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Emerging trends in flame retardancy of rigid polyurethane foam and its composites: A review

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Abstract

Owing to the superior thermal insulating attributes of rigid polyurethane foam (RPUF) compared to other insulating materials (expanded and extruded polystyrene, mineral wool), it remains the most dominant insulating material and most studied polymer foam. Like other polyurethane foam, RPUF is highly flammable, necessitating the incorporation of flame retardants (FR) during production to lower combustibility, promoting its continuous use as insulation material in construction, transportation, and others. The popular approaches for correcting the high flammability of RPUF are copolymerization and blending (with FR). The second method has proven to be most effective as there are limited trade-offs in RPUF properties. Meanwhile, the high flammability of RPUF is still a significant hindrance in emerging applications (sensors, space travel, and others), and this has continuously inspired research in the flame retardancy of RPUF. In this study, properties, and preparation methods of RPUF are described, factors responsible for the high flammability of PUF are discussed, and flame retardancy of RPUF is thoroughly reviewed. Notably, most FR for RPUF are inorganic nanoparticles, lignin, intumescent FR

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systems of expandable graphite (EG), ammonium polyphosphate (APP), and hybridized APP or EG with other FR. These could be due to their ease of processing, low cost, and being environmentally benign. Elaborate discussion on RPUF FR mechanisms were also highlighted. Lastly, a summary and future perspectives in fireproofing RPUF are provided, which could inspire the design of new FR for RPUF.

Keywords
Rigid polyurethane foam, flame retardancy, intumescent flame retardant, ammonium polyphosphate, expandable graphite

Highlights

- Emerging trends (2015–2021) in flame retardants system for rigid polyurethane foam (RPUF) are reviewed.
- Preparation methods and properties of RPUF are discussed.
- Factors responsible for the flammability of polyurethane foam are detailed.
- Inorganic nanoparticles, lignin, and intumescent flame retardant systems have been mostly used for RPUF.
- Future directions in flame retarding RPUF are proposed.

Introduction

Based on the report from Statista Research (2020), the worldwide market for polyurethane (PU) is estimated to increase from 18.4 million metric tons in 2019 to 22.5 million metric tons by 2024.[1] The anticipated increase in demand for PUs is due to their resilience and flexibility for thermal insulation in construction, refrigeration, and automotive[2,3] and space travel, sensors, oil absorbents, fireproofing and electrical (as cable jointing).[4–6]

As a clear proof, it can be observed that the available scientific articles comprising PU and PU foam (Figure 1) increased by over 100% between 2010–2020 compared to 1996–2009. The most prominent use of PUs across its primary market is PU foam,[7] constituting up to 67% of total global foam consumption, followed by polystyrene (PS) and poly (vinyl chloride) foams,[8,9] and it remains the most studied of all polymer foams (Figure 1). Generally, foam is a type of engineering material that is made up of a variety of components such as plastic, ceramic and others. Overall mass, strength, stiffness and thermal qualities are all defined by the cellular architectures of foams.[10]

Based on the application outlook, PU foam is majorly categorized as flexible and rigid[6,7] both differs by the type of polyol used in their synthesis and the functionality. While flexible foam is synthesized from a long chain polyether polyol and has the functionality of 3, rigid foam is prepared from short-chain polyol and has functionality between 3–8.[11] More functionality enhances better reticulation grades in the prepared PU.[12] Other applications of PU and its derivatives (such as PU elastomer or thermoplastic

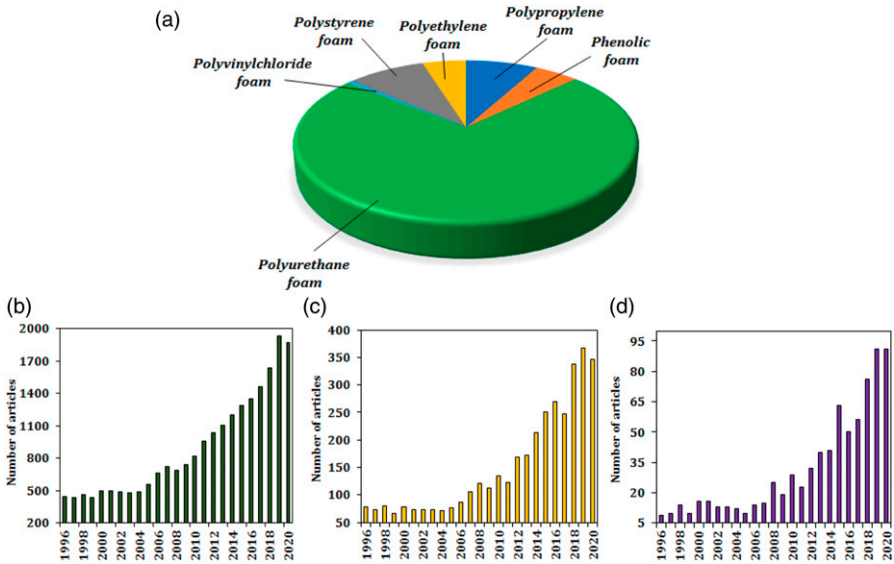

Figure 1. (a) Distribution of publications on various polymer foam from 2015–2020; Plot showing the published data for (b) Polyurethane, (c) Polyurethane foam and (d) Rigid polyurethane foam. Source: Web of Science database with the keywords polyurethane, polyurethane foam, rigid polyurethane foam OR polyurethane composites OR rigid polyurethane foam composites.

PU) include medical devices due to their flexibility, good resistance to solvent and high tensile.[13,14] Thermoplastic PU is widely employed in electronic textiles and flexible displays due to earlier listed properties[15,16] and for oil-water separation due to their low cost.[17] Other types of PU are waterborne polyurethane. Waterborne polyurethane are popular due to their environment unfriendliness and are widely use as coating and finishing materials on wood, fabric, leather and others.[18,19] However, the focus of this review is on rigid polyurethane foam (RPUF).

In recent times, RPUF is the most studied and like other PU foam, its properties can easily be modified for various end-use applications such as insulation material,[20,21] sealants,[22,23] transportation,[24,25] construction,[26] domestic appliances,[27,28] and packaging.[29,30] More so, due to lower thermal conductivity (0.02 W/mK) than most thermal insulating materials such as expanded PS and extruded PS (0.03–0.04 W/mK, 0.034–0.044 W/mK), mineral wool (0.037–0.055 W/mK),[31] and their closed-cell structure,[32,33] excellent adhesion property,[34] low density and moisture permeability,[35–37] durability, and good energy absorption.[38,39] Almost half of the global PU foam supply is RPUF[34,40] and superior thermal insulating attributes than other insulating materials (expanded PS, softwood, fireboard, and brick). However, these are less costly but need more material to achieve the same insulating efficiency as RPUF. This attribute is credited mostly to RPUF cell size and cell morphology, trapping the low thermal conductive gas.[41,42]

Against the good features of RPUF, it exhibits a low limiting oxygen index (LOI) value between 16-18%,[43,44] making it highly flammable and exhibits low thermal resistance, a major drawback undermining its use[45,46] in its stronghold; insulation (building and appliance) and packaging.[47,48] Hence, it is pertinent to strengthen RPUF with flame retardants (FR) during production to lower combustibility and suppress smoke emitted from burning.[49,50] Toxic smoke is harmful to human health when inhaled. Two major routes are being accepted to correct the drawbacks of RPUF: copolymerization (chemical modification of polymers' surface and core),[22,51] and incorporation of additives (FR) within the polymer matrix either by mixing or coating.[52–54] Meanwhile, the second option has proven to be the most viable and cost-effective route for virgin RPUF as there are minimal trade-offs in material properties.[55] Therefore, the review is limited to RPUF composites incorporated with a few selected additive-type FR for advanced engineering applications. These are preferred because of their unique properties such as low cost, small loading requirement, outstanding processability, and eco-friendly.[56] When incorporated into virgin RPUF, they typically form char structures and generate inert gas during combustion, thereby enhancing flame retardance.[57] In the last 5 years, expandable graphite (EG), ammonium polyphosphate (APP), and nanoparticles (mostly halloysite nanotubes', carbon nanotubes', and montmorillonite), remain the dominant as well as most investigated FR publicized to confer good performance in rigid foam. From Figure 1(d), a swift increase in interest for RPUF can be seen, which indicates that researchers globally continuously work on RPUF.

Several reviews have been produced on protection of flexible PU against fire via layer-by-layer technology,[58] phosphorus and nitrogen based-FR for PU and other polymers,[59] soft PU FR[60] and different surface coating methods for FR flexible PU foams.[61] Other reviews that have briefly discussed flame-retardants RPUF are produced by Akindoyo et al., 2016[34], and Gama et al.,[4] 2018. Yang Chunguang et al.[62] wrote a review on the effect of phase change materials on RPUF. Similarly, Mahmood Nubla et al.[63] discussed how depolymerized lignin is used in the preparation of polyols and RPUFs. Nevertheless, it is imperative to produce a review dedicated solely on flame retardancy of RPUF.

Herein, we can carefully assume that with the rising applications of RPUF, its flame retardancy will perform an important role in its demand. Therefore, it is apt to produce a research report on recent advances in flame retardancy of RPUF as this topic has not been explicitly reviewed in the literature. This in-depth review is centered on emerging trends in FR systems developed to enhance the flame retardancy of RPUF. We focus only on inorganic nanoparticles, lignin, APP, EG, and hybrids with other FR. Thereafter, emphasis on how flame retardancy of RPUF will be elaborately discussed. An overview on the preparation and properties of RPUF is also discussed, then the flammability in PU foam is explained, current trends in FR strategies for RPUF (2021–2022) was described. The final section provides an outlook on the future of FR for RPUF.

Rigid polyurethane: Synthesis, structure, and properties

Synthesis and structure

Polyurethane is produced (Figure 2) by polyisocyanate reaction with hydroxyl-containing compounds, mostly during processing, but PU foams are extended materials, and their composition emerges from several processes combined.[7] Two primary ingredients in the synthesis of PU foams are isocyanates and polyols; both provide the foam's physical and mechanical characteristics. FR, surfactants, fillers, catalyst, crosslinkers, and blowing agent are often required to monitor and improve the reaction scheme and performance properties.[64] By choosing a particular form of isocyanate and polyols or combining isocyanates and polyols, the structure can be customized to achieve the desired properties.[65] Nevertheless, understanding the correlations between the structure, and characteristics of PU is essential as the freedom to modify the structure at the time of manufacturing is among PU's critical strengths over other polymers.[34,66]

The synthesis of a rigid PU involves mostly isocyanate and a polyol, and others such as a crosslinking agent, blowing agent (chemical or physical), catalyst, and a surfactant, each playing a particular function (Table 1) in the chemical reactions responsible for the development of the foam.[47] The reaction scheme involves urethane formation, crosslinking reactions, together with foaming reactions when a chemical-type blowing agent is employed. Figure 3 represent the typical reaction of the formation of urethane linkage and in Figure 4, the developed urethane group react further with an isocyanate group to produce allophanate and the reaction leads to the chemical crosslinking in the polymer.

In rigid foam manufacture, aromatic-type isocyanates (Figure 5(i) and (ii)), such as methylene diphenyl diisocyanate (MDI) and toluene diisocyanate, are mostly used; both are highly reactive and cost-effective compared to others.[34,66] Quite importantly, PUs developed out of aromatic isocyanates usually have higher tensile strength, modulus, and glass transition temperature (T_g), although elongation and impact resistance may be lower. In contrast, those out of aliphatic isocyanates (Figure 5(iii) and (iv)) such as

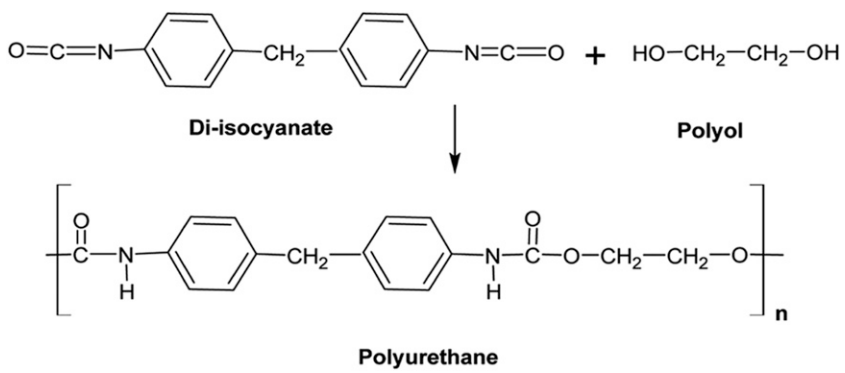

Figure 2. Possible reaction scheme involved in PU synthesis.[34]

Table 1. Various components for the preparation of rigid polyurethane; component types and functions[34,47,88,89].

Components	Commonly used	Preparation method	Specific function/ advantages	General function
Isocyanates	-Methylene diphenyl diisocyanate	The reaction between phosgene and amine precursors (aromatic or aliphatic)	-Increase functionality -Low volatility -Increase crosslinking	Provides foam reactivity and curing properties
	-Toluene diisocyanate	Nitration of toluene with H_2SO_4 to form nitrotoluene; this is hydrogenated to a comparable amine, and lastly, the diamines are phosgenated thereby forming diisocyanates	-High reactivity -Low cost	
Polyol	-Poly (oxypropylene) glycol	-Alkaline polymerization of propylene oxide	-Offers good flexibility -Cost-effective	Contributes long flexible segment which produces soft elastic polymers
	-Polytetra methylene ether glucol	-Acid polymerization of tetra hydrofuran	-Confer high strength, abrasion resistance, resilience, and engineering toughness	
	-Glycerine -Caprolactone	-Ring-opening polymerization	-Improves resistance to hydrolysis	
Catalysts	-Trialkyl amine, dibutyl tin dilaurate, N-alkylmorpholin, tindioctoate, diazobiscyclooctane (DABCO)			-Increases reaction rate of isocyanate and polyols -Lower the reaction temperature

(continued)

Table 1. (continued)

Components	Commonly used	Preparation method	Specific function/ advantages	General function
Chain extender/ cross-linking agents	1,4-butane diol, water, diamines and ethylene glucol		-Responsible for the elastomeric properties of polyurethanes (PU) -Provide the hard segment to the PU elastomers responsible for modulus and ultimate strength	-To modify the PU molecule and provide mechanical support that will improve the material properties
Blowing agents	Physical type such as pentanes, hexane, CO_2,1,1,1,3,3 -Pentafluoro propane Chemical type such as water		-Require little or no water -Zero ozone depletion rate -Cost-effective -Produce CO_2 gas and expand the foam	-Helps in the preparation of the foam by controlling the formation of bubbles -Control foam cell structure
Surfactants (for rigid foams)			-To strengthen cell walls and protect against foam collapse -Helps secure low thermal conductivity	-Helps to combine raw materials evenly -Eliminate surface defects
Fillers	-Organic filters (e.g., glass fibres) -Inorganic fillers (e.g., nanoparticles and graphene)	-Reaction injection moulding -Injection moulding	-Improved rigidity and strength -Improve both compressive and impact strength	-To reduce processing cost and increase mechanical strength like tensile, compression, and stiffness
Flame retardants (FR) and smoke suppressants	-Additive-type FRs* (e.g., APP*, melamine) -Layered FRs* (e.g., graphene, EG*.) -Nanoclay, Sepiolite, montmorillonite			-To enhance foam flammability and lower the amount of smoke generated during their combustion

*FRs - Flame retardants; APP; ammonium polyphosphate, EG – expandable graphite.

