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# Evaluating the use of calcium hydrogen phosphate dihydrate (DCPD) as a mineral-based fire retardant for application in melamine-urea-formaldehyde (MUF)-bonded wood-based composite materials

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## Summary

Calcium hydrogen phosphate dihydrate (DCPD) was evaluated for its potential as a mineral fire retardant (FR) for application in melamine-urea-formaldehyde (MUF)-bonded wood composites. The efficacy as FR was studied in melamine-urea-formaldehyde (MUF)-bonded three-layer particleboard as a function of addition quantities of 10-, 20- and 30 wt%. Resistance to fire and mechanical properties were determined by measuring the self-extinguishing time after flame exposure and internal bond strength, respectively. Combustion behavior was examined on samples with 20 wt% DCPD addition by performing cone calorimetry experiments. The efficacy of DCPD was evaluated by determining the heat release, total heat release rate, smoke production and smoke production rate and compared to another promising mineral-based fire-retardant composition (FRC) based on hydroxyapatite (HA) with deliquescent salt and HA alone. The effect of FR on curing behavior of MUF in relation to mechanical properties was determined through viscosity measurements of MUF with 10 wt% addition of FR. The results confirmed the fire-retardant characteristics of DCPD in wood composites, albeit at higher application rates when compared to the FRC, however with no negative impact on resin curing time or mechanical strength. Based on the demonstrated compatibility in MUF, DCPD is considered a promising mineral extender of other FRs for application in UF-based wood composites.

**Keywords:** *calcium orthophosphate, fire retardant; hydrated mineral; mineral extender; resin curing; water vapour release*

## Introduction

The application of minerals in wood and wood-based materials has attracted increased attention. <sup>1-6</sup> Among the various advantages of the application of mineral additives in wood-based

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3 materials, such as the potential cost reduction, the applications as a fire retardant (FR) is  
4 considered one of the most promising fields. Recent research on the incorporation of minerals  
5 in wood highlighted their potential for application as fire retardants (FRs).<sup>3,7,8</sup> The approach  
6 discussed in those works utilizes the technology of mineral precipitation from different salt  
7 solutions with the goal of modifying the wood structure by incorporating minerals directly in  
8 the cell wall. This approach allows for considerable amounts of minerals to be precipitated in  
9 the wood structure with a lumen filling ratio close to 50% (ratio of mineral volume to pore  
10 volume) <sup>8</sup>, however requires an impregnation step in order to achieve efficient penetration of  
11 the wood structure. While this approach is suitable for modification of solid wood structures,  
12 the technology is considered less appropriate for applications in composite structures, which  
13 includes many of the engineered wood-based composites. The incorporation of FR in the  
14 composite formulation as a functional additive is considered to be the preferred method in the  
15 manufacture of composite materials. These materials are usually manufactured from several  
16 components in a single process, in which individual components are mixed and then bonded  
17 together under the influence of temperature to form the final product. The direct incorporation  
18 of mineral-based FRs by mixing with the matrix during manufacturing is more suitable in  
19 comparison to a post-impregnation step.

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22 The use of minerals as FR in various types of polymer-based composite materials, including  
23 wood- and cellulose fiber-based reinforced composites is well known.<sup>9-11</sup> The use of mineral  
24 additives in engineered wood-based composites products, a special group of composites  
25 manufactured by binding of wood strands, particles, fibers, or veneers and often using a  
26 thermosetting adhesive <sup>12,13</sup>, is less studied.<sup>14-16</sup> Traditionally, mineral additives are not  
27 utilized in the manufacture of such products due to the already competitive costs of the raw  
28 wood-based materials.<sup>17</sup>

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31 Recent studies demonstrated the feasibility of the incorporation of mineral-based additives in  
32 selected engineered wood-based composites.<sup>14-16</sup> The results of these studies demonstrated  
33 that calcium carbonate-based mineral additives can be incorporated in existing products, such  
34 as medium density fiberboard (MDF) or particleboard, without substantially affecting the  
35 material properties and potentially decreasing production costs. Furthermore, the industrial  
36 feasibility of this approach has been demonstrated in fiberboard products.<sup>18</sup> A promising  
37 mineral-based fire retardant composition (FRC), consisting of a mineral carrier material and  
38 deliquescent salt for application in particle-based wood composites has been further  
39 evaluated.<sup>19</sup> The authors demonstrated the efficacy of the mineral-based FRC as a fire  
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3 extinguisher and that the FRC can be easily incorporated into the structure of a particle-based  
4 wood material.

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6 Building on the promising results from the application of calcium carbonate and the mineral-  
7 based FRC in wood-based products,<sup>15,16,18,19</sup> this study investigates the use of another  
8 potential mineral for application in wood panels. Calcium hydrogen phosphate dihydrate  
9 (DCPD), a hydrated mineral, is proposed as a functional mineral additive for application in  
10 wood-based composites, which is expected to exhibit fire retardant properties similar to other  
11 non-halogenated inorganic phosphorous compounds, such as ammonium polyphosphate  
12 (APP).<sup>20–22</sup> In general, such inorganic phosphorous flame retardants are known to act  
13 primarily in the solid phase of burning materials, in which the formed polyphosphates create a  
14 char layer that can further intumesce to shield the material from oxygen. In addition, they can  
15 present a partial gas phase contribution to the flame extinguishing effect<sup>23</sup>. Similar to other  
16 hydrated minerals, such as ATH, magnesium oxides or struvite often described as FR in  
17 connection to wood-based materials,<sup>8,24</sup> DCPD is also expected to release water vapour in the  
18 event of fire, which can contribute to improved fire retardancy by diluting flammable gases,<sup>19</sup>  
19 in addition to the known char formation of polyphosphates. The fire retardant properties of  
20 DCPD have been previously demonstrated in cotton fabric.<sup>25</sup> However, its application in  
21 wood-based composites has not yet been investigated, to the best of our knowledge. The  
22 potential fire retardant effect of DCPD addition, as well as the effect of addition quantity on  
23 the mechanical properties, is compared to the previously reported FRC.<sup>19</sup> To this end, we  
24 investigated material compositions of 10-, 20- and 30 wt% FR with the aim of determining  
25 the optimum addition amount in terms of fire retardancy and the mechanical properties. It is  
26 expected that considerable amounts, e.g. up to 20 wt%, can be added without significantly  
27 deteriorating the material thermomechanical properties.  
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## 48 **Material and methods**

