Abstract: Nowadays, epoxy composites are elements of engineering materials and systems. Although they are known as versatile materials, epoxy resins suffer from high flammability. In this sense, flame retardancy analysis has been recognized as an undeniable requirement for developing future generations of epoxy-based systems. A considerable proportion of the literature on epoxy composites has been devoted to the use of phosphorus-based additives. Nevertheless, innovative flame retardants have coincidentally been under investigation to meet market requirements. This review paper attempts to give an overview of the research on flame retardant epoxy composites by classification of literature in terms of phosphorus (P), non-phosphorus (NP), and combinations of P/NP additives. A comprehensive set of data on cone calorimetry measurements applied on P-, NP-, and P/NP-incorporated epoxy systems was collected and treated. The performance of epoxy composites was qualitatively discussed as Poor, Good, and Excellent cases identified and distinguished by the use of the universal Flame Retardancy Index (FRI). Moreover, evaluations were rechecked by considering the UL-94 test data in four groups as V0, V1, V2, and nonrated (NR). The dimensionless FRI allowed for comparison between flame retardancy performances of epoxy composites. The results of this survey can pave the way for future innovations in developing flame-retardant additives for epoxy.

Keywords: epoxy; Flame Retardancy Index (FRI); fire retardancy; cone calorimetry

1. Introduction

Innovations are mainly born in a very disciplined manner, but sometimes they arise from serendipity. Regardless of the origin of innovative materials and systems, the identification and classification of systems in terms of explanatory variables requires the use of universal, well-accepted criteria. Nowadays, epoxy-based composites are elements of advanced systems [1–3]. There has been continued interest in the use of epoxy for developing a wide variety of general- and specific-purpose products such as adhesives, coatings, and medical devices thanks to the versatility of this thermosetting material [4–7]. Nevertheless, research outcomes reveal that epoxy is highly flammable, and one principally requires flame retardant materials for applications where epoxy should stand against
fire [8–12]. In general, it has been understood that careful selection of additives is the first step in development of flame retardant polymer composites, but the performance of the material may additionally depend on the type and the amount of additives used individually or simultaneously [13,14]. Particularly, flame retardant epoxy composites consisting of phosphorus flame-retardant additives were the subject of different reports [15,16]. Moreover, combination of phosphorus and nonphosphorus additives was considered in the quest of higher flame retardancy performance [17–19]. In almost all reports, however, there was a lack of a correlation between the crosslinking state of resin in the presence of additives and flame retardancy.

In a previous work, we used two dimensionless indexes to correlate cure state with corrosion inhibition and flame-retardant properties of epoxy/Fe3O4 nanocomposites [20]. By the use of dimensionless Cure Index [21] and dimensionless Flame Retardancy Index (FRI) [22], it was demonstrated that the quality of cure in epoxy composites (Poor, Good, or Excellent) can be correlated to the performance of flame retardancy (Poor, Good, or Excellent). The FRI was also powerful in exploring the complementary actions of mineral and organic additives in polymer systems in terms of the peak of HRR (pHRR), the total heat release (THR), and the time to ignition (TTI) of neat polymer and polymer composites [23]. In this work, with the aim of recognizing the future ahead of innovations in flame-retardant epoxy composites, reports on flame-retardant epoxy composites were comprehensively reviewed and then classified as a function of their flame retardancy performance by the use of the FRI criterion. Classification was performed on account of phosphorus (P)-, nonphosphorus (NP)-, and combined P/NP-incorporated epoxy composites. In each class, comprehensive master tables were provided in which the polymer matrix, the additives, the content of additives, and cone calorimetry data including TTI, THR, and pHRR and the calculated FRI values were summarized. Moreover, the available UL-94 test data were provided and plotted similar to the FRI curves, but in four groups of V0, V1, V2, and nonrated (NR).

2. Epoxy Resins Containing Phosphorus-Based Flame Retardants

According to the literature, a variety of phosphorus-based flame retardants have been used in epoxy resins. Table 1 summarizes pHRR, THR, and TTI and the FRI values of epoxy/P systems. The percentage of incorporated flame retardant (FR) as well as the results of limiting oxygen index (LOI) and UL-94 test are given.

Table 1. The flame retardancy performance of epoxy containing phosphorus-based (P) flame retardants in terms of FRI (* the name and percentage of incorporated flame retardant is given after each epoxy resin). Notes a to l on the bottom of the table are representative of composite systems containing woven or nonwoven fibers.

| Epoxy Resins and Incorporated Phosphorus FR * | wt.% | TTI (s) | pHRR (kW m⁻²) | THR (MJ m⁻²) | FRI | LOI | UL94 | Ref. |
|---------------------------------------------|------|--------|---------------|--------------|-----|-----|------|------|
| N, N'-diallyl-p-phenylphosphonic diamide (FP1) | 0    | 49     | 1477          | 118          | —   | 27  | NR   | [24] |
| N, N'-diallyl-p-phenylphosphonic diamide (FP1) | 4    | 46     | 831           | 106          | 1.85| 33  | NR   | [24] |
| N, N'-diallyl-p-phenylphosphonic diamide (FP1) | 6    | 42     | 500           | 115          | 2.59| 36  | V-1  | [24] |
| N, N'-diallyl-p-phenylphosphonic diamide (FP1) | 8    | 40     | 587           | 109          | 2.22| 38  | V-0  | [24] |
| (bis(4-hydroxyphenyl) methyl) diphenylphosphine oxide (DPO-PHE) | 0    | 31     | 1068          | 76           | —   | 23.7| NR   | [25] |
| 1-(bis(4-hydroxyphenyl)methyl)-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO-PHE) | 11.68| 41     | 657           | 59           | 2.76| 32.1| V-0  | [25] |
| Reaction between 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide & cyanuric chloride (DOPO-T) | 12.03| 39     | 956           | 57           | 1.87| 30.5| V-0  | [25] |
| Reaction between 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide & cyanuric chloride (DOPO-T) | 0    | 47     | 1208          | 80           | —   | 22.5| NR   | [26] |
| Reaction between 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide & cyanuric chloride (DOPO-T) | 2.34 | 38     | 836           | 69           | 1.35| 32.5| NR   | [26] |
| Reaction between 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide & cyanuric chloride (DOPO-T) | 4.67 | 36     | 727           | 62           | 1.64| 34.6| V-1  | [26] |
| Reaction between 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide & cyanuric chloride (DOPO-T) | 6.99 | 32     | 629           | 56           | 1.86| 36.2| V-1  | [26] |
| Reaction between | wt.% | TTI (s) | pHRR (kW m\(^{-2}\)) | THR (MJ m\(^{-2}\)) | FRI | LOI | UL94 | Ref. |
|-----------------|------|---------|------------------------|-----------------------|-----|-----|-------|------|
| 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide & cyanuric chloride (DOPO-T) | 9.34 | 30 | 613 | 54 | 1.86 | 33.4 | V-0 | [26] |
| Aluminum ethylphenylphosphinate (AEPP) | 0.13 | 131 | 495 | 179 | — | 21.3 | V-2 | [27] |
| Aluminum ethylphenylphosphinate (AEPP) | 5 | 119 | 254 | 131 | 2.41 | 33.3 | V-2 | [27] |
| Aluminum ethylphenylphosphinate (AEPP) | 10 | 105 | 241 | 124 | 2.37 | 25.7 | V-1 | [27] |
| phenethyl-bridged | 15 | 91 | 223 | 119 | 2.31 | 28.2 | V-0 | [27] |
| phenethyl-bridged | 0 | 32 | 827 | 116 | — | 21.8 | NR | [28] |
| 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide derivative (DiDOPO) | 3 | 41 | 387 | 104 | 3.05 | 32.7 | V-0 | [28] |
| phenethyl-bridged | 0 | 32 | 781 | 116 | — | 21.8 | NR | [29] |
| Aluminum ethylphenylphosphinate (AEPP) | 5 | 119 | 254 | 131 | 2.41 | 23.3 | V-2 | [27] |
| Aluminum ethylphenylphosphinate (AEPP) | 10 | 105 | 241 | 124 | 2.37 | 25.7 | V-1 | [27] |
| aluminum ethylphenylphosphinate (AEPP) | 15 | 91 | 223 | 119 | 2.31 | 28.2 | V-0 | [27] |
| phenethyl-bridged | 0 | 32 | 827 | 116 | — | 21.8 | NR | [28] |
| Phenethyl-bridged | 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide derivative (DiDOPO) | 10 | 38 | 508 | 83 | 2.35 | 38 | V-0 | [29] |
| phenethyl-bridged | 11 | 43 | 441 | 96 | 2.65 | 37.4 | V-0 | [29] |
| phenethyl-bridged | 0 | 32 | 781 | 116 | — | 21.8 | NR | [30] |
| Phenethyl-bridged | 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide derivative (DiDOPO) | 5 | 35 | 491 | 81 | 2.29 | 35.8 | V-0 | [31] |
| phenethyl-bridged | 0 | 32 | 781 | 116 | — | 21.8 | NR | [31] |
| Phenethyl-bridged | 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide derivative (DiDOPO) | 15 | 41 | 436 | 72 | 3.41 | 33.6 | V-0 | [32] |
| phenethyl-bridged | 0 | 32 | 781 | 116 | — | 21.8 | NR | [32] |
| Phenethyl-bridged | 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide derivative (DiDOPO) | 20 | 16 | 298 | 68 | 2.06 | 27.5 | V-0 | [32] |
| phenethyl-bridged | 0 | 19 | 1324.6 | 95.7 | — | 19.2 | HB | [33] |
| Phenethyl-bridged | pentaerythritol phosphate melamine salt (PPMS) | 15 | 20 | 491.6 | 74 | 3.66 | 22.8 | V-2 | [33] |
| Phenethyl-bridged | pentaerythritol phosphate melamine salt-functionalized Expandable graphite (PPMS-EG) | 15 | 16 | 414.3 | 66.7 | 3.86 | 25.8 | V-1 | [33] |
| Phenethyl-bridged | Pentaerythritol phosphate melamine salt-functionalized Multiwalled carbon nanotube (PPMS-MWCNT) | 5 | 13 | 1013.4 | 93.7 | 1.21 | 21.5 | HB | [34] |
| Phenethyl-bridged | Pentaerythritol phosphate melamine salt-functionalized Multiwalled carbon nanotube (PPMS-MWCNT) | 10 | 8 | 680.7 | 90.7 | 1.15 | 22.6 | V-2 | [34] |
| Phenethyl-bridged | diphenyl 1H-imidazol-1-ylphosphonate (DPIPP) | 7.5 | 56 | 535.2 | 61.3 | 1.77 | 27.5 | NR | [35] |
| Phenethyl-bridged | diphenyl 1H-imidazol-1-ylphosphonate (DPIPP) | 0 | 66 | 793.5 | 86.3 | — | 21 | NR | [35] |
| Phenethyl-bridged | 1-(diphenylphosphinyl)-1H-imidazole oxide (DPPIO) | 7.5 | 62 | 583.1 | 60 | 2.66 | 31.5 | V-0 | [35] |
| Phenethyl-bridged | 1-(diphenylphosphinyl)-1H-imidazole oxide (DPPIO) | 15 | 63 | 432.9 | 48.4 | 3.11 | 38 | V-0 | [35] |
| Phenethyl-bridged | 1-(diphenylphosphinyl)-1H-imidazole oxide (DPPIO) | 0 | 57 | 730.1 | 82.6 | — | 20.5 | NR | [35] |
| Phenethyl-bridged | imidazolium dibenzo[c,e][1,2]oxaphosphate (IDOP) | 5 | 65 | 617.5 | 65.8 | 1.78 | 27 | NR | [36] |
| Phenethyl-bridged | imidazolium dibenzo[c,e][1,2]oxaphosphate (IDOP) | 10 | 67 | 586.5 | 64.2 | 1.98 | 34.5 | V-1 | [36] |
| Phenethyl-bridged | imidazolium dibenzo[c,e][1,2]oxaphosphate (IDOP) | 15 | 68 | 485.6 | 51.2 | 3.05 | 37 | V-0 | [36] |
| Phenethyl-bridged | polyphosphoric acid piperazine (PPAP) | 5 | 38 | 511.9 | 92.5 | 0.96 | 30.8 | V-0 | [37] |
Table 1. Cont.

| Epoxy Resins and Incorporated Phosphorus FR | wt.% | TTI (s) | pHRR (kW m\(^{-2}\)) | THR (MJ m\(^{-2}\)) | FRI | LOI | UL94 | Ref. |
|--------------------------------------------|------|---------|------------------|-----------------|-----|-----|------|------|
| diglycidyl ether of bisphenol A epoxy resin/epoxy/hollow glass microspheres (foam) | 0    | 17      | 444.92           | 138.2           | --- | 21.5 | NR   | [38] |
| aluminum disubarylphosphinate (AlPBu)      | 10   | 17      | 272.28           | 113.2           | 1.99 | 26.5 | NR   | [38] |
| aluminum disubarylphosphinate (AlPBu)      | 12.5 | 17      | 264.98           | 110.8           | 2.09 | 21.2 | V-1  | [38] |
| Aluminum disubarylphosphinate (AlPBu)      | 15   | 17      | 260.77           | 109.3           | 2.15 | 20   | V-0  | [38] |
| aluminum disubarylphosphinate (AlPBu)      | 0    | 53      | 1484             | 86.4            | ---  | 26   | NR   | [39] |
| 6-morpholino-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide (MPL-DOPO) | 2.5  | 46      | 1296             | 74.3            | 1.15 | 29.5 | V-1  | [39] |
| 6-morpholino-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide (MPL-DOPO) | 5    | 45      | 1145             | 67.1            | 1.44 | 30.5 | V-0  | [39] |
| 6,6′-((methylenebis(4,1-phenylene))bis(azanediyl))bis(6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide) (DDM-DOPO) | 2.5  | 51      | 1236             | 76.5            | 1.30 | 30.5 | V-0  | [39] |
| 6,6′-((methylenebis(4,1-phenylene))bis(azanediyl))bis(6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide) (DDM-DOPO) | 5    | 48      | 999              | 69.7            | 1.66 | 31.5 | V-0  | [39] |
| 6-(((1H-tetrazol-5-ylamino)(4-hydroxyphenyl)methyl)dibenzo[c,e][1,2]oxaphosphinine 6-oxide (ATZ) | 0    | 71      | 1511.7           | 115.8           | ---  | 19.4 | NR   | [40] |
| 6-morpholino-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide | 0    | 71      | 1205.4           | 77.1            | ---  | 25   | NR   | [41] |
| 6,6′-((methylenebis(4,1-phenylene))bis(azanediyl))bis(6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide) (DDM-DOPO) | 2.4  | 51      | 947.6            | 67.3            | 0.97 | 31.7 | V-1  | [44] |
| 6,6′-((methylenebis(4,1-phenylene))bis(azanediyl))bis(6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide) (DDM-DOPO) | 4    | 57      | 705.4            | 57.6            | 1.71 | 32.5 | V-0  | [44] |
| 1-methyl-3-6-(6-oxidodibenzo[c,e][1,2]oxaphosphinin-6-yl)(methyl)-1H-imidazol-3-ium 4 methylbenzenesulfonate | 7.5  | 51      | 767              | 56.2            | 1.44 | 33.9 | V-0  | [44] |
| poly(pentaerythritol phosphate phosphinic acyl piperazine) (PPAP) | 0    | 32      | 1111             | 18.2            | ---  | 20.5 | NR   | [45] |
| poly(pentaerythritol phosphate phosphinic acyl piperazine) (PPAP) | 10   | 38      | 1008             | 12.4            | 1.92 | 23.5 | NR   | [45] |
| poly(pentaerythritol phosphate phosphinic acyl piperazine) (PPAP) | 15   | 40      | 846              | 12.2            | 2.44 | 24.5 | V-1  | [45] |
| poly(pentaerythritol phosphate phosphinic acyl piperazine) (PPAP) | 20   | 41      | 545              | 12.2            | 3.96 | 26.5 | V-0  | [45] |
| melamine phenylphosphate (MPhP)             | 0.96 | 79      | 1426.4           | 75.4            | 0.92 | 31   | V-1  | [46] |
| melamine phenylphosphate (MPhP)             | 1.9  | 79      | 1299.5           | 74.2            | 1.06 | 32   | V-1  | [46] |
| melamine phenylphosphate (MPhP)             | 3.75 | 79      | 915.3            | 67.1            | 1.59 | 35.6 | V-0  | [46] |
| melamine phenylphosphate (MPhP)             | 7.24 | 67      | 660.7            | 60.2            | 2.11 | 38   | V-0  | [46] |
| melamine phenylphosphate (MPhP)             | 0    | 70      | 1491             | 81              | ---  | 19   | NR   | [47] |
| bisphenol-A bridged penta(phenoxycyclophosphazene (A-BP) | 9    | 62      | 783              | 55.9            | 1.92 | 33.9 | V-0  | [48] |
| cage-ladder-structure, phosphorus-containing polyhedral oligomeric silsesquioxane (CLEP-DOPO-POSS) via the hydrolytic condensation of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO)-vinyl trimethoxysilane (VTMS) with 2,3,4-epoxycyclohexyl)ethyl trimethoxysilane (CLEP-DOPO-POSS) | 0    | 95      | 939              | 98             | ---  | 23   | NR   | [49] |
| copper phenylphosphate nanoflake (Cu-PF)     | 10   | 100     | 531              | 93              | 2.09 | 23.4 | NR   | [49] |
| copper phenylphosphate nanoflake (Cu-PF)     | 2    | 80      | 466              | 83              | 2.00 | 35.5 | V-1  | [49] |
| copper phenylphosphate nanoflake (Cu-PF)     | 4    | 88      | 454              | 82              | 2.28 | 38.2 | V-1  | [49] |
| copper phenylphosphate nanoflake (Cu-PF)     | 6    | 88      | 448              | 72              | 2.64 | 37.8 | V-1  | [49] |
| copper phenylphosphate nanoflake (Cu-PF)     | 8    | 86      | 401              | 73              | 2.84 | 34.6 | V-1  | [49] |
Table 1. Cont.

