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ENHANCED FIRE RETARDANCY OF VINYL ESTER RESINS BY COMBINATION OF ADDITIVES

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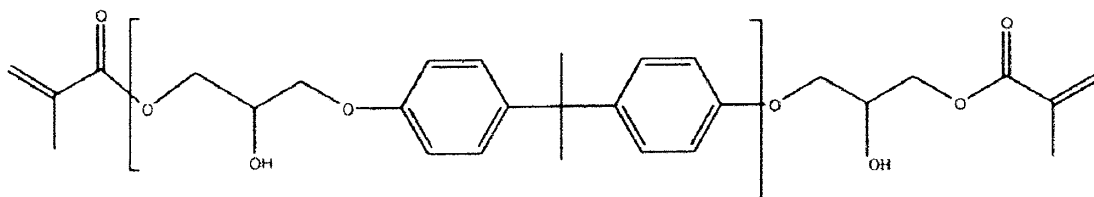
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ABSTRACT

In pursuit of fire-retarded materials, vinyl ester resins were combined with various commercially available fire retardants at lower loadings than that at which they are usually effective when used alone. The thermal stability and flammability of the various combinations of fire retardants were evaluated by thermogravimetric analysis and cone calorimetric analysis. With some combinations, the 50% degradation temperature was improved by about 5-10°C. Different additives affected the flammability to varying extents and some combinations resulted in an enhanced fire retardancy compared to the additives used alone. The combinations that showed the best reductions in the peak heat release rate (PHRR) were further used to prepare glass reinforced resins and the flammability of these systems was also evaluated using cone calorimetry.

INTRODUCTION

Vinyl ester resins are mixtures of methacrylated epoxy (the vinyl ester) (VE) and styrene (St) monomers. The VE monomer has reactive groups at either end, while St has one reactive double bond. The structure of the vinyl ester is shown below in **Scheme 1**. During polymerization the VE monomer provides cross-linking capacity and branching points for the network, while the styrene monomer provides linear chain extension. The development of the network greatly affects the physical, chemical and mechanical properties of the polymer [1, 2].



Scheme 1: Structure of the vinyl ester moiety

Vinyl ester resins have a vast number of applications both in industry and the military [1, 3, 4]. Like all other polymers, the VE resins are flammable. Over the years a number of both halogenated [5, 6] and non-halogenated [7-9] fire retardants (FRs) have been identified and are currently in use. Despite some environmental concerns, to date halogen-containing FRs are mainly used either as additives or are chemically attached [10] to the vinyl ester resin. Other flame retardants, like hydrated mineral fillers ($Mg(OH)_2$, $Al(OH)_3$), phosphorus containing compounds, such as resorcinol diphosphate (RDP), tris(2-chloroethyl) phosphate (TECP), and inorganics (silicates, $CaCO_3$) have also been examined as possible FRs for these VE resins; a review by Kicko-Walczak [11] explains in detail how some of these additives function as fire retardants.

Vinyl ester-clay nanocomposites have been prepared and flammability properties evaluated [12, 13]. In previous work from this laboratory [14], the effect of nanocomposite formation using different types of organically-modified clays and synergy between nanocomposite formation and phosphorus containing additives on the flammability of VE resins was evaluated. From this study, it was concluded that clay and phosphorus additives compliment each other, as shown by improvements in mechanical properties and reductions in both the peak heat release rate and the total heat released from cone calorimetric measurements. Weil *et al* [15] and others have combined additives with the polymer and evaluated the flammability using oxygen index and the UL94 protocol.

In the work reported herein, a similar strategy was used, however using cone calorimetry and thermogravimetric analysis, TGA, to determine how the thermal and flammability properties may be improved using a combination of two or more additives at relatively low levels. The additives used in this study are ATH, zinc borate, melamine, melamine polyphosphate, melamine cyanurate, organically modified clay, and resorcinol diphosphate, RDP. If inorganic additives, such as alumina trihydrate (ATH), which are effective in improving the fire retardancy, but only in very large amounts, can be combined with other additives and show efficacy at lower levels, this would be a significant advance of knowledge.

EXPERIMENTAL

Materials. The organically-modified montmorillonite, containing a dimethyl dihydrogenated tallow ammonium cation (hydrogenated tallow is a mixture of ~65% C18, ~30% C16 and ~14% C14) substituted clay, Cloisite-15A, was supplied by Southern Clay Products, Inc. Other clays used in this study, Np clay [16], BTL clay [17] and 5AC [17] have been prepared in this laboratory. Vinyl esters resin bisphenol-A/Novolac epoxy based vinyl ester, a combination of bisphenol-A epoxy based vinyl ester and novolac epoxy based vinyl ester, mass fraction of 67% in styrene, (Derakane 441-400) was obtained from the Dow Chemical Company and Ashland Chemical Co. The initiator, 2-butanone peroxide, BuPO, was supplied by Aldrich Chemical Company and cobalt naphthenate, CoNp, mass fraction 6% in mineral spirits, was obtained from OMG Americas, Inc. Great Lakes Chemical Company provided resorcinol diphosphate, RDP. Hydrated zinc borate (fire brake ZBFNG) (ZnB) and anhydrous zinc borate (fire brake 415) (FB), were supplied by US Borax. Alumina trihydrate, ATH, OL-1071C, was obtained from Albemarle Co, while melamine, melamine polyphosphate and melamine cyanurate (MM, MPP and MC respectively) were kindly provided by Ciba Specialty Chemicals.

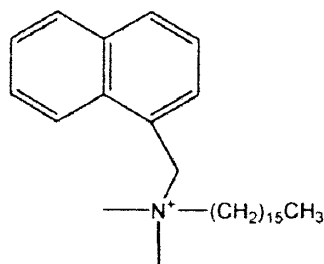
Preparation of vinyl ester composites. 120 g samples of vinyl ester composites were prepared at room temperature by mixing the resin and additives using a mechanical stirrer for three hours. The initiator, BuPO (1.25%), was then added and mixture stirred for a few minutes, followed by the addition of the catalyst, CoNp (0.3%), and stirring was continued until the catalyst was well distributed in the mixture. The sample was quickly transferred to aluminum dishes, making ~30 g samples for cone calorimetric analysis and thin samples for TGA measurements. The samples were cured at room temperature overnight and post cured at 80 °C for 8 hrs. The amount and identity of the fire retardant additives was varied to ascertain how the thermal stability and flammability of the polymer is affected by the quantity of the fire retardant that was used.

