Unsaturated polyester/expanded polystyrene composite: thermal characteristics and flame retardancy effects

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Abstract. Panels for energy efficient buildings have to meet certain requirements such as low thermal conductivity and inherent flame retardancy characteristics, before being eligible for buildings and construction applications. Expanded Polystyrene (EPS) as waste material had been incorporated as filler in Unsaturated Polyester Resin (UPR) composites. The composite are fabricated as flat panel window or glazing to replace glass. In this study, different EPS content incorporated was found to affect flammability and thermal characteristics. Core additives such as Flame Retardant (FR) and Antioxidant (AO) were added to the composite for imparting flame retardancy and prevent aging of the composite. The result obtained via the comparison of the various composite systems studied had revealed that organic and metal oxide flame retardant (FR) additives imparts higher flame retardancy levels than others, but each type of additives had interacted with the polymeric matrixes differently. The thermal conductivity, k value, as measured from a handheld thermal probe had showed a minimum of ~0.124 W/m.K for the 1%wt zinc oxide sample, while the highest k value of ~0.280 W/m.K was exhibited by the 2%wt tin oxide sample. The first 1%wt of either metal oxide FR initially decreases both the thermal conductivity, k value; and volumetric specific heat, C_p,v of the samples. At 2%wt, increases in k value were obtained. The flammability was reduced with the use of organic Phosphate Ester FR, which had reduced the flame speed to about 37.1% of the original flame speed. With the equivalent mixture of all three organic FR system, the flammability reduced less than 30%, while the metal oxide FR additive doesn't reduces the flammability.

1. Introduction

All products applied in exterior glazing units must able to withstand the climate exposure during several decades of use; this includes the use of glass panelling or polymer sheets [1]. Aiding the conservation of energy usage are now a prerequisite for modern green materials. High insulation materials and daylight harvesting, for example, are some of the energy management techniques that reduces overhead lighting via utilization of the ambient (natural & artificial) light present in a space; flame retardancy characteristic is another prerequisite [2]. Green Technology can contribute to the glazing industry by the development of new materials using recycled plastic, which could also impart some insulation characteristic, while fulfilling the building requirement for flame retardancy.

Sustainable building is the practice of designing, constructing, operating, maintaining, and removing buildings in ways that conserve natural resources and reduce pollution. Rating systems
provide an effective framework for assessing most buildings’ environmental performance. A good Green Building Rating System (GBRS) should cover key indicators reflecting a building’s characteristics while keeping their performance in balance [3].

Composite employing Unsaturated Polyester Resin (UPR) matrix have been used for many years in a broad technology fields such as naval construction, offshore applications, waterlines, and building construction. UPR is the chosen thermoset material due to its excellent processing ability; good cross-linking tendency, as well have good mechanical and weathering properties. Studies had also been done to improve its thermal properties by incorporation of Expanded Polystyrene (EPS) into UPR with relevant diluents [4,5].

In the light for an alternative building material, EPS had been used as a filler for thermoset insulating panels; and tests were performed for thermal insulation studies and flame retardancy. Thus, the preparation and characterization of recycled EPS filled UPR composite systems had systematically been investigated. Core additives such as flame retardant (FR) agents, metal oxides and antioxidant (AO) for preventing aging were added to the UPR-EPS composite for imparting selected properties.

Flame retardant functions to increase the resistance of a material to ignition and, once ignited, reduces the rate of flame spread via combustion suppression by acting either through the vapour phase or the condensed phase by chemical and/or physical mechanisms [6,7]. The use of a flame-retardant additive may prevent a small fire from becoming a catastrophe, to which most fires involving polymer composites often quickly evolved as it consume the volatile combustible material generated from the thermal degradation of polymers. Flame ignition itself depends on numerous variables such as oxygen availability, temperature, physical and chemical properties of polymer [8,9].

The fire resistance of polyester based resins could improved via blending with flame retardant additives such as triphenyl phosphate and antimony trioxide; such of which are generally utilized for production of fume hoods, electrical equipments, building panels and navy boats as noted by Nazan, 2016 [5].

