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The Reuse of Municipal Solid Waste Fly Ash as Flame Retardant Filler: A Preliminary Study

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Abstract: The growing increase in the production of municipal solid waste incinerator (MSWI) ashes has led to the research of new possibilities to reuse these by-products. This work aims to use MSW fly ash (FA) as a flame retardant filler. The FA was stabilized according to a simple stabilization process involving the mixing of only different ashes: bottom ash (BA), flue gas desulphurization (FGD) residues and coal fly ash (CFA). Stabilized FA, calcite and commercial flame retardants were compared as additives in an epoxy resin or polypropylene (PP) matrix. The self-extinguish performance of fillers was evaluated by fire resistance tests: the vertical burning test (UL94-V) and glow wire test (GWT) at 750 °C and 850 °C. A life cycle assessment (LCA) evaluation was also performed to estimate the reduction in environmental impact related to the production of the flame retardant with stabilized FA. The results show that this new filler is a promising alternative to traditional flame retardant. The ignition time of composites with calcite was lower than the corresponding sample with FA. From an environmental point of view, the replacement of calcite in an epoxy resin matrix or commercial flame retardant in a PP matrix with stabilized FA allows for a reduction in the impact of about 24.1% and 49.5%, respectively.

Keywords: flame retardant; stabilized FA; LCA; circular economy

1. Introduction

The combustion of municipal solid waste (MSW) in thermal power plants is recognized as a fundamental treatment in sustainable waste management systems. The main advantages of waste-to-energy (WtE) plants are a reduction in residual streams to landfilling, with the consequential saving of land, a reduction in pollutant emissions from landfills, the prevention of environmental impacts resulting from the use of fossil fuels and electricity production. WtE plants could contribute to the achievement of the SDGs targets of the Agenda 2030 with an increase of 27% of renewable resources and a reduction of about 40% of greenhouse gases (GHG) by 2030 compared to 1990 [1]. In 2015, the production of MSW in Europe was estimated to be about 255 million tons, of which 27% was treated by incineration, particularly in Germany, a country with the largest amount of waste incinerated (16 million tons) followed by France (about 12 million tons) and the UK (about 10 million tons). The number of WtE plants in Europe was 512, of which 121 was located in France, 98 in Germany and 52 in Italy. Currently, the largest electricity production from MSW is from Germany (5768 GWh) [2]. The disadvantages of the incineration treatment are the production of by-products such as fly ash (FA), bottom ash (BA) and air pollution control residues. More than 500 million tons of MSW incineration FA and 1.5 billion tons of BA are produced in the world every year [3]. The increase in landfill costs and lower availability of storage sites encourage the search for technologies and methods of BA and FA reuse.

FA contains a high quantity of soluble salts (NaCl, KCl) and leachable heavy metals such as Cd, Pb and Zn. FA is classified as a special dangerous waste. Therefore, pretreatments are necessary to reuse these ashes. Instead, BA is classified as a non-hazardous waste and, therefore, can be reused with minimal treatment [4]. In recent years, research has been extremely active in finding new possibilities to reuse each type of ash as a filler in different applications. The most widespread FA reuse field is building construction, as cement and concrete additives [5]. The literature reveals that FA can be used as an adsorbent of heavy metals [5], micropollutants [6] and as a material for CO_2 sequestration [7]. The reuse of FA shows several advantages, such as the use of waste as a secondary raw material for achieving circularity in anthropogenic material cycles, the preservation of natural resources and the reduction in waste landfilling [8].

It has been reported that the use of FA in polymer composites increases their thermal stability and minimizes the smoke generated during combustion [5,9].

There are different types of flame retardants (FRs)—more than 175—subdivided, mainly, into four groups: inorganic, halogenated organic (brominated and chlorinate), organophosphorus and nitrogen-based [10,11]. Flame retardants have different applications in construction, electrical and electronic devices, plastics or fabric materials and transportation [12]. In 2006, the European Flame Retardants Association (EFRA) estimated the production of flame retardant to be about 465 kt in Europe, of which 93 kt was phosphorus flame retardant (PFRs) and 46.5 kt was brominated flame retardant (BFRs) [13]. Organophosphate esters are widely used in different type of products, such as plastics, foams, textiles and building materials [14]. Their use is increasing due to the restriction for BFRs. Indeed, the disadvantages of many BFRs are their low biodegradability, persistence, accumulation and toxicity, not only for the environment but also for humans and animals [10]. There is a growing need to search for green products with fire resistance. Previous studies focused on the evaluation of environmental impacts attributable to flame retardants and commented on the importance of applying overarching methodologies such as a life cycle assessment (LCA) to orient a product of more sustainable materials and goods [10,15–17].