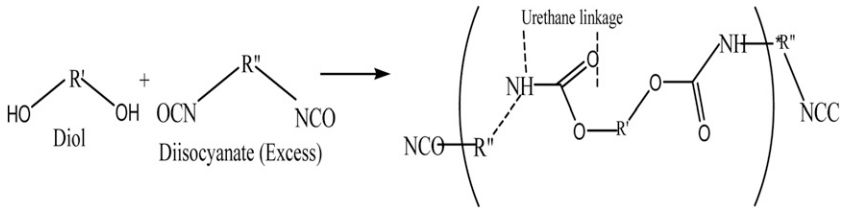

Figure 3. Mechanism of urethane linkage formation.[67]

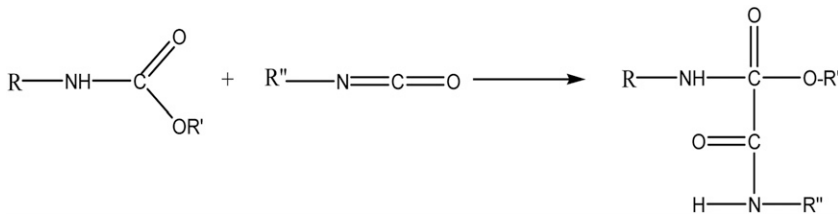

Figure 4. Formation of allophanate.[47]

hexamethylene diisocyanates and isophorone diisocyanate are usually flexible materials with higher elongation and lower tensile strength.[68] In addition, polymeric MDI has gained much popularity lately[11] because of three vital functions: (1) It can react with water, forming CO_2, which is a desirable gas for foaming, (2) It acts as a di- (or poly) functional reactant, linking polyol molecules together through the reaction among isocyanate and hydroxyl groups. The reaction is highly exothermic, thus supplying the heat needed to burn the inert blowing agent and the heat needed to guarantee a successful foam cure, (3) Isocyanate generates polyurea urea linkages and this becomes part of the polymer structure, providing the foam with rigidity and thermal resistance.[41,47]

In PU synthesis, NCO/OH, known as the isocyanate/hydroxy ratio is vital, denoted as isocyanate index ([NCO]/[HO] × 100) (IC) index. The sum of PUR bonds and isocyanurate rings is linked to IC index. It has been documented that the commercial rigid PU (RPU) IC index typically ranges from 105 to 125, however that of RPU-polyisocyanurate foams range from 180 – 350.[69] Utilizing an excess of –NCO helps provide higher strength and more porous foam.[70,71] To support this point, Aiga Ivdre et al.[72] recently examined how different IC indices based on polyols synthesized from waste PET and rapeseed oil (RO) influence the foaming parameters (tack-free time, gel-time and cream time) and compressive strength of RPUF. All the foaming parameters increases as the IC indices of the polyols increased from 110–150. Similarly, the compressive strength of RPUF/RO/PET marginally rise from 0.30 MPa (specimen with IC index of 110) to 0.35 MPa (IC index of 130). Furthermore, Sung et al.[73] studied the effect IC index (90–130) on some properties of RPUF using a physical blowing agent (HFC 365mfc). There was slight reduction in gel time but increase tack-free time and dimensional stability of the rigid PU

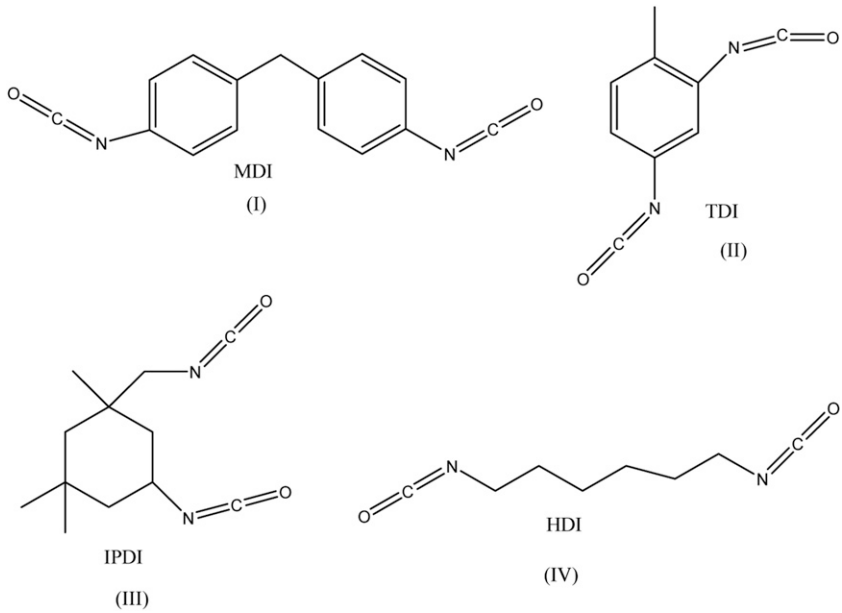

Figure 5. Molecular structure of different isocyanates.[68]

foam as the IC index increases. Attributed to improved mixture mobility, and increased glass transition temperature of the foam, respectively. Rigid foams are synthesized from lower molecular weight (Mn of 290–670 g/mol),[12] highly branched resins.[66] The length and grade of polyols contribute significantly to the overall physical properties, from long polyols producing low-modulus PU elastomers to short or multifunctional polyols producing RPUs. It also determines the foam type (rigid or flexible), brittle (or nonbrittle), as well as level of its porosity to gas or moisture.[74,75] Polyols used for RPUF preparations are classified into two, the first being primary and secondary hydroxyl-terminated polyether polyols, and the second are polyester polyols. This pattern stems from the huge class of molecular structures involving hydroxyl functionality as well as polyether polyols' molecular weight.[41,76] Generally, the polyol can either be petro-based such as glycerine, which contains primary OH group or plant-based oil from soybean, palm olein, and castor, which contains secondary OH groups.[34,76,77] More so, reacting polyol from the secondary OH group with isocyanate is a slow process compared to polyol from the primary OH group and isocyanate. Sometimes, a mixture of both types of polyols is used in foam to lower the consumption of petro-based polyol (62,64), reducing energy usage and promoting sustainable development.

Properties and preparation of rigid polyurethane

Rigid foam is commonly used as cushioning in furniture and automotive insulating, in refrigeration and as packaging materials, and is use as cushioning in furniture and

automotive is ascribed to its low thermal conductivity and lightness.[78,79] RPUF is substantially used in the heat insulation industry due to its low thermal conductivity.[80] Thermal insulation is related to the lowering of heat flux that penetrates through the material.[81,82] PU is categorized as multiblock copolymers, consisting of alternate segments (hard and soft) connected in succession by covalent (urethane or urethane-urea) bonds.[83] While urethane and urea moieties are connected to hard PU foam segments, polyol produces soft segments.[84] As a result, higher isocyanate concentration will confer extra hard segments, creating a more rigid PU foam. The soft segment is produced in a continuous rubbery (polyol) phase, and sometimes partially crystalline compared to the hard segment that contains the rigid part compared to the hard segment containing the rigid part joined by hydrogen bonds and crystallization.[85] The hard segment contributes to foam chemical resistance, tensile and tears strength, and high-temperature performance. In addition, more urethane hydrogen bonding promotes plastic features and lower intermolecular motion compared to the soft segment that promotes elastomeric properties, namely, flexibility, hardness, compression, and low-temperature efficiency.[86] The morphology of PU hard and soft segment is shown in Figure 6. Besides polyols and isocyanate, other constituents for rigid foam synthesis are the catalyst, blowing agents, surfactants and additives that are needed to achieve specific properties. Table 1 gives a description of the functionality of these constituents. However, one of the most essential additives for rigid foam is FR due to their inherent flammable nature. Considerable work has been done to allow rigid foams to comply with stringent flammability regulations, especially in foam used in building insulation.[70,87]

Conventional methods of preparing RPUF are water-blown, batch foaming, and one-pot free rise. However, for the first method, water is used as blowing agent, a demerit in the preparation of flame-retardant RPUF. The second route utilized both carbon dioxide and nitrogen as the blowing agent, making it an expensive method.[2] Previously, many works adopted batch foaming to prepare PU composite foams. However, this method affects the dispersion of filler (especially nanoparticles) and forming behaviour of PU's.[90,91] Nowadays, the preparation of PU and PU-based foams by free-rising/pouring,[39,92] one-step one shot,[93] and quasi pre-polymer[94] foaming system are widely adopted, especially in small-scale foam production due to their low cost and ease of preparation. This method can blend polyols, catalysts, surfactants, blowing agent, and polyisocyanate in sequence in disposable plastic cups or molds, and the mixture is degassed and afterwards stirred. The foam is then allowed to rise in the mold for several hours at room temperature to achieve curing. However, complete curing is achieved by oven drying at a specific temperature and time. Figure 7(a)–(c) depicts the schematic of these foaming system, their features, merit, and demerits. Kerche et al. (2020)[92] recently cured their RPUF in an electric oven under 2 h at 60°C and proceeded further to a post-cured at 20°C, 65% relative humidity over 2 weeks. For Shi et al. (2018),[39] their foam cured in an oven at 70°C for 24 h.

Similarly, Modesti et al. (2018)[95] oven-cured foam at the same temperature as Shi et al. but over a shorter duration (12 h). The difference in curing conditions is an indication that there is no condition that fits all samples as PU foams are prepared with different components and processing conditions, one of the major strengths of PU over other

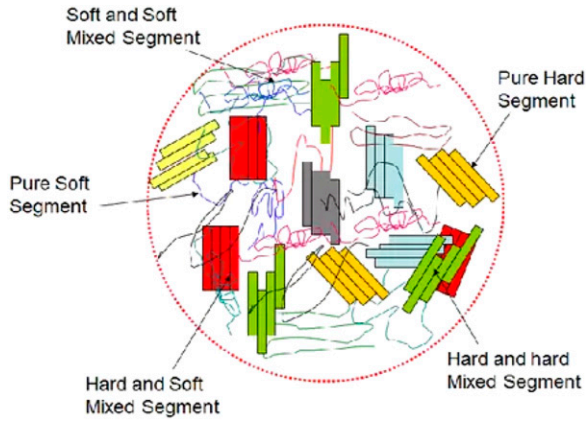

Figure 6. Morphology of polyurethane.

polymers. For instance, plant-based polyol versus petrol-based polyol, and different blowing agents (chemical vs biological).

Flammability of PUF

In the last decade, the growing market for PU foam (Figure 1(a) and (c)) and highly flammable is the justification for lots of studies devoted to their flame retardancy compared to other properties. The flammability of PUs, in particular PU foams, fully relies on the structure of the polyol and the isocyanate/hydroxy ratio and very important, foam density, which determine the flame spread during combustion.[96,97] PUs are very combustible polymers with a low LOI value of between 16-18%,[43,44] attributed to low split up temperature of urethane linkage (bond). Hence, the thermal stability of PU goods is awful, as shown by their low initial and maximum degradation temperature.[28,49,98] Similarly, the neat rigid foam has poor FR attributes due to its vast specific surface area and combustible hydrocarbon chains.[99,100] Through combustion, conventional PU foams release highly toxic smoke, primarily carbon monoxide (CO) and hydrogen cyanide (HCN), due to the substantial presence of nitrogen in their structure.[49,101] These gases could cause severe damage to human health or even death when inhaled. Moreover, a rapid temperature rise occurs during a burn, leading to the breakdown of PUFs emitting tiny molecules in the gaseous cycle. The mixing of these small molecules with air will produce an explosive mixture. When this mixture and temperature level exceeds the flammability threshold, the substance begins to burn.[49] More so, the amount of HCN released from PUs is typically higher than other nitrogen-based polymers such as polyamide and polyacrylonitrile.[102] Levchik and Weil documented the thermal decomposition of PUs in their review; they explained that it usually begins with allophanate and biuret (being the thermally weaker side) and then urea, urethanes and Isocyanurate units followed. Also, the burning stage of PUs were categorized into two; solid-phase and liquid-phase. The former show

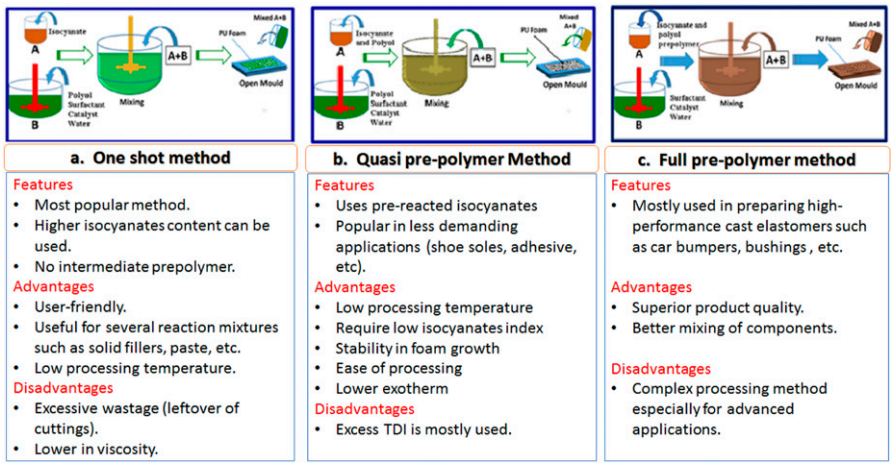

Figure 7. Polyurethane foaming method, and their features.[7,90–94]

combustion of isocyanate part of the foam; the latter represent that of polyol. In the early stage, the isocyanate part of the foam is discharged as yellow smoke; at the advanced stage of combustion flames, the yellow flame will further decay to HCN and flammable organic compounds. Later, nitrogen oxides are produced from the combustion part of the HCN. At the final stage, the burning of polyol is responsible for the vital part of the heat, carbon dioxide and CO let-off.[97]

Additionally, PU foams have low thermo-oxidative properties, which greatly restrict their practical application because oxidation of PU foams can happen at low temperatures. Thus, low thermo-oxidative properties will increase the polymer degradation rate.[103] PU foam low flammability is attributed to its large surface area, porous structure, geometry, and low density of foam properties.[104] PU material morphology is the key cause of the bad fire behaviour of PU foam, as it can quickly diffuse oxygen into the foam's porous structure thereby accelerating the combustion process.[29] Another factor contributing to the flammable PU foam is the gas within the cells. If the gas is flammable (CO and HCN) as the case in many PU foams, the fire activity is far worse as it is another fuel for flame propagation during pyrolysis.[4,96] In polymers, the combustion process is complex as it entails instantaneous combination of heat together with mass diffusion and decomposition chemistry. It involves four key steps, namely, ignition, combustion, pyrolysis, and feedstock as shown in Figure 8.[105] Aided by abundant heat source, the polymer will breakdown generating ignitable gases through the pyrolysis process. Subsequently, the ignitable gases unite with oxygen and initiate the combustion cycle of polymer. According to the flammability threshold of the polymer, if the heat that originates from the flame in the ignition process is sufficient to retain the degradation level of the polymer is above that required to sustain the mass of the flammable volatiles, then a self-unending combustion process will occur.[106,107] As such, disrupting the three components (fire, oxygen, and fuel)

responsible for combustion to occur, either alone or combined will provide efficient FR attributes for the polymeric material exposed to heat flux.[108,109]

Flame properties and flame test

The FR attributes of polymer composites are primarily measured through heat release amount and rate, evolved smoke amount and rate, ease of ignition, combustion gas-burning time, surface flame spread rate and toxicity.[70,110,111] Material actions regarding fire are majorly categorized into: (a) resistance to fire, (b) reaction to fire. Fire resistance gives data on how good a building component, like a wall, door, among others, will preserve its surface and intricate properties on exposure to fire. In contrast, fire reaction is a measure of a material or device contribution to the fire's growth and expansion/spread.[4,107] To evaluate the flammability properties of polymers, several characterization methods are employed, commonly used are Underwriters' Laboratories (UL-94) burning test categorized into vertical and horizontal test (both differ mostly by the sample orientation during testing), cone calorimetry (CC), as well as LOI or simply oxygen index (IO) and lately, pyrolysis combustion flow calorimeter (PCFC) was introduced. CC test defines the continuous link amongst the heap of oxygen absorbed from the air, the quantity of heat emitted amid the polymer combustion process, and the entire flame retardancy mechanism. It reveals fire parameters like smoke production (rate, temperature), heat release rate (HRR), total heat release (THR), time to ignition (TTI), mass loss rate or char residue/yield, peak heat release rate (pHRR), among others.[112,113] HRR is the topmost parameter that influences fire; hence, high HRR induces rapid combustion and flame expansion, conversely the pHRR reflects the spot in a fire at which heat is prone to migrate and burn surrounding materials. This test's measurement concept, standardized as ISO 5660 and ASTM 1354, depends on oxygen consumption.[4,114] For the UL-94 vertical burning test, a simple Bunsen burner is used to obtain an upward flame spread vertically. The test has been standardized as ASTM D3801 and is reported to be the most widely

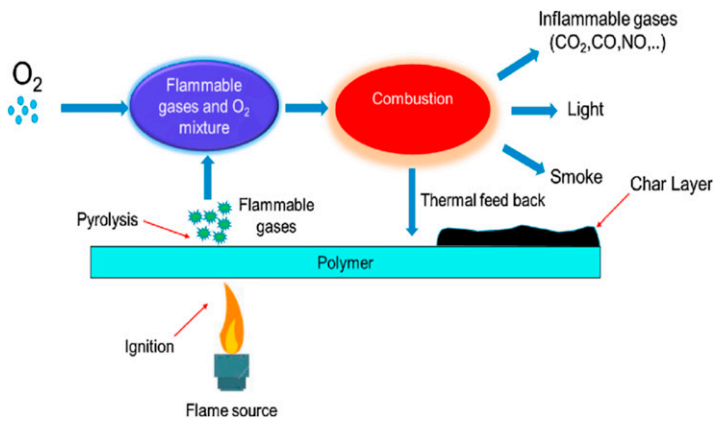

Figure 8. Combustion cycle of polymers.[105]

used small-flame test for polymeric materials.[115,116] UL-94 test measures a material's readiness to quench or expand the flame after withdrawing the ignition source.[117] It assessed the flame retardancy of polymeric materials based on their burning characteristics (vertical or horizontal) such as V- 0, V-1, and V- 2 ratings, or HB (horizontal burning). HB rating is recorded if the material being tested failed the UL-94 test. The precise characteristics needed for each rating are summarized in Table 2.[118,119]

Furthermore, LOI evaluates the minimal oxygen concentration needed to start and sustain a flame or combustion of the polymer in an oxygen-nitrogen (O_2/N_2) atmosphere for more than 3 min or 5 cm size of the sample length consumed. The sample is positioned vertically in a glass chamber and lit from its top edge. A slow O_2/N_2 mixture is supplied from underneath the chamber to sustain burning flames, and then oxygen concentration is steadily lowered until the sample ceases burning. The testing procedure has been standardized through ASTM D2863 (or ISO 4589). Limiting oxygen index test is reproducible, requires only small samples, and presents a single data (number) used for material flammability rating.[120,121] Polymers or materials with an LOI value above 27% or sometimes 28% are defined as self-extinguishing.[122] Those below 21% are highly combustible (in the air)[123,124] and those with LOI values between 21-27% are categorized as slow-burning.[125] Typically, a higher LOI value signifies that more oxygen is needed for combustion, i.e., the material is hard to burn. Thus, the fire will retard, signifying better flame retardancy of the polymer or material.[126–128] The LOI value of untreated PU foam is within 16–18% range[43,44]; once PU foam starts to burn, it will not self-extinguish, and the flame will propagate swiftly due to the foam's cellular structure,[27] necessitating the inclusion of FR to improve their performance. The UL-94 and other tests are generally insufficient to measure the critical pyrolysis and combustion characteristics of some composite materials such as wire and cable sheath. For instance, it is challenging to use the CC test to analyze cables and wires flammability behaviour due to their complex internal structure and special form. This led to the introduction of PCFC (Figure 9) in 2007, also known as micro-scale combustion calorimetry (MCC).[129,130] PCFC has a dynamic capability and can measure the flame properties of polymers, cables, and materials with similar structure by obtaining specific heat release data, namely, HRR,

Table 2. UL-94 classification used for polymers.

