

Synergistic effect of aluminum hydroxide and antimony trioxide on the flammability of phosphorous modified epoxy resin

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Abstract

In this study, aluminum hydroxide (ATH) and antimony trioxide based phosphorous modified epoxy resin (Bisphenol A diglycidyl ether) is synthesized and subsequently cured with tri-ethylene tetra-amine (TETA) at room temperature to enhance the flame retardancy of phosphorous based epoxy resins. The structure of the modified flame retardant epoxy resin (FREP) is characterized using Fourier transform infrared spectroscopy (FTIR), UL-94 and by thermogravimetric analysis (TGA), moreover, mechanical properties are analyzed to study the effect of such additives addition on epoxy resin. Introduction of both antimony and aluminum hydroxide together in phosphorous modified epoxy resin brings the success to enhance the flame retardant properties of the epoxy resin. The addition of 40 weight % of aluminum hydroxide and antimony trioxide mixture in phosphorus-modified epoxy resin demonstrated optimal composition among all selected compositions i.e. 10 %, 20%, 30%, 40% and has shown eminent flammability along with balance mechanical strength. The obtained findings confirm the functionality of demonstrated modified resin as an effective flame retardant material.

Key Words: Fire retardant, epoxy Diglycidyl ether of bisphenol-A, Aluminium hydroxide, Antimony trioxide

1. Introduction

The epoxy resin is considered as a vital material due to excellent adhesion properties to different substrates, preferable chemical and corrosion resistance, less shrinkage and balanced electrical and mechanical properties, moreover, epoxy resins possess excellent dimensional stability [1-3]. The growing demands of fire retardant materials in aerospace, electronics, and wind energy industries has opened new challenges to address and need is to investigate new processing techniques and approaches to synthesize materials demonstrating high flame retardancy and enhance thermal properties.

The most optimistic approach employed to enhance the flame retardant properties of epoxy resin is the incorporation of additive and reactive type flame retardant into the epoxy resins [4-6]. Additive type fire retardants are commonly employed in the coating, whereas reactive flame retardants are of main attention due to the consequential effect on mechanical, physical properties and have authoritative effect to sustain flame retardant properties for a longer time period. Previously, halogen-based flame retardants were actively used to enhance the retardancy of epoxy resins but due to their adverse effects i.e. toxic smoke, emission of corrosive gases during

burning, the trend shifted towards halogen-free compounds to circumvent aforementioned challenges [3, 7-9]. Among the halogen-free compounds, phosphorus-containing retardants have shown good flame retardancy incorporated in epoxy resin and also produce less toxic and smoke as compared to the halogen-based system. Polymers modified with phosphorus functions as a reactive flame retardant and associated to an integral part of the chain to enhance flame retardancy and proved to address the issues associated with the physical blend of the polymeric materials and the flame retardants [5, 10]. A lot of work has been done in this aspect and series of glycidyl phosphinates, diglycidyl phosphates, and diglycidyl phosphonates have been prepared. Numerous works have been presented on fire retardant plastics (polypropylene-based composites) and elastomers with aluminum hydroxide additives [11, 12]. Dyakonov. et. al. [13] worked on the flame retardancy of the polyurethane-based elastomer with aluminum hydroxide incorporated flame retardant additive. Antimony trioxide proved to enhance the flame retardant properties of halogen-based epoxy resins, mainly have found its synergic effect with bromine where it formed a white cloud of antimony tribromide which attenuate the oxygen concentration by excluding it from the flame [14] but still, no proper investigation has

taken place to study the effect of antimony trioxide on the non-halogen based flame retardant epoxy resins.

In this study, a novel route of modified epoxy resins synthesis is introduced by modifying the epoxy resin in two steps, initially, the phosphorous group is incorporated in epoxy resin (Diglycidyl ether of Bis-phenol-A) and then further modified the resultant with various concentrations of aluminum hydroxide and antimony trioxide mixture. The synergic effect of antimony and aluminum hydroxide on flame retardant properties of phosphorous modified epoxy resin has been characterized by FTIR, TGA, UL-94, and by mechanical testing at numerous mass ratios of aluminum hydroxide and antimony trioxide in phosphorous modified resin to investigate the flame retardant nature, thermal properties, and degradation behavior of resultant composite. The findings demonstrated that synthesis materials structures have an influential effect on thermal stability and flame retardant properties of phosphorous modify epoxy resins.