This paper aims to evaluate that stabilized FA is a promising alternative to traditional flame retardants from technical and environmental perspectives. To this goal, FA, BA, coal fly ash (CFA) and flue gas desulphurization (FGD) residues (all together named stabilized FA hereafter) undergo a stabilization process to enable their use as flame retardant fillers. Stabilized FA is tested at the laboratory scale and compared to the self-extinguishing performance of similar additives in use today. Then, we apply screening LCA to estimate the theoretical potential to decrease the environmental impacts related to the production of commercial flame retardants, achievable using stabilized FA.

2. Experimental Section

2.1. Materials and Methods

Stabilized FA, calcite ($CaCO_3$) and commercial flame retardant were used as additives. Epoxy resin and polypropylene (PP, Moplen 500N) were used as matrix. Scheme 1 reports a synthetic representation of the Section 2 and the materials involved in this study.

The stabilization of FA was performed according to [18]. FA and BA were derived from an MSW incinerator plant in Brescia (Italy). FGD residues and CFA were provided by the coal thermal power plant in Brescia. FA (59%), FGD (18%), CFA (14%) and BA (9%) were mixed with 200 mL of Milli-Q water (Millipore DirectQ-5 TM, Millipore S. A. S., 67120, Molsheim, France). The stabilization time considered was 11 months. The results of total X-ray fluorescence (TXRF) analysis of leaching test of raw materials and stabilized samples at 1, 2, 3 and 11 months were reported in [18]. In particular, a significantly reduction in heavy metals was obtained; Pb and Zn concentrations were reduced by two orders of magnitude in stabilized material compared to starting FA.
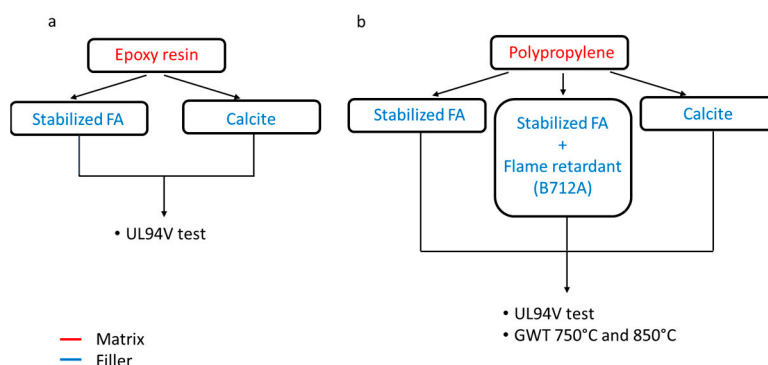
Scheme 1. Synthetic representation of the Section 2 and the materials involved in this study. Epoxy resin (**a**) and polypropylene (**b**) were used as matrix.

Calcite V40, with particle size lower than 60 μm, was bought from Sigma-Aldrich. Phoslite^{TM} (B712A), a commercial flame retardant, was provided by Italmatch Chemicals s.p.a.

Epoxy resin (E-227) was provided by Prochima. It was composed of two components: A (base) and B (hardener). The ratio used was 2:1, respectively.

A mixer of 95% silicone glue (SIL33) and 5% hardener (83Y) was used for sample mold construction.

Fire resistance tests, the vertical burning test (UL94-V) and glow wire test (GWT), were performed.

UL94-V is a direct method in which the flame is applied directly on the sample, placed in vertical position, while GWT is an indirect method. In this test, a coil was heated up at 750 °C or 850 °C and was put into contact with sample for a set time.