| Epoxy Resins and Incorporated Phosphorus FR | wt.% | TTI (s) | pHRR (kW m⁻²) | THR (MJ m⁻²) | FRI | LOI | UL94 | Ref. |
|--------------------------------------------|------|--------|---------------|--------------|-----|-----|------|------|
| reaction of 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphinane-2-oxide & 2-aminothiazoline (DOP-ATZ) | 0.55 | 1139.7 | 75.7 | — | 25.2 | NR [50] |
| reaction of 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphinane-2-oxide & 2-aminothiazoline (DOP-ATZ) | 1.75 | 508.9 | 40.6 | 6.48 | 27.5 | V-0 [50] |
| reaction of 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphinane-2-oxide & 2-aminothiazoline (DOP-ATZ) | 2.0 | 238.9 | 28 | 9.72 | 28.3 | V-0 [50] |
| reaction of 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphinane-2-oxide & 2-aminothiazoline (DOP-ATZ) | 0.11 | 1301 | 64.6 | 1.58 | 35.1 | V-1 [50] |
| reaction between 1,4-Phthalaldehyde & 2-benzothiazolamine & 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (BPD) | 3.38 | 1313 | 78.5 | 1.32 | 34.5 | V-1 [50] |
| reaction between 1,4-Phthalaldehyde & 2-benzothiazolamine & 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (BPD) | 6.71 | 1273 | 69.8 | 1.44 | 34.3 | V-1 [50] |
| reaction between 1,4-Phthalaldehyde & 2-benzothiazolamine & 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (BPD) | 10.04 | 1220 | 63.8 | 1.70 | 36.9 | V-0 [50] |
| reaction between 1,4-Phthalaldehyde & 2-benzothiazolamine & 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (BPD) | 13.41 | 1071 | 59.1 | 1.97 | 39.1 | V-0 [50] |
| reaction between 1,4-Phthalaldehyde & 2-benzothiazolamine & 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (BPD) | 0.11 | 828 | 61.6 | 1.68 | 34.5 | V-1 [50] |
| reaction between 1,4-Phthalaldehyde & 2-benzothiazolamine & 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (BPD) | 7.77 | 52 | 63.1 | 2.47 | 32.5 | V-1 [50] |
| reaction between 4-(hydroxymethyl)-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane & 6-(2,5-dihydroxyphenyl)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide (DOPO-TPMP) | 2.5 | 1683.9 | 91.1 | 1.26 | 28.2 | V-1 [50] |
| reaction between 4-(hydroxymethyl)-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane & 6-(2,5-dihydroxyphenyl)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide (DOPO-TPMP) | 5 | 1544.8 | 82.9 | 1.44 | 34.8 | V-1 [50] |
| reaction between 4-(hydroxymethyl)-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane & 6-(2,5-dihydroxyphenyl)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide (DOPO-TPMP) | 7.5 | 1483.6 | 75.7 | 1.64 | 35.6 | V-0 [50] |
| reaction between 4-(hydroxymethyl)-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane & 6-(2,5-dihydroxyphenyl)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide (DOPO-TPMP) | 10 | 819.3 | 69.2 | 2.84 | 36.1 | V-0 [50] |
| reaction between 4-(hydroxymethyl)-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane & 6-(2,5-dihydroxyphenyl)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide (DOPO-TPMP) | 54 | 880 | 187 | 24.1 | NR [54] |
| reaction between 4-(hydroxymethyl)-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane & 6-(2,5-dihydroxyphenyl)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide (DOPO-TPMP) | 2 | 800 | 162 | 1.52 | 29.3 | V-0 [54] |
| reaction between 4-(hydroxymethyl)-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane & 6-(2,5-dihydroxyphenyl)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide (DOPO-TPMP) | 21 | 594 | 53 | 3.90 | 33 | NR [55] |
| ammonium polyphosphate (APP) | 53 | 1121 | 102 | — | 20 | NR [55] |
| ethanediamine-modified ammonium polyphosphate (EDA-APP) | 61 | 398 | 54 | 6.12 | 33 | V-0 [55] |
| hexakis(4-boronic acid-phenoxy)-cyclophosphazene (CP-6B) | 45 | 1091 | 83 | — | 22.8 | NR [56] |
| N,N'-diamyl-p-phenylphosphonicdiamide (PM) | 30 | 608 | 71 | 1.95 | 30.8 | V-0 [56] |
| N,N'-diamyl-p-phenylphosphonicdiamide (PM) | 57 | 1108 | 96 | 1.44 | 34.8 | V-0 [56] |
| N,N'-diamyl-p-phenylphosphonicdiamide (PM-βCD) | 2 | 905 | 73 | 1.55 | 26.5 | NR [56] |
| N,N'-diamyl-p-phenylphosphonicdiamide (PM-βCD) | 50 | 541 | 68.8 | 2.51 | 26.8 | NR [56] |
| N,N'-diamyl-p-phenylphosphonicdiamide (PM-βCD) | 43 | 469 | 66.2 | — | 24.7 | NR [56] |
| poly(4,4-diamo diphenyl sulfone | 10 | 149 | 33.2 | 4.08 | 28 | V-1 [58] |
| poly(4,4-diamo diphenyl sulfone | 26 | 218 | 21.7 | 7.33 | 31 | V-0 [58] |
| bisphenol A bridged penta(anilino) cyclotriphosphazene (BPA-BPP) | 2 | 457 | 78.4 | 2.48 | 28.7 | V-1 [59] |
| 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) | 9 | 1291 | 87.2 | — | 23 | NR [60] |
| 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) | 9 | 1093 | 59.6 | 1.19 | 30.2 | NR [60] |
Table 1. Cont.

| Epoxy Resins and Incorporated Phosphorus FR | wt.% | TTI (s) | pHRR (kW m⁻²) | THR (MJ m⁻²) | FRI | LOI | UL94 | Ref. |
|-------------------------------------------|------|---------|----------------|--------------|-----|-----|------|------|
| reaction between 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide-1-oxo-4-hydroxymethyl-2,6,7-trioxa-1 phosphabicyclo[2.2.2] octane (DOPO-PEPA) | 5.7 | 44 | 873 | 60.9 | 2.02 | 30 | V-0 | [60] |
| reaction between 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide-1-oxo-4-hydroxymethyl-2,6,7-trioxa-1 phosphabicyclo[2.2.2] octane (DOPO-PEPA) | 7.4 | 48 | 683 | 46.3 | 3.71 | 35 | V-0 | [60] |
| reaction between 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide-1-oxo-4-hydroxymethyl-2,6,7-trioxa-1 phosphabicyclo[2.2.2] octane (DOPO-PEPA) | 9.1 | 42 | 595 | 45.9 | 3.76 | 35 | V-0 | [60] |
| polycrystalline polymeric silsesquioxane containing 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO-POSS) | 5.8 | 839 | 129 | — | — | NR | [61] |
| polycrystalline polymeric silsesquioxane containing 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO-POSS) | 7.4 | 48 | 683 | 46.3 | 3.71 | 35 | V-0 | [60] |
| polycrystalline polymeric silsesquioxane containing 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO-POSS) | 9.1 | 42 | 595 | 45.9 | 3.76 | 35 | V-0 | [60] |
| 58 | 839 | 129 | — | — | NR | [61] |
| polymeric polymeric silsesquioxane containing 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO-POSS) | 2.5 | 58 | 631 | 104 | 1.64 | 27.1 | V-1 | [61] |
| polymeric polymeric silsesquioxane containing 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO-POSS) | 5 | 62 | 404 | 87 | 3.29 | — | NR | [61] |
| polymeric polymeric silsesquioxane containing 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO-POSS) | 10 | 61 | 346 | 79 | 4.16 | — | NR | [61] |
| Hexaphenylcyclophosphazene (HPCP) | 7.6 | 56 | 918 | 94 | 1.44 | 26.2 | V-1 | [62] |
| Hexaphenylcyclophosphazene (HPCP) | 11.9 | 54 | 796 | 83 | 1.78 | 28 | V-0 | [62] |
| Hexaphenylcyclophosphazene (HPCP) | 14.9 | 54 | 840 | 78 | 1.83 | 28.6 | V-0 | [62] |
| 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO-PEPA) | 6.97 | 56 | 947 | 92 | 1.30 | 25.9 | V-1 | [62] |
| 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO-PEPA) | 10.46 | 50 | 850 | 88 | 1.48 | 27.4 | V-0 | [62] |
| 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO-PEPA) | 13.94 | 46 | 785 | 81 | 1.60 | 27.8 | V-1 | [62] |
| 2-(hydroxy(phenyl)methyl)-5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxide (TP) | 12.42 | 23 | 312.6 | 59 | 1.60 | 31.8 | V-1 | [63] |
| [4-(2,4,6-Tris[24]dioxaphosphinan-2-yl) hydroxymethyl]phenoxyl-1(3,5,5)-triazine (TNTP) | 14.36 | 34 | 253 | 65.8 | 2.62 | 32.4 | V-1 | [63] |
| 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) | 7 | 32 | 556 | 61 | 1.96 | 31.5 | V-0 | [65] |
| 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) | 10 | 33 | 453 | 55 | 2.75 | 33.2 | V-1 | [65] |
| 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) | 14.7 | 34 | 410 | 50 | 3.45 | 32.5 | V-0 | [65] |
| 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) | 18.4 | 33 | 400 | 47 | 3.65 | 33.3 | V-0 | [64] |
| 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) | 7 | 32 | 556 | 61 | 1.96 | 31.5 | NR | [65] |
| 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) | 10 | 33 | 453 | 55 | 2.75 | 33.2 | V-1 | [65] |
| 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) | 15 | 34 | 425 | 54 | 3.08 | 35.6 | V-0 | [65] |
Table 1. Cont.

| Epoxy Resins and Incorporated Phosphorus FR | wt.% | TTI (s) | pHRR (kW·m⁻²) | THR (MJ·m⁻²) | FRI | LOI | UL94 Ref. |
|------------------------------------------|------|---------|----------------|---------------|-----|-----|-----------|
| tri(phenylenemaleimide-phenoxy)-triazine (DOPO-TMT) | 13.9 | 53 | 776 | 60.6 | 1.79 | 36.2 | V-0 [68] |
| tri(phenylenemaleimide-phenoxy)-triazine (DOPO-TMT) | 17.3 | 48 | 556 | 56.5 | 2.43 | 37.5 | V-0 [68] |
| hexa(4-maleimido-phenoxyl)cyclotriphosphazene (HMCP) | 3.4 | 39 | 751 | 77 | 1.39 | 27 | NR [69] |
| hexa(4-maleimido-phenoxyl)cyclotriphosphazene (HMCP) | 6.8 | 38 | 469 | 66.5 | 2.52 | 29 | V-1 [69] |
| hexa(4-maleimido-phenoxyl)cyclotriphosphazene (HMCP) | 10.2 | 36 | 506 | 63 | 2.33 | 33.4 | V-0 [69] |
| hexa(4-maleimido-phenoxyl)cyclotriphosphazene (HMCP) | 13.6 | 36 | 467 | 58 | 2.75 | 35 | V-0 [69] |
| addition reaction between DOPO and Schiff base obtained in advance by condensation of 4,4‘-diaminodiphenyl methane & 4-hydroxybenzaldehyde (DOPO-bp) | 3.4 | 48 | 757.1 | 154.1 | 1.65 | 30.5 | V-1 [70] |
| addition reaction between DOPO and Schiff base obtained in advance by the condensation of 4,4‘-diaminodiphenyl methane & 4-hydroxybenzaldehyde (DOPO-bp) | 6.7 | 47 | 633.9 | 145.2 | 2.05 | 39.7 | V-0 [70] |
| hexa-[4-(phosphoxyanilino-phosphaphenanthrene methyl)-phenoxyl]-cyclotriphosphazene (CTP-DOPO) | 10.6 | 52 | 349.9 | 51.7 | 2.19 | 36.6 | V-0 [71] |
| polymelamine tetramethylene phosphonium sulfate (PMTMPS) | 11 | 59 | 489.9 | 80.9 | 1.78 | 32.5 | V-0 [72] |
| poly(tetraethylenepropane) tetramethylene phosphonium sulfonate (PTEPS) | 12 | 57 | 525.8 | 79.2 | 1.63 | 31.3 | V-0 [73] |
| aluminum poly-hexamethylenephosphinate (APHP) | 2 | 54 | 742 | 98 | 2.71 | 29.3 | NR [74] |
| aluminum poly-hexamethylenephosphinate (APHP) | 4 | 58 | 540 | 95 | 4.12 | 32.7 | V-1 [74] |
| aluminum poly-hexamethylenephosphinate (APHP) | 6 | 55 | 603 | 93 | 3.58 | 33.1 | V-0 [74] |
| reaction between triallyl isocyanurate & 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (TAD) | 4 | 46 | 1106 | 82 | 1.80 | 33.6 | V-1 [77] |
| reaction between triallyl isocyanurate & 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (TAD) | 6 | 57 | 691 | 81.6 | 1.65 | 32.6 | V-0 [78] |
| reaction between triallyl isocyanurate & 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (TAD) | 8 | 56 | 590 | 53.7 | 2.32 | 32.6 | V-1 [78] |
| reaction between triallyl isocyanurate & 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (TAD) | 10 | 54 | 452 | 57.7 | 2.72 | 34.2 | V-1 [78] |
| reaction between triallyl isocyanurate & 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (TAD) | 12 | 55 | 641 | 55.7 | 2.02 | 33.5 | V-0 [78] |
| reaction between triallyl isocyanurate & 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (TAD) | 4 | 46 | 1106 | 82 | 1.80 | 33.6 | V-1 [77] |
| diethylenetriamine-modified ammonium polyphosphate (DETA-APP) | 10 | 35 | 388 | 12.7 | 9.60 | 28.5 | V-0 [80] |
| diethylenetriamine-modified ammonium polyphosphate (DETA-APP) | 15 | 32 | 310.5 | 11.4 | 12.23 | 30.5 | V-0 [80] |
| diethylenetriamine-modified ammonium polyphosphate (DETA-APP) | 52 | 995 | 93.3 | 22.5 | NR [81] |
| reaction between triallyl isocyanurate & 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (TAD) | 3 | 57 | 437.2 | 60.6 | 3.84 | 31.7 | V-1 [81] |
| reaction between triallyl isocyanurate & 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (TAD) | 11.7 | 48 | 390.8 | 70.4 | 3.11 | 33.9 | V-0 [81] |
| reaction between triallyl isocyanurate & 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (TAD) | 14 | 44 | 420.7 | 67.9 | 2.74 | 36 | V-0 [81] |
| reaction between triallyl isocyanurate & 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (TAD) | 61 | 1420 | 144 | 16.4 | NR [82] |
| Epoxy Resins and Incorporated Phosphorus FR * | wt.% | TTI (s) | pHRR (kW m⁻²) | THR (MJ m⁻²) | FRI | LOI | UL94 | Ref. |
|---------------------------------------------|------|--------|---------------|-------------|-----|-----|------|------|
| addition reaction of 1,3,5-triglycidyl isocyanurate & 9,10-dihydro-9-oxa-10-phosphophenanthrene-10-oxide & 10-(2,3-dihydroxyphenyl)-10-H-9-oxa-10-phosphophenanthrene-10-oxide (TOD) | 2    | 61     | 852           | 89          | 2.69 | 32.8 | V-1  | [82] |
| addition reaction of 1,3,5-triglycidyl isocyanurate & 9,10-dihydro-9-oxa-10-phosphophenanthrene-10-oxide & 10-(2,3-dihydroxyphenyl)-10-H-9-oxa-10-phosphophenanthrene-10-oxide (TOD) | 4    | 61     | 830           | 77          | 3.19 | 35.9 | V-0  | [82] |
| addition reaction of 1,3,5-triglycidyl isocyanurate & 9,10-dihydro-9-oxa-10-phosphophenanthrene-10-oxide & 10-(2,3-dihydroxyphenyl)-10-H-9-oxa-10-phosphophenanthrene-10-oxide (TOD) | 6    | 61     | 720           | 69          | 4.11 | 38   | V-0  | [82] |
| 9,10-dihydro-9-oxa-10-phosphophenanthrene-10-oxide, 4,4-diaminodiphenyl methane (DOPO-DDM) | 68   | 1730   | 110           | —           | —    | —    | NR   | [83] |
| 9,10-dihydro-9-oxa-10-phosphophenanthrene-10-oxide-4,4-diaminodiphenyl ether (DOPO-DDS) | 61   | 893    | 112           | —           | —    | —    | NR   | [84] |
| 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide-4,4-diaminodiphenyl methylene (DOPO-DDM) | 64   | 433    | 91.1          | 2.66        | 30   | V-1  | [84] |
| 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide-4,4-diaminodiphenyl sulfone (DOPO-DDE) | 69   | 961    | 96            | —           | 20   | NR   | [85] |
| 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide-4,4-diaminodiphenyl ether (DOPO-DDS) | 70   | 1000   | 89            | 21.5        | —    | NR   | [86] |
| bisphenol-S bridged 1,3,5-triazinane-2,4,6-trione (PN) | 47   | 71     | 652           | 72          | 1.94 | 33.5 | V-0  | [87] |
| bis[2,6-dimethylphenylphenylphosphonate (BDMP)] | 75   | 685    | 65            | —           | 20.3 | NR   | [88] |
| amine-terminated cyclophosphazene (ATCP) | 57   | 713    | 64            | 28          | V-1  | [89] |
| amine-terminated cyclophosphazene (ATCP) | 52   | 610    | 58            | 1.17        | 34   | V-0  | [89] |
| 9,10-Dihydro-9-oxa-10-phosphophenanthrene-10-oxide (DOPO) | 4.5  | 83     | 724           | 73          | 2.02 | 31.5 | V-1  | [91] |
| 10-Dihydro-9-oxa-10-phosphophenanthrene-10-oxide & 2-amino(benzothiazole (DOPO-ABZ) reaction between 9,10-Dihydro-9-oxa-10-phosphophenanthrene-10-oxide & 2-amino(benzothiazole (DOPO-ABZ) reaction between 9,10-Dihydro-9-oxa-10-phosphophenanthrene-10-oxide & 2-amino(benzothiazole (DOPO-ABZ) reaction between 9,10-Dihydro-9-oxa-10-phosphophenanthrene-10-oxide & 2-amino(benzothiazole (DOPO-ABZ) reaction between 9,10-Dihydro-9-oxa-10-phosphophenanthrene-10-oxide & 2-amino(benzothiazole (DOPO-ABZ) reaction between 9,10-Dihydro-9-oxa-10-phosphophenanthrene-10-oxide & 2-amino(benzothiazole (DOPO-ABZ) reaction between 9,10-Dihydro-9-oxa-10-phosphophenanthrene-10-oxide & 2-amino(benzothiazole (DOPO-ABZ) reaction between 9,10-Dihydro-9-oxa-10-phosphophenanthrene-10-oxide & 2-amino(benzothiazole (DOPO-ABZ) reaction between 9,10-Dihydro-9-oxa-10-phosphophenanthrene-10-oxide & 2-amino(benzothiazole (DOPO-ABZ) reaction between 9,10-Dihydro-9-oxa-10-phosphophenanthrene-10-oxide & 2-amino(benzothiazole (DOPO-ABZ) reaction between 9,10-Dihydro-9-oxa-10-phosphophenanthrene-10-oxide & 2-amino(benzothiazole (DOPO-ABZ) reaction between 9,10-Dihydro-9-oxa-10-phosphophenanthrene-10-oxide & 2-amino(benzothiazole (DOPO-ABZ) reaction between 9,10-Dihydro-9-oxa-10-phosphophenanthrene-10-oxide & 2-amino(benzothiazole (DOPO-ABZ) reaction between 9,10-Dihydro-9-oxa-10-phosphophenanthrene-10-oxid |
Table 1. Cont.

| Epoxy Resins and Incorporated Phosphorus FR * | wt.% | TTI (s) | pHRR (kW m⁻²) | THR (MJ m⁻²) | FRI | LOI | UL94 Ref. |
|---------------------------------------------|------|---------|---------------|--------------|-----|-----|----------|
| aluminum poly-hexamethylenephosphatinate (APHP) | 10   | 56     | 855           | 90           | 1.03 | 31.5 | NR [95]  |
| bisphenol-A bis(diphenyl phosphate) (BDP)     | 10   | 50     | 746           | 86           | 1.11 | 33.4 | NR [95]  |
| isopropylphenyl phosphate (FIPP)              | 20   | 47     | 722.7         | 86.7         |       | 20.5 | NR [96]  |
| tertbutylphenyl phosphate (FTBP)              | 20   | 50     | 361.8         | 61.4         | 2.51 | 30.3 | V-0 [96] |
| phenolphosphonic di-benzothiazolyl amide (PBDAB) | 10   | 65     | 966           | 96           |       | 22.5 | NR [97]  |
| aluminum poly-hexamethylenephosphatinate (APHP) | 5    | 46     | 892           | 91           | 1.60 | 26.8 | V-1 [98] |
| bisphenol-A bis(diphenyl phosphate) (BDP)     | 9    | 47     | 805           | 89           | 1.11 | 29.2 | V-0 [96] |
| isopropylphenyl phosphate (FIPP)              | 9    | 47     | 805           | 89           | 1.86 | 33.4 | V-0 [96] |
| phenolphosphonic di-benzothiazolyl amide (PBDAB) | 15   | 46     | 602           | 84           | 2.58 | 31.5 | V-1 [98] |
| polystyrene encapsulating ammonium polyphosphate (PS-APP) | 2    | 21     | 1092.2        | 86.4         | 0.58 | 23.2 | NR [99]  |
| polystyrene encapsulating ammonium polyphosphate (PS-APP) | 5    | 20     | 939.5         | 92.6         | 0.59 | 25.7 | V-1 [99] |
| polystyrene encapsulating ammonium polyphosphate (PS-APP) | 10   | 10     | 614.2         | 85.8         | 0.49 | 26.8 | V-1 [99] |
| isopropylphenyl phosphate (FIPP)              | 20   | 25     | 733.7         | 81.7         | 1.09 | 28.7 | V-1 [99] |
| polystyrene encapsulating ammonium polyphosphate (PS-APP) | 48   | 58     | 631           | 104          | 1.64 | 27.1 | V-1 [99] |
| polystyrene encapsulating ammonium polyphosphate (PS-APP) | 2.5  | 62     | 404           | 87           | 3.29 | 26.2 | V-1 [99] |
| polystyrene encapsulating ammonium polyphosphate (PS-APP) | 10   | 61     | 346           | 79           | 4.16 | 24.8 | NR [100] |
| polystyrene encapsulating ammonium polyphosphate (PS-APP) | 45   | 58     | 588           | 92           | 2.28 | 28.5 | NR [100] |
| polystyrene encapsulating ammonium polyphosphate (PS-APP) | 76   | 57     | 393           | 33           | 8.91 | 30   | V-0 [100] |
| 1-oxo-4-hydroxymethyl-2,6,7-trioxa-l-phosphabicyclo[2.2.2] octane (PEPA) | 5.2  | 53     | 538           | 78           | 2.43 | 27   | NR [100] |
| Ammonium polyphosphate (APP)                  | 50   | 860    | 112           | 23           | NR   |       | 100%     |
| ammonium polyphosphate montmorillonite nanocomposite (APP-MMT) | 50   | 860    | 112           | 23           | NR   |       | 100%     |

