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Sustainable Enhancement of the Mechanical and Flammability Performances of Keratinous Feather-PP Composites: The Effects of Processing Temperature and Solvent Choice

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Abstract: This paper discusses two major issues: (i) understanding the influence of the solvent used for fibre processing to obtain flame-retardant chicken feathers, and (ii) establishing the importance of the fibre–matrix blending temperature before composite manufacturing. Three temperature profiles for the extrusion die have been taken into consideration: a low-temperature profile (40 °C) (LT-FRCF), a medium-temperature profile (120 °C) (MT-FRCF), and a high-temperature profile (200 °C) (HT-FRCF). Due to better mixing, the tensile strengths for the medium- and high-temperature profile specimens improved by approximately 44% and 83%, respectively. The cone calorimeter results for the samples with water as the solvent for the feather modification showed a 22% reduction in the peak heat release rate compared to those of the samples with ethanol as the fibre treatment solvent, inferring the importance of the solvent used for the processing and making the process more sustainable with a lower water footprint. The research findings provide clear evidence of how the mixing (extrusion) temperature and choice of solvent for modifying chicken feather fibres affect the composites' mechanical and flame-retardant properties. These insights contribute to our understanding of how keratinous fibres can effectively serve as flame-retardant reinforcements in polymeric composites.

Keywords: fibre reinforced composite; processing parameters; flame/fire retardancy

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1. Introduction

Natural-fibre-reinforced composites (NFRCs) have garnered increasing attention as sustainable alternatives to traditional synthetic fibre-reinforced composites, owing to their renewable and biodegradable fibres [1,2]. In recent years, the quest for sustainable and eco-friendly materials has driven researchers to explore innovative solutions that merge natural resources with advanced composites technology. The promotion of circular economies necessitates the repurposing or reuse of various industrial wastes. For instance, the waste resulting from chicken processing contributes to many landfills, which requires costly waste management systems. Therefore, it is desirable to reuse chicken feathers in composites manufacturing whenever possible, in order to offset the related energy and environmental impacts. Until now, chicken feathers have been repurposed to make fibreboards and alternatives for producing eco-friendly motar and several other products [3–5].

Chicken feather fibres offer biodegradability and potential carbon neutrality (depending on the processing methods). They also have the potential to enhance the mechanical properties and improve the flame-stalling abilities of composites [6–8]. Due to their moderate aspect ratios and partial adherence to polymeric matrices, chicken feather fibres, which exhibit both hydrophilic and hydrophobic qualities as a result of polar and non-polar proteins, can be used as reinforcements [6,9,10]. A porous honeycomb structure [11] adds to their benefit, as they help in promoting excellent reinforcement to polymeric composites and also act as a medium for transferring materials [12,13].

Previous research work has led to the understanding that, in order to promote keratinous-fibre-reinforced composites, it is imperative to find techniques to improve the fibre/matrix bonding. The interfacial bonding between natural fibres and the matrix is strengthened as a result of surface changes in the fibres, which improves the eventual mechanical characteristics [6,14]. The surface morphology of the fibre, the chemical structure, and the matrix polarity primarily determine the mechanical/chemical bonding at the interface [15–17]. Processing techniques that generate heat from solvents enable keratinous fibre modification as a result of the successive loading of materials, which causes chemical and/or structural changes, thereby improving the resulting composite's properties [18].

Apart from the fibre, the matrix plays an important role in acting as a support for better composites manufacturing. The mechanical properties of polypropylene can be controlled or altered to suit specific applications by adjusting the processing temperatures [19]. The processing temperature during the fabrication of NFRCs plays a crucial role in determining the final material's performance and characteristics. At elevated temperatures, the thermoplastic matrix, such as polypropylene (PP), exhibits an increased flow and enhanced wetting of the feather fibres, leading to improved interfacial adhesion and mechanical properties of the resulting composites [20]. However, excessively high temperatures may also cause the thermal degradation of the natural fibres, compromising their inherent strength and resulting in a reduced overall performance of the composite. Striking the right balance in the processing temperature is imperative to achieving the necessary dispersion and alignment of the natural fibres within the PP matrix, thereby enhancing the composite's mechanical properties while retaining the inherent characteristics of the natural fibre reinforcement. A thorough understanding of the influence of the processing temperature on NFRCs is essential to harnessing the full potential of these composites, offering a green solution for various industrial applications that demand both performance and environmental responsibility. The effects of the processing temperatures and solvents used to treat chicken feathers to create flame-retardant polymeric composites are currently unknown and warrant additional investigation. In this regard, it is crucial to comprehend whether the extrusion temperatures affect the flammability and mechanical properties of polypropylene composites reinforced with treated keratinous feather fibres to create acceptable and sustainable composites.