### 49 **Materials**

#### 50 *Calcium hydrogen phosphate dihydrate (DCPD)*

51 Calcium hydrogen phosphate dihydrate (DCPD),  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ , was obtained from Sigma  
52 Aldrich.  
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### *Hydroxyapatite (HA)*

Hydroxyapatite-based mineral consisting of 59 wt% of hydroxyapatite (HA)  $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$  and about 41 wt% calcium carbonate ( $\text{CaCO}_3$ ) was provided by Omya International AG. The detailed characteristics of the material are provided in Ozyhar et al. 2021.<sup>19</sup>

### *Mineral-based fire retardant composition (FRC)*

The mineral-based fire retardant composition (FRC), described in detail in Ozyhar et al. 2021,<sup>19</sup> was supplied by Omya international AG and used as a benchmark FR in this study. The FRC consists of the above-mentioned HA-based mineral as a carrier material and contains 26 wt% calcium chloride ( $\text{CaCl}_2$ ) (dry/dry) stored within the porous structure of the carrier.

### *Wood material*

Wood particles for composite manufacturing originated from spruce (*Picea abies* (L.) Karst.) and were provided by Rauch Spanplattenwerk GmbH, Germany. The quality of the particles complied with the commercial grade utilized in particleboard production (surface- and core layer). The moisture content of the particles was 3% and the packing density was *ca.* 250 kg m<sup>-3</sup>.

### *Resin*

Melamine-Urea-Formaldehyde (MUF) resins with the trade name Kauramin 620 (MUF1) and Kauramin 621 (MUF2) was kindly provided by BASF SE. The solid content of MUF1 is 65 % and 65.6 % for MUF2 respectively. The MUF2 has a higher melamine content and is known to be less reactive compared to MUF1. For this reason, MUF2 was used in curing experiments since it allowed to emphasize the potential effects on the curing behavior.

## **Experimental**

### *Manufacturing of three-layer particleboard with addition of FRs*

Three-layer particleboard with 0 (served as reference), 10-, 20-, and 30 wt%, of DCPD, FRC and HA in the outer layer, with respect to dry wood mass, were manufactured to investigate the effect on 1) mechanical properties and 2) fire retardant behavior (self-extinguishing and burning behavior). The amount of HA mineral was normalized to the amount of HA contained in the FRC for accurate comparisons.

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3 The manufacturing procedure involved three steps: 1) addition of MUF1 resin to the previously  
4 dried fiber, 2) incorporation of the mineral additive (HA, DCPD, FRC, respectively) to the  
5 wood particles and homogeneous mixing and 3) pressing to the final plate. In the case of the  
6 FRC, samples that were previously dried overnight at 120°C were utilized for the second  
7 manufacturing step (moisture content < 3 %), however moisture is known to be completely  
8 reabsorbed, reaching its capacity after a 48 h equilibration period.<sup>19</sup> The addition of the MUF  
9 prior to mineral additive ensured the adhesion of the additive to wood particles and prevented  
10 separation of the two components.  
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12 The surface layer of the three-layer particleboards contained 15 wt% of MUF resin, while  
13 12 wt% of MUF resin was used for the core (both based on the dry wood mass). The surface  
14 layer was made using a fine material, whereas the core layer utilized a coarse material *i.e.* the  
15 core layer quality material. Ammonium sulphate as hardener at a rate of 3 wt% (based on solid  
16 resin) was applied to both the surface- and the core layer. The core layer material was mixed  
17 again using a mixer (Lödige FM 300D, Gebrüder Lödige Maschinenbau GmbH, Paderborn,  
18 Germany), and the surface layer particles were mixed in a second mixer (Drais T-100,  
19 Draiswerke GmbH, Mannheim, Germany). The particleboards were manufactured using a  
20 laboratory press (Höfer HLOP 210, Höfer Presstechnik GmbH, Taiskirchen, Austria) at a  
21 temperature of 200°C utilizing a press factor of 15 s·mm<sup>-1</sup>, resulting in a press time of 240 s.  
22 The target density was 650 kg m<sup>-3</sup> and 16 mm thickness. The ratio of surface to core layer was  
23 50/50 with a symmetric structure *i.e.* 4mm surface layer – 8 mm core layer – 4 mm surface  
24 layer.  
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## 26 **Methods**

### 27 **SEM**

28 Scanning electron microscope micrographs were taken by a field emission scanning electron  
29 microscope (FESEM, Zeiss Sigma VP) using a secondary electron detector (SE) to  
30 qualitatively evaluate the distribution of the DCPD and its distribution in the surface layer of  
31 the particleboard.  
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### 33 **Thermogravimetric analysis (TGA)**