Flame retardants can be incorporated into polymeric materials either as additives or as reactive materials. Additive types are widely used by blending directly into the polymeric material. Problems such as poor compatibility, leaching and reduced mechanical properties are often the commonly encountered drawbacks of utilizing additive type FR. Reactive type FR overcome these shortcomings by directly co-polymering the FR with the polymer itself, thus making the flame retardancy quality inherent to the material itself. The main concern and limitation however of this method is the toxicity due to use of halogenated monomers [8–12].
Thus, this paper shall emphasise on the flammability and thermal aspects of a UPR/EPS composite system with varying organic and metal oxide FR additives utilized both with and without antioxidant inclusion.

2. EXPERIMENTAL

2.1 Materials and Method

The selected thermoset matrix material used for fabricating these composite systems is the Reversol UPR system, consisting of vinyl ester oligomers having a density of 1.12 g/cc, a viscosity of 450-600 cps with 41-44% styrene content. Methyl Ethyl Ketone Peroxide (MEKP) and Cobalt solution used as initiator and promoter each, were supplied together with the UPE resin by Revertex Sdn Bhd. These ingredients are similar to materials used by Rashida, et al. [8], which was the basis for this study.

The EPS or Styrofoam filler was obtained from waste material; Irganox, an antioxidant was supplied by Ciba Geigy; Phosphate Ester, Silesquioxane, and Melamine as flame retardants were supplied by Tina Organics (P) Ltd. Plasticizers & Allied Chemicals; Zinc Oxide and Tin Oxide solutions were supplied by Merck KGaA.

2.2 Composite Fabrication and Testing

Recycled EPS, fixed at 10% parts by weight (%wt) of UPR resin, was blended together with the resin by utilizing a high speed agitation mixer until complete mixture dissolution was attained. The gaseous contaminates present were eliminated from the mixture via vacuum suction, while any solid contaminates were removed from the mixture after a gravity settling phase of 24 h.

Designated additives were then added to the mixture before the samples were cured. The FR content was varied between 0 to 2.5%wt. Each FR are designated a code for distinction. The organic-based FRs of phosphate ester, silesquioxane, and melamine were designated as FRA, FRB, and FRC respectively. Tin oxide and zinc oxide representing metal oxide-based FRs were respectively designated as FRD and FRE.

The AO content was set to 0.5 g for samples impregnated with organic FR additives, which was absent for the samples impregnated with metal oxide FR additives. The MEKP and cobalt solution usage was limited to just 2.5%wt and 1 drops respectively for each sample.

The samples were shaped using compressive moulding process onto an aluminium mould, where the mixture made to partially jellifies in the mould before any pressure was applied upon it. The gelling time was set to be about 20 to 30 min. Once sufficient gel forms, low pressure press were applied for 1 h at 70°C to retain the required shape, and complete curing was done by leaving the
sample outside the mould for 24 h at room temperature. These steps are also similar to the process used by the study of Rashidan, et al., (2009) [8].

This paper was then written upon the conduction of sufficient qualitative analysis of the manufactured samples. The flammability testing of the sample was subjected to the procedures underlined under the ASTM D635 standard. This particular standard utilizes prepared specimen size of 125 mm x 20 mm x 3 mm. A fixed distance of 75cm for combustion was used to complete flame propagation, with the sample being placed to burn in a horizontal position. Flame initiation was performed by using a candle flame at room temperature. The linear burning rate were assessed from time taken to reach the specified distance. The flame speed as defined by its equation:

$$\text{Linear Burning Rate, } V(\text{mm/s}) = \frac{L}{t}$$

Where:  
$L = \text{the burn length between two reference marks, in millimetres (The designated length is 75mm)}$

$t = \text{the time(s) (The flame's elapsed time between the two reference mark)}$

The samples with metal oxide FR additives were also tested via a thermal probe to determine their thermal conductivity, thermal diffusivity and volumetric heat capacity. The thermal properties of samples were determined by use of a KD2 Pro Hand-held Thermal Probe which adheres to ASTM Standard D5334-08 and IEEE Standard 422-03.