*FR = Flame Retardant
| Epoxy Resins and Incorporated Phosphorus FR * | wt.% | TTI (s) | pHRR (kW m$^{-2}$) | THR (MJ m$^{-2}$) | FRI | LOI | UL94 | Ref. |
|---------------------------------------------|------|--------|-------------------|-----------------|-----|-----|------|------|
| glycidyl methacrylate microencapsulated ammonium polyphosphate (GMA-APP) | 15 | 68 | 283.09 | 44 | 18.91 | 38.5 | V-0 | [108] |
| ammonium polyphosphate (APP) | 62 | 1192 | 184 | 6.97 | 31 | V-0 | [109] |
| modified ammonium polyphosphate (MAPP) | 12 | 41 | 200 | 104 | 6.97 | 31 | V-0 | [109] |
| hexa-(phosphophenanthrene) | 66 | 893 | 68 | 32.5 | V-0 | [111] |
| epoxy Resins and Incorporated Phosphorus FR * wt.% TTI (s)pHRR (kW m$^{-2}$) THR (MJ m$^{-2}$) FRI LOI UL94 Ref. |
| 9,10-dihydro-9-oxa-10-phosphophenanthrene-10-oxide units linked to the star-shaped aliphatic ground body tetra-[acyloxyloxy]ethyl] pentarythrit (DOPP) | 19.6 | 40 | 1191 | 44.8 | 2.73 | 37.9 | V-1 | [113] |
| 9,10-dihydro-9-oxa-10-phosphophenanthrene-10-oxide units linked to the star-shaped aliphatic ground body tetra-[acyloxyloxy]ethyl] isocyanurate (DOPP) | 23.1 | 36 | 869 | 41.5 | 3.63 | 34.2 | V-0 | [113] |
| polyanion polyphosphate (APP) | 5 | 61 | 283 | 111 | 5.09 | 27.1 | V-0 | [117] |
| cardanol derived benzoxazine monomer (CBz) | 10 | 49 | 1119 | 80.5 | 1.09 | 31 | V-1 | [118] |
| cardanol derived benzoxazine monomer (CBz) | 15 | 50 | 920 | 79.4 | 1.38 | 32 | V-0 | [118] |
| reaction of spirocyclic pentaerythrit bisphosphorate disphosphoryl chloride & 2,4-dihydroxybenzophenone (MFR) | 10 | 26 | 402.3 | 53.3 | 1.69 | 29.6 | V-1 | [9] |
| reaction of spirocyclic pentaerythrit bisphosphorate disphosphoryl chloride & 2,4-dihydroxybenzophenone (MFR) | 15 | 17 | 479.7 | 47.8 | 1.03 | 30.8 | V-0 | [9] |
| reaction of spirocyclic pentaerythrit bisphosphorate disphosphoryl chloride & 2,4-dihydroxybenzophenone (MFR) | 20 | 22 | 241.6 | 42.3 | 3.00 | 32.2 | V-0 | [9] |
| poly (piperazine phosphophenanthrene) (DOPMPA) | 4 | 55 | 658 | 86.9 | 1.33 | 25.3 | V-1 | [116] |
| poly (piperazine phosphophenanthrene) (DOPMPA) | 13 | 67 | 285 | 27.4 | 11.26 | 34 | V-0 | [119] |
| poly (piperazine phosphophenanthrene) (DOPMPA) | 28 | 673.7 | 56 | 22.3 | V-0 | [9] |
| poly (piperazine phosphophenanthrene) (DOPMPA) | 10 | 68 | 393 | 56.3 | 4.21 | 29 | V-1 | [115] |
| poly (piperazine phosphophenanthrene) (DOPMPA) | 60 | 920 | 90.5 | 22.7 | NR | [116] |
| poly (piperazine phosphophenanthrene) (DOPMPA) | 5 | 54 | 461 | 70 | 2.01 | 33.7 | V-1 | [115] |
| poly (piperazine phosphophenanthrene) (DOPMPA) | 64 | 821 | 74.2 | 25 | HB | [113] |
| poly (piperazine phosphophenanthrene) (DOPMPA) | 0.4 | 70.2 | 1295 | 133.4 | 1.30 | 23.5 | NR | [17] |
| poly (piperazine phosphophenanthrene) (DOPMPA) | 0.8 | 64 | 1086 | 125.3 | 1.50 | 24 | NR | [17] |
| poly (piperazine phosphophenanthrene) (DOPMPA) | 1.6 | 58.6 | 1227 | 131.1 | 1.16 | 24.5 | NR | [17] |
Table 1. Cont.

| Epoxy Resins and Incorporated Phosphorus FR * | wt.% | TTI (s) | pHRR (kW m⁻²) | THR (MJ m⁻²) | FRI | LOI | UL94 | Ref. |
|---------------------------------------------|------|---------|----------------|---------------|-----|-----|------|------|
| 9,10-dihydro-9-oxa-10-phosphaherrene-10-oxide-covalent organic framework nanosheets (reaction between melamine & o-phthalaldehyde) (DOPO-COFs) | 3.2  | 60.7  | 1117 | 110.5 | 1.57 | 25 | NR | [17] |
| melamine coated ammonium polyphosphate (Mel-APP) | 20  | 22  | 312.6  | 30.8  | 17.54 | 32.6 | V-0 | [120] |
| phosphorus and nitrogen-containing flame retardant (FR) | 1  | 43  | 1631  | 69.6  | 1.16 | 22.5 | NR | [121] |
| poly(4,4′-diamino diphenyl sulfone phenyl phosphonamide) (ArPN₂) | 15.6  | 30  | 546  | 59.4  | 2.65 | — | NR | [122] |
| ionic liquid-based metal–organic hybrid = Phosphomolybdic acid hydrate:PMA & 1-ethyl 3-(diethoxyphosphoryl)-propylimidazolium bromide:IL (PMAIL) | 6  | 85  | 674.4  | 99  | 1.65 | — | V-0 | [123] |
| oligo[DOPAc-2-tris(acryloyloxy)ethyl isocyanurate] (oDOPI) | 13.8 | 52  | 426  | 86  | 2.08 | — | V-0 | [124] |
| Phosphazene (PZ) | 10.8  | 50  | 466  | 80  | 1.97 | — | V-0 | [124] |
| Melamine coated ammonium polyphosphate (Mel-APP) | 29.7  | 24  | 261  | 23  | 18.81 | — | V-0 | [125] |
| Melamine (PAlP) | 20  | 40  | 540  | 60  | 1.85 | — | HB | [127] |
| Melamine poly(zinc phosphate) (MnPzP) | 20  | 43  | 298  | 57.3  | 3.86 | — | V-1 | [127] |
| Melamine poly(magnesium phosphate) (M MPgP) | 20  | 44  | 244  | 26.6  | 8.77 | — | V-0 | [127] |
| Melamine polyphosphate (MPP) | 15  | 45  | 370  | 86  | 2.08 | — | V-1 | [127] |
| diethyl aluminium phosphinate (AlPi-Et) | 20  | 41  | 492  | 55.8  | 2.23 | — | V-0 | [127] |
| 6H-dibenzo[c,e][1,2] oxaphosphorin-6-propanoic acid, butyl ester, 6-oxide (DOPAc-Bu) | 20  | 44  | 624  | 50.2  | 2.10 | — | V-0 | [128] |
| Tetraphenylphosphonium modified montmorillonite (TPP-MMT) | 5  | 110  | 482  | 140  | 1.68 | 25 | HB | [130] |
| Tetraphenylphosphonium modified montmorillonite (TPP-MMT) | 5  | 53  | 571  | 138  | 1.92 | 25 | HB | [130] |
| Tetraphenylphosphonium modified montmorillonite (TPP-MMT) | 5  | 25  | 694  | 105  | 2.05 | 25 | HB | [130] |
| hyperbranched poly(phosphoester) (hpPPE) | 10  | 49  | 506  | 62  | 2.73 | 23.6 | HB | [131] |
| hyperbranched poly(phosphoester) (hpPPE) | 20  | 49  | 699  | 53  | 2.31 | 25 | HB | [131] |
| polycyclotriphosphazeno-[4,4'-sulfonyldiphenol] (PZS) hybrid | 3  | 61  | 586.5  | 91.89  | 1.31 | 28.6 | — | [132] |
| poly(cyclotriphosphazeno-4,4′-sulfonyldiphenol) (PZS) | 3  | 60  | 801.2  | 88.96  | 1.64 | 29.5 | — | [132] |
| 1-oxo-4-hydroxymethyl-2,6,7-trioxa-l-phosphabicyclo[2.2.2] octane modified trimellitic anhydride chloride (PEPA-TMAC) 1-oxo-4-hydroxymethyl-2,6,7-trioxa-l-phosphabicyclo[2.2.2] octane modified trimellitic anhydride chloride (PEPA-TMAC) | 16.5  | 30.1  | 523.7  | 42  | 2.14 | 23.4 | — | [133] |
| 1-oxo-4-hydroxymethyl-2,6,7-trioxa-l-phosphabicyclo[2.2.2] octane modified trimellitic anhydride chloride (PEPA-TMAC) | 33  | 33.9  | 337.2  | 36.9  | 4.27 | 26.9 | — | [133] |
| 1-oxo-4-hydroxymethyl-2,6,7-trioxa-l-phosphabicyclo[2.2.2] octane modified trimellitic anhydride chloride (PEPA-TMAC) | 50  | 986  | 91.1  | — | 25 | — | [134] |
| polycyclotriphosphazeno-c-sulfonyldiphenol (PCPS) | 1  | 49  | 979  | 92.1  | 0.97 | 27 | — | [134] |
| polycyclotriphosphazeno-c-sulfonyldiphenol (PCPS) | 3  | 44  | 500  | 85.8  | 1.84 | 29.8 | — | [134] |
| polycyclotriphosphazeno-c-sulfonyldiphenol (PCPS) | 5  | 43  | 542  | 78.7  | 1.81 | 30.5 | — | [134] |
| Boron phosphate: reaction between boric acid & phosphoric acid by calcining at 300 °C (BP1) | 5  | 53  | 652  | 31  | 2.80 | 29.6 | — | [135] |
| Boron phosphate: reaction between boric acid & phosphoric acid by calcining at 400 °C (BP2) | 5  | 53  | 654  | 34  | 2.54 | 29.7 | — | [135] |
### Table 1. Cont.

| Epoxy Resins and Incorporated Phosphorus FR  *                  | wt.% | TTI (s) | pHRR (kW·m⁻²) | THR (MJ·m⁻²) | FRI | LOI | UL94 | Ref. |
|---------------------------------------------------------------|------|---------|----------------|---------------|-----|-----|------|------|
| Boron phosphate: reaction between boric acid & phosphoric acid by calcining at 500 °C (BP3) | 5    | 54      | 661            | 33            | 2.57| 29.6| —    | [135]|
| Boron phosphate: reaction between boric acid & phosphoric acid by calcining at 600 °C (BP4) | 5    | 56      | 710            | 38            | 2.22| 29.3| —    | [135]|
| Boron phosphate: reaction between boric acid & phosphoric acid by calcining at 700 °C (BP5) | 5    | 56      | 754            | 38            | 2.09| 29  | —    | [135]|
| 3-((Methoxydiphenylsilyl)oxy)-9-methyl-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane 3,9-dioxide (SDPS) | 10.4 | 62      | 1378           | 203           | 0.90| 28.9| —    | [136]|
| dicyclonaphosphinolic acid modified aluminum hydroxide (AOHP-NR) | 4.25 | 79      | 789            | 101           | 2.30| 28  | —    | [137]|
| diallylphosphinolic acid modified aluminum hydroxide (AOHP-C1) | 4.25 | 80      | 1092           | 107           | 1.59| 23.4| —    | [137]|
| bis(3-methoxy-3-oxopropyl)phosphinolic acid modified aluminum hydroxide (AOHP-C2) | 4.25 | 58      | 1063           | 99            | 1.28| 23.6| —    | [137]|
| N,N-bis(2-hydroxyethyl acrylate) aminomethyl phosphonic acid diethylester (BHAAPE) | 10   | 25      | 590            | 23.7          | 1.09| 30  | —    | [136]|
| dibenzylphosphinolic acid modified aluminum hydroxide (AOPH-NR) | 4.25 | 79      | 1378           | 203           | 0.90| 28.9| —    | [137]|
| dibenzylphosphinolic acid modified aluminum hydroxide (AOPH-C1) | 4.25 | 80      | 1092           | 107           | 1.59| 23.4| —    | [137]|
| diallylphosphinolic acid modified aluminum hydroxide (AOPH-C2) | 4.25 | 58      | 1063           | 99            | 1.28| 23.6| —    | [137]|
| Polyphosphazene functionalized black phosphorus nanosheets (BP-PZN) | 0.5  | 78      | 1363.4         | 86.8          | 1.82| —   | —    | [141]|
| Polyphosphazene functionalized black phosphorus nanosheets (BP-PZN) | 1    | 85      | 1082.1         | 73.5          | 4.84| —   | —    | [141]|
| Polyphosphazene functionalized black phosphorus nanosheets (BP-PZN) | 2    | 81      | 859.5          | 60.8          | 7.02| —   | —    | [142]|
| Dimethyl methylphosphonate loaded halloysite nanotube (DMMP-HNT) | 20   | 24      | 578.1          | 73.8          | 2.44| —   | —    | [146]|
| melamine poly(magnesium phosphate) (S600) | 20   | 44      | 298.0          | 57            | 3.89| —   | —    | [147]|
| aluminium diethylphosphinate (AlPi) | 20   | 41      | 492            | 56            | 2.23| —   | —    | [147]|
| melamine polyphosphate (MPM) | 20   | 38      | 244            | 26            | 9.00| —   | —    | [147]|
| poly-(cyclophosphazene-co-4,4′-diaminodiphenyl ether) surface modified silica nanospheres (SiC8@PZM) | 1    | 80      | 1363.4         | 86.8          | 1.88| —   | —    | [148]|

*FR = flame retardant, pHRR = peak heat release rate, THR = total heat release, FRI = flame regression index, LOI = limiting oxygen index, UL94 = Underwriters Laboratories 94.
| Table 1. Cont.                                                                 |
|-----------------------------------------------------------------------------|
| **Epoxy Resins and Incorporated Phosphorus FR**                             |
| **wt.%**  **TTI (s)**  **pHRR (kW m⁻²)**  **THR (MJ m⁻²)**  **FRI**  **LOI**  **UL94**  **Ref.** |
| poly-(cyclophosphazene-co-4,4'-diaminodiphenyl ether) surface modified silica nanospheres-cuprous (SiO₂@PZM@Cu) | 1  | 74 | 1289.3 | 78 | 2.04 | — | — | [148] |
| poly-(cyclophosphazene-co-4,4'-diaminodiphenyl ether) surface modified silica nanospheres-cuprous (SiO₂@PZM@Cu) | 2  | 80 | 1188.8 | 73.9 | 2.53 | — | — | [148] |
| functionalized polyphosphazene nanotubes wrapped with a cross-linked DOPO-based flame retardant (FR@PZS) | 0.5 | 82 | 1584.2 | 87 | 1.31 | — | — | [149] |
| functionalized polyphosphazene nanotubes wrapped with a cross-linked DOPO-based flame retardant (FR@PZS) | 1  | 82 | 1298.2 | 80.8 | 1.72 | — | — | [149] |
| functionalized polyphosphazene nanotubes wrapped with a cross-linked DOPO-based flame retardant (FR@PZS) | 3  | 82 | 982.6 | 72.4 | 2.54 | — | — | [149] |
| polyphosphazene nanotube (PZS) | 3  | 82 | 1152.5 | 83.9 | 1.86 | — | — | [149] |
| ammonium polyphosphate (APP) | 5  | 36 | 543 | 58.8 | 1.68 | — | — | [150] |
| 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO-POSS) | 20 | 57 | 431 | 91 | 3.25 | — | — | [151] |
| Epoxy acrylic | 32 | 223.4 | 30.8 | — | — | [152] |
| ammonium polyphosphate (APP) | 30 | 35 | 225.2 | 30.7 | 1.08 | — | — | [152] |
| Co-microencapsulated ammonium polyphosphate and pentaerythritol (M(APP & PER)) | 30 | 58 | 232.2 | 27.3 | 1.95 | — | — | [152] |
| Triphenylphosphate (TPP) | 15 | 21 | 504 | 114 | 5.09 | — | — | [153] |
| Triphenylphosphine oxide (TPPO) | 15 | 34 | 1310 | 126 | 2.87 | — | — | [153] |
| — | 32 | 2572 | 184 | — | — | [154] |
| poly(phenylene methyl 1phosphonate) (PMP) | 11.4 | 7 | 1286 | 100 | 0.80 | — | — | [154] |
| Polyhedral oligomeric silsesquioxane containing 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO-POSS) | 20 | 57 | 431 | 91 | 3.25 | — | — | [151] |
| Epoxy acrylic | 32 | 223.4 | 30.8 | — | — | [152] |
| ammonium polyphosphate (APP) | 30 | 35 | 225.2 | 30.7 | 1.08 | — | — | [152] |
| Co-microencapsulated ammonium polyphosphate and pentaerythritol (M(APP & PER)) | 30 | 58 | 232.2 | 27.3 | 1.95 | — | — | [152] |
| Triphenylphosphate (TPP) | 15 | 21 | 504 | 114 | 5.09 | — | — | [153] |
| Triphenylphosphine oxide (TPPO) | 15 | 34 | 1310 | 126 | 2.87 | — | — | [153] |
| — | 32 | 2572 | 184 | — | — | [154] |
| poly(phenylene methyl 1phosphonate) (PMP) | 11.4 | 7 | 1286 | 100 | 0.80 | — | — | [154] |
| Polyhedral oligomeric silsesquioxane containing 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO-POSS) | 20 | 57 | 431 | 91 | 3.25 | — | — | [151] |
| Epoxy acrylic | 32 | 223.4 | 30.8 | — | — | [152] |
| ammonium polyphosphate (APP) | 30 | 35 | 225.2 | 30.7 | 1.08 | — | — | [152] |
| Co-microencapsulated ammonium polyphosphate and pentaerythritol (M(APP & PER)) | 30 | 58 | 232.2 | 27.3 | 1.95 | — | — | [152] |
| Triphenylphosphate (TPP) | 15 | 21 | 504 | 114 | 5.09 | — | — | [153] |
| Triphenylphosphine oxide (TPPO) | 15 | 34 | 1310 | 126 | 2.87 | — | — | [153] |
| — | 32 | 2572 | 184 | — | — | [154] |
| poly(phenylene methyl 1phosphonate) (PMP) | 11.4 | 7 | 1286 | 100 | 0.80 | — | — | [154] |
| Polyhedral oligomeric silsesquioxane containing 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO-POSS) | 20 | 57 | 431 | 91 | 3.25 | — | — | [151] |
| Epoxy acrylic | 32 | 223.4 | 30.8 | — | — | [152] |
| ammonium polyphosphate (APP) | 30 | 35 | 225.2 | 30.7 | 1.08 | — | — | [152] |
| Co-microencapsulated ammonium polyphosphate and pentaerythritol (M(APP & PER)) | 30 | 58 | 232.2 | 27.3 | 1.95 | — | — | [152] |
| Triphenylphosphate (TPP) | 15 | 21 | 504 | 114 | 5.09 | — | — | [153] |
| Triphenylphosphine oxide (TPPO) | 15 | 34 | 1310 | 126 | 2.87 | — | — | [153] |
| — | 32 | 2572 | 184 | — | — | [154] |
| poly(phenylene methyl 1phosphonate) (PMP) | 11.4 | 7 | 1286 | 100 | 0.80 | — | — | [154] |
| Polyhedral oligomeric silsesquioxane containing 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO-POSS) | 20 | 57 | 431 | 91 | 3.25 | — | — | [151] |
| Epoxy acrylic | 32 | 223.4 | 30.8 | — | — | [152] |
| ammonium polyphosphate (APP) | 30 | 35 | 225.2 | 30.7 | 1.08 | — | — | [152] |
| Co-microencapsulated ammonium polyphosphate and pentaerythritol (M(APP & PER)) | 30 | 58 | 232.2 | 27.3 | 1.95 | — | — | [152] |
| Triphenylphosphate (TPP) | 15 | 21 | 504 | 114 | 5.09 | — | — | [153] |
| Triphenylphosphine oxide (TPPO) | 15 | 34 | 1310 | 126 | 2.87 | — | — | [153] |
| — | 32 | 2572 | 184 | — | — | [154] |
A brief yet informative view of the effect of the used P family of FRs on the flame retardancy performance of epoxy resins is given in Figure 1. It is apparent from the figure that all sorts of behavior, including Poor, Good, and Excellent flame-retardant performance, are achieved. This is the characteristic of dependency of flame retardancy performance on both the type and the content of the P type of FR. It can be observed that the majority of epoxy systems contains less than 20 wt.% of phosphorus flame retardant used. Precise detection of the performance of each class of FR: contains melamine phosphate (IFR) [164]

\[ \text{IFR: contains melamine phosphate (IFR)} \]

