Fire and mechanical properties of polymeric composites with keratin-based flame retardants

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Abstract. Due to the high flammability of polymeric materials, the development of a flame retardant with high-performance, low-toxicity and cost-effectiveness has been one of the most important issues in the polymer industry. To address these requirements, keratinous fibres have been employed for a novel intumescent flame-retardant fabrication. Phosphate loaded keratinous fibres through the sequential infiltration of phosphoric acid and reactive amines have shown a successful demonstration of the self-extinguishment (V0 grade) and ~80% reduced peak heat release rate in the vertical burn test (UL94) and cone calorimeter test, respectively. Owing to the unique char formation behaviour of the fibres with the combined effects of phosphorus compounds, the composites have achieved the improvement of flame retardancy compared to the commercial ammonium polyphosphate/polypropylene composite. Furthermore, the fibre addition has contributed to enhance the mechanical properties of the composites. For the practical application of the new FR, cost reduction capability depending on the type of reactive amine used for the phosphate production in the fibre, has also been investigated.

1. Introduction

Along with the increasing applications of polymeric materials, demand for safer materials against fire hazard has been increasing [1,2]. Although halogenated flame retardants have been studied for several decades, stringent regulations considering health and safety issues have recently limited their usage in fire protection applications. Therefore, polymer industries need an alternative methodology to replace the conventional flame retardants and impart customised flame retardant (FR) property to the polymer with environment-friendly, biocompatible and cost-effective manner. Additionally, maintaining the intrinsic property of the matrix should be considered for adapting traditional processes and applications [3]. Figure 1 shows the current trend of FR market. Although the halogenated flame retardants are still occupying one-third of the market, metal hydroxides take up the largest portion and phosphorus compound follows. Due to the cost-effectiveness and adaptable flame retardancy, metal hydroxides are used for wide applications, but their high loadings to polymeric composites cause the deterioration of mechanical performance, an issue that has been ignored in the past. Therefore, it has been envisaged that a phosphorus-based FR may help relieve the deterioration of mechanical properties due to its better fire performance with low loading requirement [4,5]. For olefins, intumescent flame retardant (IFR), mainly composed of phosphorus compounds, has shown an
excellent FR performance and low toxicity [6]. However, the addition of IFR also causes a strength drop (~20% at V0 grade for polypropylene in UL94 test) and relatively high cost compared to conventional FRs.

As one of the most promising approaches towards producing IFR, utilisation of natural resources has been studied because of their non-toxicity and cost reduction potential. Among them, protein-based materials have demonstrated their effectiveness for an improved flame retardancy of polymeric materials. For instance, Alongi et al. have used animal DNA and casein [8,9] as IFRs for several types of synthetic polymer and cotton fabric. The hybridisation of protein and polymer has achieved ~50% reduction of heat release rate (HRR) and the significant increase in time to ignition which allow the composite decreasing the potential fire risk. However, the composites modified by only natural protein could not demonstrate self-extinguishing property. There are many reasons for this, but the lack of phosphorus is one of the most prominent reasons because phosphorus works as a catalyst to speed up the char formation, stopping the fire propagation. Therefore, in our previous research [4,5,10] keratinous fibres, such as coarse wool and chicken feathers, have been used with the combination of phosphorus compounds. Kim et al. [4] have demonstrated that the wool fibres hold notable fire-resistance properties due to the sulphur and nitrogen in their molecular structure. Further ammonium polyphosphate (APP) addition was essential to achieve the self-extinguishment. Jung et al. [5,10] produced a hybrid of keratinous fibre and ethylenediamine phosphate for simultaneously improved flame retardancy and mechanical property. Notably, addition of the FR keratinous fibres makes the modified polypropylene (PP) composite avoid the strength drop generally appearing with phosphorus-based FR. Although various types of keratins can be used for the fibre modification (Figure 4), chopped coarse wool and chicken feather (Figure 2) have been studied in our research. Despite the comparable FR performance due to their similar chemical structure, the cost of the fibres varies (Table 1). Therefore, it can be concluded that chicken feather, which normally goes to incineration or landfiling, is more suitable for the FR fabrication. Figure 3 shows a new cost composition after replacing the keratinous fibre from coarse wool to chicken feather fibre (CFF). The portion of raw keratinous fibre cost is remarkably reduced (down to 15%) after the replacement of coarse wool by CFF.

**Figure 1.** Global flame retardants market by additives [7].
Figure 2. Optical microscopic image of untreated a) wool and b) CFF [5].

