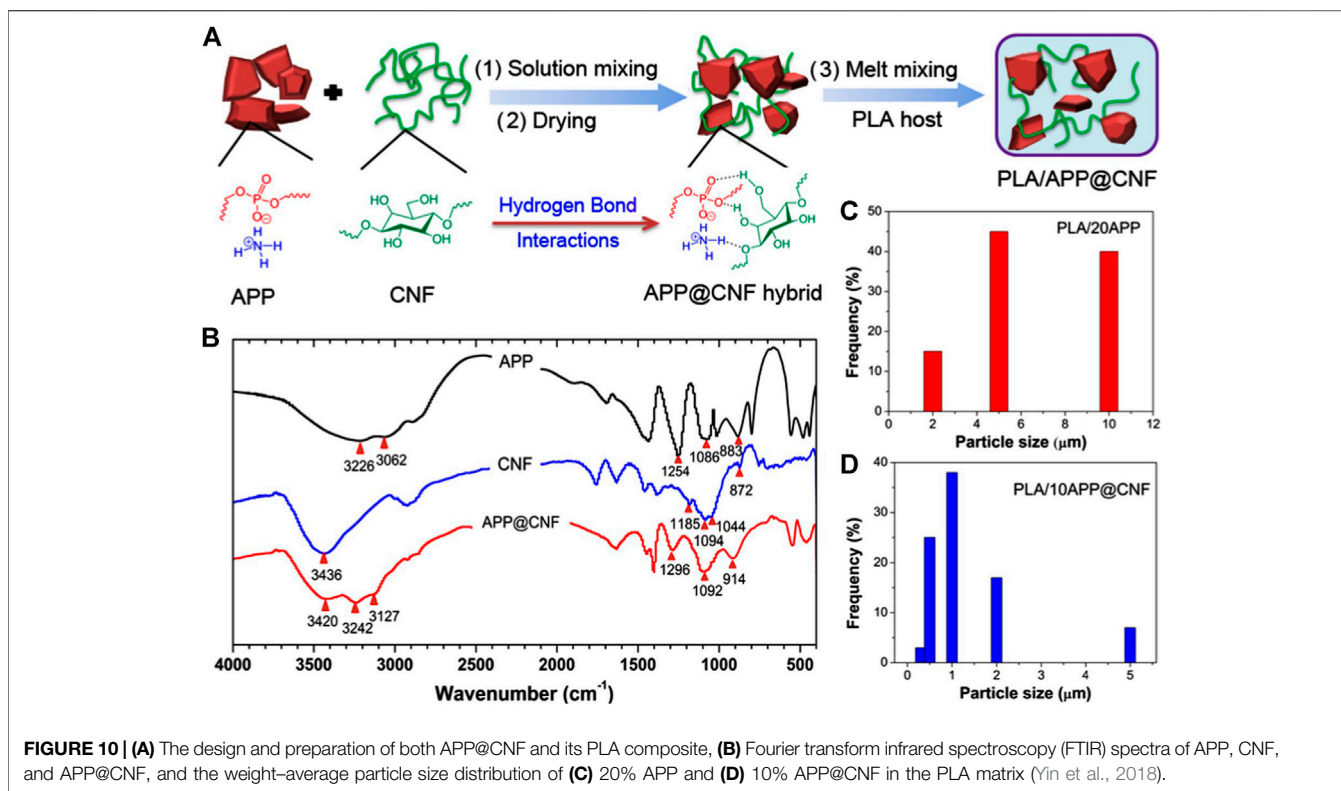
composite is increased from 14.1 wt% of the neat epoxy thermoset to 23.4 wt% with the incorporation of bagasse@TGIC@DOPO, indicating the positive effect of bagasse@TGIC@DOPO on the carbonization of epoxy matrix. Such an effect is conducive to the formation of compact char layers during the combustion of epoxy thermoset. Zabihi et al. (2020) used waste fish DNA as a surfactant to prepare a graphene-based flame retardant (GnPD). Notably, introducing only 10 wt% GnPD brings about ~86, ~80, and ~61% increases in the LOI values of epoxy thermoset, poly (vinyl alcohol) (PVA), and polystyrene (PS), respectively. They also used waste fish DNA to modify the clay structure and fabricated high-performance flame-retardant epoxy resins based on this fish DNA–modified clay (Zabihi et al., 2016). Additionally, the waste-based flame-retardant epoxy coatings were prepared

FIGURE 7 | Digital photographs of the epoxy coatings after LOI tests (Xu et al., 2018).

FIGURE 8 | The fabrication of PA-B (Kong et al., 2020).