Instrumentation. Thermogravimetric analysis, TGA, was performed on a Cahn TG-131 under flowing nitrogen (60 mL/min) at a scan rate of 20 °C per minute from 20 °C to 600 °C; all TGA experiments have been performed in triplicate and the reproducibility of temperature is ±3 °C

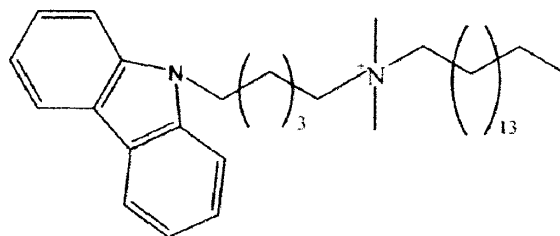
while amount of nonvolatile residue is reproducible to $\pm 2\%$. Cone calorimeter measurements were performed at flux of 35 kWm^{-2} for the vinyl esters and 50 kWm^{-2} for the glass fiber reinforced vinyl esters using an Atlas Cone 2 according to ASTM E 1354; the spark was continuous until the sample ignited. Curing and post curing of samples in pre-formed aluminum foil was used to prepare samples for cone calorimetry. All samples were run in triplicate and the average value is reported. The results from cone calorimeter are reproducible to $\pm 10\%$, based on the work of Gilman [13].

RESULTS AND DISCUSSION

Clays used in this study. Four different clays were used in this study, one of these was a commercial material while the other three were originally prepared in this laboratory and have been reported in the literature [16, 17]. In addition to the reports on the preparation of the clays, nanocomposites have been prepared with these clays and the XRD and TEM data has been reported and this is not repeated in this paper. The structures of the four clays used in this study are shown in **Scheme 2**.

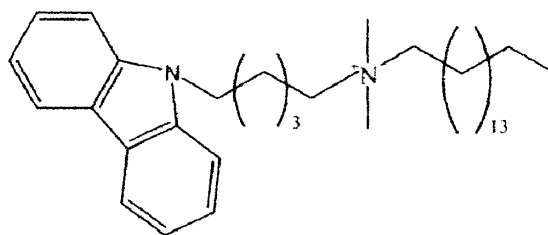


Np surfactant



BTL surfactant

$(\text{HT})_2(\text{CH}_3)_2\text{N}^+$ Cloisite 15A



SAC surfactant

Scheme 2: The structure of the surfactants of the clays used in this study

Thermogravimetric analysis. In order to determine how the thermal stability of the vinyl esters was affected by the presence of the additives, thermogravimetric analysis (TGA) of the composites was carried out. The parameters of interest from TGA are the onset temperature of the degradation, denoted as the temperature at which 10% degradation occurs, T_{10} , the temperature at which 50% degradation occurs, T_{50} , another measure of thermal stability, and the material that remains at 600°C , denoted as residue. This residue consists of both the polymeric char and the non-volatile portion of the inorganic additive.

One of the most striking properties of vinyl ester resins is their high thermal stability. It is likely that the high thermal stability is associated with the high degree of cross-linking that occurs during polymerization. From previous work [14], a reduction in thermal stability in the presence of clay, Cloisite 15A, or phosphate, or combination of both was observed; all information on both the systems containing only the clay or only the phosphate, as well as the binary combinations, were presented in this work [14]. In this study the thermal stability of some well-known fire retardant additives was investigated.

Table 1 and **Figures 1 to 3** show the TGA data obtained when different additives were used alone. In the table of data, the residue that is obtained is shown along with that expected from a consideration of the residue of each of the materials at 600°C. For most samples, the amount of residue is reasonably close to that expected; only the samples with anhydrous zinc borate, ZnB, are not in agreement and these show a significantly smaller amount than expected. This must indicate that some reaction occurs between the additive and the polymer which leads to volatilization.

In many cases, these systems contain a large fraction of additive. The TGA curves are presented including all of the components; if one only plots the amount of polymer remaining, subtracting the mass of additive, the temperatures that one records for the various mass loss positions are not significantly different from those obtained when all of the sample is counted.

It is clear that the additives affect the thermal stability of the vinyl esters to different extents, with some additives showing improvement in the initial degradation temperature, T_{10} , and some not showing this improved thermal stability. Notable improvements in the 50% degradation temperature, T_{50} , were observed, particularly for ZnB and ATH at higher additive loading. For all the additives used, the thermal stability seems to be dependent on the additive loading. Different organically-modified clays were used and there was no improvement in thermal stability for any of these clay containing systems.

Thermogravimetric analysis data obtained for binary combinations of additives is shown in **Table 2** and **Figures 4 to 6**. It is apparent that combining additives did not lead to an improvement in thermal stability, since both the initial and 50% degradation temperatures were reduced. The amount of residue correlates quite well with that expected from the composition, with a few exceptions, and this likely means that no chemical reactions occur between the components.

For all the additives studied here, there is very little change in any of the TGA parameters. The temperatures at which 10% degradation occurs may be, in general, slightly decreased while the temperature for 50% degradation is slightly increased but these are relatively small changes. For comparison, in the clay and phosphate systems both the T_{10} and T_{50} degradation temperatures were lowered at all loadings studied [14]. One must conclude from these TGA studies that these additives do not have any significant effect on the thermogravimetric analysis data in an inert atmosphere.