	Interpretation		
Test conditions	V-0	V-1	V-2
t_1 or t_2 for each individual sample	≤10 s	≤30 s	≤30 s
t_1 plus t_2 below 50 s for 5 tested samples	≤50 s	≤250 s	≤250 s
t_1 plus t_3 below the 30 s for each individual sample	≤30 s	≤60 s	≤60 s
After flame was not observed for any sample up to clamp holder	NO	NO	NO
No flame drops to ignite underneath cotton	NO	NO	YES

Note: t_1 = denote the first after the flame time (sec) following the taken-off of flame.
t_2 = denote second after the flame time (sec) following the taken-off of flame.
t_3 = time needed for the fire flare to disperse is recorded as the after-flow time t_3.

pHRR, ignition temperature, and THR. The test requires a few milligrams sample size according to the required oxygen intake in a non-flaming/combusting oxidation process at 900°C inside a combustor. PCFC test has been standardized by ASTM 7309–13 and can be generally used to analyze the flammability of solid materials.[129,131,132] Studies have documented that the results from PCFC tally with results of other flame tests (CC, UL-94 and LOI).[133,134] However, PCFC has some obvious drawbacks regarding some combustion parameters: shrinking, quenching, swelling/expanding (intumescence), and dripping.[135]

FR for RPUF

For RPUF, their immense utilization has highlighted its poor fire safety issues namely heat release, heavy production of smoke as well as harmful gases in fire. Polymeric materials (such as foams) with robust fire retardancy have utmost tendency of lowering fire risks and economic falls in useful applications.[136,137] Therefore, to expand the use of RPUF to emerging applications such as (sensor and space travel) and maintain its use in its strongholds (construction, refrigeration, transportation, and packaging). It is imperative to adjust the design of fire properties of rigid foam. In the last 5 years, emerging trends in different methods employed for the flame retardancy of RPUF are described in this section, namely nano clay and nanoparticles, lignin, intumescent system, APP, and EG.

Nanoclay and other nanoparticles

Nowadays, because of their low price, flexibility, and accessibility, clay nanosheets are already recognized as a suitable inorganic constituent for high-performance composites. Typically, such inorganic nanometer-sized sheets are negatively charged with various hydroxyl groups usable for crosslinking on edge.[138] Clays are an essential group of fillers formed by weathering or secondary sedimentary processes.[139] Nanoclay (two-dimensional nanofiller) confer significant improvements on thermal and mechanical properties when embedded into a foam/polymer matrix, ascribed to their platelet structure.[140] The flat surface of the clay is an effective nucleation site, making it possible to control clay's

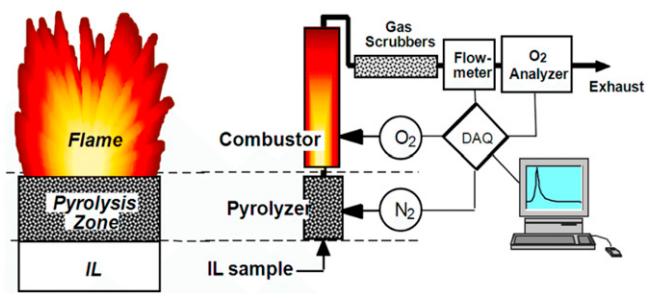

Figure 9. Schematic diagram of pyrolysis combustion flow calorimeter.[129]

dispersion, and a uniform cell size formation and rich intercalation chemistry would lead to substantial clay dispersion. The nanoclay lamella structure can indeed be exfoliated, a key advantage, thereby increasing the interfacial adhesion with the polymer matrix.[141] This will strengthen the polymer matrix as many vital chemicals and physical interactions are controlled by surfaces.[142,143] Several clays such as montmorillonite (MMT) and halloysite nanotubes (HNT) with nanosized dimensions, have been found to act as an effective cell opener in foams (rigid, semi-rigid and flexible). Due to their IC index and the presence of propylene carbonate, the flexible foam was said to have higher open-cell content than others.[90] MMT is a layered silicate with a layered structure, whereas HNT has a tubular structure, lumen with nanoscale and low OH groups on the surface. HNT has been an efficient FR among all inorganic nanofillers, and their incorporation in polymers have produced nanocomposites with enhanced mechanical and flammability properties.[144,145] One of the types of nano-sized components is nano-silica,[146] such as MMT, and the incorporation of nano clay silicates improves the efficiency of the polymer matrix by boosting the polymer's thermal stability, providing barrier action and preventing the movement of polymer molecular chains.[147,148] More so, when MMT nanosheets are combined with a polymer matrix, they perform exceptionally well in blocking heat and gases, resulting in increased protection and security for a variety of uses, notably flame retardancy.[149] As an advantage over halogenated FR, nano-silica is halogen-free FR; it present eco-friendly flame, smoke and toxicity capability even at very low concentration because of their high aspect ratio.[150] The mechanism of clay alone supports their FR capability. Clay appears to spread to the polymer matrix surface during combustion and form a strong silica layer that acts as a protective barrier.[151] The barrier formation can delay the transfer of mass and heat even during the burning process. The polymer is shielded from heat by the silicate layer, minimizing oxygen flow and preventing volatiles; these acts would hinder the combustion process, limiting the amount of combustible available.[152,153] Though nano clay has excellent physical properties, such as high surface area, large aspect ratio, and strong bond,[154] but their FR attributes can be disturbed by loading, morphology and chemical composition.[130] For carbon nanotubes (CNT), our focus is the multi-walled CNT with a large diameter in the range of 10–100 nm and being a 1-dimensional (ID) nanofiller for carbon nanotubes (CNT). Typical CNTs is lightweight, has a high aspect ratio, ultra-high tensile strength though CNT is flexible, it has high surface to volume ratio and thermal conductivity in the range of 2000-6000$Wm^{-1}k^{-1}$.[155,156] These special attributes of CNTs are attributed to its robust SP^2 carbon-carbon linkage and geometric arrangement, making it to enhance the performance properties (thermal, flammability) of polymers.[157,158] This section is an overview of the flame retardancy of RPUF composites with nanoclays such as montmorillonite (MMT), halloysite nanotubes (HNT) and other nanoparticles like carbon nanotubes (CNT) without the compliment of any conventional FR. In section 4.1.1, the synergistic effect of MMT, HNTs, and CNTs on conventional FRs will be discussed according to recent studies of FR RPUF.

In a study conducted by Adilah Alis et al.[159] on the flame retardancy as well as thermal stability of nano clay, HNTs were prepared then blended with bio-based RPUF. The authors found that incorporation of 1wt.%, 3wt.%, and 5wt.% HNTs enhanced the thermal

stability of RPUF, increasing with increased HNT loading. However, 5wt.% loading of HNT in RPUF gives the highest increase of weight loss; for instance, at 80% weight loss (T_{80}), the increment was 18% compared to pure RPUF. Similarly, RPUF/HNT5wt.% presented the highest residual char of 18.1% at 600°C relative to pure RPUF with 7.6%. This outcome can be attributed to the higher surface area of HNT, promoting better adhesion between HNT and RPUF. This boosted the activation energy of the foam and enhanced its thermal stability. Moreover, compared to pure RPUF, RPUF/HNT5wt.% LOI value marginally increases to 19.5% from 17%. It is opined that the presence of discrete cells hinders the formation of long physical char layers on the RPUF surface. Hence, it poorly delays the combustion process.

For Ciecierska et al.,[50] they employed carbon nanotubes (CNT) as standalone nanoparticles to boost the flame retardancy and mechanical performance of RPUF. The CNT loadings were 0.01%, 0.05%, and 0.1%. Compared to neat RPUF, RPUF/CNT0.01% composite LOI value increased to 25% from 20%, while other composites LOI values were closer to neat RPUF. Due to the presence of CNTs, there was an equal discharge of heat flux throughout the neat RPUF. This minimizes the degradation temperature at which volatilization of gases occurred. CNT add-ons lead to the formation of a char layer, serving as a shield for the underlying foam. Incorporating 0.01wt.% of CNT increased the composite bending strength and Young's modulus by 21% and 6%, respectively. It can be said that CNT has strengthened the composite and the porous structure.

Similarly, Espadas et al. investigated how multiwall CNT alone influenced the flame-retardant performance of RPUF.[160] RPUF/CNT composites were fabricated through the free rising foaming method, and the CNT loadings were 0.1, 1 and 2wt.%. It was found that the presence of CNTs affects the flammability of RPUF composites noticeably. Incorporating 0.1wt.% of multiwall CNT increased the burning rate of the composite; however, as the loading rises above 1wt.%, the burning rate remarkably decreases. Similarly, the time to extinction of flame after ignition was shorter at above 1wt.% CNT content. Hence, multiwall HNT successfully modifies the cellular structure of the foam. Lastly, compared to pristine RPUF, the thermal conductivity of RPUF composite marginally increased to 0.069 W/mK from 0.020 W/mK, increasing with multiwall CNT loading. This can be ascribed to the good stability of the covalent bonds (carbon-carbon) present in the multiwall CNT crystalline structure.

Nanoparticles/conventional FR in RPUF. As previously mentioned in section 4.1, nanoparticles offer unique roles in the fire retardancy of polymeric materials due to their exceptional fire behaviour.[161] In the last decade, there have been new advances in nanoparticles as synergistic agents to boost polymer fire response. These have attracted significant interest from industrial and academic researchers due to proven improvements in anti-dripping, mechanical and barrier properties of polymers at low loading.[162] The presence of nanoparticles in RPUF favours the formation of the carbonized layer, inhibiting the combustion process. They prompted a successful decline in the number of ensuing products of thermal decomposition.[163] It is widely documented that the FR

system blended with appropriate nanoparticles can generate a continuous and solid protective char, causing higher FR performance.[161,164]

In that regard, Czlonka et al.[165] studied the effects of montmorillonite (MMT) and salvia (SO) filler on fire behaviour, thermal stability, the compressive and flexural strength of rigid polyurethane (PUR) composites. SO filler was extracted from *Salvia officinalis* (popularly called sage); it is an aromatic plant and contains a large bioactive compound. The loading of SO in MMT is 1, 2, and 5wt.%. The authors found that the best interfacial adhesion of SO filler and MMT were achieved with 1 and 2wt.% SO filler. At 5wt.% loading, the foam structure is less uniform with visible agglomeration (Figure 10).

From LOI and cone calorimetry results (Figure 11); compared with pure PUR, PUR/SO-MMT2wt.% LOI increased to 21.3 from 20.4, and PHRR decreased by 5.66% (both results are the best performance), total smoke release (TSR) decreases by 7.38% for PUR/SO-MMT2wt.% (lowest value of all the filler content) relative to pure PUR.

Based on TG results (Figure 12), PUR/SO-MMT5wt.% showed the highest weight loss at 50% ($T_{50\%}$), final decomposition temperature (T_{max}) and char residue (at 600°C) of 457°C, 317°C, and 31.0%, respectively compared to pure PUR with 397°C, 315°C, and 27.6%. An indication of improved thermal stability for the modified PUR, presence of SO filler and MMT remarkably boosted the resistance of PUR to a higher temperature. Furthermore, by incorporating 1 and 2wt.% SO/MMT n RPUF, the composite compressive strength increased by 13 and 15%, respectively, while flexural strength increased by 4 and 5%, respectively. For 5wt.% loading of SO/MMT, a decrease in compressive and flexural strength was recorded. The improvement in mechanical properties is attributed to the presence of MMT, which stiffen the movement of the molecular foam chain and confer a better reinforcing effect.

A similar study was reported that multi-walled carbon nanotubes (MWCNTs) could play synergistic FR effects in RPUF/zinc borate (ZnB).[163] The total loading of MWCNT was maintained at 0.5wt.% and ZnB was 15wt.%. Compared to virgin RPUF, incorporating 0.5wt.% MWCNT in the composite decrease the PHRR by 12%, and TTI increased by 50% from 2s to 4s. It was also found that the presence of MWCNT in the composite further enhanced the thermal stability by increasing the thermal decomposition temperature.

It has been documented that the charring action of polymers has an immense connection with their FR properties.[49,166] Hence, amid the combustion of polymers, nanoparticles tend to migrate to their surface, thereby advancing the formation of unified and solid char layers.[167] In that regard, organically modified MMT (OMMT) was prepared and added as a charring agent to develop eco-friendly FR RPUF composites based on an APP-triphenyl phosphate (TPP) system.[168] The preparation process of the modified MMT is depicted in Figure 13(a). Zheng Xiaorui et al. found that based on cone calorimeter results, compared to virgin RPUF, the joint action of 12wt.% APP/TPP at a mass ratio of 2:1 decreased the PHRR value substantially by 33% (Figure 13(b)). However, the TSR was nearly the same for both virgin RPUF and RPUF/APP/TPP composites, but the total combustion time (Figure 13(c)) of the composite was twice that of virgin RPUF (300 s vs 150 s). The TG test result revealed that the char residue of RPUF/APP/TPP was 26.5%, whereas the residual char yield of the composite incorporated with 5wt.% OMMT

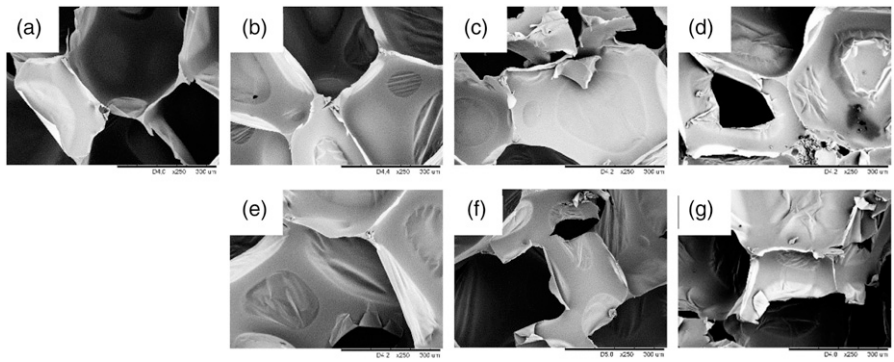

Figure 10. SEM images (a) Pure PUR (b) PUR/SO1wt.% (c) PUR/SO2wt.% (d) PUR/SO5wt.% (e) PUR-SO/MMT1wt.% (f) PUR/-SO/MMT2wt.% (g) PUR-SO/MMT5wt.%.[165]

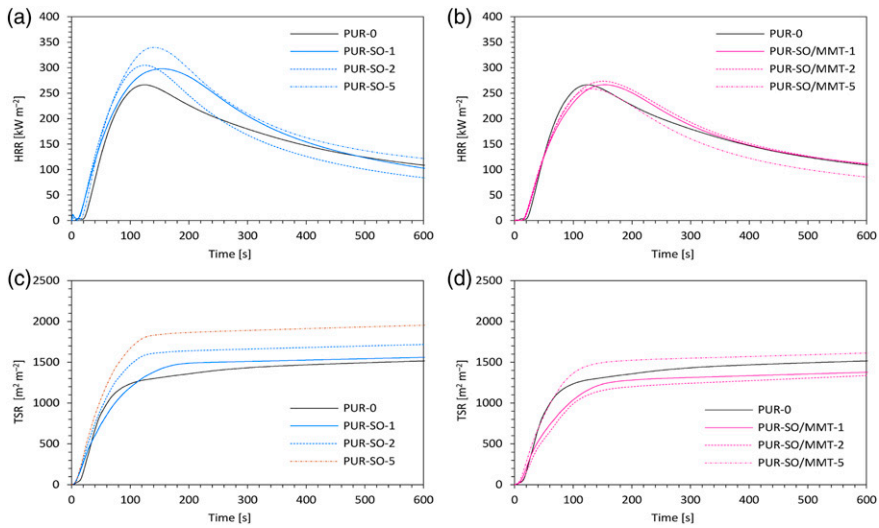

Figure 11. Heat release rate and total smoke release of pure PUR, PUR-SO and PUR-SO/MMT composites.[165]

marginally reduced to 26.4%. Although it is higher than virgin RPUF at 6.6%. An indication that OMMT in the APP/TPP FR system has not enhanced the char yield of the RPUF composite. But the good news is that incorporating OMMT in RPUF/APP/TPP composite increased their compressive strength, increasing with OMMT loading up to 5wt.%. Above 5wt.%, the compressive strength decline shows that high loading OMMT did not disperse properly in the polymer matrix.