The research comprises two aspects: (i) understanding the influence of the solvent used for the fibre processing to obtain flame-retardant chicken feathers (FRCF), and (ii) the fibre–matrix blending temperature before composites manufacturing. The impacts of the various solvents used and the processing temperature profiles on the CF are characterised using scanning electron microscopy, mechanical tests, and cone calorimeter tests. The flammability and thermal properties of the flame-retardant chicken feathers and polypropylene composites are evaluated via vertical burning (UL-94) and cone calorimeter tests. These tests provide essential insights into how the materials respond to fire exposure, helping researchers to assess their fire safety and potential applications. The findings could be useful in determining the desirable processing parameters for obtaining the necessary properties of composite materials containing feather fibre reinforcements.

2. Materials and Methods

2.1. Materials

The raw chicken feathers received from the New Zealand company Wallace Group Ltd. Melamine and phosphoric acid (PA, concentration: 85 weight percent in water) were purchased from Sigma-Aldrich. Polypropylene (PP, K515, MFI: 19) and Maleic anhydride grafted PP (MA-g-PP, Licocene PP MA 6452) were bought from Clariant NZ Ltd. A flame retardant of the injection moulding grade (Exolit AP 766, supplied by Clariant NZ Ltd., Auckland, New Zealand) was used.

2.1.1. Chemical Treatment of Chicken Feather

The flame-retardant chicken feather preparation followed a similar procedure as outlined by Mishra et al. in an earlier paper [2]. In this research, the solvents used for treatment were either ethanol or water, in order to study their impacts on the composites' properties. The PA-treated CFs were combined by weight proportion with reactive amines (melamine), and then dried at 70 °C until a consistent weight was achieved. The ammonium polyphosphate (APP) treatment of the chicken feathers was performed in the specified ratios (Table 1) to obtain flame-retardant chicken feathers (FRCFs).

Table 1. Sample formulation in wt.%.

Sample	Solvent	PP (wt.%)	MA-g-PP (wt.%)	FRCF (wt.%)	FRCF				
					PA (wt.%)	CF (wt.%)	Melamine (wt.%)	Solvent (ml)	APP (wt.%)
PP		100	–		–	–	–	–	–
E-FRCF/PP	Ethanol	57	3	40	27.5	32.87	35.50	100	4.13
W-FRCF/PP	Water	57	3	40	27.5	32.87	35.50	70	4.13

2.1.2. Preparation of Flame-Retardant Keratinous Fibre/PP Composites

A powder mixer was employed to mix the FRCFs, APP, maleic anhydride grafted polypropylene (MA-g-PP), and polypropylene. Two separate batches of flame-retardant chicken feathers were prepared based on whether they were ethanol treated or water treated.

A co-rotating LTE 26-40 extruder was utilized for the extrusion of the FRCF/PP composites. The extrusion process was carried out under three scenarios: a low temperature (LT) set at 40 °C, a medium temperature (MT) set at 120 °C, and a high temperature (HT) set at 200 °C (Table 2). The base material for the extrusion consisted of 40% FRCF, 57% PP, and 3% compatibliser (MA-g-PP), by weight, mixed in the powder mixer. The resulting melt blend was processed to form pellets, which were then compression moulded into test samples for further characterisation (Figure 1).

Table 2. Temperature zones for the extrusion process at 40 °C, 120 °C, and 200 °C.

	Die Temperature (°C)	Z9 (°C)	Z8 (°C)	Z7 (°C)	Z6 (°C)	Z5 (°C)	Z4 (°C)	Z3 (°C)	Z2 (°C)	Z1 (°C)
(LT-FRCF)	40	40	40	40	40	30	30	30	25	25
(MT-FRCF)	120	120	120	120	120	100	80	80	70	70
(HT-FRCF)	200	200	200	200	180	165	140	140	120	120

2.1.3. Material Characterisations

Flammability tests were conducted on the samples following the ASTM D 3801-10 standard, which is equivalent to the UL-94 standard. The samples were prepared and preconditioned according to the ASTM E1354-11 guidelines. The tests involved vertical burning and the results were reported based on the average values of five specimens, determining the ratings, such as V-0, V-1, V-2, or no rating (NR). Additionally, the flammability parameters were quantitatively analysed using a cone calorimeter (Fire Test Technology, East Grinstead, UK), following the ASTM E1354-11 standard.

To examine the morphology, the treated feathers and reinforced composites underwent observation and an elemental analysis using field emission environmental scanning electron microscopy (SEM Quanta200, FEI, Columbus, OH, USA).