34 Thermogravimetric analysis (TGA) was carried out on HA, DCPD and FRC using a Mettler  
35 TC10A/TC15 analyzer (Mettler Toledo, Greifensee, Switzerland). Approximately 10 – 30 mg  
36 of each test samples were analyzed at a heating rate of 10 °C/min in a temperature range of 30  
37 to 800°C under air atmosphere with a flow rate of 20 mL·min<sup>-1</sup>. The experiments were  
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3 performed on sample which was previously acclimatized at a temperature of 20°C and relative  
4 humidity (RH) of 65% until mass constancy.  
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### 8 **Halogen moisture analysis**

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10 Water loss of DCPD sample was determined by exposing the sample for 240s at 200 °C in a  
11 halogen moisture analyzer (Hal. Moisture Analyzer HE73 (230V), Mettler Toledo), simulating  
12 the three-layer particleboard manufacturing conditions.  
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### 16 **Self-Extinguishing time measurements**

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18 The efficacy of the DCPD, FRC and HA was determined by measuring the self-extinguishing  
19 time of the composites in an adapted test setup following ISO 11925-2 (2010)<sup>26</sup> using a burning  
20 chamber (KBK Taurus instruments GmbH, Weimar, Germany) and following the same  
21 procedure as used in Ozyhar et al. 2021.<sup>19</sup> Samples with dimensions of 200 mm x 14.5 mm x  
22 16 mm (thickness) were exposed to a flame for a period of 30 s at an angle of 45°. A total of 12  
23 samples was tested per variant.  
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### 30 **Evaluation of MUF resin curing time**

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32 The influence of the addition of DCPD, FRC and HA on the curing time of the MUF resin was  
33 examined by the rotational rheometry method using an Anton-Paar MCR302 rheometer  
34 equipped with a P-PTD200 temperature-control cell (heating plate) and a disposable PP25  
35 (plate/plate, 25 mm diameter) measuring system. A mixture of 20g of MUF2 with 3% catalyst  
36 (ammonium sulphate-based on solid resin) was prepared by homogenizing at room temperature.  
37 The mixture was then applied immediately onto the measurement plate and the curing time was  
38 recorded following the test protocol shown in Table 1. The procedure was repeated after adding  
39 10% of mineral-based materials to the mixture (based on dry weight of resin).  
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### 50 **Cone calorimetry**

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52 The combustion properties were examined by carrying out cone calorimetry testing using a  
53 Cone Calorimeter apparatus by Dr.-Ing. Goerg Wazau Mess- + Prüfsysteme GmbH, Germany.  
54 The measurements were performed utilizing a heat flux of 50 kW·m<sup>-2</sup>. The experiments were  
55 performed on samples with dimensions of 100mm x 100 mm with the back and edges of the  
56 samples sealed with aluminum foil with a thickness of 0.02 mm.  
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3 Heat release rate (HRR), total heat release rate (THR), smoke production rate (SPR) and total  
4 smoke production (TSP) were determined following the ISO 5660-1 (2015)<sup>27</sup> on samples  
5 containing 20 wt% of DCPD and FRC, HA, respectively.  
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### 10 **Determination of physical and mechanical properties of wood panel**

11 Internal bond strength (IB) and density of the composites were determined for samples  
12 acclimatized under standard climatic conditions (20 °C and 65% RH) following the procedures  
13 described in SN EN 319:1993<sup>28</sup> using a universal testing machine (ZwickRoell Z030,  
14 ZwickRoell, Ulm, Germany). The IB and density were determined for 6 samples per variant  
15 and the moisture content for 10 samples per variant.  
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### 22 **Determination of the density profile**

23 The density profile of the samples was measured with an X-ray density scanner (DAX 5000,  
24 Fagus-GreCon Greten GmbH & Co. KG, Alfeld-Hannover, Germany). Prior to the scanning,  
25 each specimen was measured in width, height and thickness using a digital caliper and weight  
26 using a digital balance to calculate the mean density. The density profile was then automatically  
27 plotted over the mean density.  
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## 33 **Results and discussion**

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36 Similar to the mechanism known for other hydrated minerals,<sup>29</sup> the release of water vapour  
37 from the mineral structure of DCPD is expected to play a role in its fire retardant properties,  
38 along with the known char formation of non-halogenated inorganic phosphorous  
39 compounds.<sup>21,22,30</sup> The release of water vapour has also been suggested as one of the primary  
40 mechanisms contributing to the fire retardancy of the FRC based on a modified calcium  
41 carbonate mineral.<sup>19</sup> Keeping in mind that the FR reaction mechanism of the FRC is a  
42 combination of multiple factors, such as decomposition of active components, the basic nature  
43 of the carrier and the release of water vapour, we have included the FRC as a benchmark FR  
44 in this study. In addition, the effect of a hydroxyapatite (HA)-based mineral, which is a  
45 component of the FRC, was considered. The direct comparison of the effect of DCPD and HA  
46 to the FRC, respectively, is of particular interest, as both represent water-insoluble minerals.  
47 Although DCPD and HA cannot be directly compared with each other due to their different  
48 chemical compositions, they belong to the same group of calcium orthophosphates.<sup>31</sup> The  
49 main factor that was considered when comparing the properties of DCPD and HA to the FRC,  
50 was the effect of adsorbed water, which was not present in HA.  
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## Characterization of the DCPD in relation to its FR potential

With regard to the potential application of DCPD as FR, the total amount of water stored in the FR is of particular interest, as the release of water vapour and the associated dilution of flammable gases is a known mechanism for hydrated minerals contributing to the fire retardancy.<sup>19,32</sup> The expected fire-retardant effect and the efficacy is thus believed to be proportional to the amount of water stored in the FR.