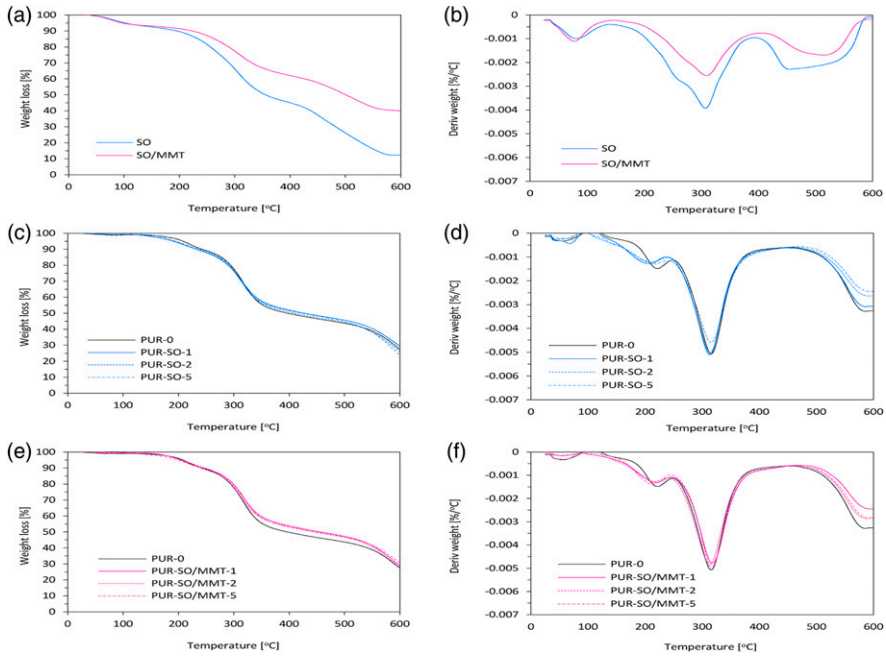

Figure 12. TG results of pure PUR and MMT-treated SO (a–b), PUR composites/pure SO (c–d), and PUR composites/MMT-treated SO (e–f).[165]

Lignin

The most numerous aromatic biopolymers on the earth are lignin. It's amorphous, and found in plant cell walls. It has been reported that only 2% of total lignin output is now commercialised, being a non-valued by-product from the paper and pulp sector.[169,170] Lignin is a renewable and biodegradable substance with a low-price tag. Furthermore, lignin gives mechanical support to polymer matrix.[171] Mu et al.,[172] extracted bio-oil from biomass lignin and reported enhanced composite anti-wear performance. Furthermore, Lignin is also an important source of hydrothermal carbon providing up to 45–60% yield compared to other sources such as wood meal and D-xylose with lower yield.[173]

As a promising renewable reinforcing filler and FR for rigid PU foam, the use of lignin has generated wide acceptance in the last decades due to its outstanding benefits such as readily available, low weight, abundant aromatic structures, substantial hydroxyl groups, and extensive carbon-carbon linkage (bonds).[174,175] The presence of aromatic structure and carbon-carbon linkage in lignin confer high thermal stability, which led to high char formation during combustion.[176,177] This attribute is a vital requirement of FR additives, as char lowers the burning rate of polymers.[178] Therefore, Lu Weimiao et al.[179] developed an eco-friendly intumescent FR (IFR) of lignin and APP and examined its influence on flame retardancy of RPUF. Lignin containing substantial aromatic rings and carbon

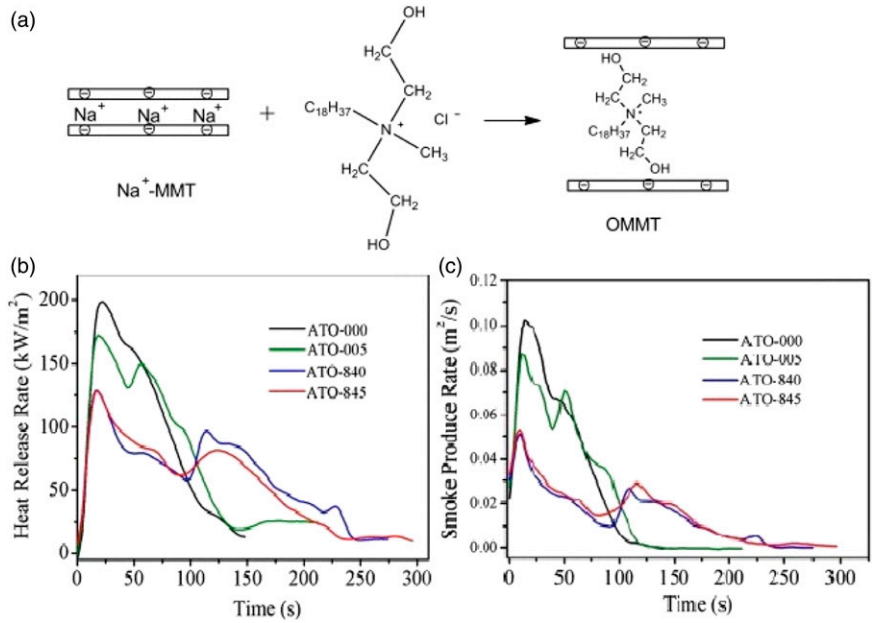

Figure 13. (a) Preparation route of organically modified montmorillonite, (b) HRR curves of pure RPUF (ATO-000), RPUF/OMMT5wt.% (ATO-005), RPUF/APP8wt.%/TPP4wt.% (ATO-840), RPUF/APP8wt.%/TPP4wt.%/OMMT5wt.% (ATO-845) (c) Smoke production rate curves of all tested samples.[168]

contents serves as the carbonizing agent, while APP has a dual function, acid source and swelling agent. It is obvious from Figure 14(a) and (b) that incorporating lignin reduces the mass loss of the foam, and further addition of lignin lowers the mass loss by up to 50% compared to pure RPUF. However, foam containing 15wt% lignin exhibited the best thermal stability.

Similarly, the char yield at 700°C increased from 30.0 wt.% for the pure foam to 33.4% for RPUF/lignin15wt%, an indication that lignin promotes the formation of char in thermal decomposition stages because of its aromatic structure and carbon-carbon bonds. Besides, a noticeable boost was recorded in the flame retardancy of RPUF with lignin/APP; for instance (Figure 14(c)), when the ratio of lignin to APP was 1:5, the foam's LOI value increased above 30%. More so, as shown in (Figure 14(d)), HRR value decreased and the time to peak of HRR was prolonged. The presence of APP during combustion led to the thermo-oxidation of lignin and its dehydration, responsible for the increased in foam's LOI value and APP/lignin interaction results in creation of protective surface barrier, results in the reduced HRR value.

It is common lately to incorporate a small amount of conventional FR into lignin to produce lignin-based FR. In the research of Zhu Haibin et al.,[180] an eco-friendly lignin-based FR was developed by the liquefaction-esterification-salication method. Lignin was chemically grafted using phosphate melamine compound (LPMC) and later blended with

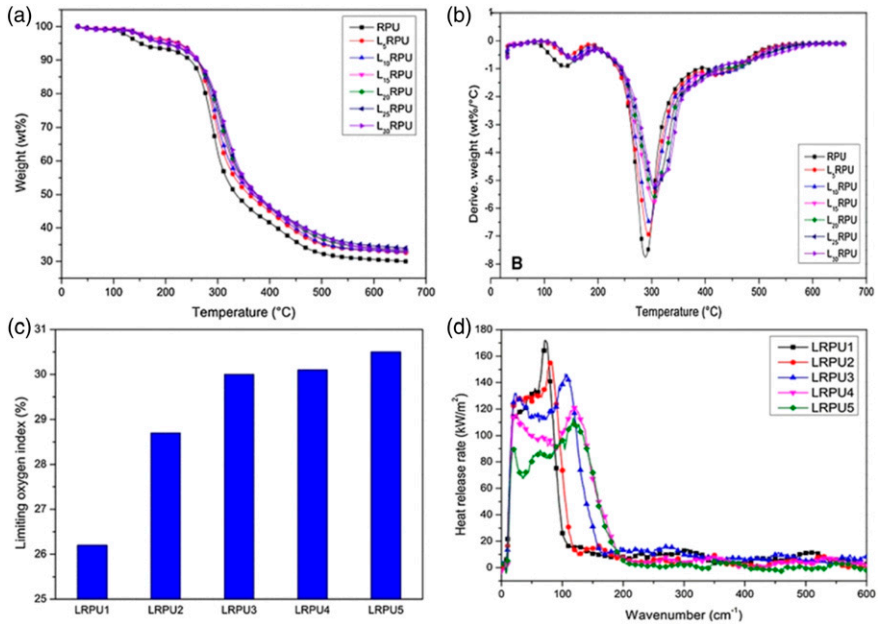

Figure 14. (a and b) TGA and DTG curves of RPU foam and of 5, 10, 15, 20, 25, and 30wt.% lignin in rigid foam in N_2 condition (c) LOI values of LRPU foams with varied lignin to-APP contents, (d) HRR curves with lignosulphonate RPUF of different lignin-to APP contents.[179]

PU foam to enhance the rigid foam's thermal stability and flame retardancy. As shown in Figure 15(a), the addition of LPMC to the foam led to an upsurge in initial and maximum degradation temperature, increasing with LPMC loading, indicating the effective influence of LPMC on thermal stability. The char residue (at 800°C, N_2 atmosphere) of PU/LPMC5wt% was 17.2wt%, and it increased to 24.4wt% for PU/LPMC15wt% compared to neat PU with 14.6wt%, implying that LPMC promoted char formation. As found by the authors, the LOI values of modified foam increase with increasing LPMC add-ons; 26.7% for PU/LPMC15wt.% and 28.3% for PU/LPMC20wt.% from 18.9% for pure PU. Additionally, only these two modified samples passed the UL-94 test, denoting the crucial role of LPMC in curbing the inflammation. In Figure 15(b)(i), the pure PU foam cannot offer a good flame barrier for the underlying polymer, evidenced by its weak and porous inner char compared to PU/LPMC15wt% (Figure 15(b)(ii)) with an unbroken and strong outer and inner layer. The char layer would retard heat alongside mass movement within the gas phase as well as the condensed phase hence restricting the underlying polymers from more attack by heat flux.

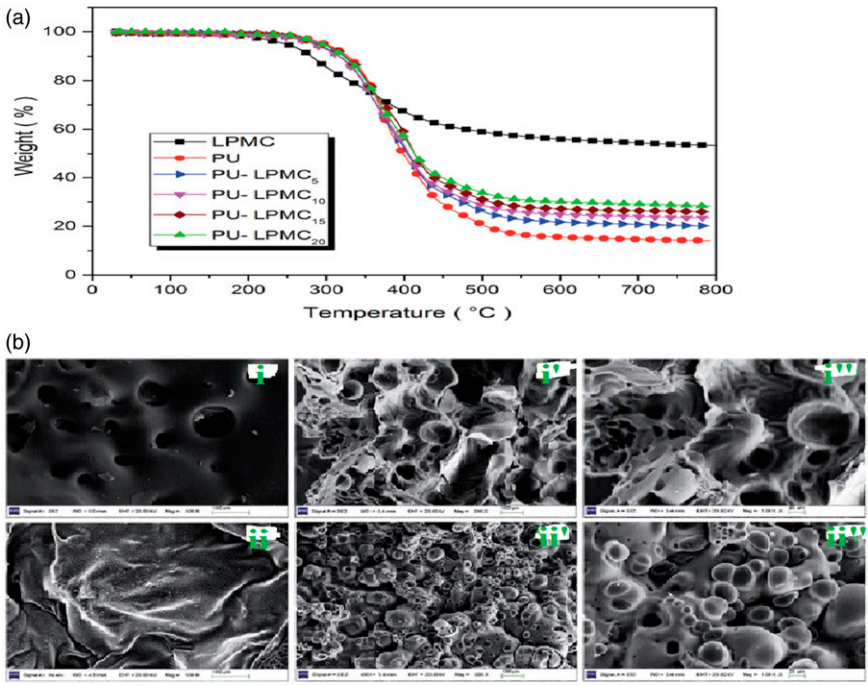

Figure 15. (a) TGA curves of pure PU and PU/LPMC composites (b) SEM of residual char after combustion (i), outer ($i^{/}$) and inner ($i^{//}$) char of neat PU (ii) outer ($ii^{/}$) and inner ($i^{//}$) of residual char of PU/LPMC15wt.%.[180]

Intumescence

Intumescence is a characteristic of some materials that expand, bubble, or rise in volume in the presence of heat. Such materials form a foamed, charred surface barrier to shield the underneath material from heat flux. The charred layer serves as a protective barrier retarding heat and mass movement amongst gas and condensed stages/phases. Furthermore, the mechanism of intumescence is commonly employed to produce flame-retarded materials.[146,181] The demerits of conventional FR, such as halogen-based and metal hydroxide, led to a new generation of FRs called intumescent flame retardants (IFR).[182,183] The creation of multipurpose intumescent fire-retardant coatings has a wide range of practical applications.[184] IFR is widely used as halogen-free additives in RPUF and other polymeric materials, and they offer less smoke, lower toxicity, excellent fire protection, and antidripping properties.[44] Typically, IFR system primarily comprises three constituents: an acid source, then a carbon source (also known as char former), and lastly, a blowing/swelling agent. Notably, the carbon source is vital for charring and material surface isolation from heat and flames. The acid is being used to enhance the compatibility between polymer components and contribute to char formation. The blowing agent breaks down in the presence of heat to allow the charred layer to swell.[185,186] It is important to say

that the precise constituents of intumescent systems should be designed according to the intended polymer matrix.

Furthermore, to additionally increase the flame retardancy of RPUF and lower IFRs cost, IFR systems can be boosted in combination with synergistic agents, this will also be detailed in this section. In brief, this section highlights the recent advances in intumescent RPUF. It would be discussed in three parts: Firstly, we majorly examine the application of the APP-based IFR system. Secondly, this is focused on the surface modification approach of APP-based intumescent RPUF composites. Due to the drawbacks of APP (prone to moisture, poor compatibility, and low water resistance), when incorporated in polymer matrix, especially as a standalone additive. Hence, it's modified to increase its compatibility and material properties (mechanical, flammability). The last part of this section is devoted to other IFR/FR systems of RPUF.

APP-based IFR systems. Ammonium polyphosphate is widely employed in intumescent formulations for different polymers. It is preferred to other FRs because of its unique properties, namely low cost, small loadings required, outstanding processability and quite significantly, its halogen-free, making it eco-friendly.[56,187,188] APP work as an IFR in either condensed or polymer phase via intumescence.[189] These attributes have made APP a commercially famous FR in the design of FR polymers.[146]

For instance, a one-shot free rise technique was used to prepare semi-rigid PU foam with enhanced FR and compressive strength and modulus using a zeolite/APP-based IFR system.[190] In their work, zeolite-treated APP was blended with the foam to produce flame-retardant foam. After this treatment, the LOI values of the foam with 15wt.% zeolite and 60wt.% APP increased from 25.2 to 26.7% (Figure 16), and V- O grade was obtained in the UL-94 test. In contrast, foam with 60wt.% untreated APP only achieved HB-1 grade, indicating the improved fire performance of the foam due to the synergism between APP and zeolite.

Furthermore, the incorporation of 15wt.% zeolite into 60wt.% APP increases the foam compressive strength and modulus, attributed to the heat of reaction being absorbed by the dehydration of zeolite contributing to the preparation of less defective foam.

In Yurtseven (66) research, the authors studied the effect of IFR of APP/melamine (mass ratio of 3:1) incorporation on the compressive strength and fire performance of RPUF. The UL –94 test results revealed that the IFR addition into the foam increased their fire resistance due to synergism between APP and melamine. In contrast, the compressive strength of the foam reduced, and the decrease rose with rising melamine content in IFR attributed to the breakdown of the polymeric and cellular structure due to high loading of APP in the IFR system. However, this study is limited by not reporting the LOI and cone calorimeter test result. Both tests would have provided more insight into the fire behaviour of their foam composites.