The mechanical properties of the specimens were evaluated using an Instron universal testing machine (UTM 5567, Buckinghamshire, UK), adhering to the ASTM D 638 standard. To obtain reliable data for the tensile characteristics, at least five specimens were tested for each sample, and the average values were calculated.

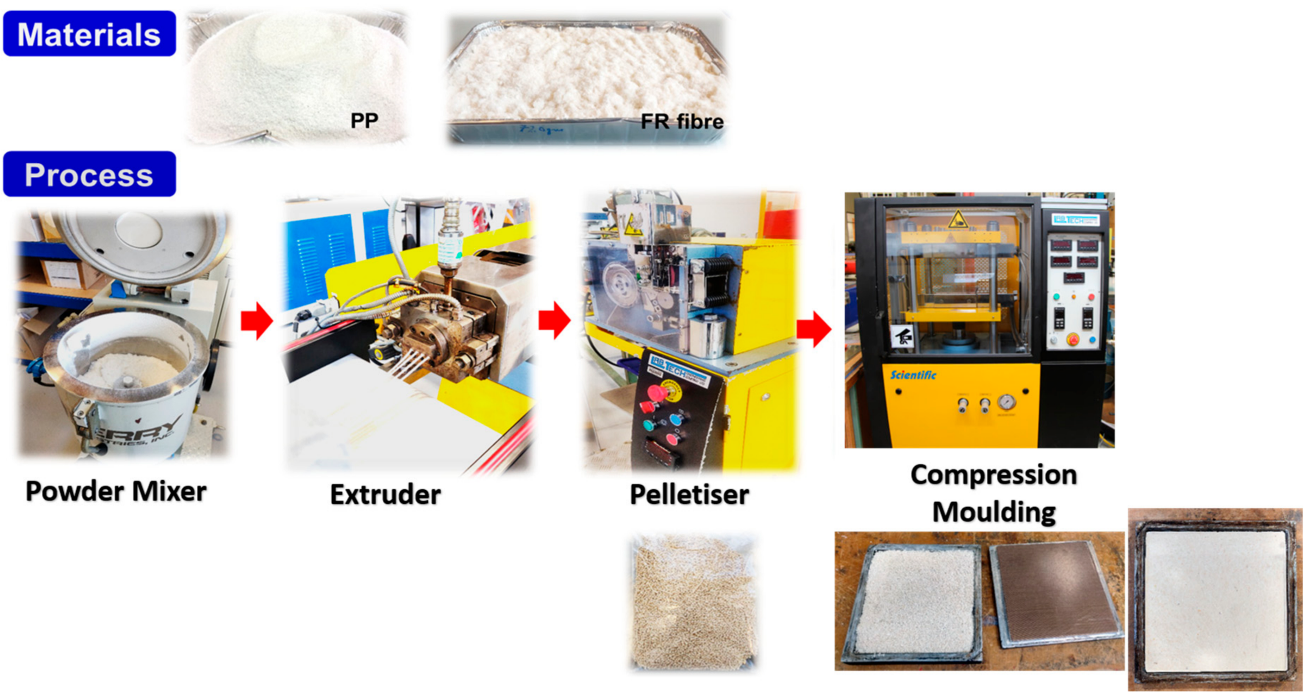


Figure 1. Pictorial representation of process followed for obtaining FRCF/PP composites.

3. Results

3.1. Fibre Modification Process

Phosphoric acid surface activation of the chicken feathers improved the acid dispersion across the composite material, leading to an improved matrix interaction [8]. The processing temperature offered an effective base for efficient, intumescent flame-retardant dispersion, preventing aggregation in some places, as seen for the ethanol-treated fibres. To understand the overall effects of the processing temperature on the manufacturing of the composites, the treated fibres under different extrusion die temperatures were assessed, followed by fire and mechanical characterisations. Figure 2 provides a concise description of the experimental methodology, as well as the conclusions that can be drawn.

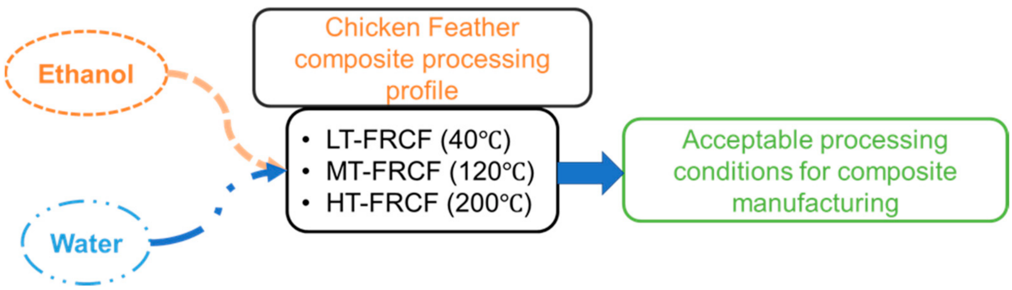


Figure 2. Schematics for fabrication of flame-retardant chicken feather/polypropylene composites.