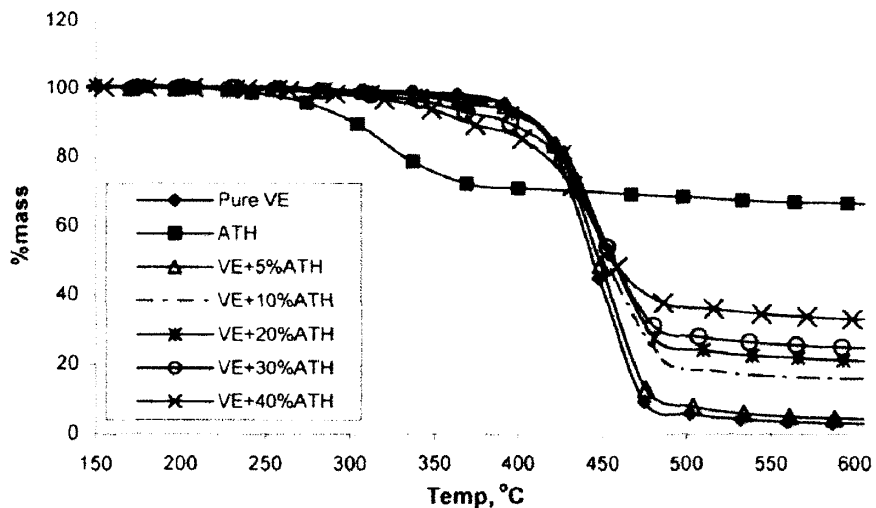


Figure 1: Thermogravimetric analysis data for vinyl esters containing ATH

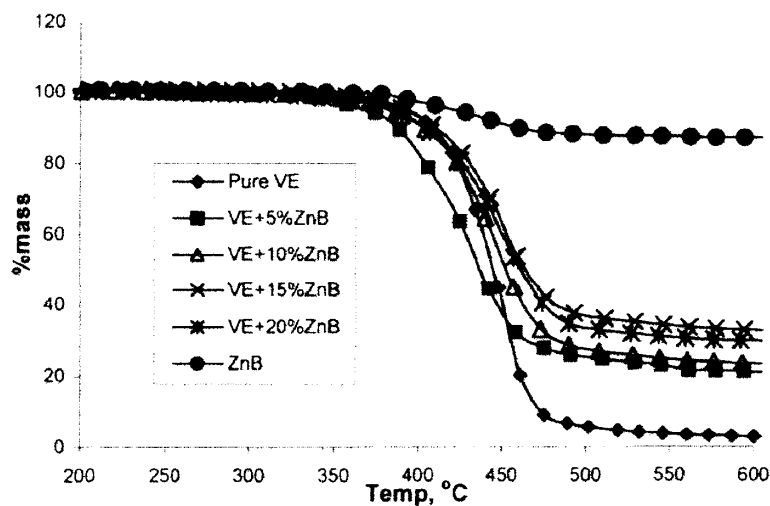


Figure 2: Thermogravimetric analysis data for vinyl esters containing hydrated zinc borate

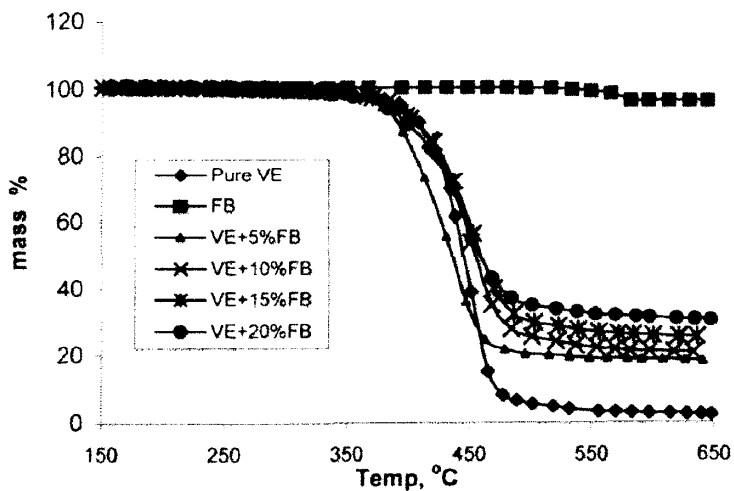


Figure 3: Thermogravimetric analysis data for vinyl esters containing anhydrous zinc borate

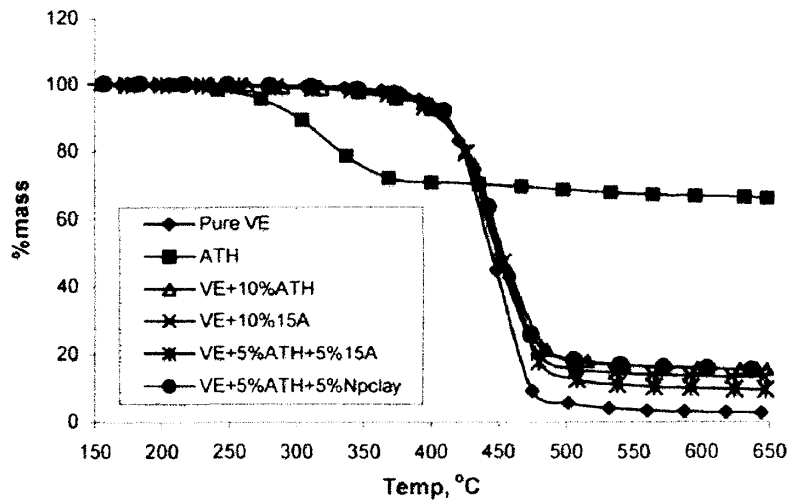


Figure 4. Thermogravimetric analysis data for vinyl esters containing mixture of ATH and Clay

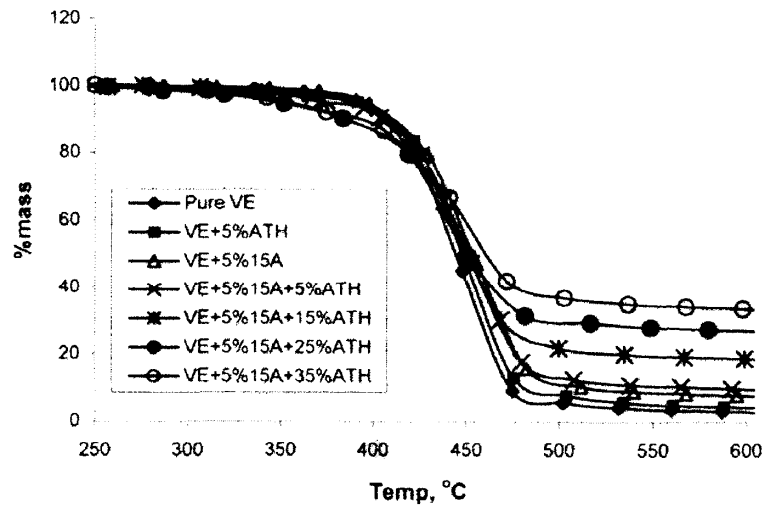


Figure 5: Thermogravimetric analysis data for vinyl esters containing mixture of ATH and 15A clay

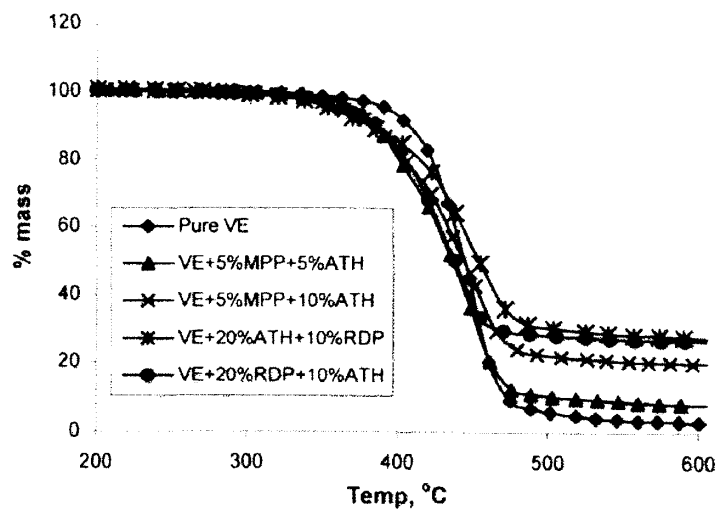


Figure 6: Thermogravimetric analysis data for esters containing mixture of ATH and MPP or RDP