In the study by Li Qimin et al., a novel bio-based char forming agent, β-cyclodextrin was employed to surface-treat APP (β-APP) (Figure 17(a)) and the blend incorporated as an eco-friendly IFR into RPUF using the box foaming method.[191] The authors reported that, compared to pure RPUF, the incorporation of 25wt.% β-APP/RPUF at a mass ratio of 3:1 lowered the THR and PHRR values of RPUF composites substantially by 38% and

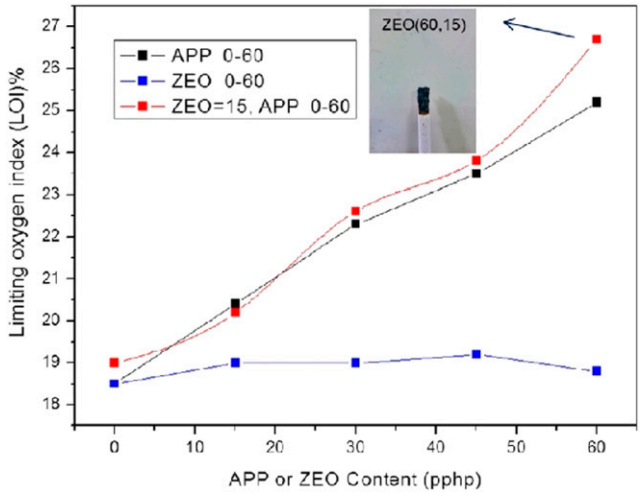

Figure 16. Limiting oxygen index results of semi-rigid PU foams with varied APP or zeolite (ZEO) loading .[190]

44%, respectively; however, for RPUF/APP20wt.% composite, THR and PHRR only reduced by 21% and 32%, respectively. Similarly, 25% β-APP in the composites confers the lowest heat parameters (THR and PHRR) relative to RPUF and APP/RPUF and provides the highest char residue of 35.7%, twice that of pure RPUF (16%) and 28% higher than APP/RPUF composite. This tremendous increase in char formation for β-APP/RPUF composites is ascribed to non-combustible gases (ammonia and water) discharged from β-APP as flame diluent. It is obvious from Figure 17(b) that pure RPUF and modified RPUFs charred rapidly after ignition and arrived their first highest PHRR. However, for 25wt.% β-APP/RPUF compared to other composites, its second and third PHRR lean towards flat and nearly vanish.

Surface modification of APP-based IFR systems. As listed at the beginning of this section, APP drawbacks are responsible for a possible breakdown in mechanical properties and FR efficiency of APP-containing composites mostly during extended use, high temperature and humid environments. This is typically experienced when high APP content ($> 15\%$) is incorporated as a standalone additive.[79,192] More so, APP freely slips out of polymer surfaces amidst processing, this negatively impart fire-retardant potency and all-round effectiveness of composite.[193] Nowadays, microencapsulation technique is among the popular surface modification approach of APP to fulfill the need for flame retardancy of polymers by using diverse surface material.[194,195]

In a study by Yang Yadong et al., gel-silica (Si) was used as the shell material to encapsulate APP (Figure 18(a)) using the sol-gel method.[196] And the emerging SiAPP revealed a reduction in thermal stability at low-temperature level, but at higher temperature ($> 260^{\circ}C$), SiAPP has higher thermal stability than untreated APP, attributed to

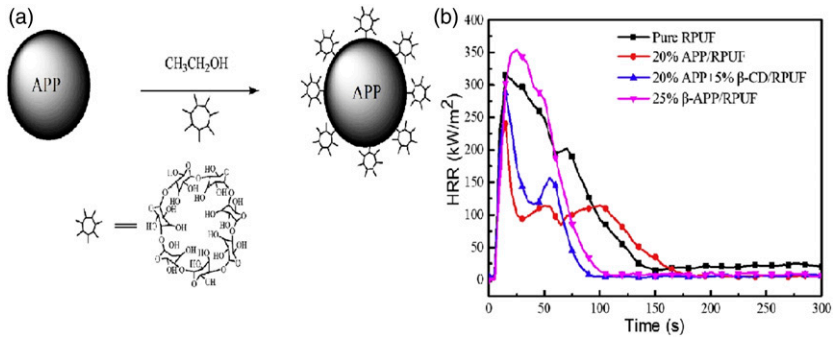

Figure 17. (a) Surface modification of APP (β-APP), (b) heat release rate curves of rigid polyurethane foam and flame-retardant rigid polyurethane foam.[191]

the silica shell addition covering the SiAPP surface that slows down the breakdown of APP (Figure 18(b)). More so, SiAPP and APP were blended in sequence with RPUF to prepare FR RPUF composites. For the RPUF/SiAPP30% (mass ratio of 70:30) system, the LOI value was increased to 22.8% from 18.8% for pristine RPUF, and the V-1 grade was achieved in the UL-94 test. It is obvious from Figure 18(c) that a rapid reduction in LOI value occurred for RPUF/APP30% with an increased period of immersion in water compared to RPUF/SiAPP30%. However, RPUF/SiAPP30% still excelled in the UL-94 test with V- 1 grade, indicating that the gel-silica shell has successfully mitigated APP loss on exposure to moisture, ensuring improved flame retardancy for RPUF/SiAPP30%, attributed to gel-silica moisture and ageing resistance. Furthermore, the thermal stability and compressive strength of the composite was also boosted after the microencapsulation. For instance, the compressive strength of RPUF/SiAPP30% increased by 12.3% relative to RPUF/APP30%

Similarly, Gang Tang et al. employed another popular shell material, melamine-formaldehyde resin, to encapsulate APP (MFAPP) through an in situ polymerization technique.[197] MFAPP was incorporated into RPUF to prepare RPUF/MFAPP composites using one-step water blowing method. However, compared to RPUF/APP (mass ratio of 70:30), RPUF/MFAPP30% composites turned out increased LOI value and excelled in the UL-94 test evidenced by V- 0 grade, a proof of improved flame retardancy for the microencapsulated composites. This could be because the MF shell successfully re-strained the breaking of APP particles. Moreover, it is clear from Figure 19(a) that the pristine RPUF revealed a porous residue with several holes due to the discharge of gas products from the foam in the decomposition process. In contrast, RPUF/APP30% confers improved compactness to the char residue (Figure 19(b)) with small holes, but RPUF/MFAPP30% showed higher char residue with no hole visible (Figure 19c). An indication that it served as a physical layer for oxygen and flammable gases, successfully retarding mass and heat movement and thereby prolonged the combustion process of the underlying polymer. Aside from this, a decent mechanism (Figure 19(d)) was recom-mended by the authors; they opined that the presence of MF resin shell in APP provides

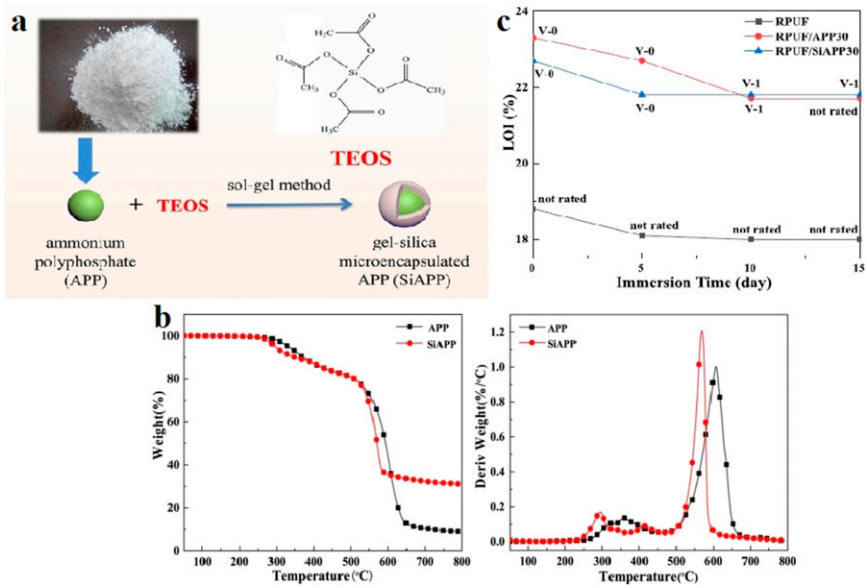

Figure 18. (a) Surface modification of APP with gel-silica (SiAPP), (b) TGA, and DTG curves of APP and SiAPP (c) LOI and UL-94 results of pure RPUF, RPUF/APP30wt.% and RPUF/SiAPP30wt.% at varied immersion time.[196] *Note:* TEOS – Tetraethyl orthosilicate.

improved flame resistance properties for the foam matrix due to the formation of solid char residues that retard the release of mass and heat movement in the fire.

The other approach to boost material properties enhancement of APP in polymer matrix includes modification with a coupling agent and surface-active agent, to enhance APP compatibility with a polymer matrix[198] and incorporation with melamine to increase flame retardancy.[199] In a study by Yajun Chen and co-workers,[198] a surface-active agent was synthesized with γ-aminopropyl triethoxysilane (KH-550) and hexachlorocyclotriphosphazene (HCCP) to modify APP and the resulting M-APP exhibited improved dispersibility and reduced particle size (Figure 20(a) and (b)). The maximum loading of APP and M-APP in PU was 40wt.%. Moreover, the LOI value of the APP-based composite increase by 14.9% relative to pure PU, but surprisingly there was a reduction in LOI value for the PU/M-APP composite. An indication that M-APP did not confer a superior flame retardancy on the foam in the LOI test. However, there was good news, both PU/APP and PU/M-APP composites were successful in the UL-94 test with a V-0 grade. The cone calorimeter results (Figure 20(c)) provides more insight into the flammability behaviour of the composite, with the incorporation of 40wt.% of M-APP, PU/M-APP40% composites attained a decline in PHRR by 51.18% compared to PU/APP40% with a higher PHRR than neat PU. The unusual outcome in flame retardancy can be ascribed to the higher density of PU-APP, change in the cell structure of the foam after APP addition, and poor aggregation of APP particles in the foam. Lastly, PU/M-APP composites produced an improved char residue at the time of burning (Figure 20(d)); it

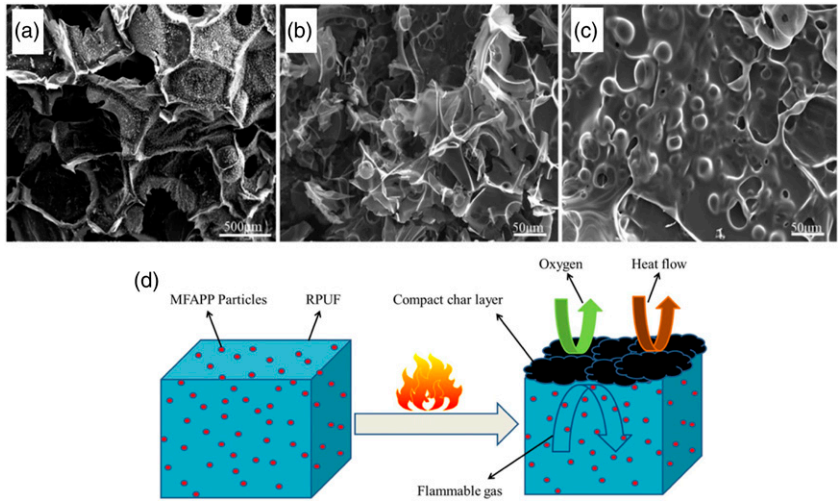

Figure 19. SEM pictures of residual char for (a) pristine RPUF (b) RPUF/APP30wt.% (c) RPUF/melamine modified APP30wt.% (d) Flame retardant mechanism of RPUF/melamine modified APP composite.[197]

formed an intumescent and solid char in combustion, resulting in better flame properties of the composites. For PU/M-APP composites, the outstanding increase in the fire performance of the foam composite can be attributed to the M-APP flame retardation and barrier effect.

In a similar study by Cui Mengjie et al.,[200] a novel triazine-modified APP (TMPD-APP) were synthesized by the reaction between APP and 4,6-dimethoxy-1.3,5-triazine)-2-methyl-propane-1,3-diol (TMPD) through a pre-polymerization technique and then adopted for PU foam matrix. The total loading of APP was maintained at 5wt.%, and the content of TMPD was kept at 6wt.%. In the case of PU/APP5wt.%, incorporating 6wt.% TMPD in pristine PUF not only increased the LOI value (from 18.0% for pristine PUF to 27.0%) but also significantly boosted the antidripping properties of the foam composite. As reported, PUF/APP5wt.% (6wt.% of TMPD) achieved V-0 grade in UL-94 test compared to PUF/APP5wt.% and pristine PUF with V-1 and no rating, respectively. Besides this, TMPD confers a synergistic influence on PUF/APP5wt.% composites, evidenced by the continuous and rigid char layer. The authors opined that the introduction of TMPD in APP promotes the emergence of a robust and solid intumescent char layer and a nitrogen-based gas confined layer, which remarkably protects the underlying composite from heat flux. In another study, a novel and green intumescent flame retardant (CWAAPP) was synthesized by Fubin et al.[201] based on the reaction between APP and cellulose whisker (CW). It was documented that the incorporation of 16.7wt.% CWAPP into RPUF/CWAPP16.7% improved the LOI value of the composite to 24.5% compared to 21.0% and 16.5% for RPUF/APP16.7%, and neat RPUF, respectively. A similar trend was recorded in the UL-94 test, as only RPUF/CWAPP16.7wt.% passed the test with a V-

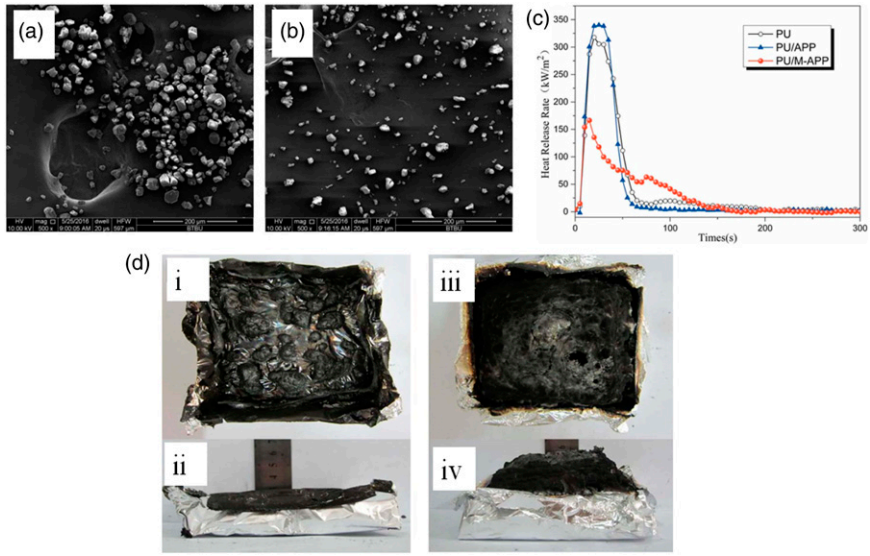

Figure 20. SEM images of (a) APP (b) M-APP, (c) HRR curves of virgin PU, PU/APP and PU/M-APP (d) Digital images of cone calorimeter residue of (i-ii) PU/APP, (iii-iv) PU/M-APP.[198]

0 grade before and after water immersion. In addition to the flame retardancy, the water resistance and compressive strength of this cellulose whisker-based composite showed considerable improvement at the same FR loading compared to RPUF/APP composite. The excellent influence of cellulose whisker on the properties mentioned above can be ascribed to its good dispersion on the surface of APP and the uniform structure of nanoscale size cellulose whisker relative to conventional cellulosic fibres.

Heng Zhu et al.[202] investigated how dimethyl methyl phosphonate (DMMP) modified APP (DMMP-APP) influenced the flame retardancy, mechanical properties as well as the thermal stability of RPUF composites. By incorporating 10wt.% each for DMMP and APP in RPUF, the LOI value of the composite substantially improved to 29.1% from 18.0% for the pure RPUF, indicating that APP and DMMP offer a synergistic influence on the fire retardancy of RPUF. However, by increasing DMMP loading to 20wt.% in RPUF/APP10wt.%, there was no further increase in their LOI value; instead, a decrease was recorded, which was close to the LOI value for RPUF/APP10w.%. More so, the authors found from cone calorimeter results (Figure 21(a) and (b)) that the PHRR and THR values of RPUF/APP10%/DMMP10% were notably reduced by 10.3% and 22.4%, respectively, compared to pure RPUF. The joint use of APP and DMMP in the composites leads a higher char residue (Figure 21(c)) based on the TGA test result; this can be credited to the generation of a ceramic-like char layer that confers higher protection for the underlying polymer in combustion. As a reference, compared to RPUF and that with APP10wt.%, RPUF/APP10wt.% (plus DMMP10wt.%) compressive strength increased by 12.6% and a

further rise in DMMP content to 20wt.% increased the composite compressive strength by 19.9%; this can be credited to DMMP cellular structure.