The comparison of the thermograms for the DCPD and FRC revealed quite a similarity in terms of the amount of water stored in both FRs (Fig. 1a). The weight loss measured at a temperature of 450 °C, which corresponds mostly to the loss of water (free and adsorbed) reveals an almost equal proportion in both FRs, indicating a water content of slightly above 25 wt%, while HA contained very little water.

Although the total amount of water in both FRs was comparable, the vapour release mechanism appeared fundamentally different (Fig. 1b), as a majority of the moisture within the FRC was released below 150 °C, whereas the water within DCPD was released at higher temperatures between 150 and 250 °C. This can be explained by the different form in which the water is present in the FRs. In the case of the FRC, the water is absorbed by the hygroscopic salt and bound (adsorbed) at the surface of the porous structure of the mineral carrier of the FRC.<sup>19</sup> In contrast, the water in the DCPD is bound within the crystal structure of the hydrated mineral. The lower energy required to release water from the surface of the porous structure of the FRC (adsorbed water) compared to the energy required for dehydration of the DCPD explained the different temperatures at which water was released from FRs (Fig. 1b) and corresponded to data reported in the literature.<sup>33</sup> The significant loss of water from the FRC below 100°C was explained by the initially high relative content of water and the adjustment of the equilibrium humidity between the FRC samples and the dry compressed air used in the TGA instrument.<sup>19</sup>

Despite the fact that both FRs are comparable in terms of the amount of water they initially contained, the exhibited contrasting thermal energy requirements for water vapour release. In addition, water vapour release from the FRC is just one of several fire-retardant mechanisms proposed to contribute to its properties.<sup>19</sup> As one of the objectives of this investigation was to understand the importance of water vapour release as one of the contributing factors in fire retardancy, the FRC was seen as a valid benchmark, as the amount of released water vapour was expected to be similar for both the FRC and the DCPD. In the case of HA, no effect of water vaporisation was expected due to the low water content (Fig. 1a-b).

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3 A significant water loss from both the FRC and DCPD samples was detected by TGA below a  
4 temperature of 250 °C. While the FRC was incorporated into the panel in dry form and is  
5 known to be reabsorb the water reaching its capacity after a 48 h equilibration period <sup>19</sup>, water  
6 loss from DCPD during the manufacturing of the three-layer particleboard could have  
7 occurred. As a consequence, the water would no longer be available in the event of a fire.  
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9 During the manufacturing process, the particleboard was exposed to a temperature of 200 °C  
10 for 240 s, although this temperature is only reached at the surface of the panels. In order to  
11 determine potential water loss during the manufacturing process, halogen moisture analysis  
12 on both the DCPD samples was performed (Fig. 2). The samples were exposed to a constant  
13 temperature of 200 °C for 240 s to accurately simulate the manufacturing conditions, while  
14 being aware that the interior of the panels does not likely reach this temperature within 4 min.  
15 As observed by the change in wt% in Fig. 2, after 240 s the DCPD sample lost only *ca.* 6  
16 wt.% as a result of water evaporation. Considering the total water loss of *ca.* 25 wt.%  
17 according to the TGA analysis (Fig. 1), it was concluded that most of the water remained  
18 bound to the DCPD samples after being exposed to the simulated manufacturing conditions  
19 and would be available in the event of a fire.  
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### 32 **Effect on self-extinguishing and burning behavior**

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34 After the manufacture of three-layer particleboard containing the FRs, the self-extinguishing  
35 and burning behavior of the panels was subsequently investigated. According to the results of  
36 self-extinguishing experiments of three-layer particleboard, DCPD addition indeed had a  
37 positive impact (Fig. 3). These observations were probably related in part to char formation of  
38 the produced polyphosphates upon dehydration of the DCPD sample.<sup>21</sup> Based on the results of  
39 halogen moisture analysis (Fig. 2), we hypothesize that the exposure time to the elevated  
40 temperature (240 s) during composite processing is not sufficient to trigger the release of  
41 substantial amounts of water and thus water vapour release upon dehydration of DCPD plays  
42 an additional role in the FR mechanism. The comparison with HA further corroborates this  
43 hypothesis, as the observed effect of the water-free HA was indeed limited, although HA was  
44 also suspected to form polyphosphate chars, as do other non-halogenated inorganic  
45 phosphorous compounds.<sup>21,22,30,34</sup> Nevertheless, the positive impact of HA on self-  
46 extinguishing time can be explained by the overall change in the ratio of combustible (organic)  
47 to incombustible (inorganic) components in the composite, which has also been demonstrated  
48 for calcium carbonate.<sup>19</sup>  
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3 Overall, the results showed that DCPD is not as effective as a flame retardant compared to the  
4 benchmark FRC when incorporated in three-layer particleboard. At 20 wt% FRC addition, the  
5 composites did not exhibit any notable afterburning and were characterized by immediate  
6 extinction of the flame. Even at rates of 30 wt%, such results were not achieved with the DCPD.  
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8 The better performance of the FRC is not surprising, considering that the effect of the FRC goes  
9 beyond the release of water vapour and is due to a synergistic effect of  $\text{CaCl}_2$  (active agent) and  
10 the inorganic carrier material of the FRC.<sup>19</sup> Nonetheless, the results demonstrated the potential  
11 of DCPD as a functional mineral additive with fire extinguishing properties, although, rates  
12 exceeding 20 wt% are believed to be required.  
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21 The evaluation of the burning behavior of the panels with DCPD was in line with the general  
22 findings observed for the self-extinguishing behavior. The DCPD addition reduced the heat  
23 release and smoke production during combustion compared to the reference and HA at the same  
24 rate of 20 wt%. (Fig. 4). Such a reduction in heat release and smoke production has been  
25 observed in a number of inorganic phosphates, which is often related to char formation and  
26 intumescence.<sup>22,23</sup> However, the performance of the FRC again exceeded those of DCPD and  
27 HA and the decrease in heat release was found to be rather low (Fig. 4a,b). In terms of smoke  
28 development, the DCPD offered clear advantages over the reference and HA in the early stages  
29 of the experiment, as demonstrated by the first shoulder in SPR diagram (Fig. 4c,d). This  
30 indicated a slowdown in the early part of the combustion reaction, most likely by prolonged  
31 ignition due to the release of water vapour.  
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39 Overall, the results demonstrated that the fire-retardant potential of DCPD for application in  
40 MUF-bonded wood composites is quite limited. The data indicated that higher addition  
41 quantities, exceeding those investigated in this study, would likely be required to achieve  
42 sufficient fire retardancy, compared to the FRC based on a modified calcium carbonate. Since  
43 the potential of DCPD is probably limited to the reaction mechanism associated with char  
44 formation and the release of water vapour, after complete dehydration of the DCPD crystal  
45 structure, there is little additional effect. Nevertheless, the use of DCPD as a functional  
46 mineral additive to support the self-extinguishing may be promising, especially if considered  
47 as an extender or in combination with other FRs. Herein, the primary advantage of using a  
48 composition containing DCPD would be its self-extinguishing potential (Fig. 3).  
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## The effect on strength properties