2. Experimental

2.1 Materials

The Epoxy Resin (matrix) is Diglycidyl ether of Bis-phenol-A (DGEBA, NPFL-128) purchased from Nan-Ya Plastics Corporation (Taiwan)). Hydroquinone manufactured by BDH laboratory England was used as an inhibitor; acetone is purchased from MERK while Triethylene tetramine (TETA, crosslinker) from AGROS was used. Antimony trioxide (ATO) supplied by Chengdu Chemphys Chemical Industry Co., Ltd. and aluminum hydroxide (ATH) manufactured by Beijing chemical works was used as a flame retardant additive.

3. Preparation of fire retardant epoxy resin

Diglycidyl ether of bis-phenol-A (DGEBA) was modified by the procedure defined in the research paper [15]. 20 g (0.6 mol) weighted DGEBA was mixed with 100 ml of acetone in a 500 ml round bottomed flask by continuous magnetic stirring in an ice bath. Phosphoric acid 0.6757 ml (0.2 mol) was added dropwise into the flask and hydroquinone (1,000 ppm over the total amount of the reactants) was added at reflux (45°C) for 3 hr. Finally, water and acetone were removed and the colorless phosphorous modified epoxy resin is obtained.

3.1 Curing of fire retardant epoxy resin

3.1.1 Formulation

Firstly, the heat treatment of ATH was done in an oven for 30 min at 100°C and then different formulations of aluminum hydroxide (ATH) mass ratios (10%, 20%, 30%, and 40 %) and combine aluminum and antimony trioxide mass ratios (10%, 20%, 30%, and 40 %) were mixed with phosphorous modified epoxy resin by continuous stirring and cured at room temperature by using tri-ethylene tetraamine (TETA). Epoxy and hardener (TETA) were mixed in the ratio 1:0.1. Several combinations of modified epoxy with additives are tested to study the effect of each additive composition on fire retardant properties of the phosphorous modified epoxy resin. Table 1 summarizes composition of varying the mass ratio of phosphorous modified epoxy resin to ATH & ATO.

Table 1: The mass ratio of aluminum hydroxide (ATH) & antimony trioxide (ATO) in phosphorous modified epoxy resin.

Sample	Wt. of ATH (g)	Wt. of ATO (g)	Wt. of the mod. DGEBA(g)	Wt. of TETA (g)
E	-	-	09	01
ME	-	-	09	01
A10	1.0	-	8.10	0.90
A20	2.0	-	7.20	0.80
A30	3.0	-	6.30	0.70
A40	4.0	-	5.40	0.60
AF10	0.50	0.50	8.10	0.90
AF20	1.00	1.00	7.20	0.80
AF30	1.50	1.50	6.30	0.70
AF40	2.00	2.00	5.40	0.60

*E stands for the virgin epoxy resin, ME stands for the phosphorous modified epoxy resin-A stands for ATH reinforced phosphorous modified epoxy resin, AF stands ATH&ATO reinforced phosphorous modified epoxy resin

3.1.2 Samples

In order to characterize the compressive and thermal analysis of the additive mixed modified resin, the samples were prepared in a cylindrical shape **ASTM D-695** [16] used for compression testing while and **ASTM E-2550** [17] used for thermo-gravimetric analysis. While for the vertical burning test **ASTM D3801** [18] was used.