Meanwhile, to further explore the effect of the APP/DMMP FR system, Xu Wei et al.[203] incorporated three nanostructured additives; montomorilite (MMT), Zinc oxide (ZnO), and zeolite in sequence into RPUF/APP/DMMP composites and examined their influence on the fire retardancy of the RPUF ternary system. In their case, the total loading of APP and DMMP were maintained at 8wt.%. The results revealed that the addition of 5wt.% of zeolite with RPUF ternary system (RPUF/APP8%/DMMP8%) confer the highest LOI value (29.5%) relative to other samples at the same nano additives content (Table 3). It is opined that zeolite has better interactions with APP/DMMP binary system due to its unique porous structure and large surface area. Moreover, the cone calorimeter results still favoured zeolite with 91 kW/m^2 PHRR compared to 119 kW/m^2 and 125 kW/m^2 for the ternary system (plus 5wt.%MMT) and ternary system (plus 5wt.% ZnO), respectively. This outcome can be ascribed to a special insulation efficiency of the char layer with the incorporation of zeolite. Evidently, the PHRR of the ternary system was 56% and 26% lower than the pristine RPUF and RPUF/APP/DMMP ternary system, further signifying the appreciable increase in fire behaviour of the RPUF composite. Table 3 provides the summary of the fire performance of modified APP-based FR RPUF.

EG

Because of its metal and non-metal characteristics, graphite is a popular choice. Whereas the thermal, electrical, and conductivity are all pretty high, as is the flame retardancy, the carbon in graphite is deemed elastic although lacks elasticity.[204] Graphite has proven record of enhancing several properties of polymer composites including flame resistance, mechanical toughness,[205] thermal conductivity, thermal stability[206] and leakage-proof especially in packaging mediums.[207]

Expandable graphite, a derivative of graphite has found considerable acceptance for the cellular polymers such as RPUF and other polymers, namely polypropylene[208] and poly (methyl methacrylate).[209] EG is prepared by chemical treatment of natural graphite and can swell up to 150–300 times in volume at elevated temperatures, changing from crispy to worm-like and later becoming a slack, curled and expanded surface structure.[210] EG low price, strong condensed-phase FR mechanism, mechanical reinforcement attributes, and high exchange surface are responsible for its popularity as an efficient platelet-like carbon-based material, making it useful as a FR in polymers.[96,211,212] The FR system/phenomenon of EG entails enclosing sulfuric acid within layers of graphite. When it is heated to high temperatures (about 200°C), EG starts to expand through the decomposition of the graphite slice. Afterwards, the expanded graphite produces a worm-like layer to protect the surface of the polymer matrix, thereby isolating heat and oxygen.[213,214] Based on past studies evidenced by (Table 4), it is clear that EG alone exhibits low FR potency for RPUF.[215] Consequently, to design a vastly efficient FR

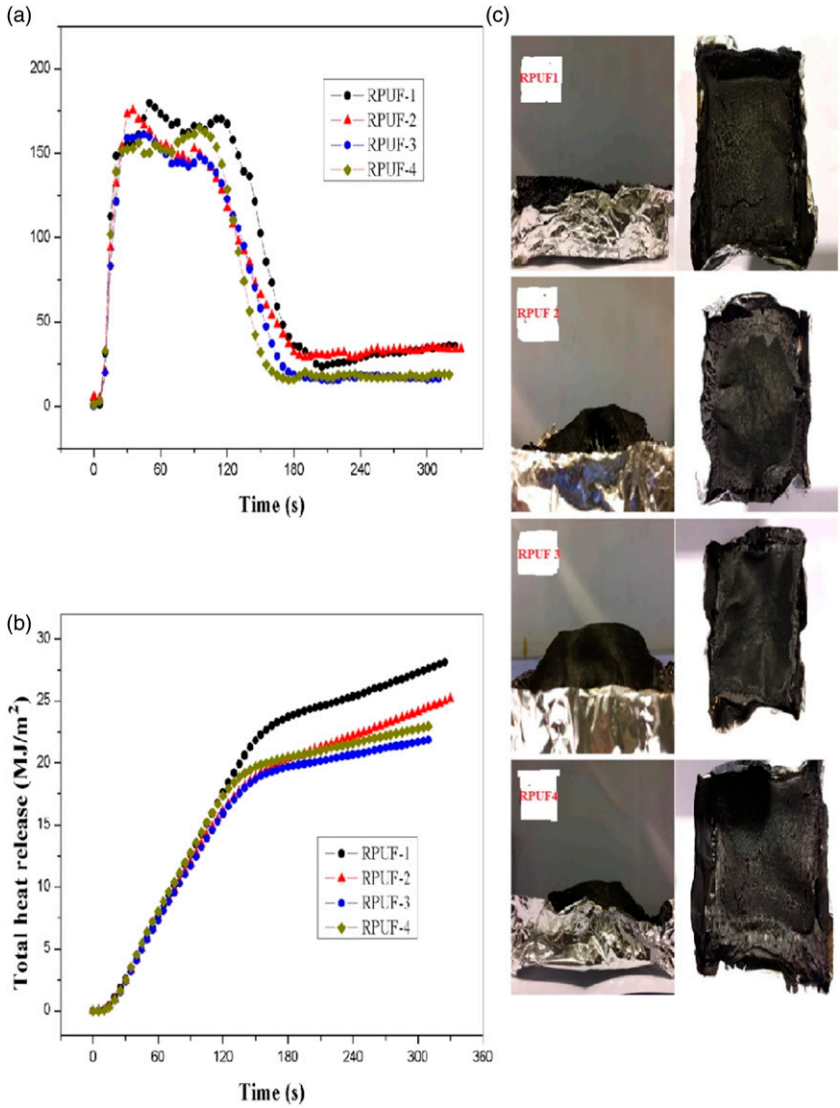

Figure 21. Cone calorimeter results (a) HRR of pure RPUF (RPUF1) and RPUF 2 (with 20wt.% APP), RPUF 3 (with 10wt.% of APP and DMMP), RPUF 4 (plus 20wt.% APP and 10wt.% DMMP) (b) THR of RPUF 1 and modified samples (RPUF 2, RPUF 3 and RPUF 4) (c) Digital pictures of residual char of RPUF 1 to RPUF 4.[202]

system, it is very vital to introduce other components into the EG system to enhance the fire resistance of RPUF. Recently, the most promising methods proposed are (a) microencapsulation of EG; (b) incorporation of synergistic agents; (c) hybridization of EG with other FR systems.

Table 3. Fire performance of modified APP-based FR and IFR systems.

APP content (wt.%)	Modifying agent and content (wt.%)	Modifying method	LOI (%)	UL-94 grade	Cone calorimeter result				REF.
					Heat flux (KW/m^2)	Δ PHRR (%)	Δ THR (%)	Char (%)	
15.0	Gel-silica,15.0	Sol-gel	22.8	V-1	—	—	—	—	196
15.0	MF, 15.0	Insitu polymerization	21.3	V-0	—	—	—	—	197
20.0	KH-550 + HCCP, 20.0	Coupling	23.1	V-0	50	−47.63	−32.83	37.9	198
5.0	TMPD, 6.0	Pre-polymerization	27.0	V-O	35	−65.69	−39.81	10.7	200
—	APP + CW, 16.7	—	24.5	V-O	—	—	—	—	201
10.0	DMMP, 10.0	—	29.1	—	35	−10.3	22.4	27.4	
8.0	DMMP, 8.0+ Zeolite, 5.0	—	29.5	—	50	−56	−26	16.3	202
	DMMP, 8.0+ MMT*, 5.0	—	28.5	—	50	−42.5	−18	24	202
	DMMP, 8.0+ ZnO*, 5.0	—	28.0	—	50	−39.6	−14	18.5	202

Note: TMPD = 4,6-dimethoxy-1,3,5-triazine)-2-methyl-propane-1, 3-diol; MF - Melamine-formaldehyde resin; KH-550 - y-aminopropyl triethoxysilane; HCCP - hexachloro cyclo triphosphazene; DMMP - dimethyl methyl phosphate; CW – cellulose whisker.

Microencapsulated EG based IFR/FR systems. It has been found from previous studies that EG would pulverize when incorporated into RPUF. Hence, to remedy the likely decline in mechanical properties, leading to the decrease of the flame retardancy of RPUF. Incorporating encapsulated EG in RPUF has proven to be an efficient approach to improve their mechanical and fire performance.[216] Through microencapsulation technology, there is an increased dispersion of EG particles within the RPUF without any negative effect on the cellular foam structure.[214,217]

In the study by Yintao Wang and co-authors,[218] magnesium hydroxide (MH) nanoparticles was the shell used to microencapsulate EG (EG@MH) (Figure 22(a)) by

Table 4. Fire behaviour of EG based flame retardant or IFR systems in conjunction with various synergistic agents.

				Cone calorimeter result				
EG content (wt.%)	Synergist content (wt.%)	LOI (%)	UL-94 grade	Heat flux (KW/m^2)	Δ PHRR (%)	Δ THR (%)	Char (%)	REF.
8.0	PPAS, 0.6	29.8	V-O	50	−45	−28	—	223
5.0	IL, 5 + DPES, 10	—	V-O	35	−60	−45	24.1	210
10.0	GP,5	32.7	—	50	−54.17	−38.5	23.1	213
14.0	DOPO-HQ,1	28.5	V-O	35	−54.58	−4.42	19.4	39
8.0	BH, 18	33	—	50	−66.5	−23.35	35.4	55
5.0	Pyrogenicsilica,1	—	—	35	−71	−21	31.8	224
	Pyrogenicsilica,1 + IL, 0.33	—	—	35	−70	−19	27.6	224
12.0	Zr-AMP, 3	30.5	V-O	35	−39.7	−54.5	51.7	225
8.0	EMD, 18	31.3	—	50	−55.4	−41.5	30.5	226
15.0	PEPA, 5	31.9	—	50	−65	−37	40.0	227

Note: PPAS - phenylphosphonic aniline salt; DPES - silane agent; GP - guanidinium phosphate; DOPO -HQ - 10-(2-5-dihydroxyphenyl)–10 hydro-9-oxa-10-phosphorylphenanthrene-10-oxide; BH - [bis (2-hydroxyethyl) amino]-methyl-phosphonic acid dimethyl ester; IL - 1-butyl-3-methyl-imidazole phosphate; Zr-AMP - zirconium amino-tris-(methylene phosphate); EMD - 5-ethyl-2-methyl-1,3,2-dioxaphosphorinan-5-yl) methyl dimethyl phosphonate P-oxide; PEPA - pentaerythritol phosphate.

heterocoagulation method and it was found to be an efficient route in flame retarding RPUF/EG@MH composites. Indeed, compared to the RPUF/EG/MH composite (the total content of FR was 11.5wt.%), the LOI value of RPUF/EG@MH increased to 32.6% from 29.8%, and this was 10.4% more than that of neat RPUF. An outcome ascribed to the substantial rise in EG expansion enhanced by the shell of MH (Figure 22(b)). EG tends to expand at elevated temperatures and produce a worm-like thermal insulation barrier that inhibits heat transfer. Similarly, compared to RPUF/EG/MH, the T_{max} of RPUF/EG@MH composite was enhanced by 13°C, 3°C, and 13.2°C, respectively, in the three stages of decomposition. However, the char residue of both composites was almost similar (8.6% and 8.9%). Based on TG results (Figure 22(c)), it was found that EG@MH particles lowered the degradation rate of the second stage above that of EG + MH particles. Moreover, the cell structure and storage modulus of the encapsulated composite was also enhanced.

In another study, poly (glycidyl methacrylate) (PGMA), a reactive polymer shell, was employed to microencapsulate EG (EG@PGMA) through an in situ emulsion polymerization method.[217] It was demonstrated that the PGMA shell remarkably boosts the expansion of EG particles by almost 67%, indicating an improved interaction (both physical and chemical) between EG and RPUF. Besides, compared with RPUF/EG10wt.% composite, RPUF/EG@PGMA10wt.% composite LOI value increased to 27.5% from 25.5% and it excelled in the UL-94 test with V-0 grade, unlike RPUF/EG@PGMA10wt.% with V-1 grade. This improved flame retardancy for the encapsulated

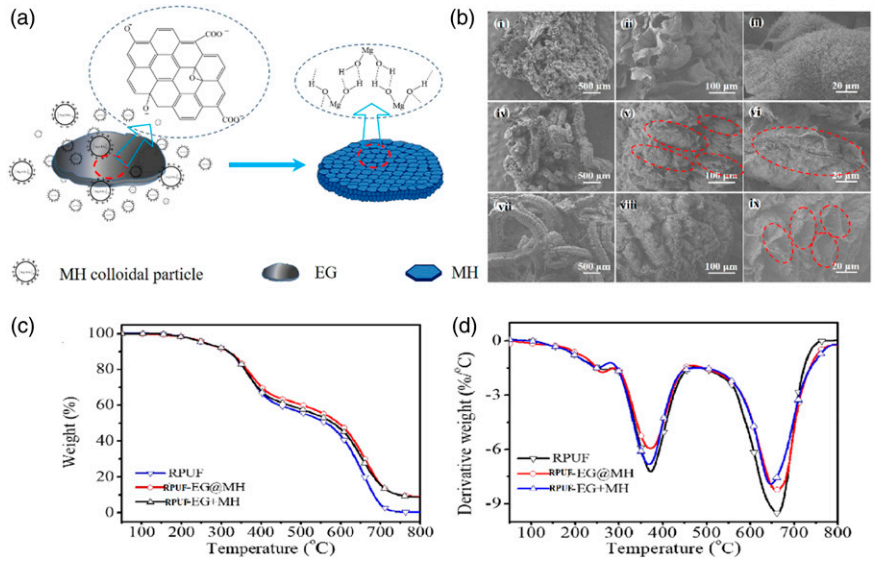

Figure 22. (a) Schematic of encapsulated EG by magnesium hydroxide particles, (b) SEM pictures of residual char from LOI test (i-iii) virgin RPUF (iv-vi) RPUF-EG@MH (vii-ix) RPUF-EG+MH (c) TG, (d) DTG curves of virgin RPUF, RPUF-EG@MH and RPUF-EG+MH under air condition.[218]

composite is credited to EG@PGMA having greater expanded volume, enabling the formation of a more carbonaceous layer during combustion. However, there was a decline in compressive strength and modulus for the RPUF composites compared to pure RPUF. However, RPUF/EG@PGMA composite performs better than RPUF/EG composite, ascribed to better physical interaction resulting from higher wettability of EG@PGMA with RPUF.

EG/synergistic agents in FR/IFR RPUF. Synergistic agents function on the synergism phenomenon; this refers to the combined effect of two or more additives (FR) being stronger than that based on the equivalence of individual effect.[219] Hence, the synergistic material would regulate the physical such as viscosity, thermal conductivity, and expansion and chemical like thermal stability and carbonization, among other properties of the FR/IFR systems.[146,220] It has been found that the fire resistance together with the LOI value of RPUFs can be enhanced by combining EG with other FR (as a synergist).[221] Recently Liu et al.[222] combined aluminum hypophosphite (AHP) with EG as a hybrid FR into RPUF and examined the composites morphology, burning behaviour, and thermal stability. From SEM images (Figure 23(a)) pure RPUF had a moderately even size with a smooth appearance and cell diameter compared to reduced regularity in cell size for RPUF/EG 30php or RPUF/AHP 30php (Figure 23(b) and (c)). The stickiness of the reaction system was raised by either EG or AHP, resulting in unequal stresses in each path during cell formation. However, for RPUF/EG15/AHP15 composite (Figure 23(d)), cell's damage trend became more severe, and the cell's diameter shrank even more. An indication of

poor compatibility amongst EG, AHP and foam matrix. LOI value of rigid foam with hybrid FR (AHP12/EG18) was the highest (27.0%) compared to 18.8%, 23.6%, and 25.6% for pure rigid foam, RPUF/AHP30 and RPUF/EG30, respectively. Signifying synergistic effect amongst AHP and EG in the foam composites. From TG and DTG results (Figure 23(e) and (f)) Combined addition of AHP and EG lowered the decomposition temperature of the composites as the amount of EG increases and highest char residue (at 700°C) of 22.4wt.% was obtained at AHP15/EG15 in the composite compared to pure RPUF (16.0wt.%). Implying that blending AHP and EG improved the thermal stability of rigid foam composites at high temperatures.