FIGURE 9 | Synthesis of P/N-containing lignin (Lig-M and Lig-F) (Dai et al., 2020).

based on vegetable compounds (ginger powder and coffee husk), which were also used as carbon source of intumescent flame retardant system (Stéphanie et al., 2017). Both vegetable compounds can effectively enhance the flame-retardant performances of the intumescent flame retardant system. Obviously, most domestic wastes can be applied as carbon

FIGURE 10 | (A) The design and preparation of both APP@CNF and its PLA composite, (B) Fourier transform infrared spectroscopy (FTIR) spectra of APP, CNF, and APP@CNF, and the weight–average particle size distribution of (C) 20% APP and (D) 10% APP@CNF in the PLA matrix (Yin et al., 2018).

FIGURE 11 | (A) HRR and (B) mass loss curves of PLA biocomposites obtained from cone calorimeter tests with an external heat flux of 35 kW/m² (Yin et al., 2018).

source for the intumescent flame-retardant system because of their OH-rich structure. All these works mentioned above pave a new route to reuse domestic wastes, which promotes the sustainable development of society and enhances the fire safety of polymers. In the future, how to prepare a high-efficiency intumescent flame-retardant system based on different domestic wastes is critical for the development of domestic waste–based flame retardants.

PLANT WASTE

There are two types of plant waste, cellulose nanofibers and lignin, that are often applied in the flame-retardant polymeric materials because of their renewable, biodegradable, and nontoxic characteristics (Zhang et al., 2015; Liu et al., 2016). Both cellulose nanofibers and lignin feature OH/C-rich structure, which can serve as charring agent during
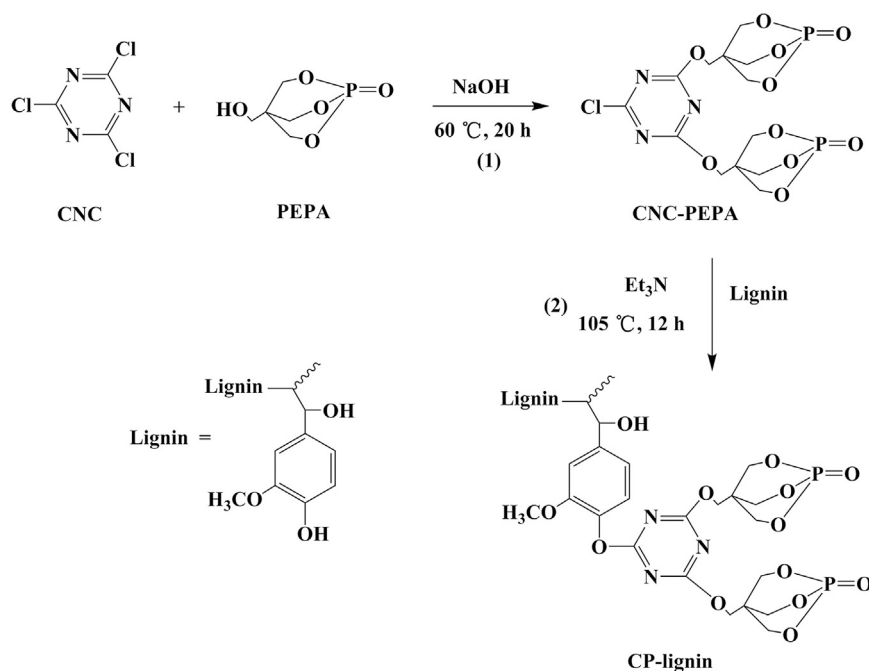
FIGURE 12 | Synthesis of CP-lignin (Chen et al., 2018).

combustion, and their flame-retardant performances can be further enhanced *via* chemically introducing different flame-retardant groups, for example, P-, N-, and Si-containing ones (Feng et al., 2017; Yang et al., 2020; Yang et al., 2021b). Dai et al. (2020) synthesized P/N-containing lignin-based flame retardants (Lig-M and Lig-F, see **Figure 9**) by introducing piperazine and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) into lignin. The Lig-containing epoxy resin exhibits improved flame retardancy and smoke suppression, of which the UL-94 rating increases to V-0, and THR and the total smoke production (TSP) are reduced by 46.6 and 53%, respectively. The flame-retardant mechanism analysis indicates that the synergistic effect of lignin, nitrogen, and phosphorus is responsible for the improved flame retardancy and smoke suppression of epoxy thermoset. Yin et al. (2018) reported a flame-retardant additive (APP@CNF) obtained from the reaction between cellulose nanofibers (CNFs) and ammonium polyphosphate, and applied it in the fabrication of mechanically robust and flame-retardant PLA biocomposites (see **Figure 10**). With 5 wt% of APP@CNF, the PLA biocomposite features reduced the heat release rate (see **Figure 11**) and improved flame-retardant and mechanical properties, which passes a UL-94 V-0 rating, achieves a high LOI of 27.5%, and shows 54% increase in impact strength. The enhancements in flame retardancy and mechanical properties of PLA biocomposite are attributed to the improved dispersion of APP@CNF and the synergistic flame-retardant effect between APP and CNF. Recently, Chen et al. (2018) also synthesized a 2,6,7-trioxa-1-phosphabicyclo-[2,2,2]octane-4-methanol-1-oxide/

