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Antioxidant and flame retardant additive effect on the thermal degradation and flammability of SBR filled EPS/UPR composite

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Abstract
Thermal Degradation and Flammability are two important specifications a composite material must passed for consideration of use in the building and construction industry application. Additives such as antioxidant (AO) and flame retardant (FR) are incorporated into the UPR/EPS composite mixture in this study to impart flammability resistance and improve its thermal decomposition characteristic. The composites thermal decomposition were characterized via Thermal Gravimetric Analyzer of 20% SBR with combinations of AO and FR additives. Flammability test were also performed to evaluate their linear burning rate. An increase in thermal stability was found for combined AO and FR additive system. A possible presence of synergistic mechanism contributing towards degradation resistance at high temperature range with combined AO and FR additives. High Residue % or Char Yield for the SBR AO and SBR AO FR systems may indicate that AO limits oxidative process and thus increases the char yield. The linear burning rate for the SBR-FR series were reduced by 60% by flame retardant incorporation. Hence, it was shown that addition of antioxidant and flame retardant additives had enhanced thermal stability of SBR/EPS/UPR composite system.

Keywords: Antioxidant, Flame Retardant, Flammability, Thermal Degradation, Unsaturated Polyester Composite

1. Introduction

Flame retardants are incorporated in most composites to achieve a desired inherent fire resistance level. Flame retardants suppress combustion either through the vapour phase or the condensed phase by utilizing chemical and/or physical mechanisms. Lu and Hammerton (2002) had summarized common types of flame retardants and mechanism of action in their studies [1]. Among others, they used Phosphorus (P–N) compounds based on phosphoramidate which was evaluated using the limiting oxygen index (LOI) and UL-94 vertical test methods to determine its flame-retarding efficiencies. Nyugen and Kim (2006) found that bisphosphoramidates are more thermally stable and produce more charred residues when compared to the corresponding bisphosphate compounds upon addition of 3– 5 wt%. With bisphosphoramidate FRs, remarkably high residues at 600 °C remained. Thermogravimetric analysis (TGA) results indicated compounds work in condensed phase rather than in gas phase [2].

Environmentally friendly fire retardant for vinyl ester resin composites could be made by blending fatty acid vinyl ester (FAVE) resins with environmentally friendly fire retardants such as polyhedral oligomeric silesquioxanes (POSS), which was also investigated recently. POSS additive maintains resin viscosity; improves its Glass Transition Temperature (T_g); increases cross-link density, and provides flame retardancy. However, Glodek *et al*. (2008) determined that the flame retardancy supplied by the relatively high performing POSS-filled composite was quite inferior to that of brominated resins [3]. Intumescent flame retardant-montmorillonite synergism in nanocomposites had also been investigated by Haiyun *et al*. (2008) [4]; while flame retardancy in Unsaturated Polyester (UPE) nanocomposites via layered double hydroxides was investigated by Pereira *et al.* (2009) [5].

Flame retardants can be incorporated into polymeric materials either as additives or as reactive materials as indicated by Burchill (1996) [6]. UPE matrix composites have been used for many years in broad technological and industrial fields such as naval construction, offshore applications, waterlines, and building construction. Unsaturated polyester is an economical thermoset material that is widely used due to its excellent process ability and good cross-linking tendency as well as mechanical properties when cured.

Studies had been done on use of EPS incorporated into Unsaturated Polyester resin (UPR) with relevant diluents. The toughening of the unsaturated polyester resin is very important to increase its impact performance especially for building structures purposes. For example, Vaidya *et al*. (2000) had used Expanded Polystyrene (EPS) sheet as the core material in a composite sandwich for an alternative to wooden door shutters in building [7]. Contrary to epoxy resins, the toughening of UPR often utilize vinyl ester and nitrile rubbers modifier incorporated within the resin as indicated by Gryshchuk *et al*. (2002) [8].

Different plastic materials possess its own unique decomposition temperature profile. The decomposition of the polymeric material can be evaluated through use of Thermo-gravimetric Analysis (TGA) and its Derivative Thermogram (DTG). In most cases, decomposition occurs via free radical chain reactions, initiated by traces of oxygen or other oxidizing

impurities trapped within the materials during its manufacturing process. The oxidative degradation of polymers usually proceeds via the formation of hydro peroxide groups as noted by Regnier *et al* (1995) [9].

Initial ignition usually depends on numerous variables such as oxygen availability, temperature, physical and chemical properties of polymer. Reaction with oxygen is often exothermic, and given sufficient energy, it overrides the endothermic pyrolytic reaction and initiates flame spread. Flame spread, or the rate of travel of a flame front under given conditions of burning, is a measure of fire hazard. The spreads of flame along the surface of a material can transmit fire. As for ignition; flammable gases formed by pyrolysis mixes with atmospheric oxygen, and upon reaching the lower ignition limit, they are either ignited by an external flame, or if the surrounding temperature is sufficiently high, self-ignition will occur.

