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Development of fire resistant wool polymer composites: Mechanical performance and fire simulation with design perspectives

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ABSTRACT

Wool, as a naturally fire resistant fibre, has been incorporated with other additives, such as ammonium polyphosphate (APP), talc and maleic anhydride grafted polypropylene (MAPP), to manufacture polypropylene (PP) based composites. A single-screw extruder, attached with a flat die, has been used to successfully produce continuous wool-PP composite sheets. Furthermore, the significant roles of nitrogen content of APP and the talc in forming the effective char to increase the composites' fire retardancy have been identified through cone calorimeter tests. In particular, it is highly interesting to note that a reduction of APP content from 20 to 15 wt% was possible to achieve a direct self-extinguishment (V-0 rating) of the composite. The decrease in APP amount has also led to the reduction of material cost due to APP's relatively high price (USD 13–14/kg) and limit the possibility of deteriorating mechanical properties due to APP addition. The MAPP has enhanced thermal stability and mechanical properties compared to those without the additive, which could be attributed to the improved interfacial adhesion between wool and PP. A computational fluid dynamics model has also been developed by Fire Dynamics Simulator to mimic the cone calorimeter tests, which agreed reasonably well with the experiments.

1. Introduction

The intensive burning behaviour of polymer composites has been a critical issue in a broad range of applications in aircraft, automobiles, civil infrastructure and consumer products as hydrocarbon structures of polymers have led to poor performance in fire [1]. Extensive studies have been performed over the last few decades to comprehend and reduce the composites' flammability. Fire retardation of polymers can be achieved by breaking or slowing down the chain branching reactions in the combustion cycle, which includes ignition, pyrolysis, combustion and feedback [2]. However, the resistance to combustion of the composites can be improved by different methods, such as the incorporation of additive compounds to the polymer matrix [3], flame retardant coating [4], heat-induced intumescence of the composites surface [5] and fibre treatments [6]. The inclusion of additives, namely fire resistant fillers or flame retardant (FR), has been widely employed as an effective method due to their direct application during the composites' fabrication. Flame retardant additives, such as halogen-based materials, have been intensely utilised, but these additives release highly smoky and toxic fire effluents by interfering with hydrocarbon oxidation and the conversion of CO into CO_2 [7]. Hydrogen chloride created from chlorine-based FR is of even greater toxicological risk than carbon monoxide [3]. Thus, it is necessary to develop a fire retardant system for polymeric composites which is simultaneously innocuous to the environment and can be integrated in the present system of manufacturing.

A halogen-free intumescent FR, ammonium polyphosphate (APP), mainly contain phosphorus and nitrogen, which can improve fire retardancy for polymers under combustion [8]. APP can derive phosphorus-nitrogen synergism under combustion, producing phosphoric acids and ammonia to form the intumescent char as a barrier, consequently hindering heat and gas transfer between the flame and underlying material [8,9]. Furthermore, the amount of nitrogen or phosphorus as the main component in APP plays a significant role in forming the effective char in the condensed phase [10]. Wool is a naturally fire resistant fibre because of its relatively high contents of sulphur (3–4 wt%) and nitrogen (15–16 wt%) [11]. It has been observed that wool fibres create char in an intumescent manner without melting and dripping when burnt, thus the fibres result in low heat of combustion (4.9 kcal/g) and high limiting oxygen index (25.2%) [10]. It is also to be noted that during initial stages of procurement, certain by-products of wool, such as noils and burr, could be combustible if improperly handled in the processing area [12]. However, wool used in composites manufacturing already went through the aforementioned processing phase, thus making the existence of by-products unlikely. As the environmental concerns regarding petroleum-based polymeric composites have increased, the effects of wool as a natural fibre on the composite's mechanical and thermal properties have been recently investigated

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[13–17]. For instance, Kim et al. [15] have found the positive effect of wool with char-forming FR on improving fire retardant performance of composites and Bertini et al. [16] have also identified the reduction of total heat release and heat release capacity of wool keratin based composites. As nitrogen is a common chemical element in wool and APP, two types of APP based on different nitrogen contents have been selected in this study to investigate the effect of nitrogen as a blowing agent on flammability of wool-PP composites.

Several additives can be used in conjunction with APP, which might benefit its char forming ability, consequently improving the fire retardancy. Mineral fillers as inert materials can decrease flame spread by reducing heat generation and can mitigate the volatile products [18]. Specifically, talc can act as a mass diffusion barrier for volatile decomposition products during combustion owing to its lamellar structure, which can simultaneously improve the processibility of polymer manufacturing due to its lubricating nature and dimensional stability [19]. Levchik et al. [20] have observed that the mixture of talc and APP with nylon creates magnesium-ammonium polyphosphate ($MgNH_4(PO_3)_3$) and silicon-ammonium tetrapolyphosphate ($Si(NH_4)_2P_4O_{13}$) under linear heating up to 600 °C. These mineral based phosphates can form a ceramic-like layer at the surface to enhance fire-protective properties. Elsewhere, Duquesne et al. [21] have investigated the effects of talc and APP on PP flammability using several combinations of their loading amounts. They reported favourable fire retardant properties under the direct flame application in UL-94 tests but having a proper balance of the loading amounts was found to be a necessity for the fire performance.