4. Characterization and Analysis

4.1 Fourier Transform Infrared spectroscopy (FTIR)

FTIR measurements were done by using FTIR-4100 to investigate phosphorous modified epoxy filled with the different incorporation of aluminum hydroxide and antimony trioxide after curing. FTIR spectra were observed by using KBR as a reference material. KBR was mixed separately with pure epoxy resin, phosphorous modified epoxy resin, aluminum hydroxide based phosphorous modified epoxy resin and aluminum hydroxide-antimony reinforced phosphorous modified epoxy resin for FTIR spectra analysis. The transmission mode was activated and set the range for wave number from 400 to 4000 cm^{-1} .

4.2 Thermo-gravimetric Analysis (TGA)

TGA is the most supported technique to instantaneous evaluates the thermal stability of fire retardant polymers. TGA analysis is performed by SDT-Q600 thermal analysis instrument, The TGA measurement is performed at a heating rate of 20°C /min under an inert atmosphere from room temperature to 600 °C.

4.3 Mechanical properties

The Young's modulus and ultimate compressive strength of modified epoxy by aluminum hydroxide and antimony were

characterized with the help of a universal testing machine (TIRA, 2810) supported by the 10 KN load cell at the Strain Rate of 1.3 mm/min. The sample of dimensions 14 mm×28mm was used for all type of materials i.e. epoxy resin, phosphorous modified epoxy resin and additives incorporated phosphorous modified epoxy resin. Mechanical properties of the composite depend on the filler's aspect ratio along with the dispersion and filler-matrix interface (interfacial adhesion). For ultimate fracture strength, the filler based composite was put in the testing machine to measure the fracture strength.

4.4 UL-94 Test

The UL-94 vertical burning test was conducted for samples of 5mm thickness, 50mm long and 15 mm wide in a vertical position in a closed glass box and total time to burn the sample were recorded. Blue flame is applied at the center for 15 sec. and three types of ratings are considered in the standard (V-0, V-1 & V-2), in the V-0 rating total after flame time is ≤ 50 sec while for v-1 & V-2 this become ≤ 250 sec. while if cotton indicator ignites by flaming particles of drops then the material will be considered as V-2 rating.

5. Results and Discussions

Modification of DGEBA was analyzed by evaluating graph between the transmittance and wave number FTIR study of phosphoric modified bis-phenol-A epoxy (MEPR) resin indicated strong stretching vibration of P=O bond at 1296 cm^{-1} and stretching vibration of P-O-C (aromatic) bond at 1242 cm^{-1} , 1182 cm^{-1} [15] as shown in Fig 01(a) while FTIR spectra of virgin epoxy resin is shown in Fig 01(b). The absorption peaks at 745 cm^{-1} and 743 cm^{-1} , 744 cm^{-1} intensity are attributed to the stretching of antimony trioxide while at 3372 cm^{-1} for aluminum hydroxide as shown in Fig 2, which confirmed the proposed structure.

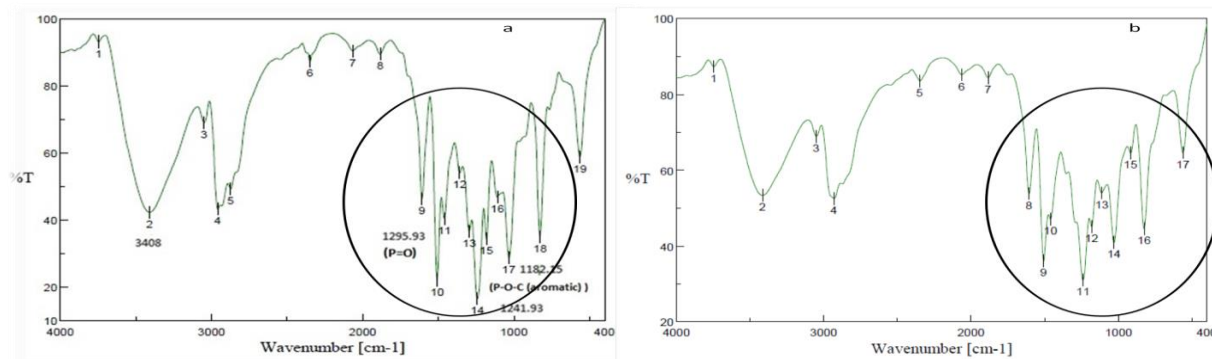


Fig 1: FTIR analysis of (a) Phosphoric acid modified Bis Phenol-A Epoxy & (b) Bis Phenol-A Epoxy.