triazine–modified lignin (CP-lignin) for polybutylene succinate (PBS), with the synthesis route shown in **Figure 12**. After incorporating 30 wt% of CP-lignin, the PHRR and THR of PBS composite are reduced by 27 and 31%, respectively, due to the promotion effect of CP-lignin on the carbonization of polymer matrix (see **Figure 13**). Ding et al. (2014) obviously enhanced the chemical activity of lignin by dripping the mixed solutions of diethanolamine and formaldehyde into the solution of lignin, and applied the modified lignin to prepare flame-retardant epoxy thermosets. Their results show that the introduction of the modified lignin brings about obvious enhancements in flame retardancy and thermal stability of epoxy thermoset. In detail, the decomposition temperature of lignin-based epoxy sample is 31°C higher than that of the neat epoxy sample. Xu et al. (2021) synthesized magnesium phytate (Mg-Phyt) and used it and rice husk ash as waste-based flame-retardants for epoxy resins. In comparison to a pure epoxy sample, the peak heat release rate, total heat release, peak smoke production rate, and total smoke release of the epoxy sample containing 5 wt% Mg-Phyt and 5 wt% rice husk ash are reduced remarkably by 28.6, 10.6, 33.0, and 7.8%, respectively. Therefore, both chemically introducing and physically combining flame-retardant groups are effective methods to improve the flame-retardant properties of lignin and cellulose nanofibers. However, lots of organic solvents are employed in the modification of lignin and cellulose nanofibers, which is not conducive to the sustainable development. In the future, more efforts should be made to create high-efficiency flame-retardant lignin and CNF *via* the green solvent or solvent-free method.
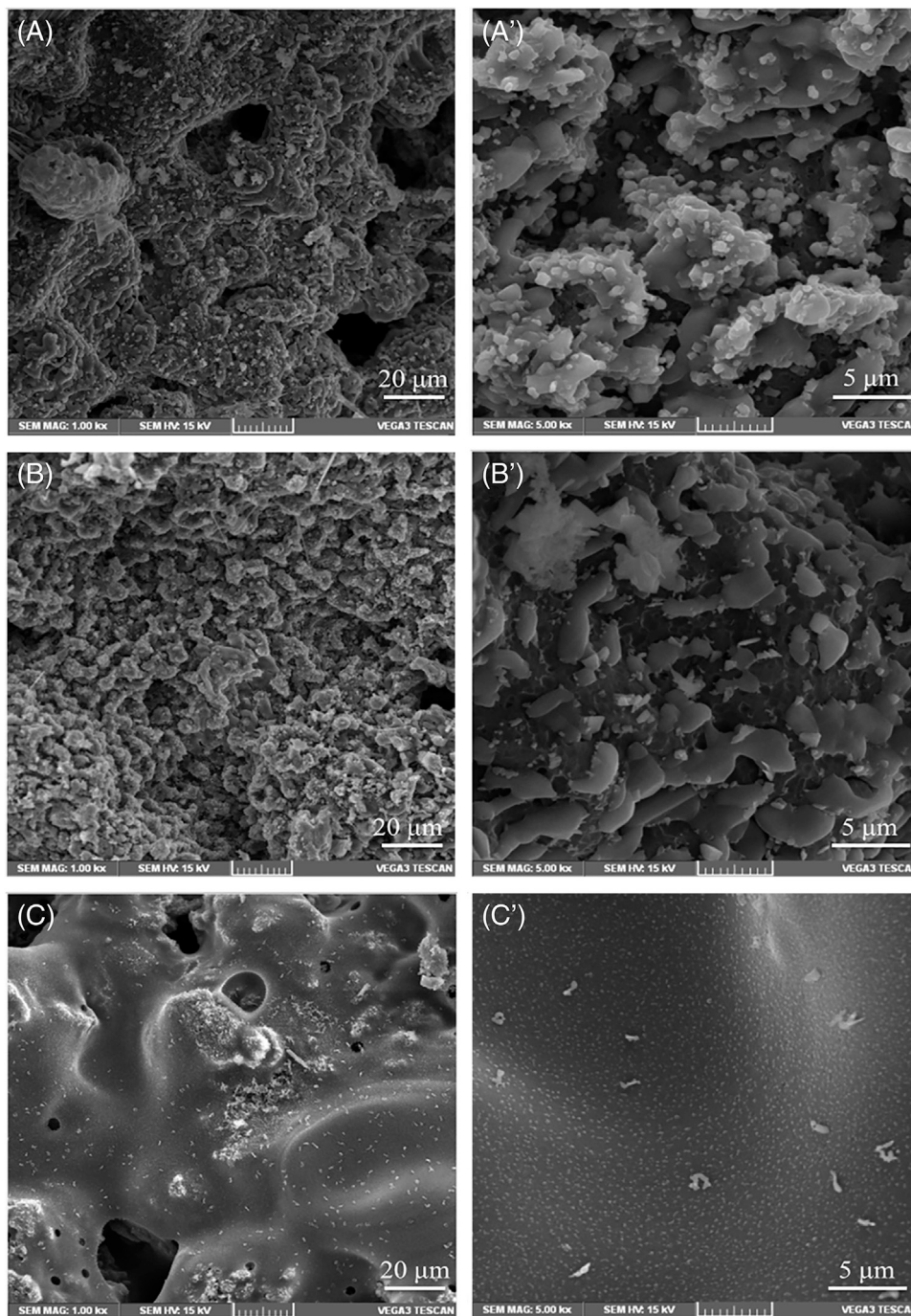
FIGURE 13 | Scanning electron microscopy (SEM) images of the chars for PBS composites with **(A, A')** 10 wt% CP-lignin, **(B, B')** 20 wt% CP-lignin, and **(C, C')** 30 wt% CP-lignin after cone calorimeter tests (Chen et al., 2018).