2.2. Epoxy Resin Matrix

2.2.1. Sample Preparation

A silicone mold was used to realize the samples with these dimensions: 125 mm height, 13 mm width and 6 mm thickness. At the beginning, a release wax was inserted into the five holes of the mold, to facilitate extraction of specimens. The samples were obtained by homogenously mixing the filler (calcite or stabilized FA) with matrix (epoxy resin) at difference percentages, reported in Table 1. The compound was inserted in the mold and kept at room temperature about 24 h to consolidate. Nine composites were realized and for each type five specimens were created. Figure 1 shows sample mold (a) and the sample after solidification (b).

Table 1. Sample composition: epoxy resin as matrix and stabilized fly ash (FA) or calcite ($CaCO_3$) as filler.

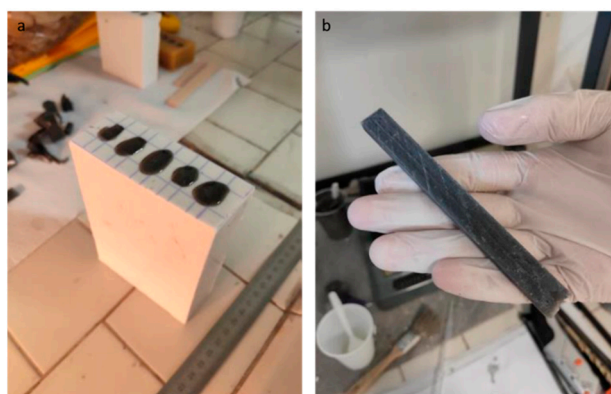| Composites	Epoxy Resin (%)	Stabilized FA (%)	$CaCO_3$ (%)
1	100	-	-
2	90	10	-
3	70	30	-
4	50	50	-
5	30	70	-
6	90	-	10
7	70	-	30
8	50	-	50
9	30	-	70

Figure 1. Sample mold (**a**) and sample after solidification (**b**). As example, sample three is reported (70% epoxy resin and 30% stabilized FA).

2.2.2. UL94-V Test

The specimens were placed in vertical position connected from the top with a clamp in such a way that the bottom of the sample was no more than 30 ± 1 cm from the work surface. Cotton wool with a thickness of 6 mm was placed below the sample. Cotton was dried for 24 h with silica gel before carrying out the experiment. A candle was used as heat source, instead of Bunsen burner. The experimental test was performed according to the following steps:

- The candle was positioned at 10 ± 1 mm from lower bound of the sample for at least 10 ± 0.5 s. After this time, the flame was removed and afterflame time (t_1) was evaluated;
- As soon as the sample stopped burning, the flame was placed again under the sample at the same distance as before for 10 ± 0.5 s;
- After this period, the flame was removed, and it was possible to calculate afterflame (t_2) and afterglow (t_3).

2.3. Polypropylene Matrix

2.3.1. Samples Preparation

The composites were realized at Rifra Masterbatches S.p.A. by mixing the PP Moplen HP500N with filler (stabilized FA, $CaCO_3$ or flame retardant B712A). The amounts of PP and filler used are reported in Table 2. After the mixing, the compound was dried for 3 h at 80 °C. Finally, the samples were printed by extrusion. The tests were carried out with twin-screw extruder, with thermal profile of 230 °C-230 °C-230 °C-230 °C (from the hopper towards the head), and screw rotation speed about 250 rpm.

Table 2. Composition of five composites (A, B, C, D and E) realized with PP Moplen HP500N as matrix, and stabilized fly ash (FA), $CaCO_3$ or flame retardant B712A as filler.

Composites	PP (%)	Stabilized FA (%)	$CaCO_3$ (%)	Flame Retardant (%)
A	70	30	-	-
B	94	6	-	-
C	70	-	30	-
D	94	-	6	-
E	74	22.50	-	3.50

For each composite, five specimens were performed.

2.3.2. GWT Test

The evaluation of the combustion resistance of samples with polypropylene matrix was carried out by GWT and UL 94 (considering only the V-2 resistance class) tests. In the GWT, the plate was fixed to a special trolley on sliding guides. which allowed contact

between the sample and heat source. For all samples, the exposure time was 30 min. The test was positive if all 5 specimens of the same composite typology were extinguished within 30 s, not completely consumed and not showing incandescent drops that burned the wadding placed under it.