3.2. Differential Scanning Calorimetry (DSC)

The endothermic and exothermic peaks and magnitudes indicate the thermal phase transformations of the composites. DSC investigated the phase behaviour of the heat flow for the chicken feathers to comprehend its impact on their flammability and mechanical properties. The data acquired (Figure 3) show that the chicken feather fractions underwent a broad change when heated from 25 °C to 250 °C: in the 40 °C–150 °C range, a broader transition was observed, with similar observations made by Tesfaye et al. [21]. No strong peak was seen in any of the feather fractions, which might be attributed to the decrease in crystallinity. Considering the polypropylene DSC, we observed a sharp transition between

150 °C and 160 °C, which could be tallied with the observations made by Baltes et al. [22]. From these observed changes in the materials, we may postulate the various processing scenarios of 40 °C, 120 °C, or 200 °C as die temperatures and analyse their subsequent impacts for a better understanding of the influence of the processing temperature on fibre–polypropylene composites.

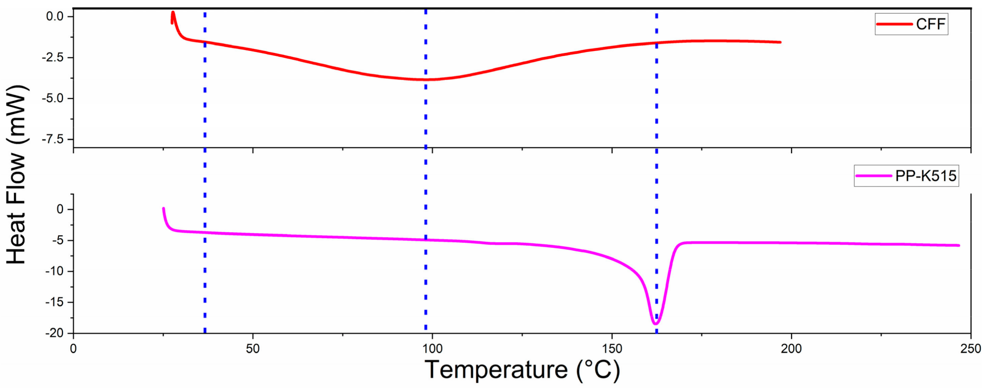


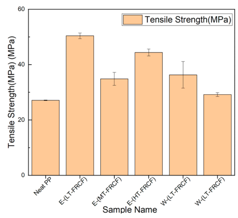
Figure 3. DSC curves for chicken feather and polypropylene.

3.3. Mechanical Properties

The different processing temperatures had a definite impact on the overall output, which is evident from the tensile strengths of the composites, as shown in Table 3. A tensile strength of 50.4 MPa, which is about 108% higher when compared with that of neat PP, was observed for the low-temperature processing profile. A similar trend was also noticed in the experiments performed by Mai et al. [23]. This increase may be attributed to the fibres not being shredded with the impregnation of chemicals during the extrusion process and the fibre property being retained without much damage. Interestingly, even though the extrusion temperature increased, the tensile strengths for the medium- and high-temperature profiles for the ethanol-treated fibre-reinforced composites improved by about 44% and 83%, respectively, compared to that of neat PP, probably due to better mixing with the matrix, improving the overall interfacial bonding.

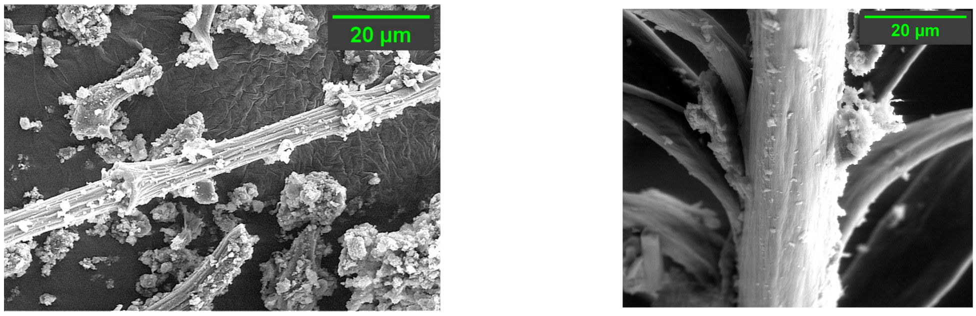
Table 3. Tensile strengths of chicken feather polypropylene composites with different solvents.

