OPTIMIZATION STUDIES IN FLAME RETARDANT FIBRE REINFORCED PLASTIC COMPOSITES FOR ROOFING APPLICATION

R. Daulath Banu, R. Vasanthakumari
Dept of Polymer Technology, B. S. Abdur Rahman University, Vandalur,
Chennai-600 048, India

ABSTRACT
Composite materials, especially, fibre reinforced plastics (FRP) are widely used in different fields such as aerospace, automobile, electrical and electronics, domestic, building and construction. It is also need of the hour in developing countries like India that low cost housing / building is to be provided within short duration at times of natural crisis such as Tsunamis, earthquake, floods etc. With this main objective the present work is aimed at carrying out studies systematically to arrive at cost effective flame retardant formulation using different Flame retardant fillers such as Aluminium tri hydrate (ATH), Antimony trioxide (Sb_2O_3), Deca Bromo diphenyl ether (DeBDE) a novel halogenated compound, Tricresyl phosphate (TCP) at different loading levels with general purpose unsaturated polyester resin and chopped strand glass fibre mat. The FRP laminates were prepared using hand lay up method and the samples were tested for various properties such as mechanical, thermal, flammability and smoke density tests. Among the various FR fillers tried, 3:2 ratio of 10% of DeBDE and Sb_2O_3 with 25% of ATH provides more cost effective FR formulation with good mechanical and flame retardant properties than the commercial FR formulation.
KEYWORDS: Flame retardant fillers, FRP, TCP, ATH, deca bromo and antimony oxide compound

1. INTRODUCTION

Composites are replacing fast all conventional materials in many applications such as aerospace, automobiles, construction, electrical and electronics due to their high strength, low cost, easy process ability & availability in various forms and shapes with good aesthetics. Considering composite materials as a whole, there are many different material options to choose from in the areas of resins, fibres and cores, all with their own unique set of properties such as strength, stiffness, toughness, heat resistance, cost, production rate etc.Thus, the selection of materials and processing method play a major role in end use application areas.

Though Fibre reinforced plastics are widely used in other fields, in building and construction their flammability is producing a major threat. Lot of studies have been carried out in the areas of usage of various flame retardant fillers / compounds in Fibre reinforced plastic composites for various applications [1-3]. Glass fibre, aramid and carbon fibre reinforced with epoxy, phenolic and polyester have been tried for building construction of structural beams and panels etc. [4-11]. The present paper is aimed at developing systematically a method of preparation of fibre reinforced plastic with V_0 flame rating to suit the needs of poor people, particularly for roofing application in place of thatched roof and asbestos sheet. Various commercial FR fillers were tried and systematically studied for their flammability characteristics and an optimum composition has been arrived at without compromise in mechanical properties.

2. EXPERIMENTAL

2.1 Materials

The materials tried in this work are Unsaturated polyester resin from M/s Vasavi bala resins, Pvt Ltd India, Chopped Glass Strand Mat-450g/mm^2 from Saint Gobain glass India limited and lab grades of ATH, DeBDE, Sb_2O_3 ,TCP Methyl Ethyl Ketone Peroxide (MEKP), Cobalt Napthenate.

2.2 FRP Composition

In all the FRP compositions the matrix resin and glass fibre were kept in the ratio 70: 30 and the various filler composition tried are

- ATH at different loadings of 15, 20, 25, 40, 50 and 60 %
- DeBDE & Sb_2O_3 combination in 3:2 ratio at different loadings of 5, 10, 15, 20 and 25 %
- TCP at 5, 10 and 15 % with respect to resin content.

2.3 Processing and Testing Methods

FRP laminate sheets (300x300x3mm) were prepared by using the above mentioned matrix material, reinforcement and fillers at different loading levels using hand lay – up technique. In all the compositions we used 1.5 % of MEKP and cobalt Napthenate for curing of the resin composite. The laminate sheets were tested for different properties as per ASTM standards as shown below:

Property details	**Standard used**
Gel time and Gel Point	ASTM D 2471
Tensile strength	ASTM D 638
Flexural strength	ASTM D 790
Izod impact strength	ASTM D 256
Barcol hardness	ASTM D 2583
Limiting oxygen Index (LOI)	ASTM D 2863
Smoke density	ASTM D 2843
Flammability	UL 94

3. RESULTS AND DISCUSSION

3.1 Studies with ATH Filler

Figure 1 shows the effect of ATH on gel time and the maximum exothermic temperature reached during the curing process. From the figure it is clear that the gel time in ATH filled formulation does not change much while there is a gradual decrease in the gel point of the resin formulation with the increase in ATH content.