This paper emphasizes on the degradation behaviour of SBR modified EPS/UPR composite system with AO, FR, and SBR content. Flame retardancy is evaluated as well. Thermal stability of the composites were investigated via TGA and DTG profiles generated from their thermal decomposition analysis. The aim of this work was to evaluate the thermal degradation, and fire resistance of different percentage of additive content within the UPE-EPS composites.

2. Material and Methods

The selected thermoset matrix materials used for fabricating composite system is the UPR resin system, by Reversol consisting of vinyl ester oligomers with a density of 1.12 g/cc, viscosity of 450-600cps, and 41-44% styrene content. Pack of methyl Ethyl Ketone Peroxide (MEKP) as initiator and Cobalt solution as promoter are supplied together with UPE resin by Revertex Sdn Bhd. EPS (expanded polystyrene) or Styrofoam from waste material and General Purpose SBR, SBR 1502 were also used. The SBR 1502 is a cold polymerized styrene-butadiene copolymer with styrene content of 23.5% supplied by Lembaga Getah Malaysia (LGM). Irganox 186, antioxidant was supplied by Ciba Geigy. Phosphate Ester as FR additive was supplied by Asachem Sdn Bhd.

2.1 Composite Fabrication and Testing

Recycled EPS was blended with UPE resin with high speed agitation mixer and complete dissolution were attained to ensure gaseous present are eliminated from the mixture with vacuum suction. SBR was masticated first via two roll mill to ease dissolution process. EPS and SBR content was fixed at 20% parts by weight of the Unsaturated Polyester resin. FR and AO additive about 0.5 % were added, followed by MEKP and cobalt to EPS/SBR solution. The mixture was poured onto aluminium mould for sample fabrication. Gelling time was set to be about 20 to 30 minutes. Once achieved sufficient gelling, low pressure press were applied to the mould to retain the required shape, and complete curing were done for 24 hours at room temperature.

TGA and DTG profile was generated from the composites by means of a Perkin Elmer Thermal Analyser at a heating rate of 50ºC/min under nitrogen atmosphere. Temperature range was 50 -1000ºC. Flammability test follows ASTM D635 with prepared specimen size of 12mm x 20mm x 3mm. Fix distance of 75mm for combustion was used to complete flame propagation and the sample been placed to burn in horizontal position by using candle flame at room temperature. Linear burning rate were assessed from time taken to reach specified distance.

3. Results and Discussion

To evaluate Thermal degradation properties of UPR/EPS/SBR composites with additive AO and FR, TGA tests were conducted and the related data were as shown in Table 1.

Table 1: Data of TGA and DTG curve

Sample	1st DTG Curve Peak	2nd DTG Curve Peak	3nd DTG Curve Peak	Temp. Dec. at early stages (°C)		Temp. Dec. at final stages (°C)		Residue (wt. loss) (%)
	Decomposition Temp (°C)	Decomposition Temp (°C)	Decomposition Temp (°C)	5%	10%	90%	95%	
SBR	251.17	451.17	-	276.23	354.2	482.41	494.54	1.21
SBR-FR	160.11	453.89	-	235.46	333.84	482.26	492.61	3.71
SBR-AO	254.81	457.08	761.52	275.68	353.37	496.92	741.8	1.25
SBR-AO-FR	308.18	529.46	897.85	318.646	403.05	546.16	836.05	2.28

There more than one decomposition products was recorded; two or three $T_{max.\ dec}$. or $T_{max\ deg}$ peaks were present for all material tested. From the sample degradation profile, $T_{max\ deg}$ composition of UPR/EPS/SBR with both AO and FR present were shown to be highest overall. Temperature at $T_{max\ deg}$ was increased significantly upon synergistic combination of both AO and FR, and similar synergistic thermal stabilization mechanisms were depicted for the 2nd decomposition product where its T_{max} deg was also increased significantly. Upon higher temperature range, 3rd decomposition product also showed higher $T_{max\ deg}$ at 897.85ºC compared to 761.52ºC without FR.

Addition of only FR in the system shows significant thermal decomposition profile with lower thermal stability level for the 1st decomposition product by lowering the 1st decomposition product temperature to 160ºC. With the AO only additive, thermal stability does not show any improvement except above 450ºC where near 90% degradation starts to occur. AO proved to significantly increase the thermal stability at high temperature range above 700ºC where temperature degradation at 95% were increased up to 741.8ºC as compared to only 494.54ºC when degradation persists without AO. AO could probably the main controlling factor for thermal stabilization at high temperature range.

