Thermosets with Flame Retardants

Subjects: Materials Science, Composites
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Epoxy and unsaturated polyester resins are the most used thermosetting polymers.They are commonly used in electronics, construction, marine, automotive and aircraft industries.Moreover, reinforcing both epoxy and unsaturated polyester resins with carbon or glass fibre in a fabric form has enabled them to be used in high-performance applications. However, their organic nature as any other polymeric materials made them highly lammable materials. Enhancing the flame retardancy performance of thermosetting polymers and their composites can be improved by the addition of flame-retardant materials, but this comes at the expense of their mechanical properties. In this regard, a comprehensive review on the recent research articles that studied the flame retardancy of epoxy resin, unsaturated polyester resin and their composites were covered. Flame retardancy performance of different flame retardant/polymer systems was evaluated in terms of Flame Retardancy index (FRI) that was calculated based on the data extracted from the cone calorimeter test. Furthermore, lame retardant selection charts that relate between the flame retardancy level with mechanical properties in the aspects of tensile and lexural strength were presented. This review paper is also dedicated to providing the reader with a brief overview on the combustion mechanism of polymeric materials, their flammability behaviour and the commonly used flammability testing techniques and the mechanism of action of flame retardants.

Keywords: epoxy resin ; unsaturated polyester resin ; flame retardancy ; mechanical properties ; polymer matrix composites ; flame retardancy index (FRI)

1. Introduction

Polymeric materials are rapidly replacing metals and ceramic materials in various applications. This is attributed to the remarkable combination of properties like low weight, easy of fabrication and low processing temperature [1][2]. Use of polymers in the electric and electronics (E&E) industry is prominent such as in electronics housings, insulators and printed circuits [3], and similarly, in transportation industry [4][5], flexible solar cells [6] and synthetic fibres in textile industry [7][8].

Reinforcing polymers with continuous fibres like glass or carbon fibres opens a new field of applications in automotive, aerospace and construction buildings. In other words, fibre reinforcements have enabled polymeric materials to replace traditional materials like aluminium, steel and concrete that are used in high performance engineering structures [9]. High specific strength and stiffness, light weight and design flexibility are the key factors behind the continuous increase in using fibre reinforced polymer (FRP) composites [10][11]. In a commercial airplane 80–90% of the interior furnishings are manufactured from FRP [9]. Recently, FRP is used in construction and rehabilitation of metallic structures [10][12]. Constructing a FRP bridge typically reduces the weight by 75% compared to steel bridge and that is beneficial in case ground condition is poor [11].

Epoxy resin, phenolic resin, unsaturated polyester resin and vinylester resin are the most used thermosetting resins in FRP composites applications [13]. Amongst all thermosetting resins, Epoxy resins are the most widely used due to their higher mechanical properties, better adhesion to various substrates and lower shrinkage after curing compared to other resins [14]. However, longer curing time and higher cost for epoxy resin compared to polyester and vinyl ester resin hinders its use as a matrix material for automotive composites [15]. However, Epoxy composites are more appropriate for higher performance applications like aircrafts [16][17].

The ever-increasing demand for light structures and increasing fuel efficiency results in replacing more metallic parts with polymers and polymer composites. Despite the benefits of using polymeric materials, the risk of fire occurrence is increased [18][19]. The high flammability of polymers and polymer composites limits their applications and more stringent requirements should be passed for fire safety concerns [20][21]. In some studies, the reason behind the reduction in time to escape during airplane crashes, accompanied by fire, is attributed to the use of several tons of polymers in overhead bins, internal panels, seat fabric and cushions in aircraft's passenger compartment [9][20]. Reducing the fire hazards accompanied by using polymeric materials can be achieved by incorporating flame retardants (FRs) [22]. The main applications that require flame retardants to be used in polymer composites are summarized in Table 1 [4][23][24][25].

Table 1. Application of flame retardants.