Figure 1 Effect of ATH on gel time and peak exothermic temperature

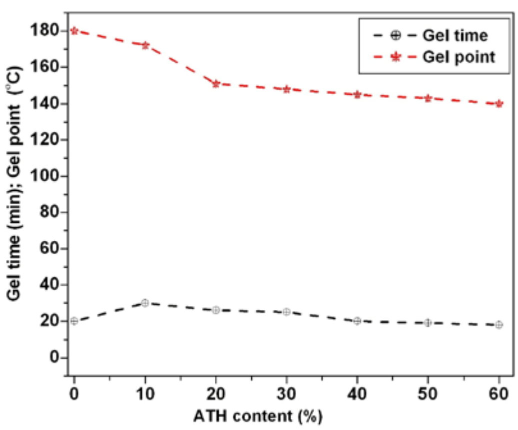

Table 1 Effect of ATH on Mechanical Properties
(Ratio of Resin : Glass fibre 70: 30)

Filler content,% ATH	Tensile Strength ($N.mm^{-2}$)	% Elongation @ break	Flexural Strength ($N.mm^{-2}$)	% Elongation @ break	Barcol Hardness	Impact Strength ($J.mm^{-1}$)
0	75.75	10.83	253.28	15.64	35.2	1.24
15	80.53	10.38	178.45	10.39	45.6	1.54
20	85.3	8.85	235.49	10.16	45.2	2.0
25	92.96	9.46	234.64	10.16	44	1.07
40	94.39	8.12	236.79	13.45	51.6	0.67
50	98.46	13.2	233.44	14.89	50.4	1.26
60	102.4	13.07	234.57	16.77	53.6	0.8

Table 1 and Figure 2 show the effect of ATH on mechanical properties of the composite. It is evident that the tensile strength is higher for the ATH filled grade and is also increasing with higher percentage of the filler. There is not much variation in flexural strength and impact strength with the increase in the ATH content. There is an increasing trend in the values of hardness with the increase in ATH content. The results show that ATH works as reinforcing filler along with the glass fiber.

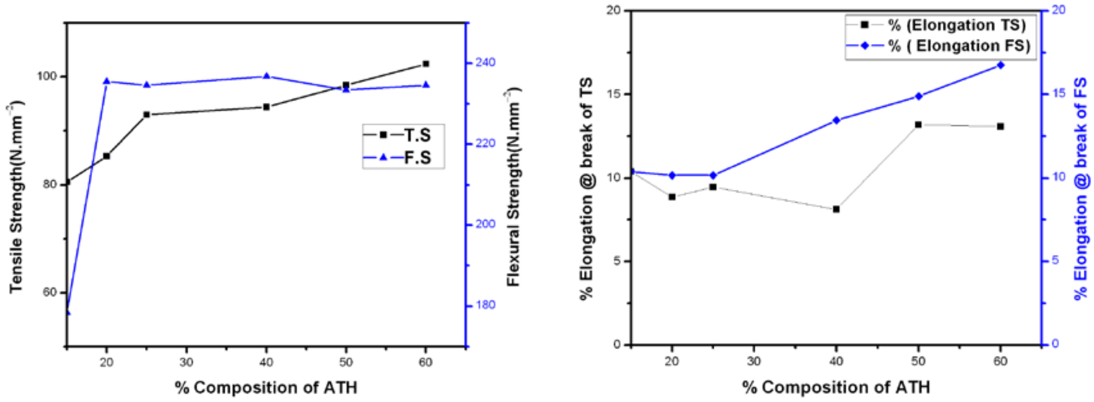

Figure 2 Effect of ATH on Tensile and flexural properties

ATH can act as a flame retardant for polymer burning since it eliminates water molecules at high temperature diluting the flammable gases thus retarding flame. Resistance to spread of flame was measured as per UL – 94 standard and the results show that even upto 60% loading of ATH to resin / Glass fibre (70/30) combination do not meet the specification of V_0 rating. Only at very high ATH filler loading (more than 130%) the laminates showed flame retardancy meeting the V_0 rating but there was a drastic decrease in mechanical properties

3.2 Studies with TCP

TCP is known as a plasticizer and also a flame retardant. The effect of TCP on mechanical properties of the composites is given in Table 2 and Figure 3.Since the cost of TCP is high only 15% loading of TCP was done and studied the properties. Tensile strength was found to increase with TCP content while there is a decrease in flexural strength observed. Impact property was found to have a marginal increase in the values with TCP content.