Table 1. Mechanical Property, application and cost of keratinous fibres.

| Keratinous fibre   | Tensile strength (MPa) | Tensile modulus (GPa) | Application                                                   | Post process                                          | Price (USD/kg) | References |
|--------------------|------------------------|-----------------------|--------------------------------------------------------------|-------------------------------------------------------|----------------|------------|
| Coarse wool fibre  | 160                    | 4.8                   | Coarse cloth, carpets, knitted articles, and felts           | Cleaning and scouring                                  | ~ 1.92         | [11]       |
| Chicken feather (barb) | 203                | 3.5                   | Raw feather                                                  | None                                                  | Incineration or land filling | [12]       |
| Toucan feather (rachis) | 78                   | 2.6                   | Feather meal as an additive for feed stock or as a fertiliser | Grinding, fermentation and rendering                   | ~ 0.47         | [13]       |
| Goose feather/down | -                     | -                     | Apparel                                                      | Washing and sorting                                   | Feather: ~1.71  \ Down: ~56.9 | -          |
| Silk               | 600                    | 10                    | Apparel                                                      | Stiffing and sorting                                  | ~ 30.1         | [14]       |
| Hair, Human        | 150                    | 1.5                   | -                                                            | -                                                     | Incineration or land filling | [15]       |

Figure 3. Production cost comparison between FR wool and FR CFF.
Feather generally consists of shaft, rachis, barb and barbule, Figure 2b. The uneven morphological structure, requiring complicated sorting process, has limited their usage for composite preparation. However, it was overcome through our chemical treatment method (Figure 4) using strong chemicals. Figure 4d shows the ground FR CFFs with an average particle size of 73 µm [5]. Although the hybrid FR with phosphate and keratinous fibre has satisfied the major requirements of modern flame retardants, such as performance and cost, there is still some room for cost reduction using more stable and inexpensive chemicals. In this work, melamine has been used for phosphate production in the fibre instead of ethylenediamine. The effects of melamine phosphate/CFF combination on mechanical property and cost of the modified PP composite have been investigated by comparing two composites with different chemical and CFF formulations.

Figure 4. Schematic diagram of fabrication of FR keratinous fibres and SEM images of a) untreated wool, b) FR wool, c) pulverised FR wool and d) FR CFF [5,10].

2. Experimental details

2.1. Materials
Raw chicken feathers were obtained from Wallace Group Ltd. (New Zealand). Phosphoric acid (PA, concentration: 85 wt% in H2O), ethylenediamine, melamine and toluene were obtained from Sigma-Aldrich and used without purification. PP (K515, MFI: 19) was manufactured by A. Schulman, Inc. Maleic anhydride grafted PP (MA-g-PP, Licocene PP MA 6452), used as a compatibilizer, was provided by Clariant NZ Ltd. Commercial intumescent ammonium polyphosphate flame retardant (Exolit AP 766) was purchased from Clariant NZ Ltd., and used for performance comparison.

2.2. Synthesis of FR CFF
Raw chicken feathers were first washed with diluted hydrogen peroxide and then again were washed three times by using hot water, mixed with laundry detergent; it was followed by complete drying at 70°C. Chicken feather, chopped by using a mechanical granulator (GR2020 granulator, MORETTO S.P.A, Italy), was mixed with PA/ethanol solution at room temperature. The PA-treated CFF was
mixed with reactive amines (ethylenediamine and melamine) and dried at 40°C until reaching a constant weight. After completing the chemical treatment, FR CFF, prior to composite preparation, was pulverized by using a centrifugal mill (ZM 200, Retsch, Germany) with a rotational speed of 10,000 rpm.

2.3. Fabrication of FR CFF/PP Composite
FR CFFs, APP, MA-g-PP and PP were dry blended by using a powder mixer. After mixing, the mixture was melt-blended at 175°C for 3 min at a speed of 70 rpm using an internal mixer (W 50 EHT, Brabender GmbH & Co., Germany) to obtain FR CFF/PP composite. The obtained compound was pelleted and then hot-pressed into sheets for further characterisations. The 20-ton hydraulic press (LP-S-20, Lab Tech Eng. Co.,Ltd., Thailand) was preheated to a temperature of 168°C and the preheating cycle was set at 5 minutes, the first pressing cycle was set at 2.5 min, ensuring the pressure to remain between 40 MPa to 50 MPa and the second pressing cycle was for 1.5 min, ensuring the pressure to be 90–100 MPa. APP/PP composites were also prepared using the same process for the performance comparison.

2.4. Flammability Test
Vertical burning tests were performed according to ASTM D 3801-10 (equivalent to UL-94 standard). Samples with length (L) =125 mm, width (W) =13 mm and thickness (T) =2.4 mm dimensions were prepared and preconditioned under 23°C and 50% relative humidity for 48 h. The tests were repeated five times for each sample and the average values were considered. The test results were classified into different grades, V-0, V-1, V-2 or no rating (NR). Cone calorimeter (Fire Test Technology, East Grinstead, UK) was used to obtain the quantitative information of flammability parameters according to ASTM E1354-11. Samples were tested in a horizontal position with an external heat flux of 50 kW/m². Samples were preconditioned at 23°C and 50% relative humidity for 48 h before the test.