The incorporation of maleic anhydride grafted PP (MAPP) as a compatibiliser enhances the mechanical properties of natural fibre filled polymer composites by creating potentially reactive groups, such as hydroxyl and carboxyl groups, upon the wool surface, which are capable of reacting with the PP matrix [22,23]. Thus, the adequate amount of the coupling agent has been a governing factor for improving the fibre/polymer interfacial bonding and fibre dispersion of composites [24]. The interface can also affect the composite's flammability- a stronger interfacial adhesion requires more energy to pull apart the constituents in the case of fire, consequently increasing the decomposition temperature and reducing the decomposition rate [22,25]. However, MAPP is less thermally stable than PP, with almost a 100 °C difference between their respective onsets of decomposition temperatures [26]. As a result, any free and unreacted MAPP present in the composite would potentially reduce the overall thermal stability.

The cone calorimeter, as a versatile bench scale instrument, has generated comprehensive fire reaction properties of materials. A wide range of parameters have been utilised to characterise the combustion behaviour of the tested sample. On the other hand, the experimental processes and measurements to quantify the fire performance of the materials can be both time consuming and expensive. To overcome this limitation and achieve the predictive ability of the fire behaviour, computational modelling has been introduced and developed. Computational fluid dynamics (CFD) as the field model is one of the major tools for analysing the full breadth of fluid flow problems [27,28]. Fire Dynamics Simulator (FDS) has been widely used as a CFD code to simulate the burning process of a single homogeneous material or large scale structure [29–31]. However, only a few researchers have dedicated their work to the composites fire simulation using the FDS [32,33].

The overarching aim of the present work is to investigate the effects of additives, such as APP types, MAPP and talc, on flammability and mechanical properties of the extruded wool-PP composites. The paper initially includes a comparative study of fire retardant performance of wool-PP-APP composites, based on different APP types. Furthermore, the burning behaviour of the composite in the presence of MAPP and talc has also been demonstrated by employing thermogravimetric analysis, cone calorimeter and vertical burn tests. The fire residue analysis using a scanning electron microscope has revealed the microstructure and chemical elements of char formed during the cone calorimeter test. Moreover, the effects of APP, MAPP and talc on the mechanical properties of wool-PP composites are presented. Finally, an FDS model has been created to simulate the combustion of wool-PP composite in the cone calorimeter test. It is to be noted that this is the first comprehensive study to investigate the effects of APP types in conjunction with talc in wool based polymeric composites.

2. Experimental details

2.1. Materials

Scoured wool fibres having Avg. 45.3 μm thickness were provided by Bloch & Behren Ltd. (New Zealand) and polypropylene (HP400L, melt flow index: 5.5 g/10 min) as the polymer matrix was supplied by Lyondell Basell. The PP grade was selected as the suitable thermoplastic polymer to improve the mechanical properties of wool-PP composites [14]. Furthermore, two types of APP were utilised as the flame retardant to investigate the effect of nitrogen content on the thermal characterisation of composites. Table 1 presents the details of the flame retardants. MAPP (Licocene 6452, Clariant Ltd.) and talc (Plustalc N625, Mondo Minerals) were also chosen as a compatibiliser and mineral filler, respectively.

2.2. Preparation of composites

Short wool fibres were dried at 75 °C in an oven to reduce the moisture content and then mixed with other constituents, such as PP, MAPP, APP and talc. A twin screw extruder (LTE 26–40, Lab Tech Engineering Company Ltd., Thailand) was operated for melt blending of the dry-mixture. The compounding process was carried out using the screws (length L/diameter D = 32) co-rotating at a 170 rpm with a temperature profile of 172/175/175/175/175/175/175/175/178/179 °C from the hopper to the die across ten heating zones. As a final moulding process, a single-screw extruder (JWS 45/30 extruder, China) with a slit die (100 × 3.5 mm), was used to fabricate the continuous composite sheets at a processing temperature of 180 °C and a screw speed of 8 rpm. A pair of calendering rolls was in operation to obtain a good surface finish and uniform thickness of the extruded product.

2.3. Characterisation

2.3.1. Thermogravimetric analysis (TGA)

TGA-50 (Shimadzu, Japan) was utilised to record the weight loss of materials, namely fibres, polymer and the composites, under heating at a constant rate. About 7 mg of sample was heated till 700 °C at a linear heating rate of 10 °C/min and argon gas with a flow rate of 50 ml/min was maintained in the chamber to reduce any secondary reaction by volatile products from the sample.

2.3.2. Fourier transform infrared (FTIR) spectroscopy

In this research, spectroscopy analysis of wool-PP composite's char formed after combustion tests was conducted by an IR-Prestige-21 spectrometer (Shimadzu, Japan) with a Pike Miracle Attenuated Total Reflectance compression clamp. Infrared spectra of the sample were recorded in the range of 4500–450 cm^{-1} with an optical resolution of 4 cm^{-1}. Data acquisition and analysis were achieved by standard software, Omnic ESP version 7.1.

2.3.3. Environmental scanning electron microscopy

Micrographs of char residues and fractured cross-sections of composites after cone calorimeter and tensile tests, respectively, were obtained by an environmental scanning electron microscope (ESEM - FEI Quanta 200F, Houston, US). Moreover, energy dispersive X-ray spectroscopy, which is a chemical microanalysis technique commonly used in conjunction with a scanning electron microscope, was also utilised to detect chemical compositions of samples during the ESEM