In the study by Acuna Pablo et al.,[223] phenyl phosphonic-aniline salt (PPAS) confer a synergistic FR effect in RPUF/EG composite. It was the incorporation of 8wt.% EG into RPUF that boosted the LOI value of the composite to 29.2% compared to 19.2% for virgin RPUF, and UL-94 V-0 grade was realized. More so, the replacement of only 0.6wt.% of EG by PPAS allowed excellent FR efficiency for RPUF/EG8wt.% evidenced by their higher LOI value (29.8%) and V-0 grade was maintained. Particularly, the cone calorimeter result revealed that compared to virgin RPUF, the PHRR of RPUF/EG8wt.% and RPUF/EG8wt.%/PPAS0.6wt.% decreased by 28% and 45%, respectively. An affirmation of synergistic effect amongst EG and PPAS, boosting the fire retardancy of the RPUF composites. Lastly, the authors proposed a flame-retardant mechanism; therein, a combination of EG and PPAS increased the char formed, thereby improving the composite's fire performance. Lastly, compared to RPUF/EG8wt.%, the compressive strengths of the composites were increased by 10% when EG was replaced with 0.6wt.% PPAS. It was found that PPAS in EG increased the density as well as the closed cell rate of the composite due to the rigid phenyl groups present in its chemical structure.

Furthermore, a new hybrid IFR system was developed by combining ionic liquid (IL), EG and a silane agent (DPES) at a mass ratio of 1:1 (for IL-EG and DPES), and this was employed in boosting the fire retardancy of RPUF.[210] The IL used is of 1-butyl-3-methylimidazole phosphate and DPES is an IFR prepared by the reaction of diphenyl phosphine chloride (DPCP) and 3-amino-propyltriethoxysilane (APTES). Compared to pristine RPUF, RPUF/IL-EG10wt.% (plus 10wt.% DPES) composite PHRR and THR values decrease by 60% and 45%, respectively. More so, increasing the loading of either of IL or DPES above 10% in the IFR system did not translate to a further reduction in PHRR and THR of the composites. An indication that 10wt.% of each is the optimum value for best performance. IL-EG decompose and swell during combustion, while DPES promote the emergence of an intumescent char layer, acting as a shield to the beneath polymer. Similarly, incorporating their optimum value of IL-EG and DPES in RPUF increased the compressive strength of the composite by 30.2% compared to pristine RPUF. The incorporation of DPES to IL-EG promotes better adhesion of IL-EG and RPUF, a factor responsible for increased mechanical performance. Recently, Chen Xiao et al.[213] explored the synergistic ability of a novel phosphorous compound, guanidinium phosphate (GP), on EG FR RPUF. In addition, hollow glass microspheres (HGM) were employed to improve the tensile and compressive strength of the RPUF composite. Incorporating EG and GP remarkably increased the composite LOI value to 32.7% from 21.1% for neat RPUF, ascribed to the production of a char layer that worked as physical barrier to impede

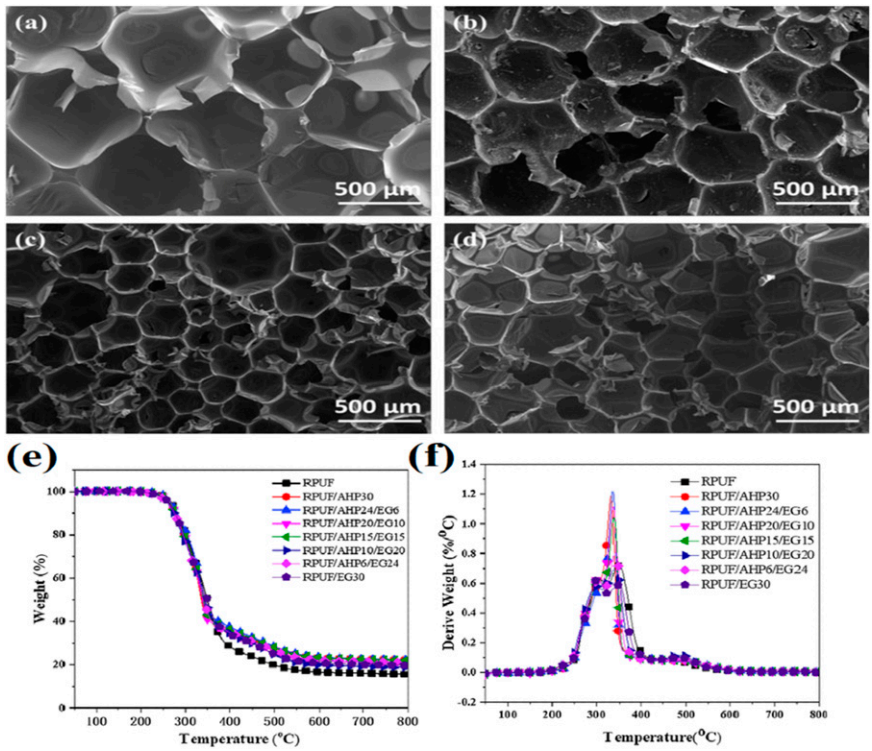

Figure 23. SEM pictures (a) pure RPUF, (b) RPUF/EG30php, (c) RPUF/AHP30php, (d) RPUF/EG15php/AHP15php (e) TG and (f) DTG results of pure RPUF and its composites.[222] ***Note**: php - part per hundred polyols.

the passing of heat and oxygen. Similarly, the co-addition of GP and EG (mass ratio of 2: 1) is responsible for a 54.17% decrease in PHRR, lowest carbon dioxide release, and the highest char residue of the composite compared to neat RPUF. GP acted as a crosslinker promoting the intumescent char layer responsible for the ceramic-like barrier to heat and oxygen. An indication of improvement in flame retardancy of the foam composite. Lastly, the presence of HGM in EG/GP FR system increased the composite mechanical properties, increasing with HGM loading. In the research of Shi Xingxing et al.[39] a new phosphorus-based FR (DOPO-HQ) was synthesized for PU foam and introduced into the foam backbone structure as a bi-phase FR with EG. Prior to this study, 10-(2-5-dihydroxy phenyl)–10 hydro-9-oxa-10-phosphorylphenanthrene-10-oxide (DOPO-HQ) has been an efficient FR in epoxy and other thermoplastics due to its good resistance to water and oxidation and high thermal stability. With this in mind, DOPO-HQ in PU/EG enhanced the composite flame retardancy with no structural change. For instance, PU/EG15wt.% presents an LOI value of 30.5% but replacing some part of EG with 1wt.% DOPO-HQ, the composite LOI value was 28.5% although it performed better than virgin PU (19.2%). Both composites (PU/EG15wt.% and PU/EG14wt.%/DOPO-HQ1wt.%) excelled in the

UL-94 test with a V-0 grade. DOPO-HQ in EG enables the reduction of EG content in the composite. EG's high loading is sometimes required to achieve increased flame retardancy but a demerit for mechanical performance and industrial processing of the composite. From cone calorimeter results (Figure 24(b) and (c)) compared to virgin PU, PU/EG14wt.%/DOPO-HQ1wt.% composite PHRR and THR decrease by 54.58% and 4.42%, respectively. Aside from this, the authors proposed an important bi-phase FR mechanism. They opined that incorporating DOPO-HQ in EG helped the formation of worm-like solid char layer (Figure 24(a)); this considerably delays the release of heat and combustible gas.

Similarly, the effect of bi-phase FR of EG and [bis (2-hydroxyethyl) amino]-methyl-phosphonic acid dimethyl ester (BH) on the compressive strength and flame retardancy of RPUF/EG/BH composite were investigated.[55] The composite was fabricated through a box-foaming method. The total loading of EG was maintained at 8wt.% while BH ranged from 10–18wt.%. Incorporating 8wt.% EG and 18wt.% BH as standalone FR in RPUF gives LOI value of 24.3% and 24.7%, respectively. However, the joint use of EG and BH (8wt.% and 18wt.%) remarkably increased the LOI value of RPUF/EG/BH composite to 33.0% (the best performance), indicating the synergistic effect of BH in RPUF/EG composite due to its superior phosphorus content and better dispersibility with isocyanate to produce RPUF. Based on the LOI test, pure RPUF presents a thin char residue relative to RPUF/EG8wt.%/BH18wt.%, which had a thicker char residue. It is notable that char amount and quality are important factors responsible for improved flame retardancy of composite. In this case, the thicker char layer retards the heat from extending to the beneath polymer. From cone calorimeter test, compared to pure RPUF, the PHRR and THR of RPUF/EG8w.%/BH18wt.% composite was substantially reduced by 66.5% and 23.35%, respectively. The reduction in PHRR was 10% higher than that of RPUF/EG8wt.% and RPUF/BH18wt.% composites. Similarly, the co-addition of EG/BH enhanced the composite char yield to above 30%, affirming their synergistic effect. The compressive strength of the RPUF composite increased marginally with increasing BH loading, BH16wt.% loading on RPUF/EG8wt.% was reported as the best result with a value of 0.28Mpa compared to pure RPUF with 0.20Mpa. Recently, Strakowska Anna et al. [224] examined the effect of ionic liquid (IL) and pyrogenic silica on the fire retardancy as well as the mechanical properties of RPUF/EG composites. The IL is synthesized from 1-ethyl-3-methylimidazolium tetrafluoroborate. Based on cone calorimeter test results, compared to neat RPUF, RPUF/EG5wt.% composite PHRR and THR values significantly lowered by 67% and 18%, respectively. Incorporating only 1wt.% silica into the composite further lowered the PHRR and THR values by 71% and 21%, respectively. Moreover, the addition of 0.33wt.% of IL into RPUF/EG5wt.%/silica1wt.% decreased the PHRR and THR values by 70% and 19%. It can be opined that the presence of silica supports the creation of a more thermal barrier and ceramic-like char layer, thereby protecting the underlying polymer. The joint use of EG and silica (5wt.% and 1wt.%) in RPUF increased their compressive strength by 37% (parallel direction) and 25% (perpendicular direction), and the increase was 10%, 16% and 36%, for hardness, flexural and impact strength, respectively. The improved mechanical performance can be credited to

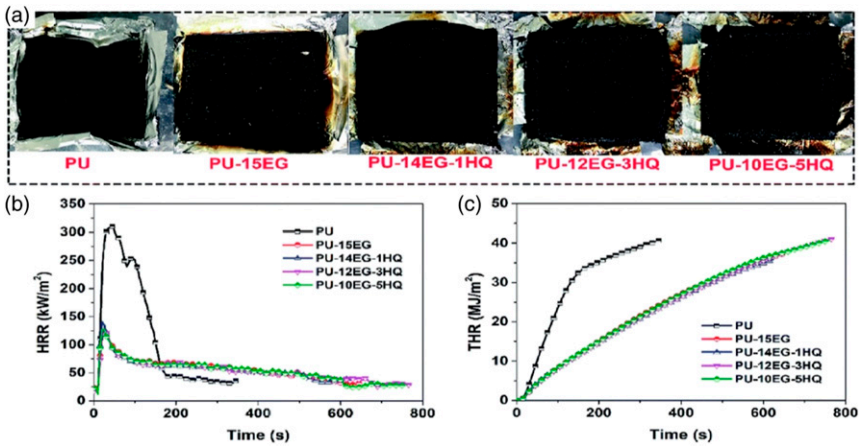

Figure 24. (a) Digital images of all samples char residue after cone calorimeter test (b) HRR curves of pure PU, PU/EG15wt.%, PU/EG14wt.%/DOPO-HQ1wt.%, PU/EG12wt.%/DOPO-HQ3wt.%, and PU/EG12wt.%/DOPO-HQ5wt.% (c) THR curves of all tested samples (pure PU and foam composites).[39]

the increased loading of polar urea groups, producing hydrogen bonds that stiffen the foam structure.

Similarly, Lei Liu et al.[225] synthesized a nano-zirconium amino-tris-(methylene phosphate) (Zr-AMP); a new phosphorus-nitrogen FR. Zr-AMP was prepared by reacting amino trimethylene phosphonic acid (AMP) with zirconium oxychloride octahydrate ($ZrOcl.8H_2O$). Afterwards the prepared Zr-AMP were blended with EG, and their synergism on the fire retardancy and compressive strength of RPUF examined. The total loading of Zr-AMP was 0.5,1,3, and 5wt.%, for EG the loadings were 10,12,14,14.5, and 15wt.%. Incorporation of 3wt.% Zr-AMP in RPUF/EG12wt.% composite substantially increased their LOI value to 30.5% from 25.5% for RPUF/EG15wt.% and only 19% for neat RPUF., The mass ratio of 4:1 for EG/Zr-AMP, confer the highest LOI value. RPUF/EG12wt.%/Zr-AMP3wt.% composite passed the UL-94 test with V-O grade relative to RPUF/EG15wt.% with V-1 grade. Moreover, 3wt.% Zr-AMP in RPUF/EG12wt.% composite significantly lowered the THR and PHRR by 54.5% and 39.7%, respectively. Again, this represents the best performance for improved flame retardancy compared to other RPUF composites. The presence of EG was responsible for the char layer formed, promoting a physical barrier, and Zr-AMP created a fire-retardant effect. An affirmation of the synergistic FR effect of Zr-AMP and EG in neat RPUF. For compressive strength, there was an increase for RPUF/EG10wt.%/Zr-AMP5wt.% (0.31Mpa) and RPUF/EG12wt.%/Zr-AMP3wt.% (0.28Mpa). The co-addition of EG and Zr-AMP boosted RPUF cell density, increasing foam density, which led to increased compressive strength. Replacing some parts of EG with Zr-AMP, minimize the negative influence of high loading of EG on RPUF structure and thus increase RPUF uniformity.

In the study by Li Linjie et al.,[226] 8wt.% EG was incorporated into RPUF to flame-retard RPUF composite. Compared to virgin RPUF, RPUF/EG8wt.% composite LOI value increased to 25.6% from 19.6%. and the composite PHRR and THR remarkably reduced by 39.5% and 18.5%, respectively based on the CC test result. Later, a non-reactive phosphonate FR of 5-ethyl-2-methyl-1,3,2-dioxaphosphorinan-5-yl) methyl dimethyl phosphonate P-oxide (EMD) was blended with EG to develop hybrid-FR RPUF composite through water blown foaming method. The simultaneous addition of EG and EMD (8wt.% and 18wt.%) greatly raised the LOI value of the foam composite to 31.3% from 25.6% for RPUF/EG8wt.% and PHRR and THR notably decreased by 55.4% and 41.5%, respectively. The authors reported increased compressive strength with the presence of EMD in the RPUF/EG composite. For instance, 18wt.% EMD in RPUF/EG8wt.% has a value of 0.30Mpa relative to virgin RPUF with 0.28Mpa. Lastly, they proposed a flame-retardant mechanism, EMD effected a gas-phase FR influence due to the release of PO fragments, while EG effected a condensed phase FR influence. Hence, a good combination of EG and EMD would confer a superior char layer as well as a physical barrier on the RPUF matrix in combustion.

For Wang Shijin et al.[227] they prepared a flame retarded RPUF composite through a similar method as Li Linjei et al. However, they use different phosphate-based FR to lower the loading of EG and further strengthen its FR effect in the RPUF composite. In their study, pentaerythritol phosphate (PEPA) was blended with EG and their synergistic influence on the fire behaviour of pristine rigid PU foam were investigated. The loadings of EG and PEPA were 10, 15, and 20wt.% and compared to pristine RPUF, 20wt.% of EG/PEPA (mass ratio of 3:1) in RPUF increased the composite LOI value to 31.9% from 19.2%. Similarly, based on the CC test result (Figure 25(a)), PHRR and THR greatly decrease by 65% and 37%, respectively. For RPUF/PEPA15wt.% and RPUF/EG15wt.% composites, their LOI values were 22.6% and 28.8%, their PHRR and THR values were higher than that of 20wt.% of EG/PEPA in RPUF but lower than pristine RPUF. The incorporation of EG/PEPA increased the charring effect of pristine RPUF (Figure 25(b) and (c)). For instance, residual char of RPUF/EG/PEPA increased to 40% compared to 1.53% for pristine RPUF and 12.4% for RPUF/PEPA15wt.%. By this outcome, the reinforced residual char provided a superior flame retardancy to pristine RPUF compared to other composites formed incorporating either PEPA or EG alone. Table 4 provides a summary of burning behaviour of EG based FR system in conjunction with various synergistic agents.