FTIR analysis of 10% to 40% mass addition of aluminum hydroxide and antimony trioxide demonstrates same spectra in the region up to 3000 cm^{-1} wave numbers. Al-OH bond stretching vibration was observed at 3375.78 cm^{-1} with the intensity of 45.95 which validate the addition of ATH while an intense band at 741 cm^{-1} in the FTIR spectrum (at 765 cm^{-1} in theoretical) is responsible for symmetric combinations of stretching vibrations for antimony trioxide as shown in the Fig. 02.

For 10%, 20% and 40% loading of the mixture (Aluminum hydroxide, antimony trioxide) initial decomposition temperatures decrease to 382.6 $^{\circ}\text{C}$, 392 $^{\circ}\text{C}$, 381 $^{\circ}\text{C}$ and 383 $^{\circ}\text{C}$ respectively.

This is lower than that of pure epoxy resin. The reduction of initial decomposition temperature

is caused by the presence of the P-O-C bond which is less stable as compared to the C-C bond. This degradation of phosphate plays a pivotal role in the formation of the char residue, which acts as a blanket for further degradation. Phosphorous modified epoxy resin promote the char formation which effectively resists the material from further depletion and reinforcement further protect it from weight loss and enhance the char formation ability of the modified epoxy resin [20]. Reduction of the onset temperature is due to the less stability of the P-O-C bond than C-C bond. Thus there is a positive effect regarding the thermal properties of all the fractioned percentages thus there is an increase in trend observed regarding the thermal properties.