Table 1: TGA data for vinyl esters containing various additives

Sample	T ₁₀	T ₅₀	% residue	% residue expected
Pure VE	415	448	7	7
VE+5% ATH	412	449	7	10
VE+10% ATH	411	453	15	13
VE+20% ATH	405	454	16	20
VE+30% ATH	395	456	21	26
VE+5% ZnB	394	440	21	11
VE+10% ZnB	405	455	24	16
VE+15% ZnB	407	461	32	20
VE+20% ZnB	401	460	30	24
VE+5% FB	387	432	11	12
VE+10% FB	406	453	18	17
VE+15% FB	402	457	26	21
VE+20% FB	400	458	31	26

Table 2: TGA data for vinyl esters containing a binary combination of additives

Sample	T ₁₀	T ₅₀	% residue	% residue expected
VE	415	449	7	7
VE+5% 15A + 5% ATH	411	452	12	13
VE+5% 15A + 15% ATH	402	447	12	20
VE+5% 15A + 25% ATH	389	451	25	27
VE+5% 15A + 35% ATH	384	459	34	34
VE+5% Np clay + 5% ATH	411	450	17	13
VE+5% MPP + 5% ATH	388	441	13	5
VE+5% MPP + 10% ATH	383	444	20	9
VE+20% ATH + 10% RDP	380	454	28	20
VE+10% ATH + 20% RDP	386	434	23	13

Cone calorimetry. The technique of choice to evaluate the fire properties of polymeric materials is cone calorimetry. The parameters that may be obtained include the time to ignition t_{ign} ; the heat release rate and especially its peak value, PHRR; the time to the peak heat release rate, t_{PHRR} ; the total heat released, THR; the average mass loss rate, AMLR; and the specific extinction area, SEA, a measure of smoke.

For all the different additives used in this study, Table 3 and Figures 7 to 10 show the cone data when clay, ATH, ZnB, FB, MM, MPP, MC additives were used individually; the following conclusions can be deduced.

For all the different types of organically modified clay used in this study, there was no change in both t_{ign} and THR compared to the virgin polymer while Np clay gave the best reduction in

PHRR. For the RDP containing system, the time to ignition, t_{ign} , PHRR and THR were reduced, with the reductions directly proportional to the amount of RDP used.

When ATH was used, a significant reduction in flammability as shown by a decrease in PHRR and THR and also an increase in t_{ign} was observed at high ATH loadings. For the two types of zinc borates used, ZnB and FB, reductions in both PHRR and THR was observed, with ZnB giving a better result at 5% loading. Except for the anomalous result for 5% FB, the reductions in both PHRR and THR are independent of the amount of additive used. This means that, unlike ATH, with zinc borates a small amount of additive provides fire retardancy with potentially a smaller effect on the physical properties of the polymer.

Three types of melamine derivatives were used, melamine, MM, melamine polyphosphate, MPP, and melamine cyanurate, MC. Of these three additives, MPP gave the best reduction in PHRR and THR, and this was used in combination with other additives. This data shows that the flammability of the vinyl ester resin can be greatly affected by the use of additives, and that these additives work effectively at different loadings. The effects of binary and ternary combinations of additives at lower loadings than at which they are normally effective when used individually was also investigated.

Figures 11 to 14 and Table 4 show the data obtained for binary combinations of additives; the following conclusions are apparent. From Table 3, 5% ATH loading gave a 4% reduction in PHRR (10% ATH gave a 22% reduction) and 5% MPP gave a 31% reduction in PHRR, however from Table 4, when 5% MPP was combined with 5% ATH, a 37% reduction in PHRR was observed. This result should be considered to be an additive effect. ATH at 15% gives a 39% reduction in PHRR while 20% ATH shows a 60% reduction, while 5% ZnB gives a 55% reduction. The combination of 5% ZnB and 15% ATH showed a 70% reduction in PHRR, which is an additive effect.

Ternary combinations were also examined and Table 5 and Figures 15 to 17 give a summary of the data obtained. For the ZnB/RDP/ATH system, comparing the reductions in PHRR, a total loading of 15% (5% of each component) is as effective as a larger amount (25% total loading) and definitely better than either RDP or ATH when used alone at 15% loading. This ternary system is about as effective as ZnB alone so this does not appear to be a synergistic effect. The same result was observed when MPP was used in place of RDP. When RDP and MPP are used in combination with other additives they have comparable effects, however when they are used alone they show quite different properties. There is probably some chemical interaction that occurs when the additives are combined and these interactions may result in a synergistic or antagonistic effect.

Since MPP and RDP are effective to the same extent in the presence of other additives, in order to decide between the two, other factors, like the effect on viscosity and cost, must be considered. RDP is a plasticizer and has the effect of reducing viscosity, which may be either an advantage or a disadvantage, and this might make it more or less preferable depending on the intended use.

In summary, it is apparent that a combination of additives results in reductions in both PHRR and THR at lower additive loadings than when some additives, such as ATH, are used alone. ZnB when used alone is effective at low loadings while RDP and MPP are effective to the same extent in the presence of ATH or ZnB. ATH also has the advantage that it increases the time to ignition. The most interesting system to further explore is one containing a mixture of ZnB, ATH and RDP. Varying the amount of each additive might result in a system with excellent

reductions in flammability, as measured by cone calorimetry. This may be due to combining the reductions in both PHRR and THR observed with a low loading of ZnB and RDP loading with a slightly higher loading of ATH, which results in an increased time to ignition.

Table 6 shows a summary of the cone data obtained for glass reinforced systems, containing 40 mass % glass fibers. It is apparent that the reference system, a brominated vinyl ester, exhibits better flammability properties compared to the samples containing mixtures of non-halogenated additives.

Even though the additive compositions tested for the glass reinforced systems did not give as good reductions in PHRR and THR as seen in the halogenated system, these resulted in higher time to ignition, a slightly lower mass loss rate and less smoke was evolved. It might be worthwhile to examine other compositions to see if it is possible to lower the peak heat release rate and or the total heat released.