Current trends in FR strategies for RPUF

In the last 2 years there have been development of new approaches to enhance the FR efficacy of RPUF, among these are the use of steel slag waste (SSW). Steel slag (SS) is a by-product from the steel production, with yearly output in the United States reported at 10–15 million tons.[228] The major chemical constituents of SS are ferric oxide (Fe_2O_3), calcium oxide, silica, manganese oxide and aluminium oxide.[229] Ferric oxide (Fe_2O_3), on the other hand, has been shown to aid charring by catalyzing crosslinking reactions during the polymer breakdown process.[230] In a recent study, Gang Tang et al.[231] improved the

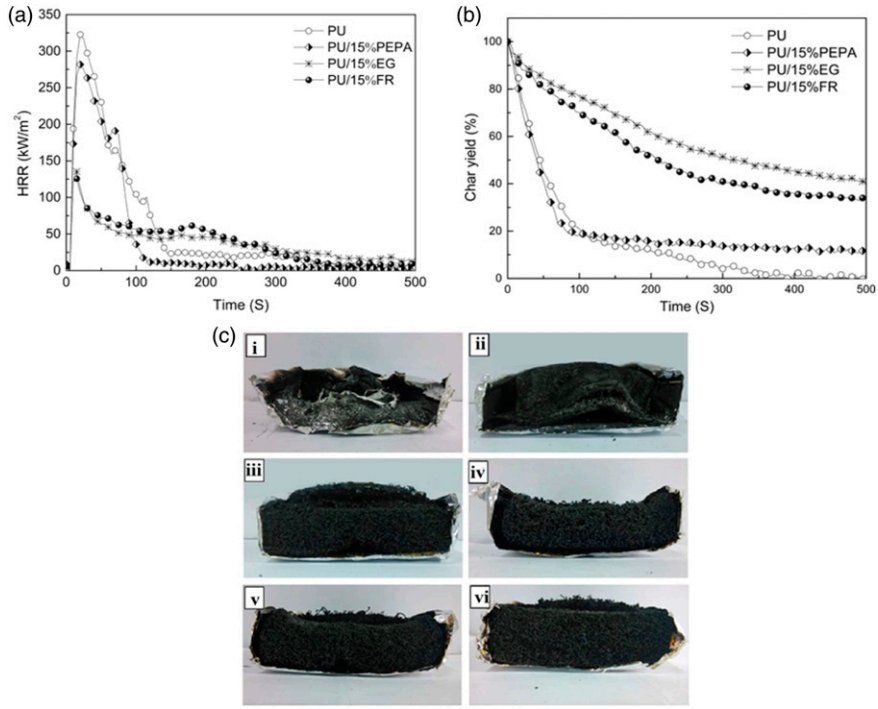

Figure 25. (a) Heat release rate and (b) mass loss curves of neat RPUF, RPUF/PEPA15wt.%, RPUF/EG15wt.%, and RPUF/EG + PEPA15wt.% (c) Digital images of char residue of all cone calorimeter tested samples (i) neat RPUF (ii) RPUF/PEPA15wt.% (iii) RPUF/EG15wt.% (iv) RPUF/EG + PEPA10wt.% (v) RPUF/EG + PEPA15wt.% (vi) RPUF/EG + PEPA20wt.%.[227]

compatibility of SS and boosted their FR effectiveness with RPUF by modifying SS with 9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) through the sol-gel process route (Figure 26(a)). Modified steel slag (mSS) was blended with EG as FR system for RPUF. Incorporating 10wt.%mSS/10wtEG into RPUF confer the highest LOI value (24.0%) and the composites passed the UL-94 test compared to pure RPUF with 17.5%. THR and PHRR for these composites reduced by 47% and 55%, respectively. The inclusion of phosphorus-silicon compound in modified steel slag may have contributed to these results by enhancing charring, which produced a superior barrier effect in burning.

In a similar study by the same research group,[232] SSW was blended with melamine pyrophosphate (MPP) to enhance the fire behaviour of RPUF. MPP and SS added together resulted in stronger fire-resistant qualities than either MPP or SS only. The LOI value for RPUF/2.5 wt% SS/7.5 wt% MPP improved to 24.0% from 17.0% for pure RPUF, while the PHRR value for the composite was lowered by 47% compared to pure RPUF. From TGA results, initial decomposition temperature slightly increases to 255°C for the composite from 252°C for unmodified foam and char residue (at 800°C) rise to 5.0% from 2.1%. The greater FR action of the composites might be attributed to the MPP promoting

char formation, which then operated as a barrier in the beginning of the thermal degradation of the RPUF. At the same, the thermally stable metal oxides in SS increased the char layer's thermal resistance. With growing interest in sustainable development policy worldwide, recent study by Marcin Zemla et al.[233] synthesized bio-polyol from rapeseed oil (RO). RPUF was formed with these RO and incorporated with varied phosphorus-based FRs such as cyclic phosphonates (CT901), triethyl phosphate (TEP), and dimethyl propane phosphate (DMPP). The amount of FRs added was maintained at 20wt.% for each of them. RPUF/20wt.%DMPP provided the highest LOI value (22.4%) compared to 19.4 for virgin RPUF. This outcome for the composite could be linked to the greater quantity of phosphorus in DMMP relative to CT901 and TEP FR. The more the phosphorus level in the modified sample, the more potent the development of char and consequently, the lower their flammability. Similarly, THR, PHRR and maximum average rate of heat emission (MAHRE) values of RPUF/DMMP composites reduced considerably by 36.80%, 14.28%, and 29.20%, respectively relative to other composites and virgin RPUF. Lu Weimiao et al.[234] synthesized a new IFR of phosphorus/nitrogen-based diphenols code named DH, DV and DS through p - hydroxybenzaldehyde (H), vanillin (V) and syringaldehyde (S) with varied methoxyl groups on its aromatic ring (Figure 27(a)). IFR of DH, DV and DS were individually incorporated into rigid PU (RPU) and their effect on the composites flame retardancy and thermal stability investigated. From LOI and cone calorimeter test results, the highest LOI value was recorded for RPU/DS (26.3%) compared to pure RPU (19.0%). More so, the HRR, THR of RPU-DS reduced by 40.66% and 40.5% respectively and char yield (at 600°C) increase to 13.6% from 4.6% for pure sample. This result is supported by the SEM images (Figure 27(b)), more solid and impenetrable structures excellently detach heat and combustible gases from beneath materials, hence decreased THR and HRR of modified samples. From TG and DTG results (Figure 27(c)), the final decomposition temperature rises to 429°C, 424°C, and 418°C for RPU/DH, RPU/DV and RPU/DS, respectively from 380°C for pure RPU. This result can be attributed to the fact that phosphorus-based acids enhance char formation at elevated temperature and perform better in the condensed phase than the gaseous phase.

In a related study by Qian et al.[235] RPUF was modified with a low-molecular weight FR reactive polyester diol (BEOPMS). BEOPMS was synthesized through the esterification reaction of 9,10-dihydro-10-[2,3-di(hydroxycarbonyl) propyl]-10- phosphaphenanthrene-10-oxide (DDP) with diethylene glycol (DG). The flame retardancy, thermal stability and compressive strength of the modified rigid foam was better compared to pristine sample. For instance, LOI value for FR rigid foam was 21.0%, total time of ignition (TTI) was 7 s (s) and PHRR (222 kW/m^2) compared to pristine foam with LOI value (17.0%), TTI (5s) and PHRR (261 kW/m^2). Wang Jingyu et al.[236] designed a bi-functional FR for rigid polyurethane foam (RPU) and the new FR was named PDEP; containing DOPO and a phosphate (DEP). Both were said to exert different roles at varied temperatures. Later, the FR system was hybridized with the incorporation of EG to form RPU/PDEP/EG system. This hybrid system (12wt.%PDEP/8wt.% EG) presents higher compressive strength composites relative to RPU/8wt.% EG and pristine RPU. From cone calorimeter analysis, the hybrid composites PHRR, THR, and TSR considerably decrease

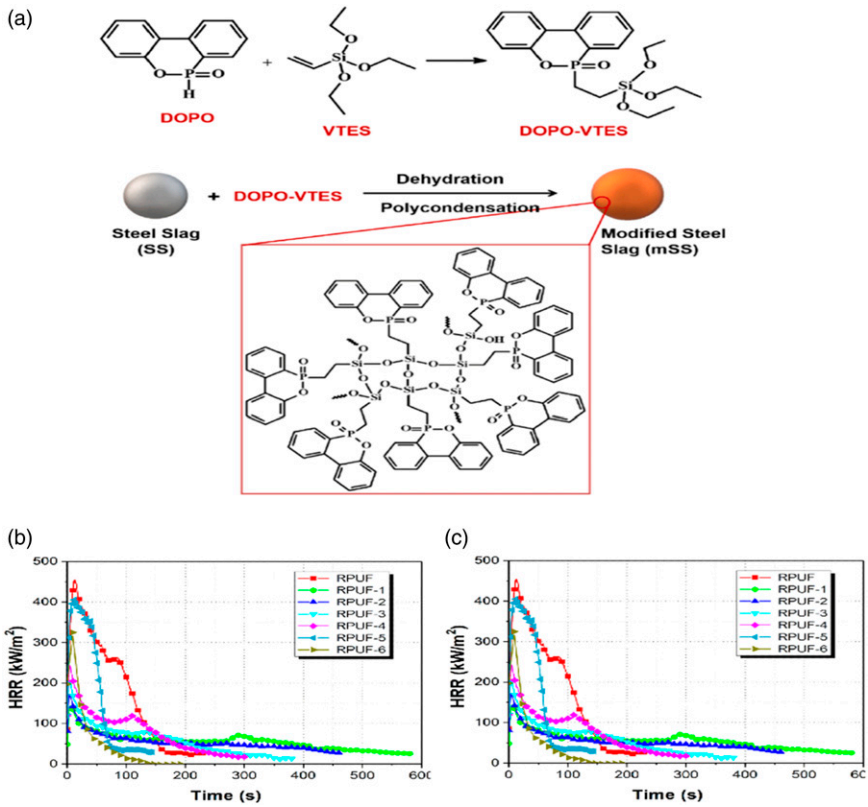

Figure 26. (a) Preparation route of microencapsulated SS (mSS) with phosphorus-based silane, (b) THR curves and (c) HRR curves of pure RPUF, RPUF/EG60.9 g (RPUF-1), RPUF/EG40.6 g/mSS20.3 g (RPUF-2), RPUF/EG30.5 g/mSS30.5 g (RPUF-3), RPUF/EG20.3 g/mSS40.6 g (RPUF-4), RPUF/mSS60.9 (RPUF-5), RPUF/EG30.5 g/SS30.5 g (RPUF-6).[231]

by 56.9%, 24.38%, and 29.27%, respectively and has highest char yield of 37.9% compared to RPUF/12%PDEP (24.7%) and pristine RPU (8.1%). An affirmation of superior flame retardancy of the hybridized composite is presented in Figure 28(a)–(d). It's important to note that PDEP/EG had a favorable impact on the primary modes of action, inheriting PDEP's flame suppression outcome in the gas stage and EG's charring outcome in the condensed phase.

Conclusions and Future Perspectives

For safety, some of the strongholds of RPUF use require stringent flame resistance, necessitating continuous research on new FR to meet market demand. RPUF remain the dominant PUF in many applications, where flame retardancy is declared as a fundamental

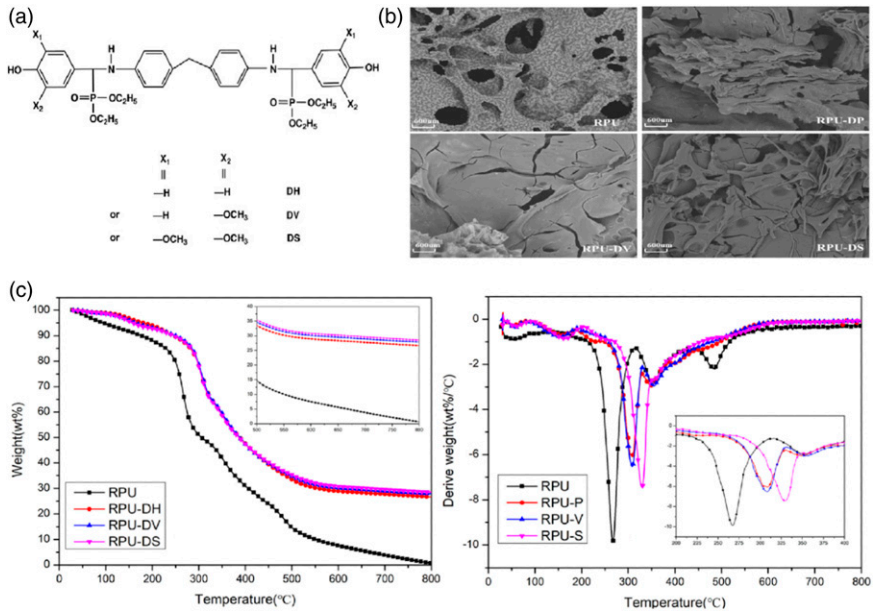

Figure 27. (a) Structural representation of DH, DS, and DV (b) SEM residual char images of pure RPU and its composites (RPU-DP, RPU-DV and RPU-DS) after cone calorimeter test, (c) TG and DTG curves of pure RPU and its composites in nitrogen atmosphere.[234]

provision. In this review, we have provided a detailed explanation of the advancements of flame retardancy of RPUF according to scientific articles published in the last half a decade. Among the FR for RPUF, conventional inorganic nanoparticles (such as montomorilite, halloysite nanotubes, carbon nanotubes), additives-based FR (APP), and layered FR (EG) are still dominant and continue to render important roles in flame retarding RPUF because of their cost-effectiveness, availability, non-toxic, and environment-friendly. Meanwhile, as a major drawback, high loading is generally needed to achieve the requirement of fire safety standard that could decrease the mechanical performance of RPUF composites. Therefore, it is apt to mention that in terms of increasing the mechanical properties, charring, and fire-resistant properties of RPUF, shell material (gel-silica, dimethyl methyl phosphate, zeolite) can be employed to microencapsulate conventional FR (especially APP and EG), thus resulting in RPUF composites with superior mechanical performance and fire behaviour.

All through this review, it was established that the formation of a stable and insulating char offers a crucial role in protecting RPUF in combustion. In this respect, one of the best potential methods for producing an enlarged char layer is to prepare an immensely efficient IFR system. To date, a lot of attention is dedicated to the design of intumescent formulations for RPUF. For example, the co-addition of APP and melamine in a mass ratio of 3:1 or EG-ionic liquid and DPES in a mass ratio of 1:1. Aside from this, synergistic agents (such as zeolite, carbon nanotubes) can be assumed as the decisive

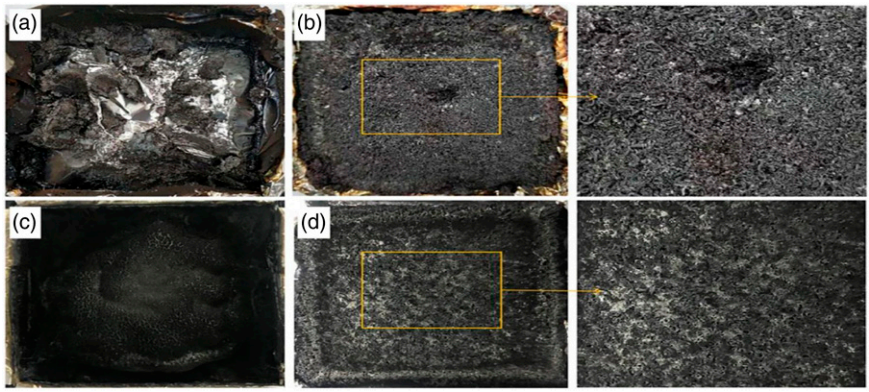

Figure 28. Pictorial of residual char after cone calorimeter analysis (a) pristine RPU, (b) RPU_EG8wt.%, (c) RPU_PDEP12wt.%, (d) RPU_PDEP12wt.%/EG8wt.%.[236]

organ for intumescent formulations since the fire behaviour of RPUF composites could be improved immensely by small synergist content in the intumescent system. In fact, from past study results, synergists help to boost the fire-retardant performance of IFR RPUF composites by producing a compact intumescent carbonaceous char with better consistency and insulation. In most of the studies, based on LOI alongside cone calorimeter test, the incorporation of FR/IFRs improved the LOI values and lowered the fire parameters (notably PHRR and THR) of RPUF composites. Evidenced by SEM and TGA test results, FR/IFR add-ons in RPUF promoted better surface morphology, increased thermal stability, and char residue.

Although several strategies have been discussed in this work, there is a need for new FR and IFR formulations to improve the fireproofing efficacy of RPUF further. From a viewpoint, upcoming developments can defer from the conventional FR and IFR constituents and explore the flame-retardant potential of bio-waste (such as keratin from chicken feather, almond shell, sea/snail shell, eggshell, walnut shell). Keratin can be explored for its lofty nitrogen content as well as protein structure. Similarly, rigid nanoparticles such as sepiolite and silver nanoparticles (AgNP) can be incorporated into RPUF as a standalone or hybridized with other FR. AgNP may stand out as a novel nanofiller (especially for RPUF) due to it environment-friendly, green preparation method, high physical and antimicrobial properties. In summary, our work provides overview of all recent FR research of RPUF, this should aid the developments of new FRs formulations for a myriad of applications.

Author Contributions

Abdulwasiu Muhammed Raji: conceptualization, writing-original draft, writing-review, and editing. **Hambali Umar Hambali**: conceptualization, writing-original draft, writing-review, and editing. **Zahid Iqbal Khan**: conceptualization, writing-review, and editing. **Zurina Binti**

Mohamad: supervision, writing-review, and editing. **Azman Hassan**: supervision, writing-review, and editing. **Raphael Ogabi:** conceptualization, writing-review, and editing.

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