A major drawback associated with the use of FR in wood composites is their negative effect on mechanical properties.<sup>20,35</sup> Therefore, there is often a trade-off between fire retardancy and mechanical properties of wood composites when utilizing FRs. For particulate FRs, the decrease in strength typically arises from the deposition of the FR on the wood particles, which interferes with the inter-particle bonding that, in turn, weakens the mechanical strength.<sup>24</sup> In addition, increasing the amount of FR additive in the composite matrix decreases the amount of wood particles in relation to the FR, reducing the fiber packing and fiber-to-fiber stress transfer, which also directly affects the mechanical properties.<sup>15,36</sup>

The influence of mineral addition on strength is best demonstrated by the decrease in internal bond (IB) strength for composites manufactured with HA and FRC (Fig. 5). The results indicated an almost linear decrease in strength with increasing additive amounts and correlate well with the results reported previously regarding application of calcium carbonate in MDF and particleboard.<sup>15,18</sup> In contrast, the addition of DCPD of up to 30 wt% did not seem to affect the strength of the composite. This is even more astonishing when one considers the nature of the mineral components, which are fine in comparison to the wood particles, which are expected to deposit on the wood particle surfaces and interfere with the inter-particle bonding (Fig. 6).

In this context, the effect of the addition of mineral FR on the density of the particleboard in the outer and inner layer should be emphasized. As can be seen, the addition of the FR results in a notably increased density in the surface layers, by roughly  $300 \text{ kg}\cdot\text{m}^{-3}$  (Fig. 7). Similar results were obtained for the addition of calcium carbonate in the surface layer of particleboard<sup>15</sup> and are attributed to the higher density of the minerals compared to the density of wood.

In contrast to the increased density in the surface layers, the density in the core layer decreases with addition of DCPD, by roughly  $200 \text{ kg}\cdot\text{m}^{-3}$ . This observation can be explained by the manufacturing process of the panels, which are produced in order to achieve the same panel thickness. When using the same amount of material by weight, the material occupies less volume due to the higher density of that material component. While the composite is densified in the surface layer, less volume is occupied in the core layer, which results in lower density. The associated fiber packing and fiber-to-fiber stress transfer was also partly responsible for the decrease in internal bond. Therefore, the decrease in IB strength upon the addition of mineral-based FR is primarily due to the decrease in density in the middle (core) layer. It should further be noted here that the fracture of the specimens almost always

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3 occurred in the core layer. Only in the FRC variants were more fractures observed at the  
4 interface between the core and middle layers.

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6 With regard to the fire-retardant properties, the use of DCPD allows for a significantly higher  
7 amount of FR to be added compared to the FRC, without a substantial impact on the  
8 mechanical properties. This thus allows to achieve self-extinguishing properties, which are  
9 analogous to those of the FRC while maintaining the material's strength, a unique feature that  
10 distinguishes the DCPD from the FRC.  
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### 15 16 **The effect on curing behavior of MUF**

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18 In view of the favorable mechanical properties of particleboard with 20 and 30 wt% DCPD,  
19 other factors affecting strength development were considered, in addition to the structural  
20 reasons discussed above. The influence of the addition of FR on resin hardening is another  
21 important factor that can affect strength development in the composite. Previous studies have  
22 shown that the addition of calcium carbonate delays the curing reaction of UF,<sup>16</sup> although its  
23 effect on strength development of the composite remains uncertain. Nonetheless, in the search  
24 of a potential explanation of the different strength characteristics for composites with different  
25 FRs (Fig. 5), we compared the curing behavior of the MUF in the presence of each FR sample  
26 via rotational rheometry (Fig. 8). Therein, increased viscosity of the resin and the curve slope  
27 is correlated with the curing reaction time and rate, respectively.  
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29 Notably, the addition of HA and FRC slowed down the curing reaction of the resin, as  
30 demonstrated by the increase in viscosity and, thus curing time compared to the reference  
31 MUF resin without additives. The longer time required to reach the same viscosity as the  
32 reference MUF with addition of HA and FRC indicated slower curing of the resin and thus  
33 demonstrated the adverse effect on the curing reaction. While we could not directly correlate  
34 the delayed and/or incomplete curing of the resin with the strength development in the  
35 composite due to the role of fiber-fiber interfacial interactions discussed above, the observed  
36 linear decrease in strength for particleboards with increasing addition of HA and FRC (Fig.5)  
37 could have also been affected by insufficient resin curing.  
38