2.4. Life Cycle Assessment (LCA) Modelling

LCA is a framework for overarching estimation of the environmental impacts associated with product-systems. The ISO standards 140440-14044 [19,20] set descriptive and quantitative LCA modelling techniques according to four phases, including (i) goal and scope definition, (ii) life cycle inventory (LCI), (iii) life cycle impact assessment (LCIA) and (iv) interpretation.

In this study, we applied LCA for screening purposes, i.e., to determine first-order estimates of the potential environmental benefits achievable employing stabilized FA as flame retardant. Specifically, we modelled inventories for epoxy resin, PP and calcite based on ecoinvent database [21]. For stabilized FA, we assumed the "zero burden" approach, i.e., environmental impacts related to life cycle phases prior to the generation of waste (i.e., fly ash and bottom ash in this study) were not included. Instead, material and energy inputs for stabilizing FA were gathered from direct measurements in the laboratory.

Further evaluation included a comparison with a selection of Br-based and P-based flame retardants. A lack of life cycle inventories on the production of flame retardants was pointed out previously in the literature [15], which would have been partially motivated by confidentiality issues. The dataset reported by [16] provides detailed inputs and outputs for a selection of BFRs and PFRs, and it was used here as the main reference for the modelling of the common production route for a set of flame retardants. The set of brominated and P-based flame retardants covered in [16] and modelled in this analysis included 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), bisphenol-A bis(diphenylphosphate (BDP), brominated polystyrene (BPS), decabromo diphenylether (decaBDE), melamine polyphosphate (MPP), resorcinol bis(diphenylphosphate) (RDP) and tetrabromobisphenol-A (TBBPA). The ReCiPe 2016 method was used for life cycle impact assessment quantification.

3. Results and Discussion

3.1. Epoxy Resin

It was not possible to measure the t_1, t_2 and t_3 for samples one, two, three and four. The combustion of the specimens occurred for all these samples, but the ignition of the cotton took place only for samples one and two. For sample five, t_1 and t_2 were evaluated, and for only one of the three specimens they were lower than 2 s.

In this case, only three specimens were realized due to mixing difficulties and the development of exothermic reactions which generated a rapid hardening of samples.

In the case of samples with $CaCO_3$ as the filler, the combustion of the specimens occurred for all these samples, but the ignition of the cotton took place only for composite six. It was possible to measure t_1 only for sample nine. In particular, the t_1 result was lower than 2 s only for two of the five specimens.

All the results obtained on the nine composites are reported in the Supplementary Materials Tables S1–S9.

Figure 2 shows a comparison of ignition times for all composites as a function of filler percentage. As expected, increasing the percentage of filler in the epoxy resin matrix increased the ignition time. This revealed that the filler reduced the ease of ignition of the substrate, so it acted as a flame retardant. This consideration agreed with Akanbi [22]. From Figure 2, it was also possible to observe that there was a discreet different in ignition times between two typologies of composites: the resin-stabilized fly ash and resin-CaCO$_3$. Figure 2 shows the effectiveness of stabilized ash as a flame retardant. The interpolating curve of the average values of these composites assumed a linear trend as the ashes increased. A greater increase was observed between composites three (30% of stabilized

ash) and four (50% of stabilized ash). Instead, an S-shaped trend was obtained by the $CaCO_3$ composites. The ignition time of sample with 70% $CaCO_3$ (7.1 s) was lower than the corresponding sample with stabilized ash (9.2 s).
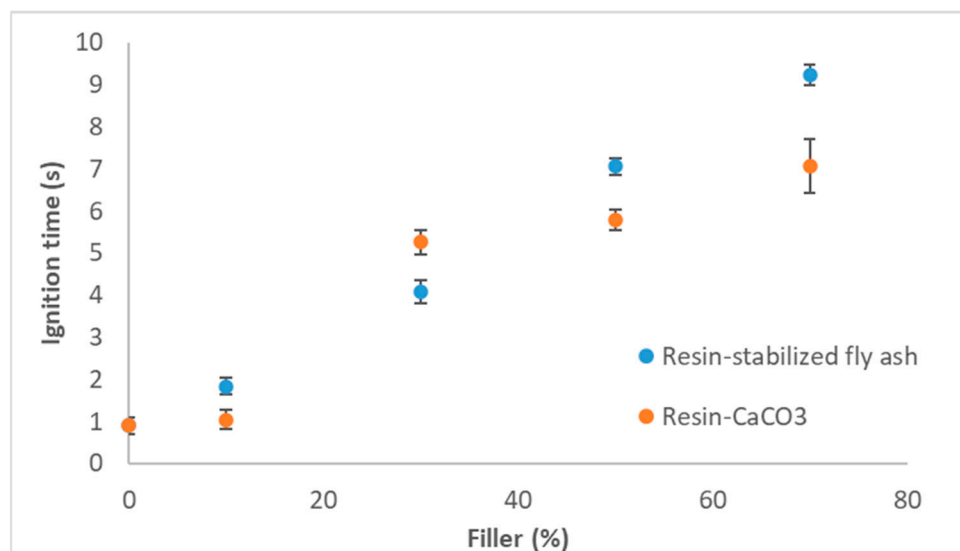