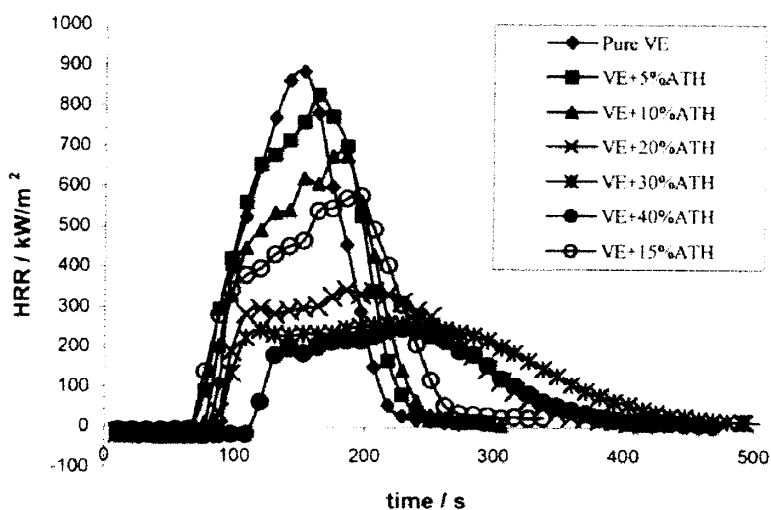


Figure 7: Heat release rate curves for vinyl esters containing ATH

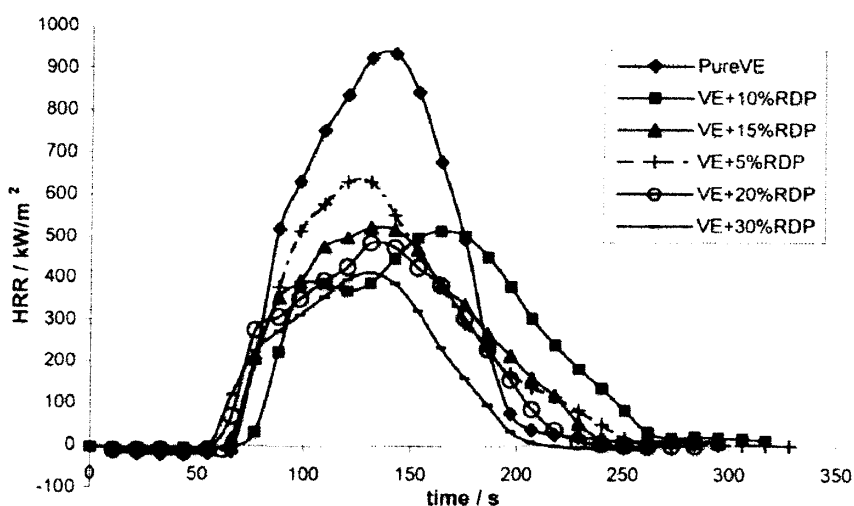


Figure 8: Heat release rate curves for vinyl esters containing RDP

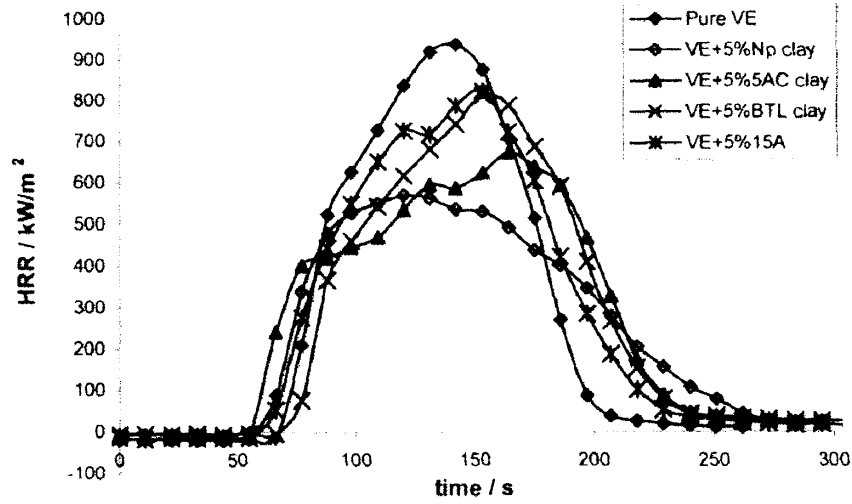


Figure 9: Heat release rate curves for vinyl esters containing clay

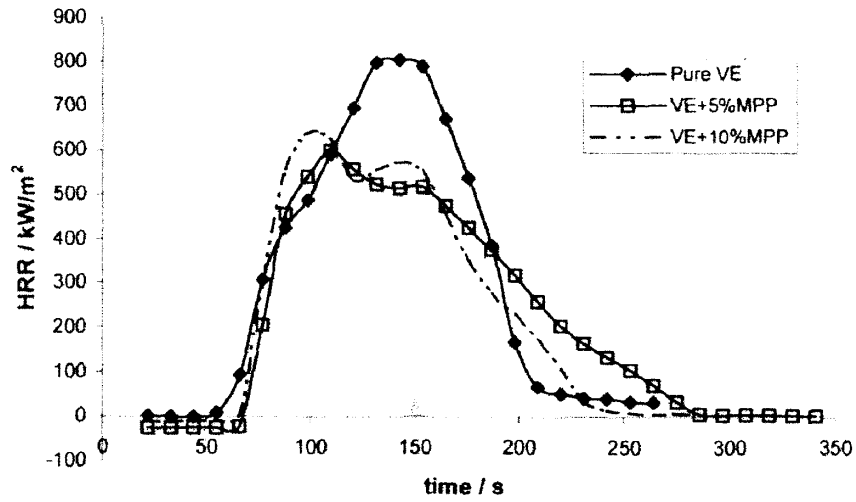


Figure 10: Heat release rate curves for vinyl esters containing MPP

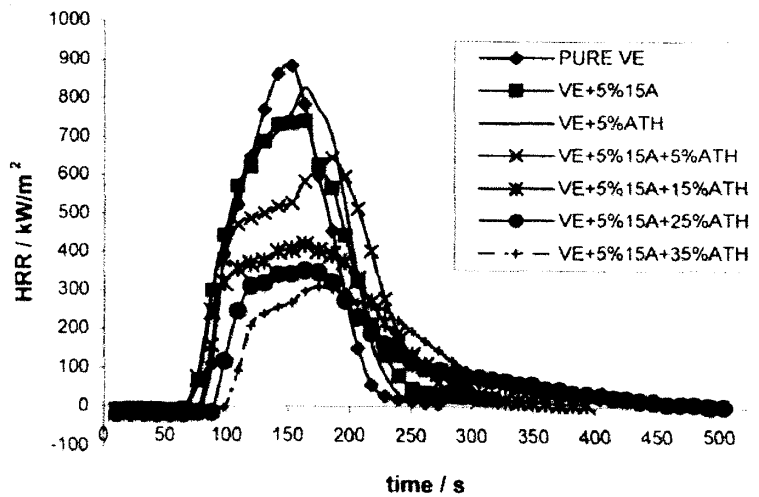


Figure 11: Heat release rate curves for vinyl esters containing mixture of ATH and Cloisite 15A clay