Sample	Solvent	Die Temperature (°C)	Average Tensile Strength (MPa)
E-(LT-FRCF)	Ethanol	40	50.41
E-(MT-FRCF)	Ethanol	120	34.87
E-(HT-FRCF)	Ethanol	200	44.39
W-(LT-FRCF)	Water	40	36.3
W-(HT-FRCF)	Water	200	29.18



For the LT-FRCF-PP composite, the tensile strength achieved was 30% lower when the solvent for the fibre treatment was changed from ethanol to water. All the other manufacturing conditions for these samples remained the same, suggesting the influence of the solvent used for modifying the chicken feathers. The observed decrement in the overall tensile strength of approximately 14% for both the solvent treatments, from the low-temperature to the high-temperature profile, indicates a consistent and significant reduction in the material's ability to withstand tension [6].

This reduction in tensile strength can be linked to several factors. First, at higher temperatures, materials generally experience an increased molecular mobility, leading to an enhanced chain mobility and segmental motion within the polymer structure. This increased mobility can result in weakened intermolecular interactions and reduced mechanical properties, including tensile strength. Additionally, the solvent treatments may have altered the material's molecular structure or caused plasticisation effects. Solvents can potentially disrupt the intermolecular forces and weaken the polymer matrix, thereby reducing the tensile strength. The observed decreases in the tensile strengths for both solvent treatments suggest that they may have had similar effects on the material's properties, as shown Figure 4.



(**a**) (**b**)

Figure 4. Fibre treated in the presence of (**a**) ethanol as solvent and (**b**) water as solvent.

It is worth noting that the specific behaviour of a material under different conditions can vary depending on the nature of the polymer and the solvent used. The observed 14% reduction in the tensile strength provides a quantitative measure of the material's performance in the given temperature range, but a further analysis and characterisation would be required to understand the underlying mechanisms in detail.

3.4. Reaction to Small Flame Test

The UL-94 tests were used for evaluating the flammability performances of the neat PP, HT-FRCF/PP, MT-FRCF/PP, and LT-FRCF/PP under burning in a vertical orientation. The tests were conducted according to the ASTM D3801 standard, where a flame was applied directly to the vertically placed samples.

When the flame was applied to the neat PP and ethanol-treated chicken feather samples, the flames eventually reached the holding clamp, with drips causing the cotton to ignite. As a result, the neat PP and ethanol-treated chicken feather samples received an apparent no rating (NR), indicating their poor flammability performance. In contrast, for the samples treated with water as a solvent, a layer of char developed at the bottom end of the specimens. This char layer acted as a barrier, preventing the flame from spreading upward. However, over time, the char layer dropped off, separating the fire's origin from the specimen. The partially burned W-HT-FRCF/PP composite exhibited continuous dripping after the second flame application. When the flames reached the holding clamp and the cotton was set ablaze by the drips, they appeared similar to those observed during the burning of the neat PP. This suggested that the intumescent char barrier formed by the composite was insufficient.

Despite the fact that there was some char formation around the margins of the composite, it proved to be inadequate in preventing the flames from reaching the clamp and preventing the continuous burning of the sample.

The treated FRCF/PP ignited while attempting to create a solid char to aid intumescence, which it failed to do. Though an apparent no rating was obtained for the UL-94 test, the observations indicated that the water-treated chicken feather composites exhibited a better flame retardancy compared to the neat PP and ethanol-treated samples. However, the char formation and barrier provided by the composites were not fully effective in preventing continuous burning, particularly when subjected to prolonged exposure to the flames. Additionally, uneven levels of surface carbonisation and poor heat source shielding could result in areas with insufficient levels of fire suppression, which made it impossible to stop the flames from penetrating the material.

3.5. Cone Calorimeter Tests

To better understand the low, medium, and high processing profiles' influence on the flammability aspects of the resulting composites, a cone calorimeter was used to evaluate the forced flame reactions of the PP and PP composites with chicken feathers. The keratinous natural filler (CF) in the composite samples made the material somewhat hygroscopic [24]. The amount of moisture trapped in a hygroscopic sample has a significant effect on the rate of heat transfer. This was evident from the heat liberation capacities of the PP, and PP composites using fire reaction parameters (Table 4).