Figure 2. Comparison of ignition time of composites with filler (stabilized fly ash or $CaCO_3$) in different percentages.

3.2. Polypropylene

Table 3 reports the result of GWT at 750 °C of composites with 4 mm of thickness. All composites showed a positive result, except the composite A. In particular, only one of the five specimens did not pass the test. This could be attributed to the inhomogeneity of the specimens. It was interesting to note that a small percentage of the flame retardant (composite E) denoted a positive interaction with the tested material.

Table 3. GWT results at 750 °C of five composites (A, B, C, D and E).

Composites	Specimen Thickness	Results
A	4 mm	Negative
B	4 mm	Positive
C	4 mm	Positive
D	4 mm	Positive
E	4 mm	Positive

Table 4 reports the result of GWT at 850 °C. The composites with stabilized FA as the filler showed a similar behavior as composites with $CaCO_3$. Despite the negative results, it was sufficient to add a small percentage of flame retardant, so that the behavior of the material (also with a small thickness of 2 mm) improved. In fact, for composites E_2 mm, only one of five specimens did not pass the test.

Table 4. GWT results at 850 °C of three composites (A, C and E).

Composites	Specimen Thickness	Results
A	4 mm	Negative
C	4 mm	Negative
E	4 mm	Positive
E	2 mm	Negative

In Table 5 the results of UL94-V2 for three composites (A, C and E) are reported. The composites created with stabilized FA showed a similar behavior with that of $CaCO_3$.

Additionally, in this case, the addition of the flame retardant in small quantities improved the sample characteristic. The shutdown time of composite E_1.6 mm (9 s) was much lower than the time imposed by normative UL 94 V-2 (30 s).

Table 5. UL94-V2 results of three composites (A, C and E).

Composites	Specimen Thickness	Results
A	3.2 mm	Negative
C	3.2 mm	Negative
E	3.2 mm	Negative
E	1.6 mm	Positive

The results obtained for three fire resistance tests revealed that a small amount of commercial flame retardant increased the material's self-extinguishing performance. In fact, the literature reveals that in industrial production, a combination of different flame retardants is often used to improve fire resistance [23].

3.3. Screening LCA Results

Figure 3 shows the endpoint results for 1 kg epoxy resin, polypropylene, calcite and stabilized FA.
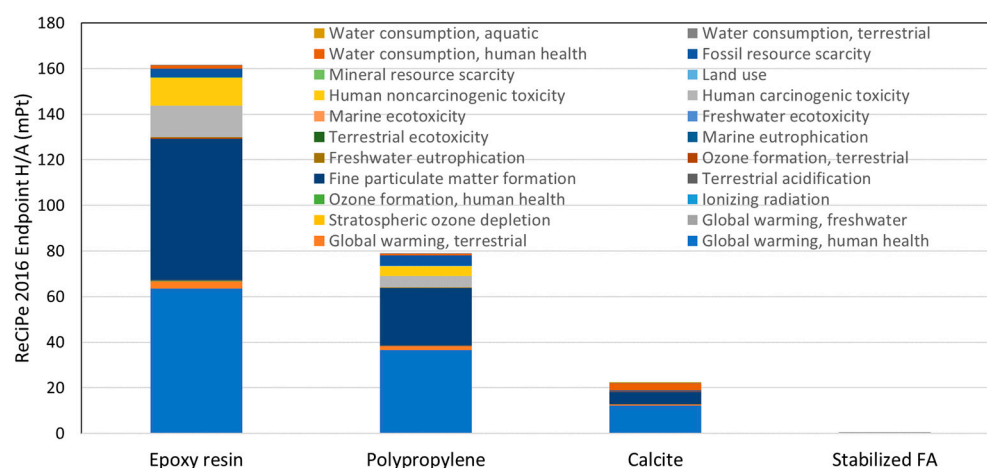