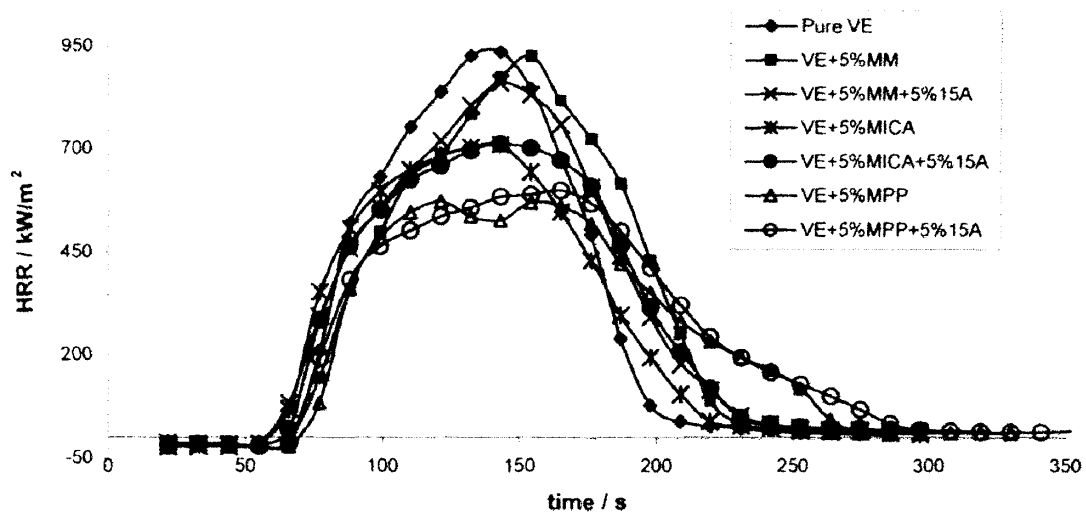


Figure 12: Heat release rate curves for vinyl esters containing mixture of clay and different types of melamine

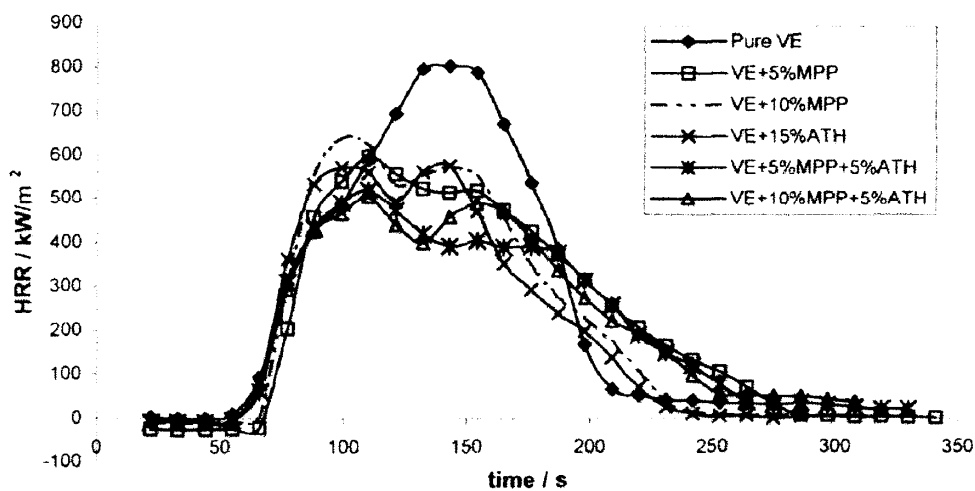


Figure 13: Heat release rate curves for vinyl esters containing mixture of ATH and MPP

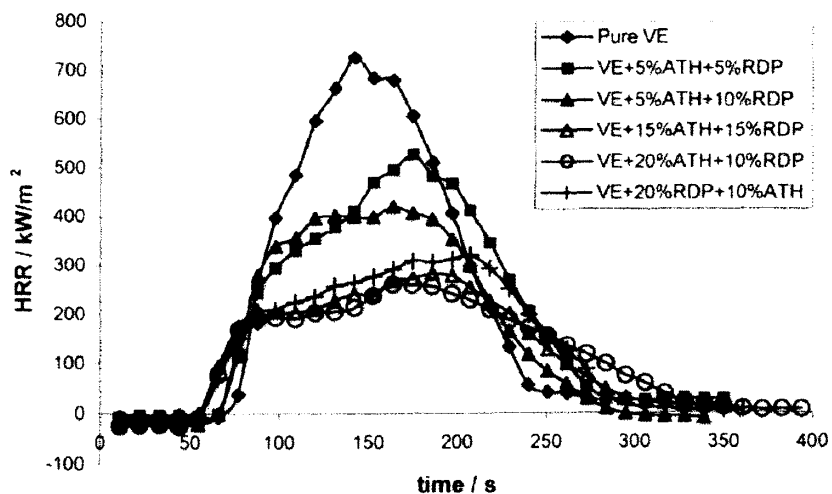


Figure 14: Heat release rate curves for vinyl esters containing mixture of ATH and RDP