Table 2 Effect of TCP on Mechanical Properties
(Ratio of Resin: Glass fibre 70: 30)

Filler content TCP %	Tensile Strength ($N.mm^{-2}$)	% Tensile Elongation @ break	Flexural Strength ($N.mm^{-2}$)	% flexural Elongation @ break	Barcol Hardness	Impact Strength ($J.mm^{-1}$)
0	75.75	10.83	253.28	15.64	35.2	1.24
5	97.99	8.94	249.68	19.32	42.4	1.39
10	80.55	10.05	181.55	15.33	38.6	1.41
15	81.06	9.88	169.10	14.32	36.6	1.47

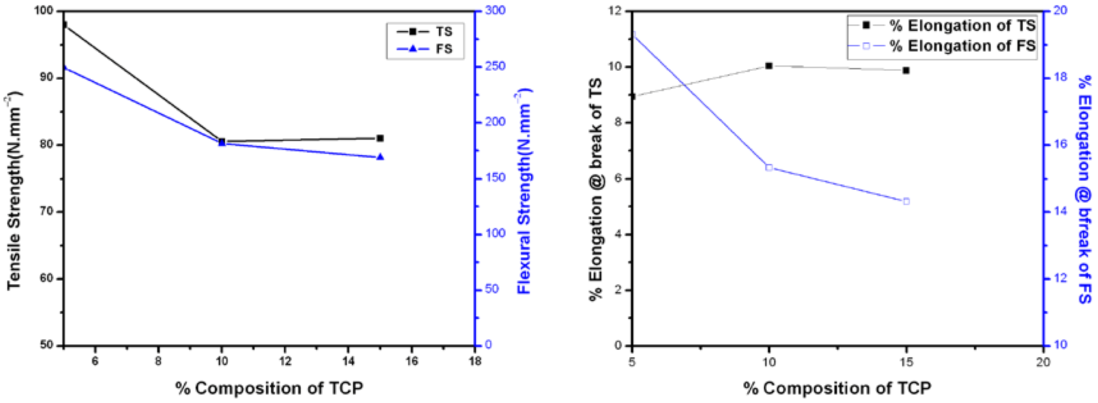

Figure 3 Effect of TCP on tensile and flexural properties

The flammability testing as per UL-94 standard showed that TCP filled compositions fail to meet V_0 specification but the rate of spreading of flame was found to be very low. Since higher concentration of TCP (more than 30%) gives better flame retardancy properties and owing to high cost, further loading beyond 15% was not considered.

3.3 Studies with DeBde and Antimony Oxide

It has been shown [12] that there is a synergistic effect in flame retardancy when a combination of antimony oxide and halogenated compound is used with engineering thermoplastic material. Here deca-bromo-dephenyl ether (DeBDE) and antimony trioxide were used in the ratio 3:2.In the present work also the same ratio of DeBDE and antimony oxide was maintained at different levels ranging from 5 to 25%

Table 3 Effect of 3:2 of Deca bromo diphenyl ether & Antimony tri oxide on Gel time & Peak exothermic temperature (ratio of Resin: Glass fibre 70: 30)

Filler content DeBDE & Sb_2O_3 %	Gel Time (minutes)	Gel Point (ºC)
0	22	180.4
5	21	190.3
10	23	186.6
15	24.3	170.3
20	26	165.2
25	28	161.3

Table 4 Effect of DeBDE & Antimony tri oxide on Mechanical Properties (ratio of Resin: Glass fibre 70: 30)