Figure 3. Endpoint results for 1 kg epoxy resin, polypropylene, calcite and stabilized fly ash (FA), according to the ReCiPe 2016 method.

In Figure 4, instead, the results for composites five and nine are reported. The endpoint results in the ReCiPe milli single point (mPt) were computed as the sum of per kg endpoint results, shown in Figure 3, multiplied by the relative content in composites five and nine (i.e., 30% epoxy resin, 70% stabilized FA or calcite, respectively). The replacement of calcite with the stabilized FA was estimated to reduce the overall environmental impact by about 24.1% (Figure 4). The contribution of the stabilized FA to the single point was negligible as a consequence of the zero-burden approach and the relatively minor resource inputs for the stabilization process.

The potential for environmental benefits was even greater when the stabilized FA was used as a substitute for BFRs or PFRs. Figure 5 shows the overall impact assessment results for a selection of commercial BFRs and PFRs, based on life cycle inventories described by [16], and further elaborated in this study. The histogram at the right-end side of Figure 5 plots the average results for the selected flame retardants, with a selection of impact categories averagely contributing for more than 1% of the total impact (cut-off). More specifically, these selected impact categories included fine particulate matter formation (39% of the endpoint single score), global warming potential (38%), human toxicity (14%), water consumption (6%) and fossil resource scarcity (2%). The average endpoint single

score was used in Figure 6 as a proxy for the B712A additive, which was added to composite E to improve the performance of that composite at the GWT analysis. B712A is known to be produced from hypophosphite salts with brominated fire-retardant compounds, the most efficient of which is melamine hydrobromide [24]. Due to confidentiality issues, the exact composition and commercial synthesis of B712A was out of our reach. However, the life cycle inventories detailed in [16] included brominated and P-based FRs and were here used as a basis for the quantification of probable environmental impacts. According to these assumptions and a substitution rate for stabilized FA to B712A in a PP matrix of 1:1, the use of stabilized FA would reduce the potential environmental impact of a traditional composite, composed of PP and B712A in the ratio 0.74:0.26 *w/w*, by about 49.5% (Figure 6).
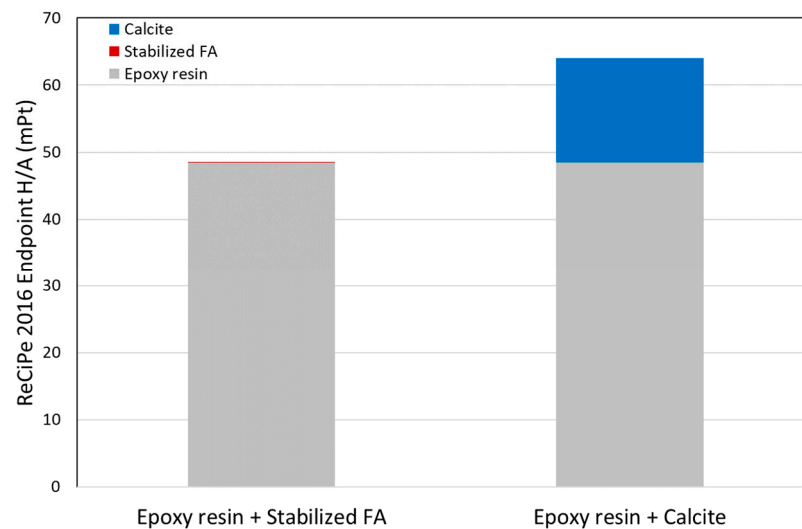