3. Result and Discussion

3.1. Thermal Characteristics

Owing to unavoidable circumstances, only the latterly produced metal oxide FR samples of FRD (tin oxide) and FRE (zinc oxide) were available for thermal characteristic testing via a thermal probe in determining their thermal conductivity, thermal diffusivity and volumetric heat capacity. These thermal characteristics are oft-considered qualities in green materials especially those involved in the construction industry. A low thermal conductivity, and the resulting thermal diffusivity, helps retain heat from dissipating against the end-users’ needs.

| Samples Code | Additive in UPE/EPS Composite | Conductivity W/m K | Diffusivity mm²/s | Volumetric Specific Heat MJ/m³ K |
|--------------|-------------------------------|--------------------|-------------------|---------------------------------|
| FRD 00       | UPR-EPS Mix.                  | 0.193              | 0.096             | 2.008                           |
| FRD 05       | 0.5%wt FRD                    | 0.190              | 0.094             | 2.030                           |
| FRD 10       | 1.0%wt FRD                    | 0.172              | 0.089             | 1.921                           |
| FRD 20       | 2.0%wt FRD                    | 0.280              | 0.089             | 3.134                           |
| FRE 05       | 0.5%wt FRE                    | 0.181              | 0.090             | 2.006                           |
| FRE 10       | 1.0%wt FRE                    | 0.124              | 0.091             | 1.368                           |
| FRE 20       | 2.0%wt FRE                    | 0.147              | 0.098             | 1.505                           |
The thermal conductivity indicated by Table 1 showed a minimum of 0.124 Wm\(^{-1}\)K\(^{-1}\) as recorded by the FRE 10 sample, while the FRD 20 sample recorded the highest at 0.280 Wm\(^{-1}\)K\(^{-1}\). Figure 3 below shows how increasing the amount of FRD/E decreases both thermal conductivity and volumetric specific heat before an excessive additives content instead reverses the trend.

The initial decrement could be postulated as an effect of the additives agglomerating caused by its insufficient amount [13], which may lead to the resin having larger contact on the probe, and thus, a larger impact on the heat flow. The latter reversal could be achieved due to the inherent metallic nature of the metal oxide FR used. Increasing its amount facilitates the heat flow which hence recorded as an increase in the latter samples.

In contrast, their thermal diffusivity is a compound characteristic obtained from the ratio of thermal conductivity to volumetric specific heat. This property measure thermal inertia in that how fast the material changes temperature due to its thermal conductivity and specific heat. In the construction industry, a material with low thermal diffusivity are preferable as the quality may indicates a material which could withstand noticeable environmental temperatures changes.

As such, FRD 10 had shown characteristic of a good green building material due to its relatively low thermal conductivity and specific heat give birth to its low diffusivity. This sample might be suitable for tropical climate such as in Malaysia.

Surprisingly, FRD 20 also sports a similar low diffusivity of FRD 10 despite its conductivity and specific heat are the highest of the set. This hypothetically makes FRD 20 a suitable alternative to FRD 10 for use in other type of climates where the temperature changes are faster or with more extreme temperature ranges.

All in all, the inclusion of metal oxide FR improves the thermal resistance quality of the polymeric system by lowering both thermal conductivity and specific heat until a certain threshold. This reduction effect may occurs due to the trapped and initially agglomerating metal oxide particles might had created thermal barrier bubbles acting similar to the air trapped in foams slows heat conduction. Further study are required to determine the validity of this hypothesis.

### 3.2 Flammability Test

Table 2. shows the time it took to burn the sample for a fixed distance.

| Sample Code | Additive in UPE/EPS Composite | Elapsed time(s) | Linear Burning (mm/s) | Linear Burning (mm/min) |
|-------------|-------------------------------|----------------|-----------------------|------------------------|
| F00         | 0.5%wt AO                     | 510.6          | 0.147                 | 8.813                  |
| FRA         | 2.5%wt FRA - 0.5%wt AO        | 812.4          | 0.092                 | 5.527                  |
| FRB         | 2.5%wt FRB - 0.5%wt AO        | 709.8          | 0.106                 | 6.340                  |
|   | 2.5%wt FRC - 0.5%wt AO   | 627.6 | 0.120 | 7.170 |
|---|---------------------------|-------|-------|-------|
| FRC | FRABC 2.5%wt FRABC - 0.5%wt AO | 805.2 | 0.093 | 5.589 |
| FRC | Similar to F00; AO absent | 408.3 | 0.184 | 11.021 |
| FRC | 0.5%wt FRD | 198.1 | 0.379 | 22.716 |
| FRC | 1.0%wt FRD | 178.5 | 0.420 | 25.210 |
| FRC | 2.0%wt FRD | 152.3 | 0.492 | 29.547 |
| FRC | 0.5%wt FRE | 184.7 | 0.406 | 24.364 |
| FRC | 1.0%wt FRE | 165.1 | 0.454 | 27.256 |
| FRC | 2.0%wt FRE | 100.4 | 0.747 | 44.821 |