Hollow symbols are indicative of fiber-incorporated composites

\[ \text{Hollow symbols are indicative of fiber-incorporated composites} \]

- Matrix: eight layers of Woven E-glass fabric reinforced epoxy; - Matrix: six layers of dry carbon fiber fabric reinforced RTM6 epoxy; - Matrix: Unidirectional carbon fiber reinforced epoxy resin; - Matrix: Carbon fibers reinforced epoxy; - Matrix: eight layers of Woven E-glass fabric reinforced epoxy; - Matrix: eight layers of Woven E-glass fabric reinforced epoxy resin; - Matrix: four fabric layers of unidirectional hemp fabric reinforced epoxy; - Matrix: eight layers of Woven E-glass fabric reinforced epoxy phenol novolak resin blend; - Matrix: eight layers of woven E-glass reinforced epoxy; - Matrix: six layers of plain weave hemp fabric-reinforced epoxy; - Matrix: six layers of plain weave Hemp fabrics treated with water glass-reinforced epoxy.

| Epoxy Resins and Incorporated Phosphorus FR * | wt.% | TTI (s) | pHRR (kW m⁻²) | THR (MJ m⁻²) | FRI | LOI | UL94 | Ref. |
|---------------------------------------------|------|--------|--------------|-------------|-----|-----|-------|-----|
| 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide-phosphonamidate functionalized reduced graphene oxide (DOPOph-RGNO) | 2    | 43     | 1248         | 55          | 1.78 | —   | —    | [161]|
| 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide-phosphonamidate functionalized reduced graphene oxide (DOPOP-RGNO) | 3    | 45     | 1117         | 54          | 2.12 | —   | —    | [161]|
| melamine coated ammonium polyphosphate (Mel-APP) * | 0    | 21     | 453.5        | 36.2        | 22.1 | NR  | —    | [120]|
| N, N'-diallyl-p-phenyl phosphonodicamidine (FPD) b | 9.59 | 20     | 290.4        | 32.2        | 1.67 | 32 V-1 | [120]|
| N, N'-diallyl-p-phenyl phosphonodicamidine (FPD) b | 0    | 53     | 387          | 24.3        | 31   | NR  | [24] |
| polyelectrolyte complexes consisting of chitosan & ammonium polyphosphate (PEC) c | 6.9  | 50     | 307.5        | 39.6        | 1.84 | 38 V-1 | [162]|
| polyelectrolyte complexes consisting of chitosan & ammonium polyphosphate (PEC) c | 8.1  | 49     | 255.9        | 35.5        | 2.42 | 40.5 V-0 | [162]|
| 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide units linked to the star-shaped aliphatic ground body tetra-[{acryloyloxy}ethyl] pentafuryl (DOPP) d | 5.9  | 56     | 248          | 19.9        | 2.02 | 45 V-0 | [113]|
| 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide units linked to the star-shaped aliphatic ground body betacyclic tris-[(acryloyloxy)ethyl] isocyanurate (DOPP) d | 6.9  | 60     | 247          | 20          | 2.16 | 47 V-0 | [113]|
| Melamine coated ammonium polyphosphate (Mel-APP) * | 14.6 | 22     | 231          | 11          | 5.96 | —    | V-1  | [126]|
| — | 42     | 385    | 21.8        | 27          | 25.0 | —    | 163, 164 | |
| IFR: contains melamine phosphate (IFR) e | 4.7  | 35     | 278          | 18.3        | 1.37 | 35 V-1 | [164]|
| ammonium polyphosphate (APP) f | 5    | 24     | 345          | 18.6        | 0.95 | —    | [150]|
| ammonium polyphosphate (APP) h | 3.15 | 20.3   | 375.3        | 42          | 2.97 | —    | [165]|
| ammonium polyphosphate (APP) h | 8.88 | 18.1   | 293.8        | 33          | 4.31 | —    | [165]|
| ammonium polyphosphate (APP) h | 16.32 | 21     | 186.7        | 27          | 9.62 | —    | [165]|
| — | 44     | 853    | 51.9        | 27          | 25   | —    | 163, 164 | |
| melamine phosphate (MP) g | 5    | 38     | 528          | 48.8        | 1.48 | —    | —    | [166]|
| 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) i | 5    | 34     | 624          | 41.3        | 1.32 | —    | —    | [166]|
| IFR: contains melamine phosphate (IFR) j | 0    | 39     | 456          | 38          | —    | —    | —    | [166]|
| IFR: contains melamine phosphate (IFR) j | 10   | 50     | 226          | 17.3        | 5.68 | —    | —    | [166]|
| IFR: contains melamine phosphate (IFR) j | 15   | 94     | 253          | 18.6        | 8.87 | —    | —    | [166]|
| ammonium polyphosphate (APP) k | 55   | 75     | 613          | 61.3        | —    | —    | —    | [166]|
| ammonium polyphosphate (APP) k | 15   | 46     | 259          | 34.4        | 4.33 | —    | —    | [166]|
| ammonium polyphosphate (APP) k | 15   | 44     | 232          | 40.1        | 4.99 | —    | —    | [166]|

* Matrix: eight layers of Woven E-glass fabric reinforced epoxy; " Matrix: six layers of dry carbon fiber fabric reinforced RTM6 epoxy; c Matrix: Unidirectional carbon fiber reinforced epoxy resin; d Matrix: Carbon fibers reinforced epoxy; e Matrix: eight layers of Woven E-glass fabric reinforced epoxy; f Matrix: eight layers of Woven E-glass fabric reinforced film of multifunctional epoxy resin; g Matrix: carbon fiber reinforced epoxy resin; h Matrix: four fabric layers of unidirectional hemp fabric reinforced epoxy; i Matrix: eight layers of plain roving glass fabric reinforced epoxy phenol novolak resin blend; j Matrix: eight layers of woven E-glass reinforced epoxy; k Matrix: six layers of plain weave hemp fabric-reinforced epoxy; l Matrix: six layers of plain weave Hemp fabrics treated with water glass-reinforced epoxy.
A brief yet informative view of the effect of the used P family of FRs on the flame retardancy of the performance of each class of P-type FR in this table from one side and the chemical structure of the used FR from the other side should be balanced towards a high-performance FR for developing flame-retardant epoxy composites.

| P-type FR | Flame Retardancy Analysis |
|-----------|---------------------------|
| MDOP-1.9  | Excellent                 |
| MDOP-3.75 | Excellent                 |
| MDOP-7.24 | Excellent                 |
| AlPi-7    | Excellent                 |
| MPP-7     | Excellent                 |
| A-BP-9    | Excellent                 |
| CLEP–DOPO–POSS-2.91 | Excellent |

Figure 1. Flame retardancy analysis of epoxy resins containing phosphorus flame retardants in terms of the FRI values as a function of P type and content. Symbols are indicative of different types of phosphorus flame retardant used. Hollow symbols are indicative of fiber-incorporated composites with details earlier given in the bottom of Table 1 as a to l notes. Here: ▲ FP-1, FP-1-5, FP-1-8 [24], 口 DPO-PHE-11.68, DPO-PHE-12.03 [25], ▲ DOPO-T-2.34, DOPO-T-4.67, DOPO-T-6.99, DOPO-T-9.34 [26], ♦ AEPP-5, AEPP-10, AEPP-15 [27], ▲ DiDOPO-5 [28], ▲ DiDOPO-10, DiDOPO-11 [29], ▲ DiDOPO-7 [30], ▲ DiDOPO-5, DiDOPO-10, DiDOPO-15, DiDOPO-20 [32], • PPMS-15, PPMS-EG-15 [33], • PPMS-MWCNT-5, PPMS-MWCNT-10, PPMS-MWCNT-15, PPMS-15 [34], + DPP-7.5, DPP-15, DPP-7.5, DPP-15 [35], ▲ IDOP-5, IDOP-10, IDOP-15 [36], ▲ PPAP-5 [37], ▲ AlPb-10, AlPb-11, AlPb-12 [38], ▲ MPL-DOPO-2.5, MPL-DOPO-5, DDM-DOPO-2.5, DDM-DOPO-5 [39], ▲ ATZ-6 [40], ▲ P-KC-30, DOPO-30 [41], ▲ DHPP-OH-BAC-5, DHPP-OH-BAC-10, DHPP-OH-BAC-15 [42], ▲ PPAP-5, PPAP-10, PPAP-20 [43], ▲ [Dmim]Tos-2.4, [Dmim]Tos-4, [Dmim]Tos-7.5 [44], ▲ MPhP-10, MPhP-15, MPhP-20 [45], ▲ MDOP-0.96, MDOP-1.9, MDOP-3.75, MDOP-7.24 [46], ▲ AIp-7, AIp-10, AIp-15, AIp-20 [47], ▲ A-BP-9 [48], ▲ CLEP-DOP-POSS-2.91 [19], ○ CuP-1, CuP-2, CuP-4, CuP-6, CuP-8 [49], ▲ DOP-ABZ-15, DOP-ABZ-17.5, DOP-ABZ-20 [50], ▲ DOP-7.11, BPD-3.88, BPD-6.71, BPD-10.04, BPD-13.41 [51], ▲ DOP-7.7, HPCP-8.2 [52], ▲ DOP-TM-2.5, DOP-TM-5, DOP-TM-7.5, DOP-TM-10 [53], ▲ HB-DPP-2 [54], ▲ APP-21, EDA-APP-21 [55], ▲ CP-68-3 [56], ▲ PM-2, PM-6, PM-βCD-2, PM-βCD-6 [57], ▲ PSA-10, PSA-20 [58], ▲ BPA-BP-9 [59], ▲ DOPO-9.1, DOPO-PEPA-9.1, DOPO-PEPA-5.7, DOPO-PEPA-7.4, DOPO-PEPA-9.1 [60], ▲ DOPO-POSS-2.5, DOPO-POSS-5, DOPO-POSS-10 [61], ▲ HPCTP-7.46, HPCTP-11.19, HPCTP-14.92, DOPO-6.97, DOPO-10.46, DOPO-13.94 [62], ▲ TP-12.42, TNT-14.36 [63], ▲ DOPO-7, BNP-7, BNP-11, BNP-14.7, BNP-18.4 [64], ▲ DOPO-7, DTB-7, DTB-10, DTB-15, DTB-20 [65], ▲ DOPO-7.7, HPCP-8.2 [66], ▲ DOPO-7.1 [67], ▲ DOPO-7, DOPO-7-TM-7, DOPO-TM-10.4, DOPO-TM-13.9, DOPO-TM-17.3, DOPO-TM-20.8 [68], ▲ HMP-3.4, HMP-6.8, HMP-10.2, HMP-13.6, HMP-17 [69], ▲ DOPO-bp-3.4, DOPO-bp-6.7, DOPO-bp-13.5 [70], ▲ CTP-DOPO-10.6 [71], ▲ PMTMS-11 [72], ▲
Although variation of FRI values according to the composition reflects the flame retardancy of epoxy composites from cone calorimeter angle (the most reliable test among those normally used for analysis of performance of flame retardants), other types of flame tests would give more insights into the real effect of one or complementary actions of two or more P type FR additives in epoxy. Based on available data, a brief view of the effect of the used P-based FRs on the flame retardancy performance of epoxy resins as a function of UL94 results is given in Figure 2. The distribution of data in this figure gives useful information about the efficiency of the FR system in harsh conditions. For instance, this figure suggests that V-0 performance in UL94 can be achieved even at the Poor category of flame retardancy performance in terms of FRI. It appears that it is not possible to roughly correlate the obtained results in UL94 to those obtained in cone calorimeter tests.
Although variation of FRI values according to the composition reflects the flame retardancy of epoxy composites from cone calorimetry angle (the most reliable test among those normally used for analysis of performance of flame retardants), other types of flame tests would give more insights into the real effect of one or complementary actions of two or more P type FR additives in epoxy. Based on available data, a brief view of the effect of the used P-based FRs on the flame retardancy performance of epoxy resins as a function of UL94 results is given in Figure 2. The distribution of data in this figure gives useful information about the efficiency of the FR system in harsh conditions. For instance, this figure suggests that V-0 performance in UL94 can be achieved even at the Poor category of flame retardancy performance in terms of FRI.

It appears that it is not possible to roughly correlate the obtained results in UL94 to those obtained in cone calorimetry tests.

**Figure 2.** Flame retardancy analysis of epoxy resins containing phosphorus flame retardants in terms of the FRI values as a function of UL-94 test results. Symbols are indicative of different types of phosphorus flame retardant used. Hollow symbols are indicative of fiber-incorporated composites with details earlier given in the bottom of Table 1 as a to l notes. The vertical variation in each category, i.e., V-0, V-1, V-2, and NR, is schematically representative of the amount of additive used. For example, among two data distinguished by different symbols having the same or very close FRI values (horizontal quantity) in a given category (e.g., V-1), which have different vertical quantity both revealed V-1 behavior in UL-94 test, but the upper was an FR used in more quantity in preparation of epoxy composites.

Another test of importance is the limiting oxygen index (LOI), which is demonstrative of flammability. A self-extinguishing behavior is expected when the LOI value is higher than 28. A brief overview of the effect of the used phosphorus-type flame retardants on the flame retardancy performance of epoxy resins as a function of LOI results is given in Figure 3. Surprisingly, the highest value obtained in LOI testing is located in the Good zone of FRI. The collection of data with FRI values below 5, where LOI% varies depending on the type of phosphorus additive and undoubtedly the content, is hidden behind these symbols.
Figure 3. Flame retardancy analysis of epoxy resins containing phosphorus flame retardants in terms of the FRI values as a function of LOI test results. Symbols are indicative of different types of phosphorus flame retardant used. Hollow symbols are indicative of fiber-incorporated composites with details earlier given in the bottom of Table 1 as a to l notes.

3. Epoxy Resins Containing Nonphosphorus Flame Retardants

According to the literature, a variety of nonphosphorus FRs have been used in epoxy resins. Table 2 summarizes pHRR, THR, and TTI and the FRI values of epoxy systems. The percentage of incorporated FR as well as the results of LOI and UL-94 test are also given for comprehensive determination of the behavior of this family of epoxy composites.

Table 2. The state of flame retardancy performance of epoxy resins containing nonphosphorus flame retardants in terms of FRI (* the name and percentage of incorporated flame retardant is given after each epoxy resin). The notes a to h on the bottom of the table are representative of composite systems containing woven or nonwoven fibers.