39 On the contrary, the addition of DCPD did not have an effect on the curing of the resin. The  
40 MUF samples with DCPD were characterized by the same curing time as the samples without  
41 addition of the FR. Interestingly, the addition of DCPD seemed to compensate for the adverse  
42 effect of FRC as demonstrated by the curing time of the MUF with a 50/50 mixture of  
43 DCPD/FRC. This indicated that diluting the FRC with DCPD promoted the curing reaction of  
44 the resin when compared to the FRC alone. This could be a result of the low pH of the DCPD,  
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3 which, when combined with the FRC, lowered the overall pH and promoted the curing  
4 reaction. With a pH between pH 3.60-4.50, DCPD can be considered as acidic<sup>37</sup> and therefore  
5 advantageous in reducing the pH when combined with the FRC. UF resins require acidic  
6 curing conditions, with pH values of around pH = 4 considered the optimum condition.<sup>38-40</sup>  
7  
8 While we hesitate to directly correlate the difference in the curing reaction obtained in this  
9 experiment using DCPD with the strength development of the composite, based on the  
10 observed results, the application of DCPD can be considered advantageous in terms of the  
11 curing of the resin. The exceptionally good mechanical properties of the panels containing  
12 DCPD compared to those with FRC and HA and the fact that the addition of DCPD did not  
13 seem to affect the curing behavior of the MUF highlights its potential as an extender with fire  
14 retardant properties for application in UF-based systems. Finally, we propose that the use of  
15 DCPD in combination with other FR additives could potentially compensate for their adverse  
16 effects on wood composite mechanical properties.  
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## 26 Conclusions

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29 Herein, the efficacy of DCPD as a mineral-based fire retardant for application in particleboard  
30 was presented. The fire-retardant potential of DCPD was demonstrated through self-  
31 extinguishing experiments and cone calorimetry, which revealed its limitations with regard to  
32 the high application rates necessary to achieve sufficient fire retardant behavior. Application  
33 rates exceeding 20-30 wt% were shown to be necessary in order to achieve a fire retardancy  
34 comparable to that of 10 wt% of FRC, the benchmark in this study. Contrary to the application  
35 of FRC, the use of DCPD seemed to have no impact on the mechanical properties of the  
36 composite, as evidenced by internal bond strength, allowing for up to 30 wt% of DCPD in the  
37 outer layer of particleboard. Confirmed by the results of the MUF curing experiments, which  
38 demonstrated that DCPD addition had no influence on curing of the resin, the exceptional  
39 position of the DCPD and its potential for applications in acid curing urea formaldehyde (UF)-  
40 based systems was confirmed. Depending on the desired level of fire retardancy, it remains  
41 open as to whether DCPD can be used as the sole FR in wood panels. More likely, DCPD can  
42 contribute to improving fire retardancy by using it as an extender for other fire retardants, such  
43 as the FRC.<sup>17</sup> Based on the minimal impact on the mechanical properties and the curing  
44 reactions, the DCPD may be a promising extender for applications in UF/MUF-bonded  
45 composite systems utilizing fire retardant mineral-based additives.  
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## Conflict of Interest:

The authors declare that they have no conflict of interest.

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## Tables

**Table 1** Test protocol for rotational rheometry method used to determine influence of FR addition on curing behaviour of MUF

	Stage 1	Stage 2	Stage 3
Temperature [C°]	40	40-130 (linear ramp-up)	130
Duration step [s]	10	40	Until complete curing of resin
Share rate [s <sup>-1</sup> ]	10		

For Peer Review

## Figure Captions

**Fig. 1** a) Thermograms and b) 1st derivative thermograms (DTG) for HA, DCPD, FRC

**Fig. 2** Halogen moisture analysis of the DCPD sample

**Fig. 3** Fire extinguishing potential of DCPD at addition quantities of 10-, 20- and 30 wt% in the outer layer of three-layer particleboard in comparison to addition of FRC and HA exemplified by the self-extinguishing time following previous exposure to flame. Whiskers show minimum and maximum values, red plus shows outliers, diamonds in box displays arithmetic mean value, box boundaries display 25th percentile and 75th percentile.

**Fig. 4** a) Heat release rate (HRR); b) total heat release rate (THR); c) smoke production rate (SPR) and d) total smoke production (TSP) determined on three-layer particleboards with 20 wt% of DCPD, FRC and HA in comparison to reference (without any addition).

**Fig. 5** Internal bond (IB) strength determined on three-layer particle with addition of 10-, 20-, and 30 wt% of DCPD in the outer layer of three-layer particleboard in comparison to addition of, HA and FRC. Whiskers show minimum and maximum values, red plus shows outliers, diamonds in box displays arithmetic mean value, box boundaries display 25th percentile and 75th percentile.

**Fig. 6** Scanning electron micrographs (SEM) of a) DCPD particles and b) the cross section of three-layer particleboard with 20 wt% addition of DCPD in outer layer.