Based on the Linear Burning formulation, the linear burning rate decreases as a longer elapsed time is recorded. As Figure 1a indicated, the burning time taken for the three types of organic FR shows how each FR affects the flame speed/burn rate either individually or in tandem.

FRA, Phosphate Ester, shows the best performance as a flame retardant additive for the system at a 37.1% flame speed reduction; even an equivalent mixture of all three in the FRABC system was second best in relation to it. FRC or melamine, on the other hand, was the least efficient FR additive for this polymeric system, although it does boast a fair 18.6% reduction in flame speed.

![Figure 1a](image1.png) ![Figure 1b](image2.png)

**Figure 1.** Linear flame speed comparison of a) Organic FR types, and, b) Metal Oxide FR levels.

As shown in Figure 1b, the use of FRD and FRE (Tin and Zinc Oxide respectively) instead showed some failure in achieving any flame retardancy effects for the polymeric system. Although the absence of AO may enable an easier ignition and a faster flame rate as seen in the difference of F00 and FRD00 in Table 2 above, each increment of either material increases the flame speed. The introduction of either into the system triggers a doubling in flame speed as compared to the organic FR, although subsequent amount only adds a small flame speed boost except the result as shown by the outlier of FRE 20 that significantly adds flame speed.

In regards to the effect of the presence or lack of AO in the systems upon material ignition and flame speed, previous studies had implied that synergism in the gas phase reaction between organic
FR and AO could have existed. The synergism mechanism may involved evolved gases, which could be intercepted by AO and causes retardancy in smoke formation and flame suppressants; which may be ascribed to the inhibiting radical formation at gas phase level [9,14,15].

In comparison, metal oxide employed by Feng et al., (2016) [16] showed that thermoplastic incorporated with CeO$_2$ and FR resulted in better flame retardancy behaviour. The CeO$_2$ played a pivotal role in the increase of LOI value of the intumescent flame retardant polypropylene composites, and presents excellent synergism. The interaction between CeO$_2$ and IFR leads to the formation of numerous closed cells without holes and formation of a compact and homogeneous char layer during burning was revealed. Similar findings are also reported by Kandare et al., (2006); Katsoulis et al., (2011); and Naik et al., (2013) [17–19].

A probable explanation to the flame speed disparity between organic and metal oxide FR might be in the manner which both FR types were integrated into the polymeric systems. Unlike the organic FR which often covalently bonded directly into the matrix, the metal oxide FR requires a suspension system to enable through mixing of the particle into the polymeric matrix. These suspensions usually utilizes relatively flammable solutions such as toluene which are counter-productive to the task expected of the additive. Until further study to determine this hypothesis, this shall be best reasoning to explain this data disparity.

4. Conclusion
In conclusion, by utilising suitable FR that easily bond with the polymeric system; the flammability, flame speed, and thus its fire hazard maybe reduced up to nearly 40%. Otherwise the effects desired may not be obtained and may even backfired due to the low capability of the additive to the system. Thus, FR compatibility should be a concern for its use.

In terms of the studied thermal characteristics, the inclusion of metal oxide FR had improved the thermal resistance quality of the polymeric system by lowering both thermal conductivity and specific heat until an observed limit. A study on how this quality improvement actually occurs within the polymeric matrix is required.

Acknowledgement
I would like to acknowledge the technicians, and staffs for their assistance during the composite fabrication and testing phases; and to my colleagues and lecturers for discussions related to this work. Special acknowledgement for Assoc. Prof. Rahmah Mohamed for her guidance and direction in
producing this publication. I also wish to thank Universiti Teknologi MARA (UiTM) for their research funding under the Research Intensive Faculty (RIF) fund [File:600-RMI/DANA 5/3/RIF (64/2012)]

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