| Epoxy Resins and Incorporated Non Phosphorus FR * | wt.% | TTI (s) | pHRR (kW·m⁻²) | THR (MJ·m⁻²) | FRI | LOI | UL94 | Ref. |
|--------------------------------------------------|------|--------|----------------|--------------|-----|-----|------|------|
| (2,4,6-tris(4-boronic-2-thiophene)-1,3,5-triazine (3TT-3BA)) | 0    | 11    | 781            | 142          | —   | 21.8| V-1  | [169]|
| graphene nanosheet (GN) | 0    | 32    | 827            | 116          | —   | 21.8| NR   | [28] |
| multiwalled carbon nanotube (MWCNT) | 0    | 32    | 781            | 107          | —   | 21.8| NR   | [29] |
| multiwalled carbon nanotube (MWCNT) | 0.8  | 40    | 473            | 97           | 2.27| 21.2| NR   | [29] |
| multiwalled carbon nanotube (MWCNT) | 0    | 32    | 781            | 107          | —   | 21.8| NR   | [30] |
| Organically modified montmorillonite (DK4:two longchain alkyl ammonium modified montmorillonite) (OMMT) | 7    | 40    | 576            | 98           | 1.85| 23.7| NR   | [30] |
| organomodified magnesium aluminium layered double hydroxide (OLDH) | 0    | 32    | 781            | 107          | —   | 21.8| NR   | [31] |
| organomodified magnesium aluminium layered double hydroxide (OLDH) | 5    | 35    | 521            | 104          | 1.68| 23.6| V-0  | [31] |
| organomodified magnesium aluminium layered double hydroxide (OLDH) | 10   | 49    | 391            | 106          | 3.08| 22.1| V-0  | [31] |
| magnesium aluminium layered double hydroxide (MgAl-LDH) | 0    | 71    | 1146           | 56           | —   | 21.2| NR   | [170]|
| zeolitic imidazolate framework68 (ZIF8) | 2    | 63    | 865            | 49           | 1.34| 23.8| NR   | [170]|
| zeolitic imidazolate framework68 decorated magnesium aluminium layered double hydroxide (ZIF8@MgAl-LDH) | 2    | 58    | 886            | 41           | 1.44| 23.3| NR   | [170]|
| zeolitic imidazolate framework68 decorated MgAl-layered double hydroxide (ZIF8@MgAl-LDH) | 0    | 61    | 1208           | 77.3         | —   | 22.5| NR   | [52] |
| triazine-based flame retardant (TAT) | 20   | 42    | 1030           | 75.8         | 0.82| 24.1| NR   | [52] |
| triazine-based flame retardant (TAT) | 35   | 106   | 803            | 80.3         | —   | 22.9| NR   | [171]|
| Epoxy Resins and Incorporated Non Phosphorus FR * | wt.% | TTI (s) | pHRR (kW·m$^{-2}$) | THR (MJ·m$^{-2}$) | FRI | LOI | UL94 Ref. |
|--------------------------------------------------|-------|---------|---------------------|------------------|-----|-----|-----------|
| 2,4,6-tris-(4-boronphenoxy)-(1,3,5)-triazine (TNB) | 1     | 23     | 686                 | 68.1             | 1.20 | 26.1 | V-1 [171] |
| 2,4,6-tris-(4-boronphenoxy)-(1,3,5)-triazine (TNB) | 5     | 22     | 427                 | 64.1             | 1.96 | 28.3 | V-1 [171] |
| 2,4,6-tris-(4-boronphenoxy)-(1,3,5)-triazine (TNB) | 10    | 20     | 324                 | 59.3             | 2.54 | 29.4 | V-1 [171] |
| 2,4,6-tris-(4-boronphenoxy)-(1,3,5)-triazine (TNB) | 15    | 22     | 300                 | 58.3             | 2.98 | 30.4 | V-0 [171] |
| 2,4,6-tris-(4-boronphenoxy)-(1,3,5)-triazine (TNB) | 20    | 22     | 305                 | 58.0             | 3.03 | 31.2 | V-0 [171] |
| Cuprous oxide (Cu$_2$O) | 21    | 47     | 1007                | 86.1             | 1.17 | 22.8 | NR [55]  |
| magnesium hydroxide (MHI) | 3     | 38     | 751                 | 80.3             | 1.27 | 25.2 | NR [56]  |
| 2,4,6-tris-(4-boronphenoxy)-(1,3,5)-triazine (TNB) | 20    | 22     | 305                 | 58.0             | 3.03 | 31.2 | V-0 [171] |
| expandable graphite (EG) | 20    | 22     | 305                 | 58.0             | 3.03 | 31.2 | V-0 [171] |
| nucleophilic substitution reaction between N-(4-hydroxyphenyl) maleimide & cyanuric chloride (TMT) | 8     | 52     | 1395                | 88.4             | 1.08 | 27   | NR [67]  |
| organically modified montmorillonite (OMMT) | 1     | 39     | 1540                | 87.2             | 1.17 | 22.8 | NR [77]  |
| triallyl isocyanurate (TAIC) | 10    | 61     | 966                 | 89.9             | 2.04 | 23.6 | NR [78]  |
| Triphenyl-1,3,5-triazine (TPT) | 14    | 48     | 964                 | 88.7             | 1.00 | 24.5 | NR [172] |
| Halloysite nanotube (HNT) | 5     | 56     | 1170                | 93.3             | 0.83 | 26.1 | NR [172] |
| Halloysite nanotube (HNT) | 10    | 65     | 1002                | 95.0             | 0.94 | 25.4 | NR [172] |
| biomimetic polydopamine nanocoating functionalized Halloysite nanotube (HNT@PDA) | 5     | 65     | 1088                | 104              | 0.79 | 25.6 | NR [172] |
| biomimetic polydopamine nanocoating functionalized Halloysite nanotube (HNT@PDA) | 10    | 67     | 881                 | 91.0             | 1.16 | 25.6 | NR [172] |
| biomimetic polydopamine nanocoating functionalized Halloysite nanotube and ultrafine Fe(OH)$_3$ nanoparticles (HNT@PDA@Fe(OH)$_3$) | 5     | 61     | 695                 | 90.0             | 1.35 | 33.9 | V-1 [172] |
| biomimetic polydopamine nanocoating functionalized Halloysite nanotube and ultrafine Fe(OH)$_3$ nanoparticles (HNT@PDA@Fe(OH)$_3$) | 10    | 58     | 698                 | 88.0             | 1.31 | 33.8 | NR [172] |
| Montmorillonite (MMT) | 6     | 49     | 792                 | 100              | 1.41 | 26   | NR [94]  |
| octaphenyl polyhedral oligomeric silsesquioxane (OPS) | 5     | 60     | 712                 | 103              | 1.74 | 31.1 | NR [102] |
| Octaphenyl silsesquioxi (OPS) | 4.1   | 55     | 626                 | 112              | 1.66 | 27.2 | NR [103] |
| Polyphosphorylsiloxane (OPS) | 4.1   | 50     | 925                 | 116              | 0.99 | 27.1 | NR [103] |
| Octaphenyl silsesquioxide (OPS) | 4.1   | 55     | 626                 | 112              | 1.66 | 27.2 | NR [104] |
| Octaphenyl silsesquioxi (OPS) | 4.6   | 57     | 635                 | 110              | 1.73 | 27   | NR [104] |
| Octaphenyl polyhedral oligomeric silsesquioxide (OPS) | 10    | 58     | 698                 | 88.0             | 1.31 | 33.8 | NR [106] |
| aluminum trihydroxide (ATH) | 40    | 68     | 231                 | 41.2             | 3.17 | 23.6 | NR [173] |
| Ulexite (U) | 40    | 58     | 158                 | 34.3             | 4.75 | 23.6 | NR [173] |
| boric acid (BA) | 40    | 62     | 171                 | 38.2             | 4.21 | 22.6 | NR [173] |
| boric oxide (BO) | 40    | 68     | 132                 | 32.1             | 7.97 | 28.5 | V-0 [173] |
| melamine borate (MB) | 57    | 78     | 107                 | 26.9             | 12.05| 24.5 | V-0 [173] |
| guanidinium nonaborate (GB) | 30    | 65     | 105                 | 26.8             | 10.27| 23.6 | NR [173] |
| polyhedral oligomeric octadiphenylsulfonylsilsequioxane (ODPSS) | 5     | 59     | 417                 | 74               | 2.50 | 24.3 | NR [115] |
| Magnesium-Aluminum layered double hydroxide (Mg-Al LDH) | 5     | 40     | 835                 | 89.6             | 0.98 | 24.3 | NR [116] |
| Trisilanolisobutyl Polyhedral oligomeric silsesquioxane (TSPSS) | 10    | 99     | 774                 | 56               | 2.69 | 20.7 | NR [174] |
| triglycidyl isocyanurate (TGIC) | 10    | 86     | 1190                | 67               | 1.27 | 19.9 | NR [174] |
| reduced graphene oxide (RGO) | 1    | 47     | 1356                | 67.6             | 1.57 | 23.5 | NR [121] |
| halloysite nano-tube (HNT) | 2     | 20     | 1591                | 90.7             | 1.06 | 19.5 | NR [120] |
| layered double hydroxide (LDH) | 2     | 21     | 803                 | 87.5             | 2.29 | 20.6 | NR [120] |
| layered double hydroxide (LDH) | 4     | 22     | 861                 | 85.4             | 2.29 | 20.6 | NR [120] |
| layered double hydroxide (LDH) | 6     | 20     | 791                 | 82.9             | 2.34 | 19.7 | NR [120] |
Table 2. Cont.

| Epoxy Resins and Incorporated Non Phosphorus FR * | wt.% | TTI (s) | pHRR (kW·m⁻²) | THR (MJ·m⁻²) | FRI | LOI | UL94 | Ref. |
|--------------------------------------------------|-------|---------|----------------|---------------|-----|-----|------|------|
| epoxy novolac resin                              | 0     | 51      | 662            | 110           | —   | —   | NR   | [124]|
| Boehmite (AlO(OH))                               | 30    | 69      | 535            | 88            | 2.15| —   | V-1  | [124]|
| activated carbon spheres (ACS)                   | 0     | 50      | 992            | 91            | —   | —   | NR   | [125]|
| activated carbon spheres@SnO₂ hybrid (ACS@SnO₂) | 2     | 56      | 898            | 91            | 1.23| —   | NR   | [123]|
| activated carbon spheres@SnO₂@NiO hybrid (ACS@SnO₂@NiO) | 2   | 56      | 893            | 92            | 1.31| —   | NR   | [125]|
| activated carbon spheres@SnO₂@NiO hybrid (ACS@SnO₂@NiO) | 5    | 50      | 986            | 91            | —   | —   | NR   | [123]|
| octapropylglycidylether polyhedral oligomeric silsesquioxane (OGPOSS) | 15   | 60      | 1026           | 145           | 1.32| —   | NR   | [129]|
| Strontium hydroxystannate nanorod (SrSn(OH)₆)   | 3     | 55      | 889            | 92.6          | 1.30| 28.4| —    | [132]|
| Silica nanoparticles (SiO₂)                      | 2     | 65      | 727            | 34.4          | 1.46| 26  | —    | [175]|
| ZIF8                                             | 2     | 65      | 841            | 91            | 1.34| 28  | —    | [175]|
| molybdenum disulfide decorated titanium dioxide nanotube (MoS₂-TNT) | 1    | 63      | 859            | 43.7          | 1.53| 25.1| —    | [176]|
| molybdenum disulfide decorated titanium dioxide nanotube (MoS₂-TNT) | 2    | 60      | 701            | 37.1          | 2.10| 26.8| —    | [176]|
| molybdenum disulfide decorated titanium dioxide nanotube (MoS₂-TNT) | 3    | 61      | 627            | 32.1          | 2.76| 28.1| —    | [176]|
| Sepiolite (Sep)                                  | 0     | 58      | 1126           | 100           | —   | 26.1| —    | [137]|
| α-Manganese dioxide nanosheets (α-MnO₂)         | 0.5   | 25      | 1701           | 77            | 1.15| —   | —    | [177]|
| α-Manganese dioxide nanosheets (α-MnO₂)         | 1     | 24      | 1480           | 73            | 1.34| —   | —    | [179]|
| amorphous silicon dioxide (SiO₂)                | 20    | 49      | 870            | 65            | 1.28| —   | —    | [127]|
| amorphous silicon dioxide (SiO₂)                | 20    | 41      | 970            | 57.6          | 1.17| —   | —    | [127]|
| α-Manganese dioxide nanosheets (α-MnO₂)         | 0.5   | 25      | 1617           | 74            | 1.26| —   | —    | [180]|
| α-Manganese dioxide nanosheets (α-MnO₂)         | 1     | 26      | 1547           | 74            | 1.37| —   | —    | [180]|
| α-Manganese dioxide nanosheets (α-MnO₂)         | 2     | 27      | 1358           | 64            | 1.87| —   | —    | [180]|
| α-Manganese dioxide nanosheets (α-MnO₂)         | 1     | 60      | 2187           | 124           | —   | —   | —    | [140]|
| α-Manganese dioxide nanosheets (α-MnO₂)         | 2     | 49      | 1457           | 98            | 1.55| —   | —    | [140]|
| Octapropylglycidylether polyhedral oligomeric silsesquioxane (OGPOSS) | 15   | 60      | 1026           | 145           | 1.32| —   | NR   | [129]|
| Expandable graphite (EG)                         | 20    | 49      | 870            | 65            | 1.28| —   | —    | [127]|
| α-Manganese dioxide nanosheets (α-MnO₂)         | 54    | 49      | 616            | 65.5          | 1.28| —   | —    | [127]|
| Octapropylglycidylether polyhedral oligomeric silsesquioxane (OGPOSS) | 7.2   | 44.3    | 880            | 83.6          | 1.43| —   | —    | [180]|
| Aminopropylisobutyl polyhedral oligomeric silsesquioxane (AI-POSS) | 21.8 | 36.3    | 585            | 97.7          | 1.51| —   | —    | [180]|
| Aminopropylisobutyl polyhedral oligomeric silsesquioxane (AI-POSS) | 54    | 32.2    | 616            | 65.3          | 1.90| —   | —    | [180]|
| Expandable graphite (EG)                         | 0     | 5       | 986            | 113           | —   | —   | —    | [181]|
| halloysite nanotube (HNT)                        | 0     | 9       | 152            | 110           | 13.33| —   | —    | [181]|
| Boron Nitride with D50 = 2 µm (BN 2 µm)         | 45    | 175     | 767            | 71.5          | 3.07| —   | —    | [182]|
| Boehmite with D50 = 2 µm (BT 2 µm)              | 45    | 140     | 674            | 72.2          | 2.77| —   | —    | [183]|
| Manganese dioxide (MnO₂)                         | 2     | 27      | 1443           | 71            | 1.58| —   | —    | [183]|
Table 2. Cont.

| Epoxy Resins and Incorporated Non Phosphorus FR * | wt.% | TTI (s) | pHRR (kW·m⁻²) | THR (MJ·m⁻²) | FRI | LOI | UL94 Ref. |
|-----------------------------------------------|------|--------|----------------|--------------|-----|-----|-----------|
| Manganese dioxide@zinc hydroxyxystannate binary hybrid (MnO₂@ZHSS) | 0.5 | 24 | 1487 | 56 | 1.72 | — | — | [183] |
| Manganese dioxide@zinc hydroxyxystannate binary hybrid (MnO₂@ZHSS) | 1 | 25 | 1275 | 49 | 2.40 | — | — | [183] |
| Manganese dioxide@zinc hydroxyxystannate binary hybrid (MnO₂@ZHSS) | 2 | 23 | 989 | 61 | 2.28 | — | — | [183] |
| Diglycidyl ether of bisphenol-F epoxy | 0 | 66 | 1197 | 82.7 | — | — | — | [184] |
| ionic liquid flame retardant (ILFR) | 5 | 55 | 753 | 62.5 | 1.75 | — | — | [184] |
| boron nitride nanosheets (BN) | 5 | 70 | 813 | 68.2 | 1.89 | — | — | [184] |
| ionic liquid flame retardant functionalized boron nitride nanosheets (ILFR-BN) | 10 | 104 | 689 | 51.5 | 4.39 | — | — | [184] |
| thiol-functionalized mesporous silica (SH-mlSiO₂) | 2 | 65 | 1117 | 77.8 | 3.14 | — | — | [143] |
| ionic liquid flame retardant functionalized boron nitride nanosheets (ILFR-fBN) | 5 | 104 | 689 | 51.5 | 4.39 | — | — | [184] |
| thiol-functionalized mesoporous silica (SH-mlSiO₂) | 2 | 65 | 1117 | 77.8 | 3.14 | — | — | [143] |
| ionic liquid flame retardant functionalized boron nitride nanosheets (ILFR-BN) | 10 | 104 | 689 | 51.5 | 4.39 | — | — | [184] |
| amorphous hydrous TiO₂ solid spheres (AHTSS) | 0.5 | 52 | 1125 | 84 | 1.75 | — | — | [185] |
| amorphous hydrous TiO₂ solid spheres (AHTSS) | 1 | 72 | 902 | 89 | 2.32 | — | — | [185] |
| amorphous hydrous TiO₂ solid spheres (AHTSS) | 2 | 72 | 902 | 89 | 2.32 | — | — | [185] |
| amorphous hydrous TiO₂ solid spheres (AHTSS) | 5 | 72 | 902 | 89 | 2.32 | — | — | [185] |
| urchin-like mesoporous TiO₂ hollow spheres (UMTHS) | 0.5 | 52 | 827 | 43.3 | 1.52 | — | — | [188] |
| urchin-like mesoporous TiO₂ hollow spheres (UMTHS) | 2 | 52 | 706 | 38.5 | 2.01 | — | — | [188] |
| urchin-like mesoporous TiO₂ hollow spheres (UMTHS-2) | 5 | 1592 | 39.7 | — | — | — | — | [188] |
| chitosan-modified molybdenum disulfide nanosheets (CS-MoS₂) | 0.5 | 71 | 1243 | 35.9 | 1.54 | — | — | [189] |
| chitosan-modified molybdenum disulfide nanosheets (CS-MoS₂) | 1 | 74 | 1107 | 28.6 | 2.27 | — | — | [189] |
| chitosan-modified molybdenum disulfide nanosheets (CS-MoS₂) | 2 | 75 | 902 | 33.9 | 2.38 | — | — | [189] |
| molybdenum disulfide nanosheets (MoS₂) | 2 | 72 | 1178 | 40.1 | 1.48 | — | — | [189] |
| silica nanospheres (SiO₂) | 1 | 74 | 1777 | 95.6 | 1.21 | — | — | [148] |
| silica nanospheres (SiO₂) | 3 | 74 | 1777 | 95.6 | 1.21 | — | — | [148] |
| carbon nanotube (CNT) | 1 | 26 | 673 | 53.8 | 1.07 | — | — | [150] |
| chemical treatment carbon nanotube (CCT) | 2 | 35 | 578 | 58.4 | 1.55 | — | — | [150] |
| thermal treatment carbon nanotube (TCNT) | 5 | 35 | 578 | 58.4 | 1.55 | — | — | [150] |
| Hydrogenated fatty acid modified layered double hydroxide (OLDH) | 5 | 35 | 578 | 58.4 | 1.55 | — | — | [150] |
| Montmorillonite (MMT) | 5 | 38 | 7177 | 82.6 | 0.98 | — | — | [150] |
| Montmorillonite (MMT) | 5 | 38 | 7177 | 82.6 | 0.98 | — | — | [150] |
| Layered double hydroxide (LDH) | 5 | 35 | 578 | 58.4 | 1.55 | — | — | [150] |
| Layered double hydroxide (LDH) | 5 | 35 | 578 | 58.4 | 1.55 | — | — | [150] |
| Expanded graphite (EG) | 5 | 102 | 1911 | 124 | 0.92 | — | — | [190] |
| Expanded graphite (EG) | 10 | 80 | 1487 | 113 | 1.02 | — | — | [190] |
| Expanded graphite (EG) | 15 | 102 | 1911 | 124 | 0.92 | — | — | [190] |
| Expanded graphite (EG) | 23 | 116 | 1992 | 102 | 1.23 | — | — | [190] |
| Expanded graphite (EG) | 50 | 132 | 1800 | 81 | 1.95 | — | — | [190] |
| Bentonite (BT) | 3 | 150 | 1094 | 74 | 0.91 | — | — | [191] |
| Bentonite (BT) | 5 | 158 | 1192 | 88.1 | 0.73 | — | — | [191] |
| 6-(4-butylphenyl)1,3,5-triazine-2,4-diamine modified bentonite (BFTDA-BT) | 2 | 138 | 772 | 47.4 | 1.17 | — | — | [191] |
| 6-(4-butylphenyl)1,3,5-triazine-2,4-diamine modified bentonite (BFTDA-BT) | 3 | 140 | 966 | 74.1 | 0.96 | — | — | [191] |
| 11-amino-N-(pyridine-2)-lundecanamide modified bentonite (APUA-BT) | 3 | 138 | 772 | 47.4 | 1.17 | — | — | [192] |
| 11-amino-N-(pyridine-2)-lundecanamide modified bentonite (APUA-BT) | 5 | 139 | 814 | 74.2 | 1.13 | — | — | [192] |
| graphene nanosheets (GN) | 2 | 86 | 980 | 65.1 | 3.87 | — | — | [193] |
| Ni-Fe layered double hydroxide (Ni-Fe LDH) | 2 | 80 | 1070 | 58.9 | 3.65 | — | — | [193] |
| octaammonium polyhedral oligomeric silsesquioxane-modified montmorillonite (OAPOS-MMT) | 2 | 42 | 1207 | 103 | 0.99 | — | — | [194] |
| Epoxy Resins and Incorporated Non Phosphorus FR* | wt.% | TTI (s) | pHRR (kW·m$^{-2}$) | THR (MJ·m$^{-2}$) | FRI | LOI | UL94 Ref. |
|-----------------------------------------------|------|---------|---------------------|------------------|-----|-----|------------|
| octaammonium polyedral oligomeric silsesquioxane-modified montmorillonite (OAPOS-MMT) | 4    | 48      | 1095               | 94               | 1.36| —   | —          |
| octaammonium polyedral oligomeric silsesquioxane-modified montmorillonite (OAPOS-MMT) | 6    | 50      | 982                | 88               | 1.69| —   | —          |
| Sodium magadiite (Na-magadiite)               | 3    | 39      | 1283               | 116              | 2.38| —   | —          |
| Sodium magadiite reaction with silane coupling agent (S-Na-magadiite) | 3    | 38      | 1641               | 120              | 1.75| —   | —          |
| protonated magadiite reaction with silane coupling agent (S-H-magadiite) | 3    | 38      | 1416               | 114              | 2.14| —   | —          |
| organo-modified magadiite (OM-magadiite)      | 3    | 29      | 1332               | 105              | 1.88| —   | —          |
| silane grafting organo modified magadiite (S-OM-magadiite) | 3    | 34      | 1273               | 103              | 2.36| —   | —          |
| tetrabromobisphenol-A (TBBA)                  | 17   | 17      | 1390               | 92               | 1.96| —   | —          |
| graphene sheet (GN)                           | 90   | 1653    | 130                | —                | —   | —   | —          |
| Ce-doped MnO$_2$ (Ce–MnO$_2$)                 | 2    | 79      | 920                | 96.7             | 2.11| —   | —          |
| Ce-doped MnO$_2$ decorated graphene sheets (Ce–MnO$_2$–GN) | 2    | 100     | 765                | 83.8             | 3.72| —   | —          |
| mesoporous silica (m-SiO$_2$)                 | 2    | 107     | 1191               | 96.5             | 1.35| —   | —          |
| Co–Al layered double hydroxide (Co–Al LDH)    | 2    | 103     | 1188               | 84.3             | 1.49| —   | —          |
| mesoporous silica@Co–Al layered double hydroxide (m-SiO$_2$@Co–Al LDH) | 2    | 110     | 894                | 56               | 3.19| —   | —          |
| Zinc sulfide (ZnS)                            | 2    | 88      | 1213               | 119              | 2.00| —   | —          |
| Zinc sulfide decorated Graphene sheets (ZnS@GN) | 2    | 70      | 1141               | 108              | 1.88| —   | —          |
| hydrated pre-treated sepiolite (sep idra)     | 2    | 55      | 1370               | 101              | 0.91| —   | —          |
| hydrated pre-treated sepiolite (sep idra)     | 5    | 65      | 1157               | 99.5             | 1.30| —   | —          |
| dehydrated pre-treated sepiolite (sep anida)  | 2    | 65      | 1072               | 95.7             | 1.45| —   | —          |
| dehydrated pre-treated sepiolite (sep idra)   | 5    | 65      | 1114               | 107              | 1.26| —   | —          |
| dehydrated pre-treated sepiolite (sep idra)   | 10   | 65      | 958                | 108              | 1.45| —   | —          |
| expandable graphite (EG)                      | 5    | 111     | 463                | 142              | 2.34| —   | —          |
| chitosan modified montmorillonite intercalation iron compounds (CTS-Fe-OMMT) | 3    | 55      | 1168               | 91.4             | 1.25| —   | —          |
| cetyltrimethylammoniumbromide modified montmorillonite intercalation iron compounds (CTAB-Fe-OMMT) | 3    | 47      | 975                | 89.2             | 1.31| —   | —          |
| aminated multiwalled carbon nanotubes supplied by the Polish company (A-MWCNT(Polish)) | 0.05 | 72.8    | 1161               | 93.6             | 1.29| —   | —          |
| aminated multiwalled carbon nanotubes supplied by the Polish company (A-MWCNT(Polish)) | 0.1  | 68.8    | 992                | 93.6             | 1.43| —   | —          |
| aminated multiwalled carbon nanotubes supplied by the Polish company (A-MWCNT(Polish)) | 0.5  | 74      | 926                | 96.9             | 1.59| —   | —          |
| aminated multiwalled carbon nanotubes supplied by the Polish company (A-MWCNT(Polish)) | 1    | 71.9    | 875                | 92.6             | 1.72| —   | —          |
| aminated multiwalled carbon nanotubes supplied by the Polish company (A-MWCNT(Polish)) | 5    | 78.3    | 1141               | 98.9             | 1.34| —   | —          |
| carboxylated multiwalled carbon nanotubes supplied by the Polish company (C-MWCNT(Polish)) | 0.05 | 78.7    | 1080               | 101              | 1.40| —   | —          |
| carboxylated multiwalled carbon nanotubes supplied by the Polish company (C-MWCNT(Polish)) | 0.1  | 72.6    | 1250               | 100              | 1.12| —   | —          |
| carboxylated multiwalled carbon nanotubes supplied by the Polish company (C-MWCNT(Polish)) | 0.5  | 80.2    | 1163               | 98.8             | 1.35| —   | —          |
| carboxylated multiwalled carbon nanotubes supplied by the Polish company (C-MWCNT(Polish)) | 1    | 81.2    | 945                | 102              | 1.63| —   | —          |
| carboxylated multiwalled carbon nanotubes supplied by the Belgian company (C-MWCNT(Belgian)) | 0.05 | 76.2    | 919                | 96.3             | 1.66| —   | —          |
| carboxylated multiwalled carbon nanotubes supplied by the Belgian company (C-MWCNT(Belgian)) | 0.5  | 67.4    | 1110               | 99               | 1.19| —   | —          |
| carboxyammonium multiwalled carbon nanotubes supplied by the Polish company (CA-MWCNT(Polish)) | 0.05 | 83.9    | 1240               | 104              | 1.26| —   | —          |
| carboxyammonium multiwalled carbon nanotubes supplied by the Polish company (CA-MWCNT(Polish)) | 0.1  | 73.8    | 1162               | 99               | 1.24| —   | —          |
| carboxyammonium multiwalled carbon nanotubes supplied by the Polish company (CA-MWCNT(Polish)) | 0.5  | 76      | 1095               | 99.5             | 1.35| —   | —          |
| carboxyammonium multiwalled carbon nanotubes supplied by the Polish company (CA-MWCNT(Polish)) | 1    | 67.3    | 1192               | 97.8             | 1.12| —   | —          |
| carboxyammonium multiwalled carbon nanotubes supplied by the Polish company (CA-MWCNT(Polish)) | 5    | 69.7    | 1198               | 100              | 1.12| —   | —          |
From the comparison between Tables 1 and 2, one can simply infer that the NP family is less effective in terms of the flame retardancy of the composite epoxy with respect to the P family of FR.
The effect of the used NP-type FR on the flame retardancy performance of epoxy resins can be visually assessed in Figure 4. Moreover, detailed information about the type of NP additives is provided to the reader in the caption of Figure 4. The quality of epoxy composites containing NP additives suggests that even at high loading levels it is difficult to attain very high efficiencies. As an informative case, alumina Trihydrate (ATH, ●) has been used in a wide range of content in development of flame-retardant epoxy nanocomposites. It can be seen that at high loading rate (up to 30 wt.%), it gives the best results, Excellent in terms of FRI. It can be concluded that the NP class of additives are not individually responsible for high fire resistance of epoxy.