Figure 4. Endpoint results for 1 kg of composites five and nine (30% epoxy resin, 70% stabilized fly ash (FA) or calcite, respectively), according to the ReCiPe 2016 method.
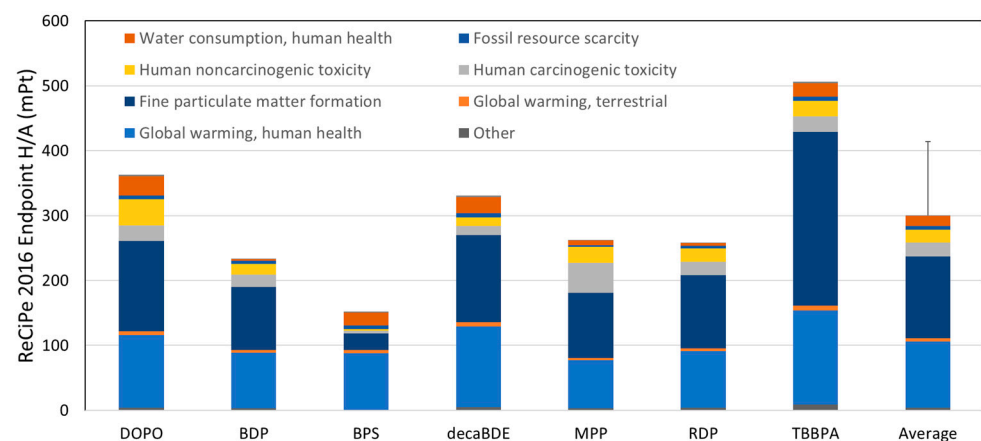

Figure 5. Endpoint results for 1 kg of selected brominated and P-based flame retardants according to the ReCiPe 2016 method based on life cycle inventories reported in (Jonkers et al., 2016) and further elaborated in this study. DOPO: 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide; BDP: bisphenol-A bis(diphenylphosphate; BPS: brominated polystyrene; decaBDE: decabromo diphenylether; MPP: melamine polyphosphate; RDP: resorcinol bis(diphenylphosphate); TBBPA: tetrabromobisphenol-A.
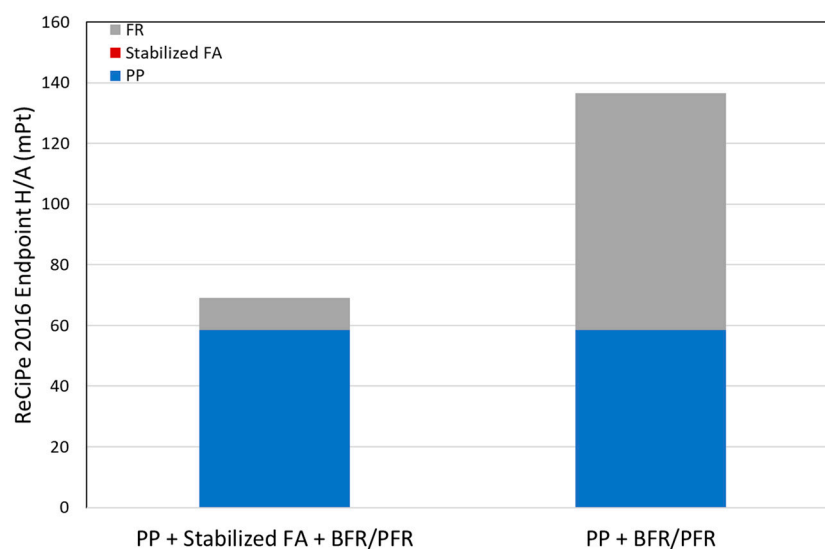
Figure 6. Endpoint results for 1 kg of composite E, according to the ReCiPe 2016 method. PP: polypropylene; FA: fly ash; BFR/PFR: brominated and P-based flame retardants average.

Although these screening LCA results were preliminary, our outcomes evidenced the importance of an environmental impact assessment for the incorporation of sustainability considerations into the production of flame retardants, which is an urgent need in this field [17,25–27]. The use of waste and residues as a source of material alternatives to virgin production is a key pillar in the setting of a regenerative and restorative economy, such as the circular economy. In the case of the stabilized FA, our results suggested that their employment as a flame retardant may determine a significant reduction in the overall environmental pressure compared to similar products in use today.