The cone calorimeter results provided some interesting insights into the flammability of the PP composites in the presence of chicken feather fibres treated with different solvents, i.e., ethanol or water. The samples with water as the solvent for the CFF modification into FRCF showed a 22% reduction in the peak heat release rate (PHRR) compared to that of the samples with ethanol as the fibre treatment solvent. This may have been due to a better bonding of the modified CFF and PP. It could also be reasoned to be due to the surface tension of water compared to ethanol, which helped to improve the wetting of the fibres with the treatment method, as seen in Figure 4. The idea of a better impregnation of flame-retardant additives onto a fibre medium with a porous honeycomb structure in the presence of a solvent does help to add reason to our findings [25]. Hence, the improved interaction of the constituents under water treatment was a probable cause that influenced the heat release rates (Table 4).

Correlating the acquired data with theoretical analogues was essential to supporting our conclusions further. According to Equations (1)–(3), the THR is proportional to the combustion efficiency (χ), heat of the combustion of the volatiles (h_c^0), specimen mass (m_0), and char yield (μ) [26,27].

$$EHC \propto \chi \cdot h_c^0 \tag{1}$$

$$HRR \propto \chi \cdot (1 - \mu) \cdot h_c^0 \tag{2}$$

$$THR \propto \chi \cdot (1 - \mu) \cdot h_c^0 \cdot m_0 \tag{3}$$

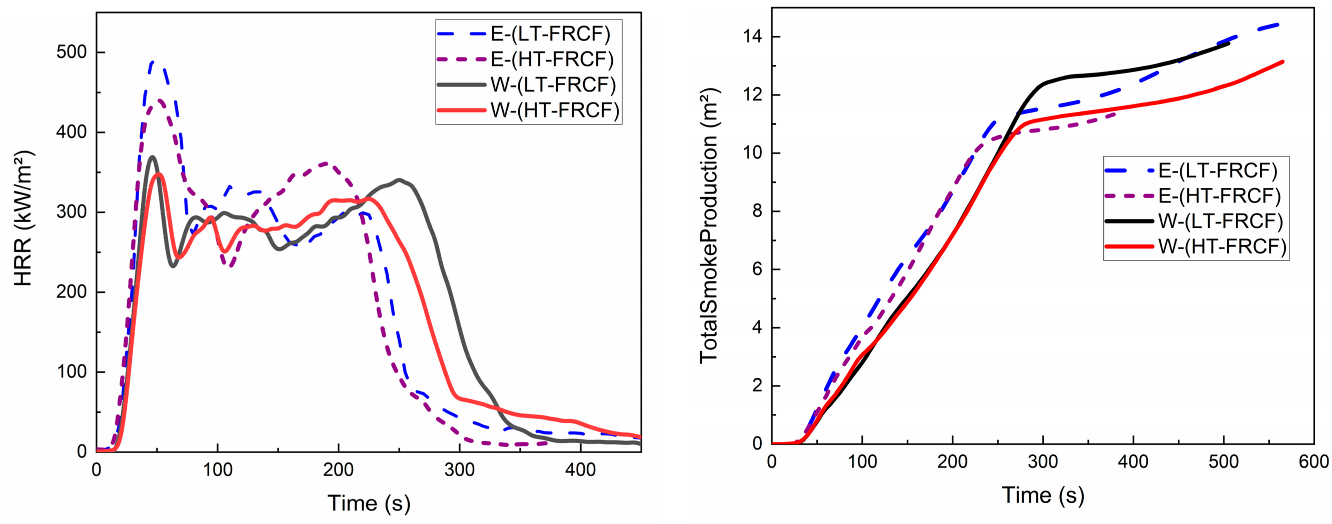
From the data in Table 4, it is evident that the sample with ethanol as the solvent had a higher mass loss rate as compared to water, which helps us to understand the suppressed peaks in the HRR curves of the samples. The decreases in the combustion efficiency are what account for the reductions in the EHC, as shown in Figure 5, for the ethanol-treated HT-FRCF/PP and water-treated HT-FRCFF/PP when compared to the PP (41.3% and 19.3%, respectively). The overall heat of the combustion was also impacted by the fuel dilution. A reduced combustion efficiency resulted in incomplete combustion, which raised the CO yield and smoke output [28]. The total smoke production (TSP) was 1.5 and 1.8 times higher for the ethanol-treated and water-treated HT-FRCF/PP, respectively, compared to that for the neat PP.

Based on the provided information, the water-treated HT-FRCFF/PP composite demonstrated a 27% reduction in fire growth rate (FGR) compared to the ethanol-treated HT-FRCF/PP composite. A lower FGR indicated slower fire propagation and a longer time to reach the peak heat release rate (PHRR), which is beneficial in terms of commercial applicability and safety, allowing more time for evacuation.