**Figure 4.** Flame retardancy analysis of epoxy resins containing nonphosphorus flame retardants in terms of the FRI values as a function of NP type and content. Symbols are indicative of different types of NP type of FR used. Hollow symbols are indicative of fiber-incorporated composites with details earlier given in the bottom of Table 1 as notes a to h. Here: ■ 3TT-3BA-20 [169], ● GN-3 [28], ▲ MWCNT-0.8 [29], ▼ OMMT-7 [30], ● OLDH-1, OLDH-5, OLDH-10 [31], ● MgAl-LDH-2, ZIF8-2, ZIF8@MgAl-LDH-2, ZIF67-2, ZIF67@MgAl-LDH-2 [170], ● TAT-20 [52], ● TNB-1, TNB-5, TNB-10, TNB-15, TNB-20 [171], ● CuO@2-21 [55], ● MH-3, [56], ● TN-3.42 [63], ● EG-20 [66], ▲ TMT-8 [67], ▲ TMT-7 [68], ▼ OMMT-1 [77], ● TAIC-10 [78], ● TPT-14 [81], ● HNT-5, HNT-10, HNT@PDA-5, HNT@PDA@Fe(OH)2-5, HNT@PDA@Fe(OH)2-10 [172], ● MMT-6 [94], ▼ OPS-5 [102], ● OPS-4.1, PPSQ-4.1 [103], ▼ OPS-4.1, OAPS-4.6 [104], ▼ OPS-4.1 [106], ● ATH-40, C-40, U-40, BO-40, MB-30, GB-30 [173], ● ODPSS-5 [115], ● Mg-Al LDH-4 [116], ● T8POSS-10, TGIC-10 [174], + RGO-1 [121], + HNT-2, LDH-2, LDH-4, LDH-6 [120], ● Al(OH)-30 [124], ● ACS-2, ACS@SnO2-2, ACS@SnO2@NiO-2 [125]. ▲ ACS@SnO2@NiO-5 [125], ● OGOPOSS-15 [129], • EG-15 [33], ▲ CP-10, CP-15 [130], ▲ CP-10, CP-15, CP-15 [130], ▼ CP-10, CP-15 [130], ▼ SrSn(OH)6-3 [132], ▲ SiO2-2, ZIF8-2, ZIF8@SiO2-2 [175], ▲ MoS2-2, TNT-2, MoS2-TNT-1, MoS2-TNT-2, MoS2-TNT-3 [176], ▼ Sep-2, Sep-2, Fe3O4-Sep-2, Fe3O4-Sep-4 [177], ▲ GNO-1, GNO-3, GN-Cu-1, GN-Cu-3 [178], ▼ Al(OH)-20 [147], ▲ Al(OH)-20, SiO2-20 [127], ▲ α-MnO2-0.5, α-MnO2-1, α-MnO2-2, δ-MnO2-0.5, δ-MnO2-1, δ-MnO2-2 [179], ▲ MoS2-2 [140], ▲ AI-POSS-7.2, AI-POSS-21.8, AI-POSS-54 [180], ▲ EG-9, HNT-9 [181], ▲ BN 2 μm-45, BT 2 μm-45 [182], ▲ MnO2-2, MnO2@ZHS-0.5, MnO2@ZHS-1, MnO2@ZHS-2 [183], ▲ ILFR-5, BN-5, ILFR-5BN-5 [184], ▲ SiH-MoS2-2 [143], ▲ SCF-0.5, SCF-0.7, SCF-1, SCF-1.5 [185], ▲ HNT-20 [146], • m-Cay-2.5, d-Cay-2.5 [186], ▲ LDH-3, β-FeOOH-3, LDH-β-FeOOH-3 [187], ▲ AHTSS-0.5, AHTSS-2, UMTHS-0.5, UMTHS-2 [188], ▲ CS-MoS2-0.5, CS-MoS2-1, CS-MoS2-2, MoS2-2 [189], ▲ SiO2-1 [148], ▲ CNT-1, CCNT-1, TCNT-1, LDH-5, OLDH-5,
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A brief overview of the effect of the NP used as FR in epoxy composite preparation and on the flame retardancy performance of epoxy resins as a function of UL-94 results is given in Figure 5. Since data are limited and spread over the plot, there is no conclusion about the relationship between FRI (cone calorimetry) and UL-94 analysis to be highlighted. Nevertheless, all sorts of behavior can be seen in the plot, depending on the type and content of NP type of FRs. It is worthy of note that the NR category of UL-94 constitutes a high proportion of the results.

Figure 5. Flame retardancy analysis of epoxy resins containing nonphosphorus flame retardants in terms of the FRI values as a function of UL-94 test results. Symbols are indicative of different types of NP type of FR used in this figure. Hollow symbols are indicative of fiber-incorporated composites with details given in the bottom of Table 2 as notes a to h. The vertical variation in each category, i.e., V-0, V-1, V-2, and NR, is schematically representative of the amount of additive used. For example, among two data distinguished by different symbols having the same or very close FRI values (horizontal quantity) in a given category (e.g., V-1), which have different vertical quantity both revealed V-1 behavior in UL-94 test, but the upper was an FR used in greater quantity in preparation of epoxy composites.
A brief overview of the effect of NP-type FR on the flame retardancy performance of epoxy resins as a function of LOI results is given in Figure 6. Surprisingly, the highest value obtained in LOI testing is located in Poor zone of FRI. On the other hand, Excellent flame retardancy seen at high FRI values has LOI of about 22%. From this perspective, it can be concluded that cone calorimetry is not monotonically representative of the character of FR when used in epoxy.

![Figure 6. Flame retardancy analysis of epoxy resins containing nonphosphorus flame retardants in terms of the FRI values as a function of LOI test results. Symbols are indicative of different types of NP flame retardant used. Hollow symbols are indicative of fiber-incorporated composites with details given in the bottom of Table 2 as notes a to h.](image)

### 4. Epoxy Resins Containing Combinatorial Flame Retardant Systems

Assessing the flame retardancy performance of P- and NP-incorporated epoxy systems unraveled the inadequacy of using one FR additive alone when a high performance is required. The antagonism or synergism may be the result of using two or more FR systems in a given polymer matrix. In the case of epoxy, there have been some attempts towards combinatorial use of P and NP additives for the sake of higher performance. Table 3 summarizes pHRR, THR, TTI, and FRI values of epoxy/P/NP combinatorial flame-retardant systems. The percentage of incorporated FR as well as the results of LOI and UL-94 tests are also given.

| Epoxy Resins and Incorporated P/NP FR * | wt.% | TTI (s) | pHRR (kW m⁻²) | THR (MJ m⁻²) | FRI | LOI | UL94 | Ref. |
|---------------------------------------|------|--------|---------------|--------------|-----|-----|------|------|
| phenethyl-bridged 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide derivative/graphene nanosheet (DiDOPO/GN) | 0    | 32     | 827           | 116          | —   | 21.8| NR   | [28] |
| phenethyl-bridged 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide derivative/multiwalled carbon nanotube (DiDOPO/MWCNT) | 10.8 | 47     | 352           | 72           | 4.84| 38.6| V-0  | [29] |
| phenethyl-bridged 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide derivative/Organically modified montmorillonite (DiDOPO/OMMT) | 7    | 46     | 396           | 95           | 3.19| 32.2| V-0  | [30] |

Notes a to i on the bottom of the table are representative of composite systems containing woven or nonwoven fibers.
Table 3. Cont.

| Epoxy Resins and Incorporated P/NFR * | wt.% | TTI (s) | pHRR (kW m⁻²) | THR (MJ m⁻²) | FRI | LOI | UL94 | Ref. |
|--------------------------------------|------|---------|----------------|-------------|-----|-----|------|------|
| phenylphosphine-bridged 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide derivative | 1    | 41      | 437            | 142         | 1.73| 25.2| V-0  | [31] |
| phenylphosphine-bridged 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide derivative | 5    | 44      | 420            | 120         | 2.28| 27.8| V-0  | [31] |
| phenylphosphine-bridged 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide derivative | 10   | 46      | 406            | 82          | 3.61| 31.5| V-0  | [31] |
| IFR: Ammonium polyphosphate & pentaerythritol & melamine(APP & PER & MEL/5:3:2) (IFR) | 0    | 30      | 1293           | 86.9        | 19  | 19.2| HB   | [208]|
| microencapsulated ammonium polyphosphate/pentaerythritol (mAPP/PER) | 10   | 27      | 961            | 39.9        | 0.89| 29.9| V-0  | [209]|
| microencapsulated ammonium polyphosphate/regenerated cotton cellulose (mAPP/RC) | 10   | 30      | 1055           | 40.5        | 0.89| 24.1| V-0  | [209]|
| microencapsulated ammonium polyphosphate/oxidized regenerated cotton cellulose (mAPP/ORCC) | 10   | 29      | 554            | 20.9        | 3.17| 29.5| V-0  | [209]|
| 2,6,7-trioxa-1-phosphacyclo[2.2.2]octane-4-methanol-trimellitic anhydride/melamine cyanurate (PEPA-TMA/MCA) | 18   | 17      | 378            | 90.4        | 1.20| 28.9| V-1  | [210]|
| 2,6,7-trioxa-1-phosphacyclo[2.2.2]octane-4-methanol-trimellitic anhydride/melamine cyanurate (PEPA-TMA/MCA) | 24   | 15      | 221            | 57.6        | 2.84| 29.8| V-0  | [210]|
| 2,6,7-trioxa-1-phosphacyclo[2.2.2]octane-4-methanol-trimellitic anhydride/melamine cyanurate (PEPA-TMA/MCA) | 30   | 12      | 296            | 74.8        | 1.31| 29.1| V-1  | [210]|
| zeolitic imidazolate framework/MgAl layered double hydroxide (ZIF67/MgAl-LDH) | 2    | 64      | 742            | 42          | 1.86| 24  | NR   | [170]|
| zeolitic imidazolate framework/MgAl layered double hydroxide (ZIF67/MgAl-LDH) | 2    | 65      | 719            | 41          | 1.99| 24.2| NR   | [170]|
| triazine-based flame retardant/9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (TAT/DOPO) | 20   | 44      | 849            | 74.3        | 1.07| 29.5| NR   | [52] |
| triazine-based flame retardant/9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (TAT/DOPO) | 20   | 44      | 682            | 64.5        | 1.53| 34  | V-1  | [52] |
| triazine-based flame retardant/9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (TAT/DOPO) | 20   | 47      | 558            | 56.3        | 2.29| 36  | V-0  | [52] |
| triazine-based flame retardant/9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (TAT/DOPO) | 20   | 41      | 500            | 48.5        | 2.59| 38.6| V-0  | [52] |
| triazine-based flame retardant/9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (TAT/DOPO) | 20   | 46      | 774            | 72.3        | 1.26| 30.1| NR   | [52] |
| triazine-based flame retardant/9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (TAT/DOPO) | 20   | 43      | 598            | 59.3        | 1.86| 33.5| V-1  | [52] |
| triazine-based flame retardant/9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (TAT/DOPO) | 20   | 48      | 484            | 52.6        | 2.89| 37.3| V-0  | [52] |
| triazine-based flame retardant/9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (TAT/DOPO) | 20   | 48      | 437            | 47.8        | 3.52| 39.6| V-0  | [52] |
| ethanediamine-modified ammonium polyphosphate/Cuprous oxide (EDA-APP/Cu₂O) | 21   | 62      | 364            | 64          | 5.74| 33.5| V-0  | [55] |
| hexakis(4-boronic acid-phenoxy)-cyclophosphazene/magnesium hydroxide (CP-68/MH) | 3.5  | 49      | 535            | 67          | 2.75| 31.9| V-0  | [56] |
| 93.6  | 851 | 91.7  | 19.7 | NR | [211] |
| Epoxy Resins and Incorporated P/NP FR | wt.% | TTI (s) | pHRR (kW m⁻²) | THR (MJ m⁻²) | FRI | LOI | UL94 | Ref. |
|--------------------------------------|------|--------|----------------|--------------|-----|-----|------|------|
| IFR: ammonium polyphosphate & pentaerythritol (APP & PER/3:1) (IFR) | 20   | 42.8   | 266            | 89.7         | 1.50 | 27.3 | V-1  | [211] |
| IFR: ammonium polyphosphate & pentaerythritol (APP & PER/3:1) (IFR) | 20   | 55.4   | 246            | 59.7         | 3.15 | 28.8 | V-1  | [211] |
| IFR: ammonium polyphosphate & pentaerythritol (APP & PER/3:1) (IFR) | 20   | 50.6   | 210            | 59.6         | 3.36 | 29.1 | V-1  | [211] |
| IFR: ammonium polyphosphate & pentaerythritol (APP & PER/3:1) (IFR) | 20   | 74.9   | 178            | 44.8         | 7.85 | 34.7 | V-0  | [211] |
| IFR: ammonium polyphosphate & pentaerythritol (APP & PER/3:1) (IFR) | 20   | 51.2   | 215            | 54.3         | 3.67 | 31.4 | V-0  | [211] |
| Microencapsulated ammonium polyphosphate (APP/PSA) | 29   | 1340   | 36.3           | —            | 22.5 | NR   | [212] |
| Microencapsulated ammonium polyphosphate & pentaerythritol (MFAPP/PER) | 12.5 | 24     | 422            | 20.6         | 4.63 | 24.9 | NR   | [212] |
| Microencapsulated ammonium polyphosphate (corn starch) (MFAPP/ST) | 12.5 | 24     | 457            | 15.2         | 5.80 | 30.1 | V-0  | [212] |
| Microencapsulated ammonium polyphosphate & pentaerythritol (MFAPP/OST) | 12.5 | 22     | 400            | 13.4         | 6.88 | 29.5 | V-0  | [212] |
| Expandable graphite/9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (EG/DOPO) | 48   | 48     | 236            | 48.4         | 7.05 | 35   | V-1  | [66]  |
| Expandable graphite/9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (EG/DOPO) | 48   | 296    | 48.8           | 5.58         | 38   | V-0  | [66]  |
| Expandable graphite/9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (EG/DOPO) | 48   | 405    | 50             | 3.98         | 42   | V-0  | [66]  |
| Expandable graphite/exa-phenoxy-cyclotriphosphazene (EG/HPCP) | 48   | 442    | 51.4           | 3.55         | 41.5 | V-0  | [66]  |
| Expandable graphite/exa-phenoxy-cyclotriphosphazene (EG/HPCP) | 48   | 259    | 49.7           | 6.26         | 33.5 | V-1  | [66]  |
| Expandable graphite/exa-phenoxy-cyclotriphosphazene (EG/HPCP) | 48   | 340    | 48             | 4.94         | 36   | V-0  | [66]  |
| Expandable graphite/exa-phenoxy-cyclotriphosphazene (EG/HPCP) | 48   | 809    | 50.6           | 1.97         | 40.5 | V-0  | [66]  |
| Expandable graphite/exa-phenoxy-cyclotriphosphazene (EG/HPCP) | 48   | 760    | 42.2           | 2.51         | 39   | V-0  | [66]  |
| Expandable graphite/exa-phenoxy-cyclotriphosphazene (EG/HPCP) | 57   | 1557   | 94.5           | —            | 24.5 | NR   | [67]  |
| Nucleophilic substitution reaction between N-(4-hydroxyphenyl) maleic & cyanuric chloride/9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (TMT/DOPO) | 11   | 45     | 1210           | 74.7         | 1.29 | 34   | V-1  | [67]  |
| Nucleophilic substitution reaction between N-(4-hydroxyphenyl) maleic & cyanuric chloride/9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (TMT/DOPO) | 12.3 | 46     | 1085           | 70.3         | 1.56 | 36.5 | V-0  | [67]  |
| Nucleophilic substitution reaction between N-(4-hydroxyphenyl) maleic & cyanuric chloride/9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (TMT/DOPO) | 13.7 | 47     | 1105           | 70.8         | 1.55 | 38   | V-0  | [67]  |
| Nucleophilic substitution reaction between N-(4-hydroxyphenyl) maleic & cyanuric chloride/9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (TMT/DOPO) | 15   | 44     | 980            | 61           | 1.90 | 40.3 | V-0  | [67]  |
| 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide/aluminum poly-hexamethylene phosphonate (DOPO/APHP) | 56   | 1420   | 116            | —            | 26.2 | NR   | [75]  |
| 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide/aluminum poly-hexamethylene phosphonate (DOPO/APHP) | 6    | 50     | 539            | 63           | 4.33 | 39.3 | V-1  | [75]  |
| 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide/aluminum poly-hexamethylene phosphonate (DOPO/APHP) | 6    | 46     | 510            | 38           | 4.57 | 39.5 | V-0  | [75]  |
| 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide/aluminum poly-hexamethylene phosphonate (DOPO/APPH) | 56   | 1420   | 140            | —            | 26   | NR   | [77]  |
| Reaction between triallyl isocyanurate & 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide organically modified montmorillonite (TAD/OMMT) | 5    | 41     | 961            | 108          | 1.40 | 36.9 | V-0  | [77]  |
| Flame retardant containing phosphorus & 4-tert-butylcalix[4]arene/ammonium polyphosphate (FR/APP) | 30   | 92     | 322            | 108          | 3.11 | 27.4 | V-1  | [213] |
| Flame retardant containing phosphorus & 4-tert-butylcalix[4]arene/ammonium polyphosphate (FR/APP) | 30   | 91     | 361            | 82           | 3.73 | 28.6 | V-1  | [213] |
| Flame retardant containing phosphorus & 4-tert-butylcalix[4]arene/ammonium polyphosphate (FR/APP) | 30   | 115    | 229            | 74           | 8.22 | 29.3 | V-0  | [213] |
Table 3. Cont.