2.5. Mechanical Property Characterisation
The tensile test was conducted by using an Instron universal testing machine (UTM 5567, UK) according to ASTM D 638. The samples were prepared into thin films of 0.45 mm nominal thickness and then cut into a dog bone shape of 6 mm width. At least five specimens for each sample were tested to obtain the average values of tensile strengths and moduli. The chord moduli were calculated between 0.05 and 0.25% strain, and strengths were measured at a crosshead speed of 50 mm/min, with the extension measured by a video extensometer.

3. Results and discussion
Two types of FR CFF/PP were prepared to investigate the effects of IFR constituents (i.e. phosphate, CFF and APP) on the FR performance and cost of the composites (Table 2). PP with 20% commercial APP was also prepared and used for the comparative analysis with the composites. Although a slightly lower amount of phosphorus has been used for the FR CFF#2 than that of the FR CFF#1, extra CFF and APP addition results in similar peak heat release rate (PHRR) compared to those of the other composites (Figure 5). Interestingly, while the FR CFF#2/PP has achieved the V0 grade in the UL94 test, the FR CFF#1/PP could not gain any grade despite the similar PHRR. It can be noted that the lower CFF loading in the FR CFF#1/PP inhibited its durable char formation during combustion. The HRR curves indicate that the FR CFF#2/PP shows the significant difference in fire reaction behaviour compared to other samples. Since the FR mechanism of IFR is highly related to the condensed phase reaction, the durability of char plays a significant role in reducing the material’s flammability. As shown in Figure 5, the time to PHRR of the FR CFF#1/PP appears at 275 s, whereas that of the FR CFF#2/PP appears at 45 s. This means that the char created by the FR CFF#1/PP combustion effectively reduces the flammability of the composite at the initial stage, but continuous degradation broke the char, finally, resulting in the highest HRR. APP/PP also shows a similar trend to that of FR CFF#1/PP.
Table 2. Compositions of FR CFF/PPs, and APP/PP.

| Sample         | FR CFF | APP | Total FR additive | MA-g-PP | PP (%) | UL94 |
|----------------|--------|-----|-------------------|---------|--------|------|
|                | PA (%) | EDA (%) | Melamine (%) | CFF (%) | APP (%) | (%); |      |
| FR CFF #1/PP   | 15     | 9    | 0                 | 6       | 0      | 30   | 3    | 67   | NR   |
| FR CFF #2/PP   | 13     | 0    | 17                | 14      | 6      | 50   | 3    | 47   | V0   |
| APP/PP         | 0      | 0    | 0                 | 0       | 20     | 20   | 3    | 77   | V0   |

On the other hand, HRR curve of the FR CFF#2 shows the continuous reduction of flammability despite slightly higher PHRR than that of the FR CFF#1/PP. This means that the IFR formulation with melamine phosphate, CFF and APP can provide the durable char formation. Due to the char formation, the FR CFF#2/PP achieved V0 grade in the UL94 test. The replacement of PP with IFR constituents, such as FR CFF and APP, was also effective for the flammability reduction. Figure 6 shows the char residues of FR CFF/PPs. While the char residue of the FR CFF#1/PP exhibits the roughness and numerous cracks with its surface, the FR CFF#2 shows a relatively smooth surface with a lower number of cracks. It can be highlighted that the combination with melamine phosphate and APP results in steady burning behaviour and more stable char formation compared to that of the FR CFF#1/PP.

Figure 5. Heat release rate curves of PP, FR CFFs and APP/PP.
As shown in Figure 7, IFR addition to PP leads to stiffness improvement for all composites. However, approximately 20% of strength drop is identified from the APP/PP. This is common for PP composites with IFR due to the lack of compatibility between hydrophilic IFR and hydrophobic polymer matrix. On the other hand, the FR CFF#2/PP not only shows higher strength than that of APP/PP but also succeeds in arresting the strength drop. The FR CFF#2/PP has more than 2 times increased tensile modulus along with 7% reduced tensile strength compared to that of PP. Furthermore, the FR CFF#2/PP also demonstrates a relatively lower production cost than those of the other composites. The substantially lower material cost of melamine compared to that of ethylenediamine and simplified process due to its less toxicity led to a 25% reduced production cost compared to that of the FR CFF#1/PP based on our estimation.
4. Conclusions

Flame retardant and mechanical properties of the FR CFF/PPs with different phosphate/CFF formulations were investigated. The FR CFF/PP with melamine phosphate and APP demonstrated improved mechanical properties and cost-effectiveness than that of FR CFF/PP with ethylenediamine phosphate at a similar level of flammability. Furthermore, the formulation was effective to arrest the strength drops normally occurring due to the addition of phosphorus-based flame retardant. Better interfacial bonding between the FR CFF and PP contributes towards improving the strength but the detailed mechanism needs more investigation. Therefore, it can be generally concluded that keratinous fibre-based flame retardant using wasted natural resources and inexpensive/less-toxic chemicals can meet the essential requirements for innovative flame retardant, such as flame retardancy, compatibility with matrix and cost-effectiveness.

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