Highest thermal stability was depicted by use of AO and FR additives in combination; specifically through the temperature at 5%, 10%, 90% and 95% decomposition stage. Residue or char yield left were greater compared with AO only. This indicated that at near 900ºC, both AO and FR are the controlling factors to enhance the stability of the composite system at high end temperature range. FR effect were also shown. But when FR is only by itself, thermal stabilisation did not work as effective as when combined with AO. Therefore, the AO and FR are required to be use together in the formulation to get highest thermal decomposition profile to enhance thermal stability of composite.

Figure 1 shows the comparison of thermogram of 20% SBR with and without AO and FR presence. Combination of AO and FR additives were found to increase thermal stability of the 20% SBR composite. There is synergistic mechanism towards degradation resistance with combined AO and FR additives. T.max. deg. was 530ºC; this value is well above the other 20% SBR filled composite systems.

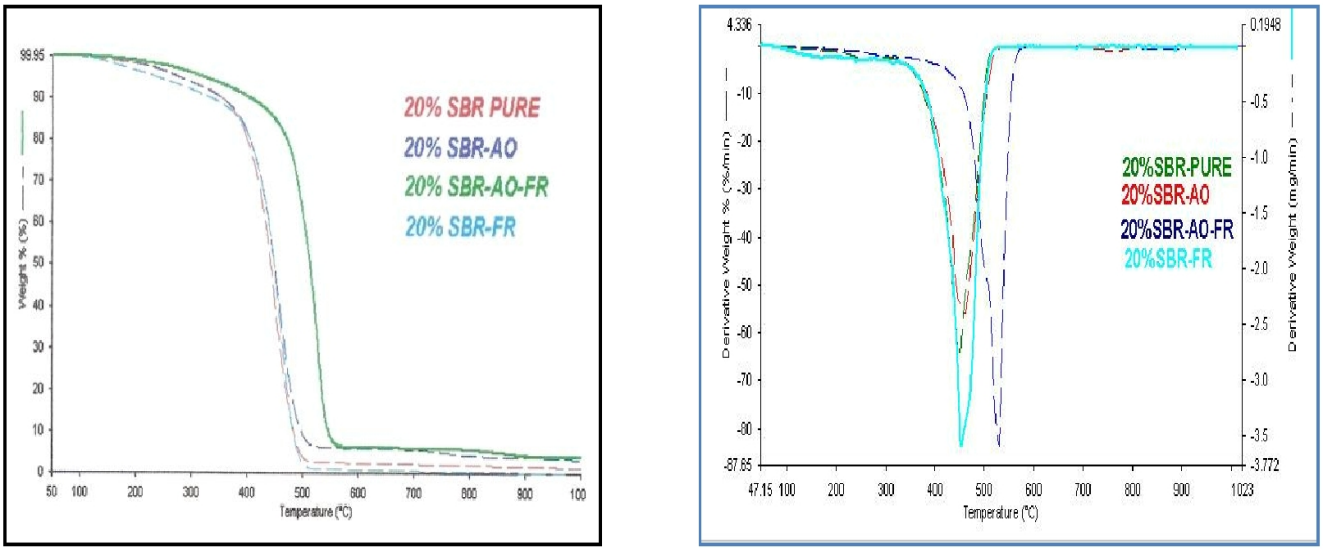

Fig 1: TGA thermogram comparison between presence and absence of AO and FR additive in 20% SBR filled composite

FR filled SBR system have similar behaviour as SBR unfilled composite. However, SBR AO and SBR AO FR do give better stability at high end temperature range above 500ºC. This showed that presence of AO cause hindrance to degradation process whereby antioxidant could have quench of the formation of free radicals which initiate pyrolysis reaction upon chain breakdown reaction. However, AO did not affect any thermal degradation for low temperature range as its T.max. deg. and % wt loss with and without AO is similar. High % Residue or char yield for system SBR AO and SBR AO FR showed that AO prevent oxidative process and increase the char yield of the product. Upon addition of these additives, thermal stability is enhanced.

3.1 Flammability test

Table 2 showed the time required to burning the sample at the fixed distance that called elapsed time(s) and the rate of combustion showed by linear burning formulation, V (mm/s) in equation 1.

$$\text{Linear Burning, } V = 60L/\,t \quad (1)$$

Where

L = the burn length, in mm between reference mark (75mm long),

t = the time (s) (elapsed time from the 25mm to 100mm reference mark)

Based on Linear Burning formulation, the rate of combustion lowers proportionally to a longer recorded time elapsed. Table 2 shows that the time taken for complete combustion will be increased when AO and/or FR are integrated into the UPE/EPS composite.