Market Area	Applications	FR Governing Aspect and Standards Used
Fabrics and apparel	**Natural fibre (cotton, wool) composites, synthetic fibre, carpets, curtain**	**Flame spread regulated by the limitations of ASTM D1230**
Electric and electronics	**Wire and cable, printed circuit boards, electronics housings, appliances**	**Ignition resistance and flame spread according to:** - International Electrotechnical Commission IEC 62441, which is an open flame "candle standard" for electronics - UL 746C Guidance for individual product standards on flame rated enclosure use
Building constructions	**Thermal insulation for roofs, facades, walls, sheetings for roofs, floor coverings, ducting and conduit, panels, linings, coverings, thermal insulating materials [foams], mattresses, furniture cushioning**	**Ignition resistance and containment flame spread according to:** - ASTM E-84 in the United States or Single Burning Item (SBI) in the European Union (EU) [13]. - ASTM E 162 which is a small-scale test for flame spread.
Transportation	- Automotive (wire and cable), seats - Aircraft (panels, overhead pins), carpets, flooring - rail vehicles (compartment linings and coverings insulation, compartment interior, seats)	- Time to escape and Ignition resistance criterion according to: - Federal Motor Vehicle Safety Standard (FMVSS) No. 302 (49 CFR 571.302) that measures the flammability resistance for materials used in the interior parts of automobiles [26] - Code of Federal Regulation (CFR) 25.853 for aircraft interiors contains three types of tests, namely, vertical burning, heat release (Ohio State University calorimeter/OSU) and smoke density measurements.

The main functions of flame retardants are to reduce smoke and delay the time of flashover, subsequently provide sufficient time for people to escape [4]. Halogenated flame retardants were commonly used, but they were banned as they evolve toxic gases during combustion [27]. Recently halogenated FRs are replaced by phosphorus-based compounds, silicon-based compounds, borates and metal hydroxides. However, these non-halogenated flame retardants should be incorporated at high loading percentages to be effective and this in turn deteriorates the mechanical properties [16][28]. Moreover, the high loading percentages influence the resin processability. For example, the added particles increase the viscosity and the curing time for the resin and that leads to changing the processing conditions [27][29]. Thus, the challenge is to develop a flame-retardant system that enhances the fire performance of polymeric composites without deteriorating their mechanical properties.

Several review articles have analysed the different approaches that can be used to enhance the flame retardancy for polymeric materials and provide an overview of various types of flame retardant additives and their modes of action to inhibit the combustion cycle [3][23][26][30][31][32][33][34][35][36][37][38]. However, limited articles have worked on introducing quantified index to allow comparison of different flame retardant systems. Vahabi et al. [39] have proposed for a first time a universal dimensionless index known as flame retardancy index (FRI). This index helps the investigators to evaluate the performance of flame-retardant system. Vahabi et al. and Movahedifar et al. [39][40][41] have applied this index on a comprehensive set of data collected from literature to evaluate the fire performance of Polypropylene (PP), Poly (methyl methacrylate) (PMMA), Ethylene vinyl acetate (EVA), Poly (lactic acid) (PLA) and epoxy resin filled with different types of flame retardants. Moreover, literature lacks a simple selection tool that can be used to correlate between the effect of adding flame retardants on the flammability behaviour of polymeric materials and their effect on the mechanical, thermal and physical properties. Elsabbagh et al. [42] introduced a material selection chart that combines the flame retardancy performance represented by UL-94 test results with the tensile strength of natural fibre polymer composites treated with different flame retardants.

2. Towards Selection Charts for Epoxy Resin, Unsaturated Polyester Resin and Their Fibre-Fabric Composites with Flame Retardants

- Phosphorus-based FRs proved their capability to enhance the flame retardancy of both epoxy and unsaturated polyester even at low loading below 10 wt.%. APP is the most effective phosphorus-based FR used. However, in order to achieve high FRI, APP should be loaded within the range 15–40 wt.% and this comes on the expense of mechanical properties. Therefore, synergizing APP with other additives or decorating APP with other FR compounds can reduce the required content of APP.