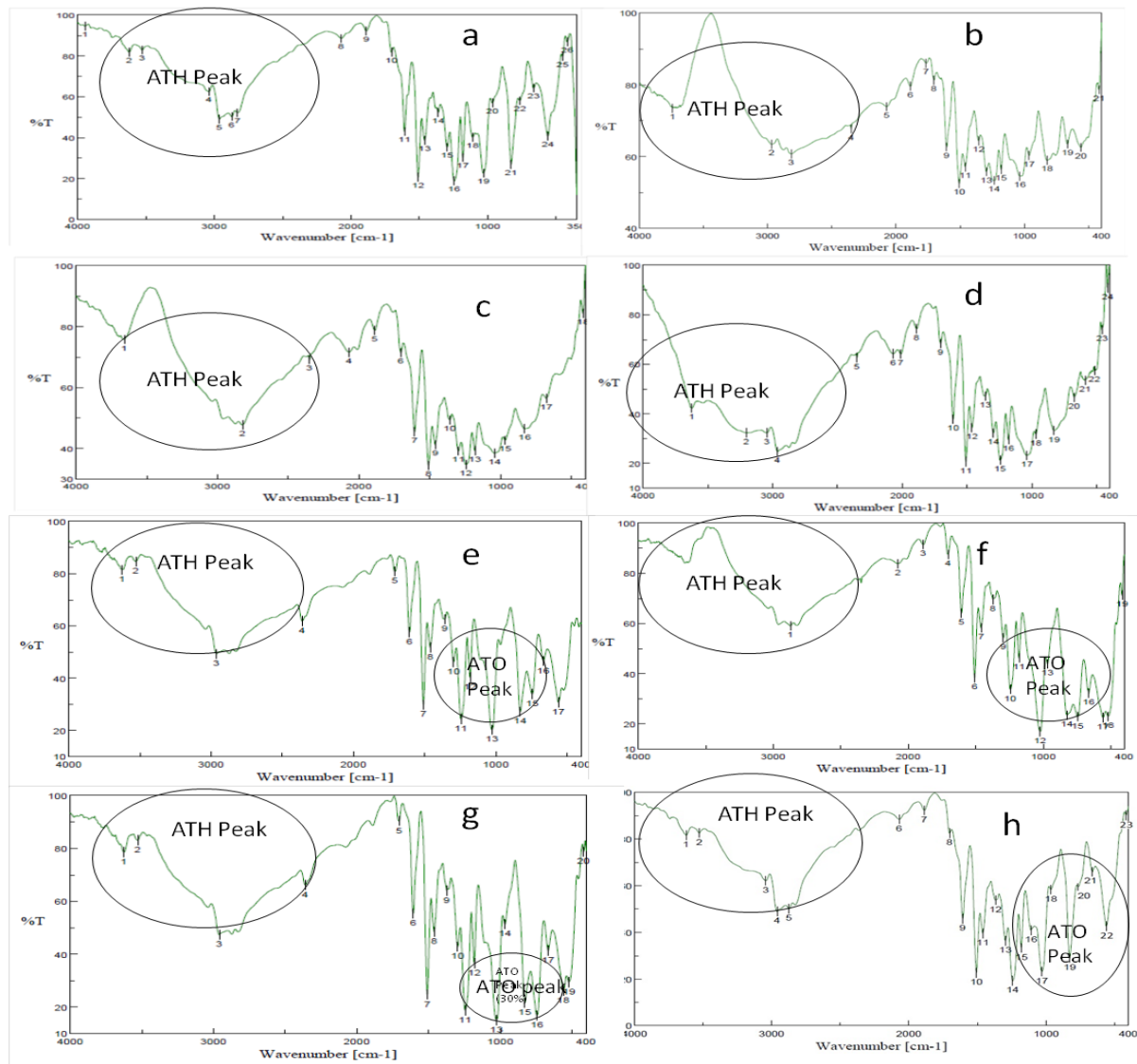


Fig 2: FTIR Spectra of ATH & ATO modified phosphoric acid epoxy resin, (a) 10% ATH addition, (b) 20% ATH addition, (c) 30% ATH addition, (d) 40% ATH addition, (e) 10% ATH & ATO addition, (f) 20% ATH & ATO addition, (g) 30% ATH & ATO addition, (h) 40% ATH & ATO addition.

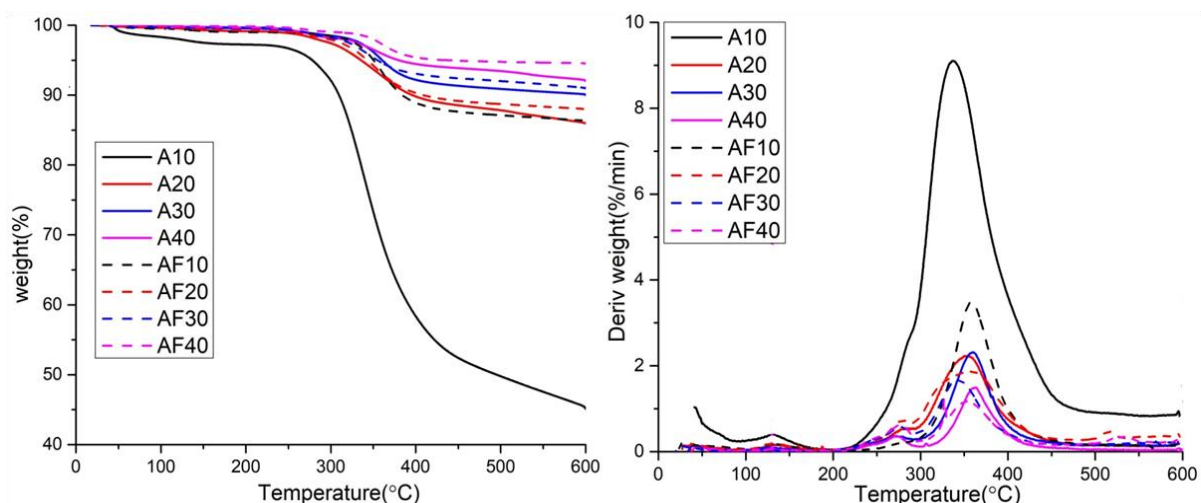


Fig 3: TGA Thermograms of Aluminium hydroxide (ATH) reinforced phosphorous modified epoxy resins, and Aluminum hydroxide (ATH) & antimony trioxide (ATO) reinforced phosphorous modified epoxy resins (ATHO).