| Epoxy Resins and Incorporated P/NP FR * | wt.% | TTI (s) | pHRR (kW m⁻²) | THR (MJ m⁻²) | FRI | LOI | UL94 | Ref. |
|----------------------------------------|------|---------|----------------|---------------|-----|-----|------|------|
| flame retardant containing phosphorus & 4-tert-butylcalix[4]arene/ammonium polyphosphate (FR/APP) | 30  | 100 | 203 | 74 | 8.07 | 30.8 | V-0 | [213] |
| amine-terminated cyclophosphazene/3-aminopropyltrimethoxy silane-functionalized rice husk ash (ATCP/FRHA) | 62  | 840 | 84 | — | 23 | V-1 | [89] |
| amine-terminated cyclophosphazene/3-aminopropyltrimethoxy silane-functionalized rice husk ash (ATCP/FRHA) | 16  | 56 | 542 | 56 | 2.10 | 44 | V-0 | [89] |
| amine-terminated cyclophosphazene/3-aminopropyltrimethoxy silane-functionalized rice husk ash (ATCP/FRHA) | 18  | 69 | 427 | 42 | 4.38 | 51 | V-0 | [89] |
| amine-terminated cyclophosphazene/3-aminopropyltrimethoxy silane-functionalized rice husk ash (ATCP/FRHA) | 20  | 77 | 340 | 30 | 8.59 | 62 | V-0 | [89] |
| amine-terminated cyclophosphazene/3-aminopropyltrimethoxy silane-functionalized rice husk ash (ATCP/FRHA) | 57  | 713 | 64 | — | — | — | — | [90] |
| amine-terminated cyclophosphazene/3-aminopropyltrimethoxy silane-functionalized rice husk ash (ATCP/FRHA) | 16  | 48 | 435 | 51 | 1.73 | 39 | V-0 | [90] |
| amine-terminated cyclophosphazene/3-aminopropyltrimethoxy silane-functionalized rice husk ash (ATCP/FRHA) | 18  | 45 | 374 | 43 | 2.24 | 45 | V-0 | [90] |
| amine-terminated cyclophosphazene/3-aminopropyltrimethoxy silane-functionalized rice husk ash (ATCP/FRHA) | 20  | 40 | 289 | 31 | 3.57 | 51 | V-0 | [90] |
| silylated modified melamine/amine-terminated cyclophosphazene (ATCP/FRHA) | 10  | 53 | 524 | 50 | 3.90 | 28 | V-0 | [93] |
| silylated modified melamine/amine-terminated cyclophosphazene (ATCP/FRHA) | 50  | 860 | 112 | — | 23 | NR | [93] |
| 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide/amine-terminated cyclophosphazene (ATCP/FRHA) | 5  | 54 | 603 | 89 | 2.14 | 29 | V-1 | [102] |
| 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide/Octaphenyl silylene (DOPO/OPS) | 45  | 855 | 112 | — | 25 | NR | [103] |
| 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide/Octaphenyl silylene (DOPO/OPS) | 5.2 | 51 | 595 | 97 | 2.05 | 31.1 | V-0 | [103] |
| 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide/Octaphenyl silylene (DOPO/OPS) | 5.2 | 49 | 895 | 100 | 1.17 | 31.2 | V-0 | [103] |
| 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide/Octaphenyl silylene (DOPO/OPS) | 45  | 855 | 112 | — | 25 | NR | [104] |
| 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide/Octaphenyl silylene (DOPO/OPS) | 5  | 54 | 540 | 82 | 2.52 | 31 | V-0 | [105] |
| octaphenyl polyhedral oligomeric silsesquioxane/octaphenyl polyhedral oligomeric silsesquioxane/9,10-di hydro-9-oxa-10-phosphaphenanthrene-10-oxide (OPS/DOPO) | 5  | 58 | 860 | 112 | — | 3 | 3.2 | [105] |
| Octaphenyl polyhedral oligomeric silsesquioxane/octaphenyl polyhedral oligomeric silsesquioxane/9,10-di hydro-9-oxa-10-phosphaphenanthrene-10-oxide (OPS/DOPO) | 50  | 860 | 112 | — | — | — | [106] |
| Octaphenyl polyhedral oligomeric silsesquioxane/octaphenyl polyhedral oligomeric silsesquioxane/9,10-di hydro-9-oxa-10-phosphaphenanthrene-10-oxide (OPS/DOPO) | 5  | 58 | 540 | 82 | 2.52 | 31 | V-0 | [105] |
| Octaphenyl polyhedral oligomeric silsesquioxane/octaphenyl polyhedral oligomeric silsesquioxane/9,10-di hydro-9-oxa-10-phosphaphenanthrene-10-oxide (OPS/DOPO) | 50  | 860 | 112 | — | — | — | [106] |
| Octaphenyl polyhedral oligomeric silsesquioxane/octaphenyl polyhedral oligomeric silsesquioxane/9,10-di hydro-9-oxa-10-phosphaphenanthrene-10-oxide (OPS/DOPO) | 5  | 58 | 540 | 82 | 2.52 | 31 | V-0 | [105] |
| Octaphenyl polyhedral oligomeric silsesquioxane/octaphenyl polyhedral oligomeric silsesquioxane/9,10-di hydro-9-oxa-10-phosphaphenanthrene-10-oxide (OPS/DOPO) | 50  | 860 | 112 | — | 3 | 3.2 | [105] |
| Octaphenyl polyhedral oligomeric silsesquioxane/octaphenyl polyhedral oligomeric silsesquioxane/9,10-di hydro-9-oxa-10-phosphaphenanthrene-10-oxide (OPS/DOPO) | 50  | 860 | 112 | — | — | — | [106] |
| Octaphenyl polyhedral oligomeric silsesquioxane/octaphenyl polyhedral oligomeric silsesquioxane/9,10-di hydro-9-oxa-10-phosphaphenanthrene-10-oxide (OPS/DOPO) | 5  | 58 | 540 | 82 | 2.52 | 31 | V-0 | [105] |
| Octaphenyl polyhedral oligomeric silsesquioxane/octaphenyl polyhedral oligomeric silsesquioxane/9,10-di hydro-9-oxa-10-phosphaphenanthrene-10-oxide (OPS/DOPO) | 50  | 860 | 112 | — | 3 | 3.2 | [105] |

Cont.
| Table 3. Cont. |
|---------------------------------|---------|--------|--------|--------|--------|--------|
| Epoxy Resins and Incorporated P/NP FR * | wt.% | TTI (s) | pHRR (kW m⁻²) | THR (MJ m⁻²) | FRI | LOI | UL94 | Ref. |
| epoxy novolac resin | 0 | 51 | 682 | 110 | — | — | NR | [124] |
| oligo[DOPac-2-tris(acryloyloxy)ethyl isocyanurate]/melamine polyphosphate (oDOP/MPP) | 32.8 | 48 | 341 | 85 | 2.44 | — | V-0 | [124] |
| boehmite/oligo[DOPac-2-tris(acryloyloxy)ethyl isocyanurate] (Al(OH)₃/oDOP) | 41.1 | 71 | 319 | 74 | 4.42 | — | V-0 | [124] |
| melamine polyphosphate/phosphazene (MPP/PZ) | 16.5 | 50 | 310 | 82 | 2.89 | — | V-0 | [124] |
| boehmite/phosphazene (Al(OH)₃/PZ) | 33.1 | 66 | 435 | 79 | 2.83 | — | V-0 | [124] |
| aluminum hypophosphate/activated carbon spheres@SnO₂@NiO hybrid (APP/ACS@SnO₂@NiO) | 5 | 54 | 714 | 76 | 1.28 | — | V-0 | [125] |
| Melamine coated ammonium polyphosphate/Talc (Mel-APP)/Talc | 29.7 | 28 | 357 | 24 | 16.60 | — | V-0 | [126] |
| melamine polyphosphate/melamine poly(zinc phosphate) (MPP/MPPZnP) | 20 | 38 | 207 | 51.1 | 5.39 | — | V-1 | [127] |
| diethyl aluminum phosphinate/melamine poly(zinc phosphate) (AlPi-Et)/MPPZnP | 20 | 43 | 405 | 51.2 | 3.11 | — | HB | [127] |
| 6H-dibenz[c,e][1,2]oxaphosphorin-6-propanoic acid, butyl ester, 6-oxide/melamine poly(zinc phosphate) (DOPac-Bu/MPPZnP) | 20 | 42 | 329 | 57.6 | 3.32 | — | V-1 | [127] |
| boehmite/melamine poly(zinc phosphate) (Al(OH)₃/MPPZnP) | 20 | 43 | 438 | 57.2 | 2.57 | — | HB | [127] |
| amorphous silicon dioxide/melamine poly(zinc phosphate) (MPZnP/SiO₂) | 20 | 37 | 525 | 62.4 | 1.69 | — | HB | [127] |
| melamine polyphosphate/melamine poly(zinc phosphate) (MPPZnP)(MPPZnP) | 20 | 41 | 211 | 32.5 | 8.96 | — | V-0 | [127] |
| diethyl aluminum phosphinate/melamine poly(zinc phosphate) (AlPi-Et)/MPPZnP | 20 | 41 | 435 | 53.8 | 2.63 | — | V-1 | [127] |
| 6H-dibenz[c,e][1,2]oxaphosphorin-6-propanoic acid, butyl ester, 6-oxide/melamine poly(zinc phosphate) (DOPac-Bu/MPPZnP) | 20 | 43 | 412 | 52.1 | 2.86 | — | HB | [127] |
| boehmite/melamine poly(zinc phosphate) (Al(OH)₃/MPPZnP) | 20 | 43 | 575 | 57.9 | 1.94 | — | HB | [127] |
| amorphous silicon dioxide/melamine poly(zinc phosphate) (SiO₂/MPPZnP) | 20 | 37 | 681 | 65.6 | 1.24 | — | HB | [127] |
| hexaphenylcycloctrophosphazene/octapropylglycidyl ether polyhedral oligomeric silsesquioxane (HCCTP/OGPOSS) | 15 | 58 | 707 | 123 | 2.20 | — | V-0 | [129] |
| hexaphenylcycloctrophosphazene/octapropylglycidyl ether polyhedral oligomeric silsesquioxane (HCCTP/OGPOSS) | 15 | 56 | 581 | 110 | 2.88 | — | V-0 | [129] |
| hexaphenylcycloctrophosphazene/octapropylglycidyl ether polyhedral oligomeric silsesquioxane (HCCTP/OGPOSS) | 15 | 56 | 560 | 105 | 3.14 | — | V-0 | [129] |
| Tetraphenylphosphonium modified montmorillonite/Silicate glass (CTIP/MMT) | 15 | 101 | 353 | 112 | 2.26 | 25 | HB | [130] |
| Tetraphenylphosphonium modified montmorillonite/Silicate glass (CTIP/MMT) | 47 | 891 | 151 | — | 21 | HB | [130] |
| Tetraphenylphosphonium modified montmorillonite/Silicate glass (CTIP/MMT) | 15 | 48 | 474 | 130 | 2.23 | 25 | HB | [130] |
| Tetraphenylphosphonium modified montmorillonite/Silicate glass (CTIP/MMT) | 22 | 1196 | 147 | — | 21 | HB | [130] |
| molybdenum disulfide/titanium dioxide nanotube (MoS₂/TNT) | 2 | 56 | 742 | 38.6 | 1.78 | 26 | — | [176] |
| 47 | 1002 | 104 | — | 18 | — | [215] |
| Ammonium polyphosphate/Pentaerythritol modified halloysite tube (APP/PER-HNT) | 25 | 33 | 562 | 51.8 | 4.93 | 24.8 | — | [215] |
| melamine poly(magnesium phosphate)/aluminum diethylphosphate (M60/AlPi) | 54 | 1068 | 76 | — | 21 | — | [147] |
| melamine poly(magnesium phosphate)/boehmite (M60/Al(OH)₃) | 20 | 44 | 479 | 46 | 3.00 | 30.4 | — | [147] |
| melamine poly(magnesium phosphate)/melamine polyphosphate (M60/MPP) | 20 | 39 | 437 | 55 | 2.38 | 28.9 | — | [147] |
| melamine poly(magnesium phosphate)/melamine polyphosphate (M60/MPP) | 20 | 43 | 208 | 54 | 5.22 | 28.4 | — | [147] |
| 3-(4-Methoxyphenyl)silyl|oxy|)-9-methyl-2, 4, 8, 10-tetraoxa-3, 9-diphosphaspiro[5. 5] undecane-3, 9-dioxide/Mono (4, 6-diamino-1, 3, 5-triazin-2-aminium) (2, 4, 8, 10-tetraoxa-3, 9-diphosphaspir [5. 5] undecane-3, 9-bis (oleate) 3, 9-dioxide) (SDPS/STPD) | 10.4 | 62 | 1122 | 207 | 1.09 | 30.8 | — | [136] |
| aluminum diethyl phosphinate/Melamine polyphosphate (AlPi/MPP) | 0 | 70 | 1491 | 81 | — | 19 | NR | [47] |
| aluminum diethyl phosphinate/Melamine polyphosphate (AlPi/MPP) | 7 | 61 | 505 | 48 | 4.34 | — | — | [47] |
| aluminum diethyl phosphinate (AlPi/MPP) | 7 | 66 | 533 | 58 | 3.68 | — | — | [47] |
| ammonium polyphosphate/char sulfonic acid (APP/CSA) | 0 | 25 | 1113 | 223 | — | — | [139] |
| ammonium polyphosphate/char sulfonic acid (APP/CSA) | 10 | 24 | 672 | 127 | 2.78 | — | — | [139] |
| ammonium polyphosphate/char sulfonic acid (APP/CSA) | 10 | 23 | 665 | 107 | 3.21 | — | — | [139] |
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Table 3. Cont.