Fillercontent, % [DeBDE/ Sb_2O_3] (3:2)	Tensile Strength ($N.mm^{-2}$)	%Tensile Elonga - tion @ break	Flexural Strength ($N.mm^{-2}$)	% Flexural Elonga - tion @ break	Barcol Hardness	Impact Strength ($J.mm^{-1}$)
0	75.75	10.83	253.28	15.64	35.2	1.24
5	48.65	9.66	171.02	14.09	41.4	1.25
10	62.72	11.63	186.24	12.69	44.30	1.45
15	65.34	8.04	192.49	8.56	47.2	1.77
20	68.59	8.36	206.78	11.68	46.6	1.94
25	78.45	10.58	250.85	11.54	49.6	2.09

The effect of DeBDE and antimony oxide on gel time and gel point during the mixing process is shown in Table 3 which reveals that the gel time is not much affected significantly while there is a decrease in the gel point with the increase in filler content. The plot of the mechanical properties (Table 4 and Fig 4) reveal that there is a drop in both tensile and flexural strength values at 5% filler content and at 25% of DeBDE and antimony oxide content they become equal to that of the unfilled material.Further there is no significant change in the elongation values. There is an increasing trend in both the hardness and impact strength values with the increasing filler content.

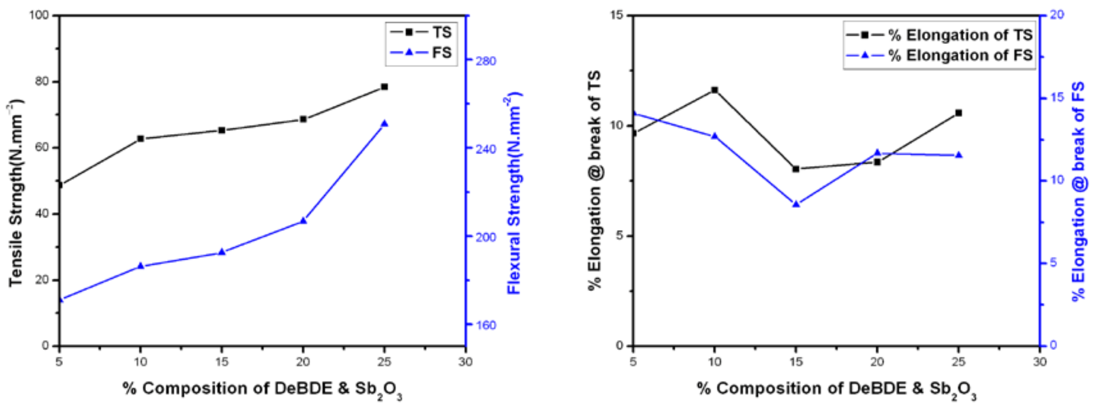

Figure 4 Effect of 3:2 of DeBDE & Sb_2O_3 on tensile and flexural properties

The flammability testing as per UL-94 standard showed that DeBDE laminates gave V_0 rating for the filler content 10% and above (Table 5) and the flame was put off within few seconds.

Table 5 Flammability tests
(ratio of Resin : Glass fibre 70: 30)

Filler content, % of (3:2 DeBDE & Sb_2O_3)	Time taken to Retard flame (Seconds) UL-94	LOI (%)	Smoke Density (%)
0	Burning	10.38	32.7
5	Burning		
10	2, V0	23.04	86.4
15	2, V0	26.56	93.9
20	2, V0	27.37	155.3
25	2, V0	25.80	160.6

DeBDE and Sb_2O_3 (3:2) follow the condensed phase mechanism at higher temperature and produce a synergistic glassy product antimony oxy bromide which puts off the fire. The limiting Oxygen Index and smoke density are additional parameters which can help in assessing the flame retardancy characteristic of the material. The LOI and smoke density measurements were made for the FRP laminates containing the DeBDE and Sb_2O_3 10 % and above, since these samples showed V_0 rating (Table 5).

There is an increase in the smoke density values with the increase in filler content which reached a maximum of 160.61 at 25% filler loading. High value of smoke density is attributed to the evolution of decomposition products such as water, carbon dioxide etc. LOI values are found to be much higher than that of the laminates without the filler.

3.4 Studies with a combination of different FR fillers

Even though DeBDE & Sb_2O_3 combination showed V_0 rating, the mechanical properties were found to be low compared to the compositions containing ATH content. Therefore to enhance the mechanical properties a combination of DeBDE, Sb_2O_3 and ATH was tried out. Table 6 gives the results obtained with FRP laminates with (10% of 3:2 DeBDE and Sb_2O_3 with 25% ATH) and without the filler. All the tested parameters showed significant improvement with the filler content. There is an increase in mechanical properties and in addition to this, flammability tests revealed excellent performance.