CONCLUSION AND PERSPECTIVES

Recent years have witnessed the rapid development of waste-based flame retardants. Some industrial, domestic, and plant wastes have been applied in the fabrication of flame-retardant polymers because of their specific flame-retardant ingredients (see **Table 1**). However, the flame-retardant efficiency and compatibility issues of waste-based flame retardants have yet to be solved, thus restricting the practical applications of waste-based flame retardants. In the future, we should

TABLE 1 | Flame retardancy and smoke suppression of the mentioned waste-containing polymers.

Waste type	Flame-retardant component	Other flame retardants	Polymer matrix	Flame retardancy and smoke suppression	References
Red mud	Fe/Al/Si elements	Al(OH)$_3$ and ammonium tetrafluoroborate	Epoxy resin	The LOI reaches 29.0%.	Kusakli et al. (2020)
Fly ash	Si/Al oxides	/	Epoxy resin	The burning rate decreases to 16.78 mm/min, and the LOI increases to 23.2%.	Nguyen (2020)
Magnesium alloy scrap	Mg/Al/Si oxides	APP, MEL, and PER	Polyacrylate	The backside temperature of the coated steel decreases to 171°C, and the char yield at 800°C reaches 27%.	Wang, et al. (2020b)
Chicken eggshell	Calcium carbonate	APP, MEL, and PER	Epoxy resin	The LOI reaches 31.5%, and the PHRR and TSR are decreased by 42.2 and 15.0%, respectively, in comparison to those of APP/PER/MEL-containing epoxy thermoset.	Xu et al. (2018)
Chicken eggshell	Calcium carbonate	APP and PER	Poly (lactic acid)	The LOI and UL-94 rating increase to 34.5% and V-0.	Urtekin et al. (2020)
Banana peel powder	Hydroxyls	Phytic acid	Poly (lactic acid)	The LOI and UL-94 rating increase to 37.5% and V-0.	Kong et al. (2020)
Bagasse	Hydroxyls	Chitosan, APP, and EG	Epoxy resin	The LOI and UL-94 rating increase to 25.8% and V-0, and the PHRR and TSR are decreased by 33.4 and 7.3%, respectively compared with those of bagasse-containing epoxy thermoset.	Chen et al. (2020)
Lignin	Hydroxyls	Piperazine and DOPO	Epoxy resin	The LOI and UL-94 rating increase to 34.3% and V-0, and THR and TSP are reduced by 46.6 and 53%, respectively.	Dai et al. (2020)
Cellulose nanofibers	Hydroxyls	APP	Poly (lactic acid)	The LOI and UL-94 rating increase to 32.5% and V-0, with 55.5 and 23.5% reductions in PHRR and THR, respectively.	Yin et al. (2018)
Lignin	Hydroxyls	Triazineand 2,6,7-trioxa-1-phosphabicyclo-[2,2,2]octane-4-methanol-1-oxide	Polybutylene succinate	The PHRR and THR are reduced by 27.2 and 31.1% compared with those of the neat polybutylene succinate.	Chen et al. (2018)

further increase the flame-retardant efficiency of waste-based flame retardants *via* the green method and prepare waste-based flame retardants with good compatibility for different polymers.

AUTHOR CONTRIBUTIONS

CG contributed to writing—original draft, review, and editing. SH contributed to conceptualization, writing—original draft, review, and editing. ZC contributed to investigation.

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