- Synergizing 20 wt.% APP with 3 wt.% of nano-clay achieved an FRI value of 20, which is the same value of loading 40 wt.% APP to epoxy resin. In addition, hybridizing 14.9% nano APP/MMT compound with 0.1 wt.% boron silicate graphene oxide achieved an FRI value of 16 for unsaturated polyester resin. Generally, the combination of different FRs is a good strategy to enhance flame retardant properties.

- Carbon-based fillers succeeded in acting as an FR at low loading percentage varied from 0.5 to 2 wt.%. However, they can just achieve FRI values between 1 and 2.5. The maximum attained FRI value of 3.7 was for the addition of 0.7 wt.% graphene oxide to epoxy. In addition to the flame retardant effect of carbon-based fillers, they can act as reinforcements. The addition of GO and carbon nanotubes to epoxy resin enhanced both FRI and tensile strength for epoxy resin.

- It can be concluded from the constructed selection charts that the mechanical properties are significantly affected by the type of FR used and its loading content. Generally, the addition of FRs reduced the mechanical properties. However, some systems enhanced both the flame retardancy performance and mechanical properties. With respect to the unsaturated polyester resin, hybridizing 20 wt.% APP with 5 wt.% nano-clay reached an FRI value of 5 and increased flexural strength by 40%. In addition, hybridizing 17 wt.% APP with 1 wt.% MMT and 2 wt.% zinc borates achieved V-0 in UL-94, an FRI value of 5 and increased tensile strength by 70%. On the other hand, increasing the APP content to 30 wt.% reduced both TS and FS by 50%. Regarding epoxy resin, the systems that enhanced both mechanical and flame retardant properties correspond to 0.7 wt.% GO (FRI value of 3.7 and relative TS value of 1.35), 8 wt.% nitrogen/sulphur-containing DOPO (FRI value of 2.5 and relative TS value of 1.2) and 7.35 wt.% biobased hyperbranched polymer-DOPO (FRI value of 1.2 and relative TS value 1.6)

- Reinforcing both epoxy and unsaturated polyester resins with carbon and glass fibre-fabric reduced the flammability behaviour of pristine resin. However, the addition of FRs to composite materials is not as effective as incorporating them with pure polymer. The presence of inert fabrics hinders the activity of FRs of forming a well-developed charring layer. The blending of different resins and coating of fabrics with FRs, instead of mixing them with the matrix, is a solution to enhance the flame retardant properties of the composites. The blending of epoxy resin with cyanate ester enhanced the flame retardancy performance of carbon fibre-fabric composites. Furthermore, the blending of unsaturated polyester with phenolic resin enhanced the flame retardancy performance of glass fibre-fabric composites.

- It can be noted that there has not been enough research performed on studying the effect of FRs on flame retardant properties, as well as mechanical properties of epoxy resin, unsaturated polyester resin and their composites. Moreover, only very few articles have studied the effect of FRs on other properties, such as thermal conductivity, optical, sound absorption and rheological properties such as viscosity and curing behaviour. Studying the effect of FRs on different properties other than flame retardancy is necessary in order to meet the end needs of the final product. In addition, properties such as viscosity and the curing behaviour of polymers can guide the manufacturer to select the appropriate processing technique.

- It is recommended that future research focuses on the following points:

- Studying the effect of FRs on other properties, besides flame retardancy, such as mechanical, physical, optical and thermal conductivity.

- The idea of material selection chart should be extended to correlate properties (such as physical, optical and sound absorption), other than mechanical with flame retardant properties for different types of polymers and polymer composites. These charts will provide a quick selection tool for the production sector to select the needed FR/polymer materials that can meet the end needs of the final product.

- Combining data from future studies together with the data collected in this review and other reviews [39][40][41] will provide a large database and open the avenue to develop numerical models that can evaluate different aspects of flame-retarded polymers.
- From the environmental perspective, research should concentrate on using biobased FRs to overcome the negative impacts of FRs on human health and the environment. Moreover, use of the life cycle assessment (LCA) tool should be considered to study the impact of flame retardant polymeric products on the environment.

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