The addition of aluminum hydroxide and antimony trioxide change the thermal rating from V-2 to V-1. The burning time against different weight addition of additives in the epoxy resin is shown in Fig 4. Antimony imparts a supportive role to enhance the flame retardant nature of aluminum hydroxide. Aluminum hydroxide reinforced modified epoxy resin exhibit the T_g value 378 °C, the addition of antimony stimulate the effect of aluminum hydroxide an approaches value of T_g in the range of 387°C.

The Young's modulus and ultimate tensile strength of the phosphorous modified epoxy resin with 10%, 20%, 30% and 40% weighted percentage of aluminum hydroxide and also with respective combination of aluminum hydroxide and antimony trioxide are shown in Fig 5. The

young modulus and ultimate tensile strength at 10 % additive weight addition of ATHO have the value of 990 MPa and 95MPa respectively. But with the further addition of additives the value of young modulus decreases and approaches to 983 MPa, 968 MPa, and 965 MPa for 20, 30 and 40 weights % addition of additives in epoxy respectively. This may be because of macromolecule chain movement when resin saturated with filler contents and create a site of stress concentration, where micro-crack initiated [15]. On the other hand only ATH addition caused initially decrease in young modulus and after that its value increased but found to be lower than aluminum hydroxide and antimony trioxide based composite.

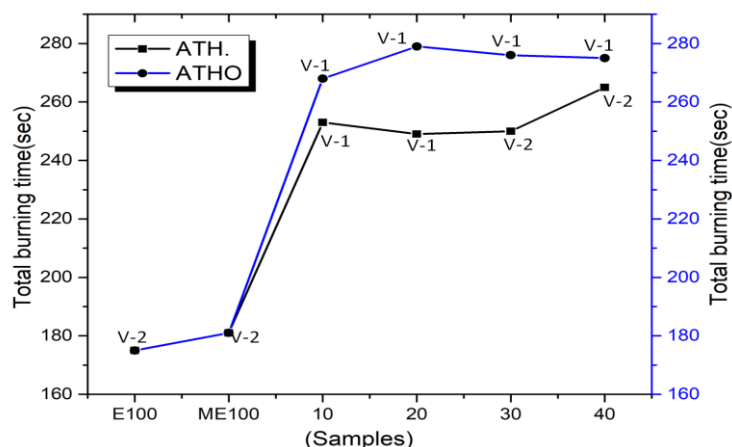


Fig 4: Burning time of the Aluminium hydroxide (ATH) reinforced phosphorous modified epoxy resins, and Aluminum hydroxide (ATH) & antimony trioxide (ATO) reinforced phosphorous modified epoxy resins (ATHO).