Table 4. Detailed cone calorimeter test results of PP, HT-FRCF/PP, MT-FRCF/PP, and LT-FRCF/PP.

Sample	Tig (s)	PHRR (kW/m^2)	TPHRR (s)	FGR (kW/m^{2}s)	THR (MJ/m^2)	EHC (MJ/kg)	MLR (g/m^{2}s)	MARHE (kW/m^2)	SPR (m^2/s)	TSP (m^2)	Av-COY (10^2 kg·kg^{-1})	FRI	TOC
PP	34.25 ± 2.22	1106.69 ± 148.11	126.25 ± 11.09	8.76	83.59	40.46	4.83	423.215	0.0153	6.56	0.025	1	48.66
E-(LT-FRCF)	16.5 ± 1.08	483.07 ± 45.78	47.5 ± 8.09	10.16989	81.18	24.33	7.81	285.71	0.0298	12.7	0.031	0.886	52.71
E-(MT-FRCF)	21 ± 1.78	500.94 ± 31.78	50 ± 7.09	10.0188	77.13	19.24	10.73	306.89	0.0355	12.6	0.0259	0.947	48.98
E-(HT-FRCF)	12 ± 1.69	456.66 ± 4.54	52.5 ± 13.23	8.698286	69.7380	23.71	10.12	306.21	0.0327	10.08	0.015	1.207	41.66
W-(LT-FRCF)	16 ± 2.74	375.08 ± 31.78	45 ± 12.09	8.335111	87.3	23.14	8.74	265.25	0.0288	13.07	0.033	1.006	52.55
W-(HT-FRCF)	15 ± 1.52	348.92 ± 20.85	55 ± 16.07	6.344	72.25	32.62	8.47	256.6	0.0258	12.2	0.0342	1.597	49.6

Note: E and W stand for Ethanol and Water, respectively for the sample names; Tig: time to ignition; PHRR: peak heat release rate; TPHRR: time to peak heat release rate; FGR: fire growth rate; THR: total heat release; EHC: effective heat of combustion; MLR: mass loss rate; MARHE: maximum average rate of heat emission; SPR: smoke production rate; TSP: total smoke production; Av-COY: Average Carbon Monoxide yield; FRI: fire retardancy index; and TOC: Total oxygen consumption.



(**a**) (**b**)

Figure 5. Cone calorimeter data of the various samples: (**a**) heat release rate of various samples, (**b**) total smoke production.

The FGR is calculated using the equation:

$$FGR = PHRR/T_{PHRR} \tag{4}$$

where T_{PHRR} represents the time to reach the PHRR. By comparing the FGR values between the different treatments, it is possible to assess the fire hazard status and evaluate the effectiveness of the flame-retardant treatments. Furthermore, another measure that can be used to assess the flame retardancy of the composites is the flame retardancy index (FRI). This is determined as the product of the total heat release and the rate of the fire growth of the polymer and its composites. A flame retardancy index value greater than 1 suggests an enhancement in flame retardancy.

In the case of the water-treated chicken feather composites, both samples showed FRI values greater than 1, indicating an improved flame retardancy compared to the untreated composite. This enhancement in flame retardancy is attributed to the water treatment, which enhanced the flame retardancy capabilities of the composite by treating the chicken feathers with melamine phosphate in the presence of water as a solvent. Moreover, the water-treated HT-FRCFF/PP composite exhibited a 24.4% higher FRI compared to the ethanol-treated HT-FRCFF/PP composite, indicating that water is a more effective solvent for the treatment of melamine phosphate in chicken feathers to improve their flame retardancy. Overall, these findings suggest that the water treatment of the chicken feather composites led to an improved flame retardancy, as evidenced by a reduction in the fire growth rate and an increase in the flame retardancy index compared to those for the ethanol treatment.