DeBDE and Sb_2O_3 retards the flame through condensed phase mechanism with the formation of antimony oxy bromide. In addition to this presence of ATH releases water vapour which dilutes the flammable gases, thereby producing double retardancy effect. Further due to the presence of ATH the mechanical properties were found to be good. The smoke emission of this sample was also found to be lower due to the presence of ATH which acts as a smoke suppressant.

Table 6 Comparison of the test parameters of the laminates at the optimum filler loading

Test Parameter	70:30 of resin and glass fiber	70:30 of resin and Glass fiber containing 10% DeBDE and 25% ATH
Gel time (min)	22	39
Gel Point ($^{\circ}C$)	180.4	161
Tensile Strength ($N.mm^{-2}$)	75.75	94.14
Elongation at break (%)	10.83	10.82
Flexural strength ($N.mm^{-2}$)	253.3	235.3
Elongation at break (%)	15.64	14.6
Barcol hardness	35.2	42.6
Impact strength ($J.\ mm^{-1}$)	1.24	1.8
Time taken to retard the flame,UL94	Burning	Flame put off in fraction of a sec, Vo
LOI (%)	10.38	28.22
Smoke density (%)	32.66	32.48

4. CONCLUSIONS

The development of Fiber Reinforced Plastics for roofing application using various flame retardant fillers has been carried out successfully. Several flame retardant fillers like ATH, DeBDE, Sb_2O_3, TCP were tried to make composites with desired properties. It has been found that ATH improved mechanical properties but even upto 60% loading of the same does not give flame retardant property. TCP addition also does not provide desirable properties in both mechanical and flame retardant properties at the loading levels under study. The combination of 3:2 ratio of DeBDE and Sb_2O_3 showed a considerable improvement in the flame retardant property but they suffered mechanical property enhancement. The major drawback in this combination has been low mechanical properties and high smoke emission which was overcome by adding 25% ATH and 10% DeBDE and Sb_2O_3. Hence, it is concluded that 10% of DeBDE and Sb_2O_3 (3:2) with 25% of Aluminum Tri hydrate meet the required mechanical and flame retardant properties and it is more cost effective than the FR formulation used by the FRP industry. The details of the formulation and process details are handed over to the industry for roofing application.

ACKNOWLEDGEMENT

The author wishes to acknowledge the support provided by M/s Urbane Industries, a FRP industry, Chennai in suggesting the problem and carrying out the lamination trials and flammability testing. The author wishes to mention that a part of the present paper is from the project work of the B Tech students R. Senthilkumar, D. Durai babu, K. Sabithadevi, R.Sheelaramani

REFERENCES

[1] Choi H J, Park SH, Kim J K and Jun J I 2000 J Appl. Polymer Sci. **75** 3
[2] Dvir H, Gottlieh M, Daren S and Trtakovsky E 2003. J Composites Sci. & Tech. **63** 1865
[3] Honda N et al, [Toshiba Chemical Corporation], European Patent EP0 795,570
111-113
[4] Bencardino F, Spadea G, Swamy N 2002 ACI Struct. Journal 99 163
[5] Chaallal O, Nollet M J and Perraton D 1998 J. Comp. Const., ASCE, **2** 111
[6] Chajes M J, Januszka T F, Mertz D R, Thomson T A and Finch W W 1995 ACI Struct. Journal **92** 295
[7] Grace N F, Abdel-Sayed G, and Ragheb W F 2002. ACI Struct. Journal **99** 692
[8] Grace N F, Ragheb W F and Abdel-Sayed G 2003 ACI Struct. Journal **100** 804-814
[9] Grace N F, Ragheb W F and Abdel-Sayed G 2004 ACI Struct. Journal **101** 237-244
[10] Harris H G, Somboonsong W and Frank K K 1998 ASCE **2** 28-37
[11] Singh N L, Sejal Shah, Anjum Qureshi, Tripathi, Singh F, Dkavasthi, and Raole P 2011 Bull. Mater. Sci. **34**, 81–88
[12] Vasanthakumari R, 1995 Research report, SRF ltd, Private publication