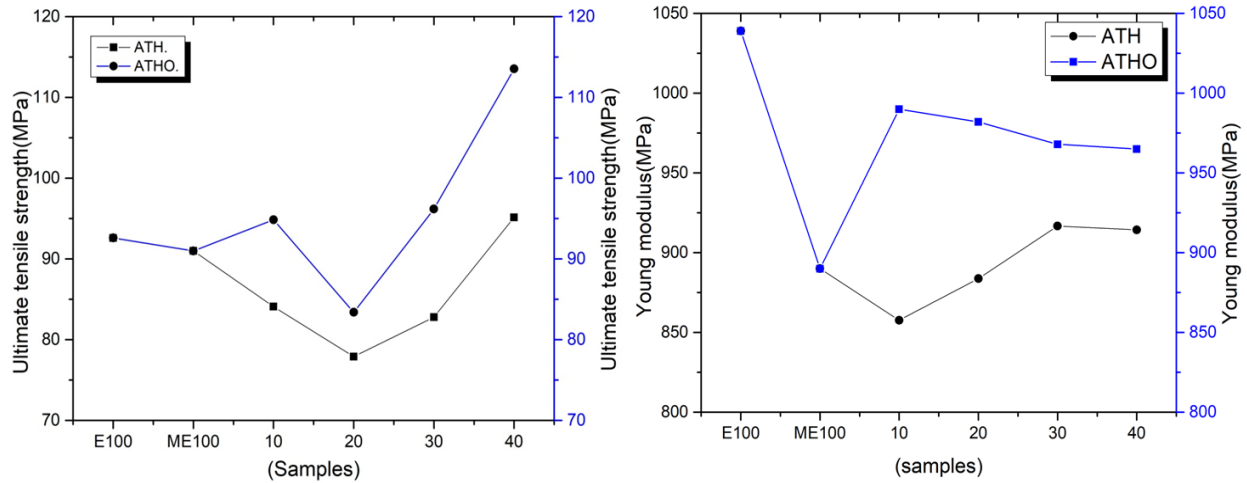


Fig 5: Young's Modulus and ultimate tensile strength of ATH based phosphorous modified epoxy resin, ATH & ATO reinforced phosphoric acid modified epoxy resin (ATHO).

That obtained value of modulus still higher compares to the phosphorous modified epoxy resin. The aluminum hydroxide and antimony trioxide addition in phosphorous modified epoxy resin demonstrated balance mechanical properties with higher flame retardant properties. Table 2 summarizes the effect of various additive compositions on mechanical and thermal properties of the phosphorous modified epoxy resin.

6. Conclusion

The introduction of both aluminum hydroxide and antimony significantly enhance the flame retardant properties of the phosphorous modified epoxy resin. The addition of 40% weight mixture of aluminum hydroxide and antimony trioxide demonstrated a balance combination of

mechanical and thermal properties. The UL-94 results showed that the total burning time increased to 275 sec compare to 175 sec of pure epoxy and 181 sec of phosphorous modified epoxy resin with the shift of flammability rating from V₂ to V₁. Furthermore, the weight loss after antimony trioxide additions reduced from 62.07% (for pure epoxy resin) to 5.45 % (for 40% addition of additives). TGA analysis presents that glass transition temperature (T_g) after additive additions almost sustain the original value of virgin epoxy resin and exhibit slightly higher value than phosphorous modified epoxy resin. The obtained findings confirm the role of aluminum hydroxide and antimony trioxide in phosphorous modified epoxy resin as influential fire retardant additives.

Table 2: The effect of various aluminum hydroxide and antimony trioxide combinations on the phosphorous modified epoxy resin.

Sample Name	Thermal Properties				Flame Retardancy	
	T _g °C (ATH)	T _g °C (ATHO)	Overall Weight loss (%)		UL-94 (sec)/ Flame rating	
			(ATH)	(ATHO)	(ATH)	(ATHO)
E100	388		62.07		62.07	
ME100	380		45.31		45.31	
10	334	73.81	73.81	13.84	253/ V-1	268/ V-1
20	380	14.00	14.00	12.01	249/ V-1	279/ V-1
30	369	9.82	9.82	9.00	250/ V-2	276/ V-1
40	382	7.82	7.82	5.45	259/ V-2	275/ V-1

*E= Epoxy; ME= Phosphorous modified epoxy; ATHO= Equivalent weight percent of aluminum hydroxide and antimony trioxide, ATH= weight percent of aluminum hydroxide.