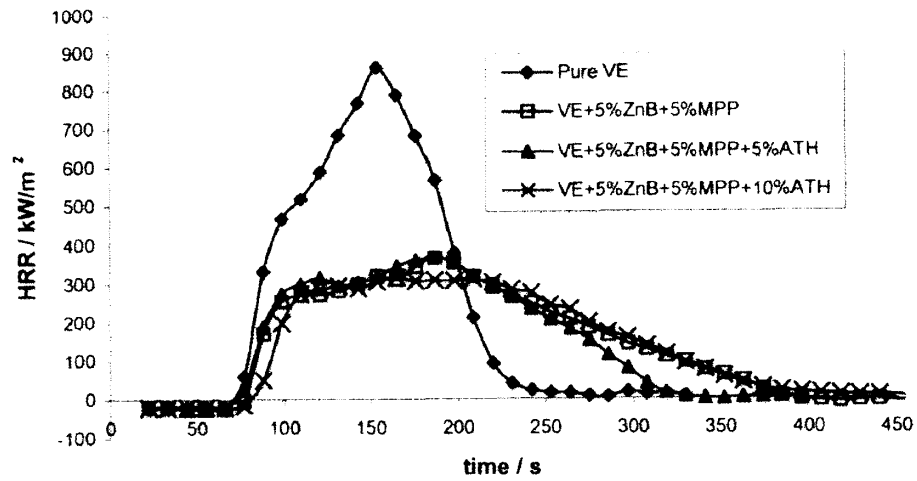


Figure 15: Heat release rate curves for vinyl esters containing mixture of ATH, ZnB and MPP

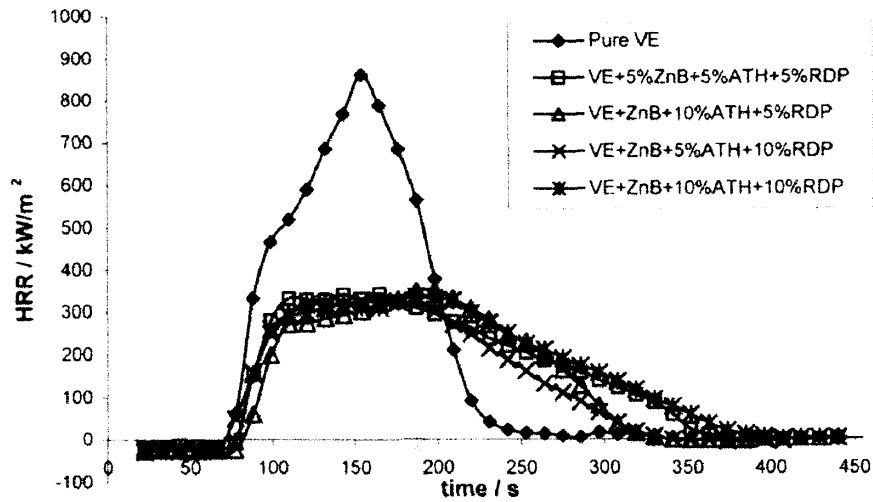


Figure 16: Heat release rate curves for vinyl esters containing mixture of ATH, ZnB RDP

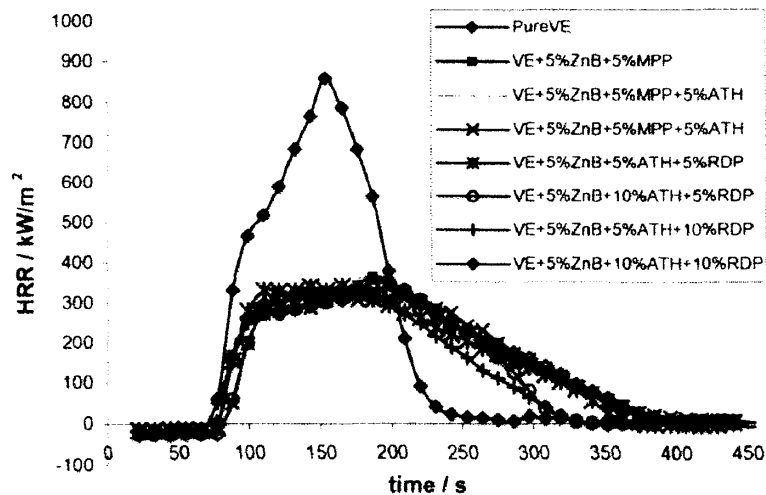


Figure 17: Heat release rate curves for vinyl esters containing mixture of ATH and various additives

Table 3: Cone calorimetry data for vinyl esters with various additives at 35 kW/m²

Sample	t _{ign} ^a , s	PHRR, kW/m ² (%redn) ^a	t _{PHRR} ^a , s	THR ^a MJ/m ²	ASEA ^a , m ² /kg	AMLR ^a g/s.m ²
VE	69±9	890±58	140±11	68±2	1118±9	28±1
VE+5% 15A	67±1	813±87 (8)	160±10	79±1	1049±18	27±1
VE +5% Npclay	62±3	597±32 (30)	108±8	73±2	1174±32	19±2
VE+10% Npclay	59±7	676±42 (21)	130±5	69±4	1059±9	24±0
VE +5% 5AC	60±6	667±62 (22)	161±19	78±4	1053±64	24±3
VE +5% BTL	76±2	754±115 (12)	162±7	81±5	1227±57	24±3
VE +10% 15A	72±2	587±37 (31)	149±26	77±3	1196±19	18±1
VE +5% ATH	62±9	852±81 (4)	164±4	81±3	1073±17	27±2
VE +10% ATH	72±4	693±123 (22)	174±16	73±2	1093±63	24±3
VE +15% ATH	72±4	530±51 (39)	181±10	70±3	1047±18	18±1
VE +20% ATH	79±2	351±18 (61)	187±16	62±7	1053±14	13±1
VE +30% ATH	83±2	282±26 (68)	219±16	59±5	1030±29	11±1
VE +40% ATH	113±3	253±22 (72)	232±9	47±3	889±14	10±1
VE +5% MM	57±4	928±61 -	150±7	84±4	1154±18	25±1
VE +10% MM	69±8	819±54 (5)	161±19	90±6	1092±15	34±9
VE +5% MC	68±8	737±60 (14)	142±10	77±7	1084±32	23±2
VE +5% MPP	72±4	585±22 (31)	124±30	70±2	1232±39	21±1
VE +10% MPP	68±1	685±34 (20)	119±27	67±4	1148±55	24±0
VE +15% MPP	65±2	590±14 (32)	124±31	63±3	1063±13	22±1
VE+5% ZnB	58±6	392±75 (55)	126±16	61±8	931±19	15±3
VE+10% ZnB	66±5	425±10 (51)	168±23	65±1	1106±43	15±1
VE+15% ZnB	71±4	380±70 (56)	179±30	62±4	1124±41	14±2
VE+20% ZnB	76±6	350±24 (60)	181±28	59±2	1088±34	14±1
VE+5% FB	55±4	644±87 (26)	118±29	68±8	1149±20	21±2
VE+10% FB	71±8	437±28 (50)	176±9	73±4	1140±6	14±1
VE+15% FB	73±3	411±22 (53)	189±16	66±3	1085±35	14±0
VE+20% FB	73±5	327±26 (63)	170±54	59±6	1094±23	12±2
VE +5% RDP	68±4	584±79 (32)	140±19	61±2	1175±17	23±2
VE +10% RDP	73±3	521±17 (39)	136±33	56±6	1495±19	24±2
VE +15% RDP	71±5	551±63 (35)	141±13	54±2	1488±84	25±1
VE +15% RDP	61±2	589±19 (32)	126±9	52±3	1480±74	28±1
VE +20% RDP	66±4	514±30 (40)	136±4	46±3	1362±7	28±2
VE +30% RDP	62±4	414±5 (51)	129±2	38±2	1454±10	28±1