On top of this, it is worth clarifying that our screening LCA effort estimated the environmental impacts from a cradle-to-gate perspective. However, possible emissions of flame retardants embedded into products may also occur during use (e.g., volatilization) and after use (e.g., by the disposal of discarded products, by leaching from landfills, incineration or recycling). On the other hand, the avoided disposal of FA may credit its recycling for reducing the environmental impacts from common end-of-life management routes. Therefore, a complete, cradle-to-grave LCA approach is preferred for overarching evaluations. In this view, more research is recommended.

The use of stabilized FA as a flame retardant has advantages, not only from an environmental but also from an economical point of view. The new filler was derived from industrial by-products; therefore, it had almost no cost. The only costs were related to the electricity consumed during the powder mixing and the water used during the stabilization process. Contrarily, the phosphorous flame retardants have a high cost (B712A is about 17 EUR /kg), while the brominated flame retardant is about 5–6 EUR /kg. Furthermore, the reuse of ashes allows the saving of landfill disposal costs (about 170 EUR /ton).

4. Conclusions

In this work, we tested the use of stabilized FA as a possible flame retardant to use in an epoxy resin and PP matrix. The self-extinguishing performance was compared to that of traditional additives, namely, calcite and PFRs. Although none of the composites with resin were defined in a resistance class, it was possible to demonstrate the effectiveness of the stabilized FA as a flame retardant. There was a difference in ignition time between the resin-stabilized FA and resin-CaCO$_3$. The ignition time of the sample with 70% of stabilized FA (9.2 s) was higher than the corresponding sample with CaCO$_3$ (7.1 s). The development of more sustainable flame retardant fillers, in terms of the economic and environmental points of view, is arousing interest. This has led to investment in the reuse of ash derived from incinerator plants. This work revealed that the use of stabilized FA as a flame retardant

is a promising alternative to traditional flame retardant such as PFR or BFRs, whose toxicity has long been discussed [28,29]. It was shown that the stabilized FA had self-extinguish properties very similar to calcite. Moreover, the new filler, unlike calcite, can be used in synergy with other flame retardants to further increase a material's self-extinguishing performance. In addition, the screening LCA results demonstrated that stabilized FA may be a valid alternative to traditional flame retardants also from an environmental perspective. The potential for reducing the overall impacts on the environment was estimated at about 24.1% when stabilized FA was used as a replacement of calcite in an epoxy resin matrix, and about 49.5% in a PP matrix after a significant reduction in the brominated and P-based flame retardants contents.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/su14042038/s1, Table S1: vertical burning test (UL94-V) of composites 1 (100% epoxy resin–0% stabilized fly ash), Table S2: vertical burning test (UL94-V) of composites 2 (90% epoxy resin–10% stabilized fly ash), Table S3: vertical burning test (UL94-V) of composites 3 (70% epoxy resin–30% stabilized fly ash), Table S4: vertical burning test (UL94-V) of composites 4 (50% epoxy resin–50% stabilized fly ash), Table S5: vertical burning test (UL94-V) of composites 5 (30% epoxy resin–70% stabilized fly ash), Table S6: vertical burning test (UL94-V) of composites 6 (90% epoxy resin–10% $CaCO_3$), Table S7: vertical burning test (UL94-V) of composites 7 (70% epoxy resin–30% $CaCO_3$), Table S8: vertical burning test (UL94-V) of composites 8 (50% epoxy resin–50% $CaCO_3$), Table S9: vertical burning test (UL94-V) of composites 9 (30% epoxy resin–70% $CaCO_3$).

Author Contributions: Conceptualization, A.Z. and L.C.; methodology, A.Z. and L.C.; software, L.C.; validation, A.Z. and L.C.; formal analysis, A.Z.; investigation, A.Z. and L.C.; resources, A.Z.; data curation, L.C.; writing—original draft preparation, A.Z. and L.C.; writing—review and editing, A.Z. and L.C.; visualization, L.C.; supervision, A.Z.; project administration, A.Z. and L.C.; funding acquisition, A.Z. and L.C. All authors have read and agreed to the published version of the manuscript.

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