7. References

- [1] Chen L, W.Y., A review on flame retardant technology in China. Part I: development of flame retardants polym Adv Technol., 2010. 21: p. 1-26.
- [2] Weil ED, L.S., A review of current flame retardant systems for epoxy resins. J Fire Sci., 2004. 22: p. 25-40.
- [3] Li, Y.X., Zongwen Mao, Liang Wang, Yong Guan, Anna Zheng, Influence of antimony oxide on flammability of polypropylene/intumescent flame retardant system. Polymer Degradation and Stability, 2012 97: p. 1737-1744.
- [4] Rachasit Jeencham, N.S., Kasama Jarukumjorn, Effect of flame retardants on flame retardant, mechanical, and thermal properties of sisal fiber/polypropylene composites. Composites: Part B, 2014 56: p. 249-253.
- [5] Banks, Mavis, John R. Ebdon, and Michael Johnson. "The flame-retardant effect of diethyl vinyl phosphonate in copolymers with styrene, methyl methacrylate, acrylonitrile and acrylamide. "Polymer 35.16 (1994): 3470-3473.
- [6] Liang, J. Z., Feng, J. Q., Zou, S. Y., Liu, D. F., & Zhang, S. D. (2015). Flame-Retardant and Flexural Properties of Polypropylene/Intumescent Composites. *Advances in Polymer Technology*, 34(3).
- [7] Marney, D. C. O., Russell, L. J., & Stark, T. M. (2008). The influence of an N-alkoxy HALS on the decomposition of a brominated fire retardant in polypropylene. *Polymer Degradation and Stability*, 93(3), 714-722.
- [8] Chen, L., & Wang, Y. Z. (2010). A review on flame retardant technology in China. Part I: development of flame retardants. *Polymers for Advanced Technologies*, 21(1), 1-26.
- [9] Laoutid, F., Lorgouilloux, M., Lesueur, D., Bonnaud, L., & Dubois, P. (2013). Calcium-based hydrated minerals: Promising halogen-free flame retardant and fire resistant additives for polyethylene and ethylene vinyl acetate copolymers. *Polymer degradation and stability*, 98(9), 1617-1625.
- [10] Kannan, P., & Kishore, K. (1991). Synthesis and spectral studies of polyamide-phosphate esters from phosphine-oxide-containing diols with aryl phosphorodichloridates and their thermal and flammability behaviour. *Polymer*, 32(10), 1909-1913.
- [11] Pinto, U. A., Visconte, L. L. Y., Gallo, J., & Nunes, R. C. R. (2000). Flame retardancy in thermoplastic polyurethane elastomers (TPU) with mica and aluminum trihydrate (ATH). *Polymer Degradation and Stability*, 69(3), 257-260.
- [12] Iqbal, M. A., Iqbal, M. A., & Fedel, M. (2018). Fire Retardancy of Aluminum Hydroxide Reinforced Flame Retardant Modified Epoxy Resin Composite. *Russian Journal of Applied Chemistry*, 91(4), 680-686.
- [13] Dyakonov, T., Mann, P. J., Chen, Y., & Stevenson, W. T. (1996). Thermal analysis of some aromatic amine cured model epoxy resin systems—II: residues of degradation. *Polymer degradation and stability*, 54(1), 67-83.
- [14] La Rosa, A. D., Recca, A., Carter, J. T., & McGrail, P. T. (1999). An oxygen index evaluation of flammability on modified epoxy/polyester systems. *Polymer*, 40(14), 4093-4098.
- [15] Jiao, C., Zhuo, J., Chen, X., Li, S., & Wang, H. (2013). Flame retardant epoxy resin based on bisphenol A epoxy resin modified by phosphoric acid. *Journal of thermal analysis and calorimetry*, 114(1), 253-259.
- [16] ASTM Committee D-20 on Plastics. (2008). *Standard test method for compressive properties of rigid plastics*. ASTM International.
- [17] ASTM International Standard Test E2550-17 Method for Thermal Stability by Thermogravimetry, ASTM International.
- [18] ASTM International Standard Test D3801,14 Method for Measuring the Comparative Burning Characteristics of Solid Plastics in a Vertical Position, ASTM International
- [19] Liang, J. Z., Li, F. J., & Feng, J. Q. (2014). Mechanical properties and morphology of intumescent flame retardant filled polypropylene composites. *Polymers for Advanced Technologies*, 25(6), 638-643.
- [20] Chen, X., & Jiao, C. (2008). Thermal degradation characteristics of a novel flame retardant coating using TG-IR technique. *Polymer Degradation and Stability*, 93(12), 2222-2225.