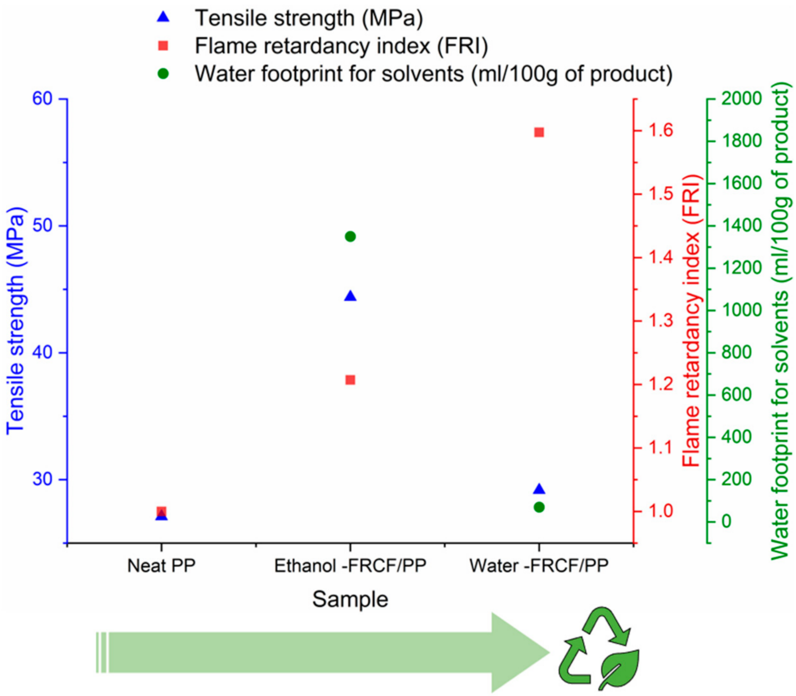
3.6. Water Footprint

The water footprint of composite manufacturing is an important aspect to consider when assessing the overall sustainability of the process [29]. In this discussion, we will focus on the preprocessing segment and specifically examine the use of water as a solvent.

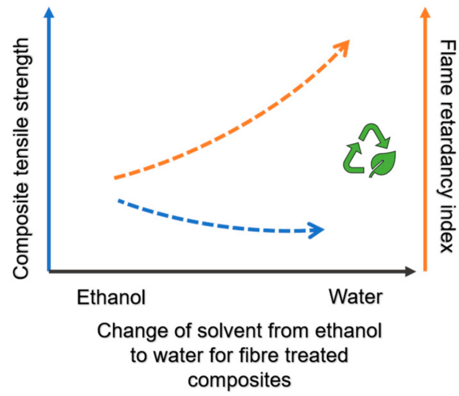
In composites manufacturing, the preprocessing stage involves various activities, such as preparing the materials and mixing and impregnating the reinforcing fibres with a polymer matrix. During the preparation of these materials, the use of ethanol as a solvent for chicken feather fibre treatment has shown improvements in the mechanical performance of the composite [6]. However, it is worth noting that using water as a solvent can be advantageous for improving the flame retardancy of polymeric composites, in terms of reducing the PHRR and obtaining a better flame retardancy index.

According to the information obtained from the literature, 10–17 L of water is used for every litre of ethanol produced [30]. This indicates the portion of the water footprint associated with the preprocessing segment of the manufacturing process. By using water instead of ethanol, the amount of water required is significantly reduced, saving approximately 10–17 times the amount of water needed. Additionally, the use of water as a solvent contributes to a ~22% reduction in the peak heat release rate of feather-reinforced PP composites compared to that of samples with ethanol as the fibre treatment solvent. Flame retardancy is an important characteristic for ensuring the safety and performance of composite materials, particularly in applications where fire hazards may be present.

By choosing water as a solvent during the preprocessing stage of composites manufacturing, the process becomes more sustainable and promising. The significant reduction in water usage and the enhancement of the flame retardancy are positive outcomes that contribute to the overall sustainability of the composites manufacturing process (Figure 6).



(a)



(b)

Figure 6. (**a**) Observed value of tensile strength, flame retardancy index, and water footprint of the solvent used for composites manufacturing; (**b**) schematic representations of solvent effects on the properties of fibre-reinforced composites.

It is important to note that specific manufacturing processes and materials can vary, and additional factors may influence the overall sustainability of composites manufacturing beyond the water footprint alone. Nonetheless, reducing water usage while maintaining or improving important properties, such as flame retardancy, is a step towards a more sustainable approach to the manufacturing of composite products.

4. Conclusions

In conclusion, this research showed new possibilities for using chicken feathers to produce flame-retardant polymeric composites, leading to reduced industrial waste and a better utilisation of renewable resources. This study also provided some insights into the effects of extrusion processing temperatures on the flammability and mechanical properties of polypropylene composites reinforced with treated keratinous feather fibres. The findings suggested that the selection of the solvent used for the fibre processing plays a crucial role in achieving a better tensile strength, a lower PHRR, and an improved overall sustainability of the composite process. With water used as the solvent for the feather modification into FRCF, the creation of tenacious polyaromatic intumescent char boosted the fuel retention, enhanced the flame retardancy of the water-treated FRCF, and produced effective protective layer effects. With flame retardancy and sustainable product manufacturing as driving forces, the use of ethanol as a solvent has been found to not be very suitable for processing chicken feather fibre-reinforced composites.

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