**Fig. 7** Comparison of density profiles for three-layer particleboard with 20 wt% DCPD in outer layer and reference board without additive.

**Fig. 8** Curing behavior of MUF as affected by DCPD, FRC, and HA at 10 wt% addition compared to the neat MUF. Each individual curve demonstrates an average value from measurements performed on three individual samples.

# Evaluating the use of calcium hydrogen phosphate dihydrate (DCPD) as a mineral-based fire retardant for application in melamine-urea-formaldehyde (MUF)-bonded wood-based composite materials

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## Summary

Calcium hydrogen phosphate dihydrate (DCPD) was evaluated for its potential as a mineral fire retardant (FR) for application in melamine-urea-formaldehyde (MUF)-bonded wood composites. The efficacy as FR was studied in melamine-urea-formaldehyde (MUF)-bonded three-layer particleboard as a function of addition quantities of 10-, 20- and 30 wt%. Resistance to fire and mechanical properties were determined by measuring the self-extinguishing time after flame exposure and internal bond strength, respectively. Combustion behavior was examined on samples with 20 wt% DCPD addition by performing cone calorimetry experiments. The efficacy of DCPD was evaluated by determining the heat release, total heat release rate, smoke production and smoke production rate and compared to another promising mineral-based fire-retardant composition (FRC) based on hydroxyapatite (HA) with deliquescent salt and HA alone. The effect of FR on curing behavior of MUF in relation to mechanical properties was determined through viscosity measurements of MUF with 10 wt% addition of FR. The results confirmed the fire-retardant characteristics of DCPD in wood composites, albeit at higher application rates when compared to the FRC, however with no negative impact on resin curing time or mechanical strength. Based on the demonstrated compatibility in MUF, DCPD is considered a promising mineral extender of other FRs for application in UF-based wood composites.

**Keywords:** *calcium orthophosphate, fire retardant; hydrated mineral; mineral extender; resin curing; water vapour release*

## Introduction

The application of minerals in wood and wood-based materials has attracted increased attention. <sup>1-6</sup> Among the various advantages of the application of mineral additives in wood-based

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3 materials, such as the potential cost reduction, the applications as a fire retardant (FR) is  
4 considered one of the most promising fields. Recent research on the incorporation of minerals  
5 in wood highlighted their potential for application as fire retardants (FRs).<sup>3,7,8</sup> The approach  
6 discussed in those works utilizes the technology of mineral precipitation from different salt  
7 solutions with the goal of modifying the wood structure by incorporating minerals directly in  
8 the cell wall. This approach allows for considerable amounts of minerals to be precipitated in  
9 the wood structure with a lumen filling ratio close to 50% (ratio of mineral volume to pore  
10 volume) <sup>8</sup>, however requires an impregnation step in order to achieve efficient penetration of  
11 the wood structure. While this approach is suitable for modification of solid wood structures,  
12 the technology is considered less appropriate for applications in composite structures, which  
13 includes many of the engineered wood-based composites. The incorporation of FR in the  
14 composite formulation as a functional additive is considered to be the preferred method in the  
15 manufacture of composite materials. These materials are usually manufactured from several  
16 components in a single process, in which individual components are mixed and then bonded  
17 together under the influence of temperature to form the final product. The direct incorporation  
18 of mineral-based FRs by mixing with the matrix during manufacturing is more suitable in  
19 comparison to a post-impregnation step.

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22 The use of minerals as FR in various types of polymer-based composite materials, including  
23 wood- and cellulose fiber-based reinforced composites is well known.<sup>9-11</sup> The use of mineral  
24 additives in engineered wood-based composites products, a special group of composites  
25 manufactured by binding of wood strands, particles, fibers, or veneers and often using a  
26 thermosetting adhesive <sup>12,13</sup>, is less studied.<sup>14-16</sup> Traditionally, mineral additives are not  
27 utilized in the manufacture of such products due to the already competitive costs of the raw  
28 wood-based materials.<sup>17</sup>

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31 Recent studies demonstrated the feasibility of the incorporation of mineral-based additives in  
32 selected engineered wood-based composites.<sup>14-16</sup> The results of these studies demonstrated  
33 that calcium carbonate-based mineral additives can be incorporated in existing products, such  
34 as medium density fiberboard (MDF) or particleboard, without substantially affecting the  
35 material properties and potentially decreasing production costs. Furthermore, the industrial  
36 feasibility of this approach has been demonstrated in fiberboard products.<sup>18</sup> A promising  
37 mineral-based fire retardant composition (FRC), consisting of a mineral carrier material and  
38 deliquescent salt for application in particle-based wood composites has been further  
39 evaluated.<sup>19</sup> The authors demonstrated the efficacy of the mineral-based FRC as a fire  
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3 extinguisher and that the FRC can be easily incorporated into the structure of a particle-based  
4 wood material.