| Epoxy Resins and Incorporated P/NFR | wt.% | TTI (s) | pHRR (kW m⁻²) | THR (MJ m⁻²) | FRI | LOI | UL94 | Ref. |
|-----------------------------------|------|--------|---------------|-------------|-----|-----|------|-----|
| ammonium polyphosphate/char sulfonic acid (APP/CSA) | 10 | 27 | 698 | 137 | 2.81 | — | — | [139] |
| 0 | 117 | 1184 | 95.3 | — | — | — | [182] |
| Boron Nitride with D50 = 12 µm/Boron Nitride with D50 = 2 µm | 45 | 164 | 918 | 757.5 | 2.28 | — | — | [182] |
| (BN 12 µm/BN 2 µm) | 45 | 163 | 729 | 65.1 | 3.31 | — | — | [182] |
| (BN 12 µm/BT 2 µm) | 60 | 923 | 124 | — | — | — | [216] |
| IFR: ammonium polyphosphate & pentaerythritol (APP & PER/3:1) (IFR) | 30 | 64 | 285 | 64.1 | 6.69 | — | — | [216] |
| IFR: ammonium polyphosphate & pentaerythritol (APP & PER/3:1)/ferric phosphate (IFR/FeP) | 30 | 46 | 170 | 56 | 9.23 | — | — | [216] |
| IFR: ammonium polyphosphate & pentaerythritol (APP & PER/3:1)/ferric phosphate (IFR/FeP) | 30 | 42 | 185 | 49.3 | 8.80 | — | — | [216] |
| IFR: ammonium polyphosphate & pentaerythritol (APP & PER/3:1)/ferric phosphate (IFR/FeP) | 30 | 39 | 167 | 39.7 | 11.20 | — | — | [216] |
| IFR: ammonium polyphosphate & pentaerythritol (APP & PER/3:1)/ferric phosphate (IFR/FeP) | 30 | 41 | 180 | 44.6 | 9.76 | — | — | [216] |
| IFR: ammonium polyphosphate & pentaerythritol (APP & PER/3:1) (IFR) | 30 | 49 | 260 | 56 | 7.68 | — | — | [217] |
| IFR: ammonium polyphosphate & pentaerythritol (APP & PER/3:1) (IFR) | 30 | 46 | 172 | 47 | 13.00 | — | — | [217] |
| IFR: ammonium polyphosphate & pentaerythritol (APP & PER/3:1)/ferric phosphate (IFR/FeP) | 30 | 53 | 166 | 36 | 20.20 | — | — | [217] |
| IFR: ammonium polyphosphate & pentaerythritol (APP & PER/3:1)/ferric phosphate (IFR/FeP) | 30 | 50 | 196 | 40 | 14.60 | — | — | [217] |
| IFR: ammonium polyphosphate & pentaerythritol (APP & PER/3:1)/ferric phosphate (IFR/FeP) | 30 | 52 | 217 | 74 | 7.39 | — | — | [217] |
| IFR: ammonium polyphosphate & pentaerythritol (APP & PER/3:1) (IFR) | 30 | 49 | 285 | 64.1 | 5.12 | — | — | [218] |
| IFR: ammonium polyphosphate & pentaerythritol (APP & PER/3:1) (IFR) | 30 | 34 | 167 | 38.3 | 10.20 | — | — | [218] |
| IFR: ammonium polyphosphate & pentaerythritol (APP & PER/3:1)/ferric phosphate (IFR/FeP) | 30 | 45 | 126 | 31 | 22.00 | — | — | [218] |
| IFR: ammonium polyphosphate & pentaerythritol (APP & PER/3:1)/ferric phosphate (IFR/FeP) | 30 | 48 | 124 | 29.3 | 25.20 | — | — | [218] |
| IFR: ammonium polyphosphate & pentaerythritol (APP & PER/3:1)/ferric phosphate (IFR/FeP) | 30 | 53 | 163 | 43.2 | 14.40 | — | — | [218] |
| Ni–Fe layered double hydroxide/graphene nanosheets (Ni–Fe LDH/GN) | 68 | 1730 | 113 | — | — | — | — | [193] |
| Epoxy acrylate | 2 | 89 | 678 | 44.2 | 8.55 | — | — | [193] |
| ammonium polyphosphate/pentaerythritol (APP/PER) | 32 | 61 | 223 | 30.8 | 2.77 | — | — | [152] |
| 70 | 934 | 124 | — | — | — | — | [219] |
| IFR: ammonium polyphosphate & pentaerythritol (APP & PER/3:1) (IFR) | 30 | 70 | 282 | 64 | 6.42 | — | — | [219] |
| IFR: ammonium polyphosphate & pentaerythritol (APP & PER/3:1)/organic-modified iron-montmorillonite (IFR–Fe–OMMT) | 30 | 20 | 243 | 70 | 1.95 | — | — | [219] |
| IFR: ammonium polyphosphate & pentaerythritol (APP & PER/3:1)/organic-modified iron-montmorillonite (IFR–Fe–OMMT) | 30 | 15 | 153 | 54 | 3.00 | — | — | [219] |
| IFR: ammonium polyphosphate & pentaerythritol (APP & PER/3:1)/organic-modified iron-montmorillonite (IFR–Fe–OMMT) | 30 | 30 | 154 | 68 | 4.74 | — | — | [219] |
| ammonium polyphosphate/onium ion modified nanoclay (APP/L30E) | 30 | 15 | 194 | 65 | 1.97 | — | — | [219] |
| 41 | 1222 | 159 | — | — | — | — | [160] |
| ammonium polyphosphate/layered double hydroxide (Mel-APP/LDH) | 23 | 149 | 363 | 92 | 21.10 | — | — | [160] |
| 0 | 21 | 454 | 36.2 | 22.1 | NR | — | — | [120] |
| melamine coated ammonium polyphosphate/layered double hydroxide (Mel-APP/LDH) | 9.55 | 21 | 259 | 22.6 | 2.81 | 31.7 | V-1 | [120] |
| melamine coated ammonium polyphosphate/halloysite nano-tube (Mel-APP/HNT) | 9.61 | 22 | 262 | 18.4 | 3.57 | 31.4 | V-1 | [120] |
| 24 | 451 | 37 | — | — | NR | — | — | [126] |
| Melamine coated ammonium polyphosphate/Talc (Mel-APP/Talc) | 14.8 | 21 | 169 | 16 | 5.40 | — | — | [126] |
| 42 | 385 | 21.8 | — | 27.5 | — | — | — | [163,164] |
| IFR contains melamine phosphate/cellulose fibre containing poylsalicic acid (IFR/Via) | 10 | 38 | 262 | 17.9 | 1.62 | 36.2 | — | [163,164] |
Table 3. Cont.

| Epoxy Resins and Incorporated P/NP FR * | wt.% | TTI (s) | pHRR (kW m⁻²) | THR (MJ m⁻²) | FRI | LOI | UL94 | Ref. |
|----------------------------------------|------|---------|----------------|--------------|-----|-----|------|------|
| IFR contains melamine phosphate/phenol-formaldehyde fibers (Kv/IFR) * | 10 | 55 | 354 | 23.2 | 1.34 | 30.2 | — | — | — |
| | 0 | 33 | 520 | 29.4 | 0.86 | — | — | — | — |
| Zinc borate/magnesium hydroxide (ZB/Mg(OH)₂) d | 1 | 32 | 572 | 41.8 | 0.64 | — | — | — | — |
| Zinc borate/magnesium hydroxide (ZB/Mg(OH)₂) d | 7.5 | 37 | 483 | 37.4 | 0.95 | — | — | — | — |
| Zinc borate/magnesium hydroxide (ZB/Mg(OH)₂) d | 15 | 38 | 439 | 35.4 | 1.13 | — | — | — | — |
| Zinc borate/magnesium hydroxide (ZB/Mg(OH)₂) d | 25 | 40 | 380 | 27.2 | 1.79 | — | — | — | — |
| Zinc borate/aluminum hydroxide (ZB/Al(OH)₃) d | 10 | 33 | 525 | 35 | 0.83 | — | — | — | — |
| Zinc borate/aluminum hydroxide (ZB/Al(OH)₃) d | 7.5 | 36 | 480 | 37.4 | 0.93 | — | — | — | — |
| Zinc borate/aluminum hydroxide (ZB/Al(OH)₃) d | 15 | 27 | 439 | 37.2 | 0.77 | — | — | — | — |
| Zinc borate/aluminum hydroxide (ZB/Al(OH)₃) d | 25 | 30 | 409 | 37.7 | 0.90 | — | — | — | — |
| melamine phosphate/Graphene (MP/CGN) * | 5 | 36 | 483 | 47.9 | 1.57 | — | — | — | — |
| 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide/Graphene (DOPO/CGN) * | 5 | 32 | 538 | 36.5 | 1.64 | — | — | — | — |
| Zinc borate/organic phosphate/Zinc borate (PFR/ZB) * | 100 | 39 | 106 | 12.3 | 1.27 | — | — | — | — |
| IFR contains melamine phosphate/cellulosic fibre containing polysilicic acid (IFR/Vis) * | 5 | 49 | 391 | 20.3 | 2.74 | — | — | — | — |
| IFR contains melamine phosphate/cellulosic fibre containing polysilicic acid (IFR/Vis) * | 7.5 | 45 | 433 | 34 | 1.36 | — | — | — | — |
| IFR contains melamine phosphate/cellulosic fibre containing polysilicic acid (IFR/Vis) * | 10 | 52 | 488 | 33.2 | 1.43 | — | — | — | — |
| IFR contains melamine phosphate/cellulosic fibre containing polysilicic acid (IFR/Vis) * | 12.5 | 54 | 488 | 31.3 | 1.57 | — | — | — | — |
| IFR contains melamine phosphate/cellulosic fibre containing polysilicic acid (IFR/Vis) * | 15 | 66 | 451 | 28.4 | 2.29 | — | — | — | — |
| IFR contains melamine phosphate/cellulosic fibre containing polysilicic acid (IFR/Vis) * | 7.5 | 39 | 379 | 32.2 | 1.42 | — | — | — | — |
| IFR contains melamine phosphate/cellulosic fibre containing polysilicic acid (IFR/Vis) * | 10 | 80 | 408 | 25.5 | 3.42 | — | — | — | — |
| IFR contains melamine phosphate/cellulosic fibre containing polysilicic acid (IFR/Vis) * | 12.5 | 59 | 379 | 24.5 | 2.82 | — | — | — | — |
| IFR contains melamine phosphate/cellulosic fibre containing polysilicic acid (IFR/Vis) * | 15 | 77 | 434 | 22.9 | 3.44 | — | — | — | — |
| IFR contains melamine phosphate/cellulosic fibre containing polysilicic acid (IFR/Vis) * | 10 | 76 | 346 | 24.3 | 4.02 | — | — | — | — |
| IFR contains melamine phosphate/cellulosic fibre containing polysilicic acid (IFR/Vis) * | 12.5 | 89 | 342 | 23 | 5.03 | — | — | — | — |
| IFR contains melamine phosphate/cellulosic fibre containing polysilicic acid (IFR/Vis) * | 15 | 90 | 442 | 20.6 | 4.39 | — | — | — | — |
| IFR contains melamine phosphate/cellulosic fibre containing polysilicic acid (IFR/Vis) * | 12.5 | 67 | 277 | 22.8 | 4.71 | — | — | — | — |
| IFR contains melamine phosphate/cellulosic fibre containing polysilicic acid (IFR/Vis) * | 15 | 89 | 339 | 20.3 | 5.75 | — | — | — | — |
| IFR contains melamine phosphate/cellulosic fibre containing polysilicic acid (IFR/Vis) * | 15 | 97 | 226 | 15.9 | 12.00 | — | — | — | — |
| IFR contains melamine phosphate/cellulosic fibre containing polysilicic acid (IFR/Vis) * | 17.5 | 100 | 236 | 23.4 | 8.05 | — | — | — | — |
| | 125 | 857 | 50 | — | — | — | — | — | — |
| Trisilanolsobutyl Polyhydral oligomeric silsesquioxane/triglycidyl isocyanurate (TISPSS/GCIC) b | 5 | 114 | 365 | 32 | 3.17 | — | — | — | — |
| | 40 | 525 | 62 | — | — | — | — | — | — |
| IFR contains melamine phosphate/cellulosic fibre containing polysilicic acid (IFR/Vis) * | 5 | 24 | 365 | 67 | 0.80 | — | — | — | — |
| IFR contains melamine phosphate/cellulosic fibre containing polysilicic acid (IFR/Vis) * | 7.5 | 31 | 290 | 41 | 2.12 | — | — | — | — |
| IFR contains melamine phosphate/cellulosic fibre containing polysilicic acid (IFR/Vis) * | 10 | 28 | 242 | 36 | 2.62 | — | — | — | — |

* Matrix: eight layers of woven E-glass fabric reinforced epoxy; b Matrix: eight layers of woven E-glass reinforced film of multifunctional epoxy resin; c Matrix: eight layers of carbon fiber reinforced system HexFlow RTM6 (matrix) and HexForce G0939 (fabric); d Matrix: eight layers of woven roving glass fabric reinforced epoxy phenol novolak resin blend; e Matrix: epoxy fiber S2-glass panels; f Matrix: eight layers of woven E-glass reinforced epoxy; g Matrix: eight layers of woven glass Fiber Reinforced epoxy; h Matrix: eight ply woven roving E-glass fiber-reinforced epoxy.

To give a more meaningful overview of the effect of combined P and NP additives on flame retardancy performance of epoxy, FRI values are calculated by using calorimetric data given in Table 3 and plotted in Figure 7. In this figure, the vertical axis shows the amount of additive system used in preparation of epoxy composites. The plot also reveals that three types of flame retardancy performances are observed, depending on the type of combinatorial systems as well as the amount
of FR additives used. Attention should be paid to the fact that even at lower loading levels, careful coupling of one or more P and NP additives could lead to superiority of the FR system used, and there was a possibility for attaining higher performances compared to highly-filled systems (FR content ≥ 40). Thus, careful selection of complementary additives with disciplined loading can result in high flame retardancy performance.

Figure 7. Flame retardancy analysis of epoxy resins containing combinatorial flame retardant systems in terms of the FRI values as a function of combinatorial flame retardants systems retardant type and content. Symbols are indicative of different types of combinatorial flame retardants systems used. Hollow symbols are indicative of fiber-incorporated composites with details earlier given in the bottom of Table 1 as notes a to i. Here: ▲ DiDOPO-1.5/GN-1.5 [28], △ DiDOPO-10/MWCNT-0.8 [29], ▲ DiDOPO-3.5/OMMT-3.5 [30], △ DiDOPO-0.5/OLDH-0.5, DiDOPO-2.5/OLDH-2.5, DiDOPO-5/OLDH-5 [31], ● IFR-40, IFR-39/CES-1, IFR-38/CES-2, IFR-37/CES-3, IFR-35/CES-5 [208], ▲ DOPO-15/P-KC-15, DOPO-20/P-KC-10, DOPO-25/P-KC-5 [41], ➤ mAPP-5/P-5, mAPP-5/RCC-5, mAPP-5/ORCC-5 [209], ● PEPA-TMA-12/MCA-6, PEPA-TMA-16/MCA-8, PEPA-TMA-20/MCA-10 [210], ☺ ZIF8-1/MgAl-LDH-1, ZIF67-1/MgAl-LDH-1 [170], ● TAT-18/DOPO-2, TAT-16/DOPO-4, TAT-14/DOPO-6, TAT-12/DOPO-8, TAT-18/HPCP-2, TAT-16/HPCP-4, TAT-14/HPCP-6, TAT-12/HPCP-8 [52], ● EDA-APP-19/Cu₂O-2 [53], ☻ CP-68-3/MH-0.5 [56], ☐ IFR-20, IFR-19.5/HGM-0.5, IFR-19/HGM-1, IFR-18/HGM-2, IFR-16/HGM-4 [211], ✲ APP-5/PSA-5 [58], MFAPP-6.25/PER-6.25, MFAPP-6.25/ST-6.25, MFAPP-6.25/OST-6.25 [212], EG-16/DOPO-4, EG-16/DOPO-6, EG-12/DOPO-8, EG-10/DOPO-10, EG-16/HPCP-4, EG-14/HPCP-6, EG-12/HPCP-8, EG-10/HPCP-10 [66], □ TMT-8.3/DOPO-2.7, TMT-8.2/DOPO-4.1, TMT-8.1/DOPO-5.6, TMT-8/DOPO-7 [67], ○ DOPO-3/APHP-3, DOPO-4/APHP-2 [75], ▲ TAD-4/OMMT-1 [77], ▼ FR-20/APP-10, FR-15/APP-15, FR-12/APP-18, FR-10/APP-20 [213], ● ATCP-15/FRHA-1, ATCP-15/FRHA-3, ATCP-15/FRHA-5 [89], ☼ ATCP-15/FRHA-1, ATCP-15/FRHA-3, ATCP-15/FRHA-5 [90], ▲ APP-4/MMT-6 [93], ● DOPO-5/MMT-1 [94], BDP-6.7/PHP-3.3 [95], ▲ OPS-2.5/DOPO-2.5 [102], DOPO-3.1/OPS-2.1, DOPO-3.1/PPSQ-2.1 [103], + DOPO-3.1/OPS-2.1, DOPO-3.1/OPS-2.3 [104], ✲ OPS-2.5/DOPO-2.5 [105], OPS-2.1/PEPA-2.6, OPS-2.1/APP-1.4, OPS-2.1/DOPO-3.1 [106], ODPS-2.5/DOPO-2.5 [115], ▲ MAPP-10/PPA-10 [214], ● T8POSS-5/TGIC-5 [174], ○ APP-4.83/CoSA-0.17 [117], ○ CBz-8/BGN-2, CBz-13/BGN-2, CBz-18/BGN-2 [118], ❏ Mel-APP-18/LDH-2, Mel-APP-18/HNT-2 [120], oDOPI-17.76/MPP-15, AlO(OH)-30/oDOPI-11.05, MPP-15/PZ-1.54, AlO(OH)-30/PZ-3.08 [124], AHP-4.5/ACS@SnO2@NiO-0.5 [125], ❏ Mel-APP-19.97/Talc-9.73 [126], ● MPP-10/MPP/ZnP-10,
When looking at the UL-94 test results (considering the fact that there were some data in Table 3 for some systems to be plotted and discussed in Figure 8), it can be seen that, except for some data, the whole systems take Poor and Good labels based on FRI values. It is also interesting to note that for a given category, e.g., V-0, the amount of additive changes the FRI, and UL-94 testing does not make sense of such variations.
The more interesting outcome of this work is that LOI percent similarly detects Poor and Good behaviors, not principally Excellent performance (Figure 9). This suggests that development of innovative FR additives by combination of P and NP and using highly efficient synthesis routes is the essential step to be taken in the near future for developing flame retardant epoxy composites.

![Figure 9](image)

**Figure 9.** Flame retardancy analysis of epoxy resins containing combinatorial flame-retardant systems in terms of the FRI values as a function of LOI test results. Symbols are indicative of different types of combinatorial flame-retardant systems used. Hollow symbols are indicative of fiber-incorporated composites with details given in the bottom of Table 1 as notes a to i.

5. Concluding Remarks and Future Perspective

In previous sections, we categorized the flame-retardant properties of epoxy resins in terms of the universal FRI criterion and the content of flame retardants of three families. We also attempted to find possible correlations between cone calorimetry (reflected in FRI variations), UL-94, and LOI analyses. Since cone calorimetry is the best way to simulate real state combustion of polymers, here, we give a general picture of flame retardancy of epoxy resins (Figure 10). The Poor, Good, or Excellent flame retardancy cases are the result of the P, NP, or P/NP types of flame retardants used in preparation of epoxy composites as well as the FR loading. Each kind of behavior can be visualized by providing a full snapshot of the Poor, Good, and Excellent regions of the FRI to see how closely the data are collected in each zone. Overall, it can be seen that Poor and Good are the cases for majority of data, while the Excellent zone contains limited data. This highlights the difficulty of achieving high flame-retardant efficiency in epoxy composites when merely using flame retardants. Thus, development of innovative flame retardants through blending different FR families and making them reactive towards epoxy may result in a fully cured 3D network with high flame resistance. This requires the knowledge and experience of chemists and engineers who can adjust the performance of the system in a very disciplined manner. Moreover, using bio-based epoxy resins with limited environmental threats would be another solution to the question of “which FR additive(s) meet the requirements of highly flame-retardant epoxy composites?”. 

* Molecules 2019, 24, x FOR PEER REVIEW 35 of 55 The more interesting outcome of this work is that LOI percent similarly detects Poor and Good behaviors, not principally Excellent performance (Figure 9). This suggests that development of innovative FR additives by combination of P and NP and using highly efficient synthesis routes is the essential step to be taken in the near future for developing flame retardant epoxy composites.

![Figure 9](image)

**Figure 9.** Flame retardancy analysis of epoxy resins containing combinatorial flame-retardant systems in terms of the FRI values as a function of LOI test results. Symbols are indicative of different types of combinatorial flame-retardant systems used. Hollow symbols are indicative of fiber-incorporated composites with details given in the bottom of Table 1 as notes a to i.

5. Concluding Remarks and Future Perspective

In previous sections, we categorized the flame-retardant properties of epoxy resins in terms of the universal FRI criterion and the content of flame retardants of three families. We also attempted to find possible correlations between cone calorimetry (reflected in FRI variations), UL-94, and LOI analyses. Since cone calorimetry is the best way to simulate real state combustion of polymers, here, we give a general picture of flame retardancy of epoxy resins (Figure 10). The Poor, Good, or Excellent flame retardancy cases are the result of the P, NP, or P/NP types of flame retardants used in preparation of epoxy composites as well as the FR loading. Each kind of behavior can be visualized by providing a full snapshot of the Poor, Good, and Excellent regions of the FRI to see how closely the data are collected in each zone. Overall, it can be seen that Poor and Good are the cases for majority of data, while the Excellent zone contains limited data. This highlights the difficulty of achieving high flame-retardant efficiency in epoxy composites when merely using flame retardants. Thus, development of innovative flame retardants through blending different FR families and making them reactive towards epoxy may result in a fully cured 3D network with high flame resistance. This requires the knowledge and experience of chemists and engineers who can adjust the performance of the system in a very disciplined manner. Moreover, using bio-based epoxy resins with limited environmental threats would be another solution to the question of “which FR additive(s) meet the requirements of highly flame-retardant epoxy composites?”. 

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Author Contributions: Conceptualization, H.V. and M.R.S.; methodology, H.V. and M.R.S.; validation, H.V. and M.R.S.; investigation, E.M., H.V. and M.R.S.; data curation, E.M.; writing—original draft preparation, H.V. and M.R.S.; visualization, H.V., S.T. and M.R.S.; supervision, H.V., S.T. and M.R.S.; writing—review and editing, H.V., S.T. and M.R.S.; funding acquisition, H.V. M.R.S.; All authors have read and agreed to the published version of the manuscript.

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