The burning rate, V of the composite with both AO and FR shows the lowest at 10.71mm/s compare to the composite without presence of both at 23.08mm/s. Addition of either AO or FR also reduce the burning rate at 17.65mm/s and 14.29mm/s respectively. This shows that incorporation of AO and FR in composition had improved the composites' ability to retard fire.

Table 2: Comparison elapsed time of combustion in different additive material

Additive utilized	Elapsed time(s)	Linear burning rate (mm/s)	Linear burning rate change (%)
SBR	65	23.08	-
SBR-AO	85	17.65	-
SBR-FR	105	14.29	- 61.92
SBR-AO-FR	140	10.71	- 60.68

As shown by Figure 2 below, the combination of AO and FR additive had some synergistic mechanism effect for improving fire retardancy, by slower the ignition of fire to the sample. Generally, FR was used to reduce the likelihood of fire starting by providing increased material resistance to ignition, and AO was used to increase the degradation of material. Therefore, synergistic effect of AO and FR as good flame retardants to retard and to delay the spread of flames. This provides extra time in which either the fire can be extinguished or an escape can be made, thus helps save lives and property and provide safer materials without compromising performance.

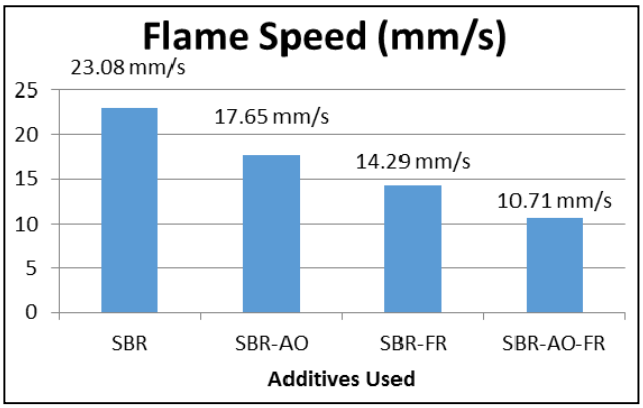

Fig 2: Flame speed comparison between presence and absence of AO and FR additive in 20% SBR filled composite

4. Conclusion

In conclusion, by using UPE as the polymer host, the EPS added with SBR and fillers could be prepared by using hot press technique. TGA profiles of UPR/EPS/SBR that contained AO-FR give better result in term of thermal stability, in order to achieve higher decomposition temperature. In terms of flammability, formulation with either AO and FR additive gave better burning rate, and both present was the best by halving the burn rate to 10.71mm/s. Properties shown so far by the UPR/EPS/SBR composite system with added FR or AO may enable it for various applications such as the building and architectural application.

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6. References

1. Lu S, Hamerton I. Recent developments in the chemistry of halogen-free flame retardant polymer. Progressin Polymer Science, 2002; 27:1661-1712.
2. Nguyen C, Jinhwan Kim. Thermal stabilities and flame retardancies of nitrogen–phosphorus flame retardants based on bisphosphorami dates. Polymer Degradation and Stability 2008; 93(6):1037-1043.
3. Glodek TE, Steven E, Boyd Ian M, Mcaninch John, Lascala J. Properties and performance of fire resistant eco-composites using polyhedral oligomeric silsesquioxane (POSS) fire retardants. Composites Science and Technology. 2008; 68(14):2994-3001.
4. Haiyun Ma, Lifang Tong, Zhongbin Xu, Zhengping Fang. Intumescent flame retardant-montmorillonite synergism in ABS nanocomposites. Applied Clay Science. 2008; 42(1):238-245.
5. Pereira CMC, Herrero M, Labajos FM, Marques AT, Rives V. Preparation and properties of new flame retardant unsaturated polyester nanocomposites based on layered double hydroxides. Polymer Degradation and Stability. Corrected Proof, Available Online. 2009,
6. Burchill Pj, Pearce Pj, Salamone Jc. Polymeric Materials Encyclopedia, Boca Raton. Crc Press, 1996; 3:2204-2210.
7. Vaidya UK, Hosur MV, Earl D, Jeelani S. Impact response of integrated hollow core sandwich composite panels. Composites Part A: App Science and Manufacturing. 2000; 31(8):761-772.
8. Gryshchuk O, Jost N, Karger-Kocsis J. Toughening Of Vinylester–Urethane Hybrid Resins by Functional Liquid Nitrile Rubbers and Hyperbranched Polymers. Journal of Polymer. 2002; 43:4763-4768.
9. Regnier N, Mortaigne B. Analysis by pyrolysis/gas chromatography/mass spectrometry of glass fibre/vinylester thermal degradation products. Polymer Degrade Studies, 1995, 419.