^a t_{ign}, time to ignition; PHRR, peak heat release rate; t_{PHRR}, time to PHRR; THR, total heat released; AMLR, average mass loss rate; ASEA, average specific extinction area (smoke)

Table 4: Cone calorimetric data for vinyl esters with a binary combination of additives at 35 kW/m²

Sample VE	t _{ign} ^a , s	PHRR, kW/m ² (%-reduction) ^a	t _{PHRR} ^a , s	THR ^a MJ/m ²	ASEA ^a , m ² /kg	AMLR ^a g/s.m ²
Pure VE	72±8	788±64	143±10	79±5	1210±54	25±2
+5% 15A+5% ATH	75±4	633±60(29)	187±19	76±3	1024±77	23±4
+5% 15A+15% ATH	73±6	419±35 (53)	170±4	69±8	1067±24	14±1
+5% 15A+25% ATH	88±4	347±23 (61)	185±27	58±7	1036±26	11±2
+5% 15A+35% ATH	103±9	300±11 (66)	194±40	54±5	1010±77	11±2
+5% MPP+5% ATH	69±2	547±24 (37)	156±44	69±7	1124±41	19±2
+5% MPP+10% ATH	67±3	540±27 (38)	186±17	68±4	1052±35	18±1
+10% MPP+5% ATH	71±6	562±53 (35)	122±13	60±7	1207±99	21±4
+5% MM+5% 15A	57±7	833±48	151±17	87±5	1173±22	24±1
+5% MC+5% 15A	65±5	739±31 (13)	144±17	80±3	1057±10	24±1
+5% MPP+5% 15A	71±2	617±55 (28)	153±17	76±3	1232±20	20±1
+5% RDP +5% ATH	72±5	546±52 (36)	171±2	66±1	1290±26	20±1
+10% RDP +5% ATH	71±3	424±29 (50)	158±27	58±3	1481±21	20±1
+5% ZnB	61±5	398±37 (52)	120±35	67±2	927±39	13±1
+5% ZnB+15% ATH	65±3	253±27 (70)	173±37	68±5	1068±58	10±1
+5% ZnB+20% ATH	64±3	272±10 (68)	186±8	65±2	1031±34	9±0
+5% ZnB+15% RDP	60±3	419±17 (50)	171±10	73±6	1103±42	13±1
+5% ZnB+25% RDP	58±4	418±49(50)	149±5	58±6	1416±207	19±1
+5% FB	61±9	547±47 (35)	108±14	73±5	1138±62	18±1
+5% FB +15% ATH	78±4	399±27 (52)	186±36	71±4	1158±31	14±1
VE+5% FB+15% RDP	64±5	525±33 (33)	150±10	59±5	1406±73	21±0
VE+5% FB+25% RDP	57±3	436±27 (48)	135±8	54±7	1445±162	19±1

^a t_{ign}, time to ignition; PHRR, peak heat release rate; t_{PHRR}, time to PHRR; THR, total heat released; AMLR, average mass loss rate; ASEA, average specific extinction area (smoke)

Table 5: Cone calorimetry data for vinyl esters with a ternary combination of additives at 35 kW/m²

Sample	t _{ign} ^a , s	PHRR, kW/m ² (%redn) ^a	t _{PHRR} ^a , s	THR ^a MJ/m ²	ASEA ^a , m ² /kg	AMLR ^a g/s.m ²
Pure VE	72±8	788±64	143±10	79±5	1210±54	25±2
+5% RDP +5% ATH+5% 15A	75±6	553±22 (35)	185±15	77±6	1204±9	18±1
+5% ZnB+5% MPP	71±4	386±35 (51)	156±13	61±3	1079±52	13±1
+5% ZnB+5% MPP+5% ATH	71±7	340±27 (57)	166±15	63±4	1092±75	12±1
+5% ZnB+5% MPP+10% ATH	66±6	288±8 (63)	187±45	61±3	1045±10	11±0
+5% ZnB+5% ATH+5% RDP	73±8	333±7 (58)	172±23	61±3	1218±61	12±1
+5% ZnB+10% ATH+5% RDP	65±4	308±17 (61)	216±14	62±2	1076±37	11±0
+5% ZnB+5% ATH+10% RDP	57±9	375±23 (52)	150±28	60±1	1175±13	12±1
+5% ZnB+10% ATH+10% RDP	58±3	346±16 (56)	169±15	57±2	1183±45	13±1

^a t_{ign}, time to ignition; PHRR, peak heat release rate; t_{PHRR}, time to PHRR; THR, total heat released; AMLR, average mass loss rate; ASEA, average specific extinction area (smoke)

Table 6: Cone calorimetry data for 40% glass reinforced vinyl esters resin at 50kW/m²

Sample	t _{ign} ^a , s	PHRR, kW/m ² (%redn) ^a	t _{PHRR} ^a , s	THR ^a MJ/m ²	ASEA ^a , m ² /kg	AMLR ^a g/s.m ²
Virgin VE	85	276		59		
Brominated VE	77	141 (49)	199	27	12	1405
VE+5% ZnB+15% ATH	89	232 (16)	241	64	10	1076
VE+5% ZnB+5% RDP+10% ATH	82	227 (18)	222	54	11	1142
VE+5% ZnB+5% MPP+10% ATH	88	249 (10)	216	52	11	1115

^a t_{ign}, time to ignition; PHRR, peak heat release rate; t_{PHRR}, time to PHRR; THR, total heat released; AMLR, average mass loss rate; ASEA, average specific extinction area (smoke).

CONCLUSIONS

Various additives affect the thermal and flammability properties of the vinyl ester resins to different extents. These additives can be combined to give significant reductions in flammability at lower additive loading than when the individual additives are used. This is particularly true for additives like ATH, which are effective at high additive loading. For the glass reinforced system, the halogen containing system seems to be the best system; perhaps increasing the additive loadings might be effective if good reductions in flammability are to be obtained with non-halogen-containing additives.

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