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6 Building on the promising results from the application of calcium carbonate and the mineral-  
7 based FRC in wood-based products,<sup>15,16,18,19</sup> this study investigates the use of another  
8 potential mineral for application in wood panels. Calcium hydrogen phosphate dihydrate  
9 (DCPD), a hydrated mineral, is proposed as a functional mineral additive for application in  
10 wood-based composites, which is expected to exhibit fire retardant properties similar to other  
11 non-halogenated inorganic phosphorous compounds, such as ammonium polyphosphate  
12 (APP).<sup>20–22</sup> In general, such inorganic phosphorous flame retardants are known to act  
13 primarily in the solid phase of burning materials, in which the formed polyphosphates create a  
14 char layer that can further intumesce to shield the material from oxygen. In addition, they can  
15 present a partial gas phase contribution to the flame extinguishing effect<sup>23</sup>. Similar to other  
16 hydrated minerals, such as ATH, magnesium oxides or struvite often described as FR in  
17 connection to wood-based materials,<sup>8,24</sup> DCPD is also expected to release water vapour in the  
18 event of fire, which can contribute to improved fire retardancy by diluting flammable gases,<sup>19</sup>  
19 in addition to the known char formation of polyphosphates. The fire retardant properties of  
20 DCPD have been previously demonstrated in cotton fabric.<sup>25</sup> However, its application in  
21 wood-based composites has not yet been investigated, to the best of our knowledge. The  
22 potential fire retardant effect of DCPD addition, as well as the effect of addition quantity on  
23 the mechanical properties, is compared to the previously reported FRC.<sup>19</sup> To this end, we  
24 investigated material compositions of 10-, 20- and 30 wt% FR with the aim of determining  
25 the optimum addition amount in terms of fire retardancy and the mechanical properties. It is  
26 expected that considerable amounts, e.g. up to 20 wt%, can be added without significantly  
27 deteriorating the material thermomechanical properties.  
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## 48 **Material and methods**

### 49 **Materials**

#### 50 *Calcium hydrogen phosphate dihydrate (DCPD)*

51 Calcium hydrogen phosphate dihydrate (DCPD),  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ , was obtained from Sigma  
52 Aldrich.  
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### *Hydroxyapatite (HA)*

Hydroxyapatite-based mineral consisting of 59 wt% of hydroxyapatite (HA)  $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$  and about 41 wt% calcium carbonate ( $\text{CaCO}_3$ ) was provided by Omya International AG. The detailed characteristics of the material are provided in Ozyhar et al. 2021.<sup>19</sup>

### *Mineral-based fire retardant composition (FRC)*

The mineral-based fire retardant composition (FRC), described in detail in Ozyhar et al. 2021,<sup>19</sup> was supplied by Omya international AG and used as a benchmark FR in this study. The FRC consists of the above-mentioned HA-based mineral as a carrier material and contains 26 wt% calcium chloride ( $\text{CaCl}_2$ ) (dry/dry) stored within the porous structure of the carrier.

### *Wood material*

Wood particles for composite manufacturing originated from spruce (*Picea abies* (L.) Karst.) and were provided by Rauch Spanplattenwerk GmbH, Germany. The quality of the particles complied with the commercial grade utilized in particleboard production (surface- and core layer). The moisture content of the particles was 3% and the packing density was *ca.* 250 kg m<sup>-3</sup>.

### *Resin*

Melamine-Urea-Formaldehyde (MUF) resins with the trade name Kauramin 620 (MUF1) and Kauramin 621 (MUF2) was kindly provided by BASF SE. The solid content of MUF1 is 65 % and 65.6 % for MUF2 respectively. The MUF2 has a higher melamine content and is known to be less reactive compared to MUF1. For this reason, MUF2 was used in curing experiments since it allowed to emphasize the potential effects on the curing behavior.

## **Experimental**

### *Manufacturing of three-layer particleboard with addition of FRs*

Three-layer particleboard with 0 (served as reference), 10-, 20-, and 30 wt%, of DCPD, FRC and HA in the outer layer, with respect to dry wood mass, were manufactured to investigate the effect on 1) mechanical properties and 2) fire retardant behavior (self-extinguishing and burning behavior). The amount of HA mineral was normalized to the amount of HA contained in the FRC for accurate comparisons.



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3 The manufacturing procedure involved three steps: 1) addition of MUF1 resin to the previously  
4 dried fiber, 2) incorporation of the mineral additive (HA, DCPD, FRC, respectively) to the  
5 wood particles and homogeneous mixing and 3) pressing to the final plate. In the case of the  
6 FRC, samples that were previously dried overnight at 120°C were utilized for the second  
7 manufacturing step (moisture content < 3 %), however moisture is known to be completely  
8 reabsorbed, reaching its capacity after a 48 h equilibration period.<sup>19</sup> The addition of the MUF  
9 prior to mineral additive ensured the adhesion of the additive to wood particles and prevented  
10 separation of the two components.  
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12 The surface layer of the three-layer particleboards contained 15 wt% of MUF resin, while  
13 12 wt% of MUF resin was used for the core (both based on the dry wood mass). The surface  
14 layer was made using a fine material, whereas the core layer utilized a coarse material *i.e.* the  
15 core layer quality material. Ammonium sulphate as hardener at a rate of 3 wt% (based on solid  
16 resin) was applied to both the surface- and the core layer. The core layer material was mixed  
17 again using a mixer (Lödige FM 300D, Gebrüder Lödige Maschinenbau GmbH, Paderborn,  
18 Germany), and the surface layer particles were mixed in a second mixer (Drais T-100,  
19 Draiswerke GmbH, Mannheim, Germany). The particleboards were manufactured using a  
20 laboratory press (Höfer HLOP 210, Höfer Presstechnik GmbH, Taiskirchen, Austria) at a  
21 temperature of 200°C utilizing a press factor of 15 s·mm<sup>-1</sup>, resulting in a press time of 240 s.  
22 The target density was 650 kg m<sup>-3</sup> and 16 mm thickness. The ratio of surface to core layer was  
23 50/50 with a symmetric structure *i.e.* 4mm surface layer – 8 mm core layer – 4 mm surface  
24 layer.  
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## 26 **Methods**

### 27 **SEM**

28 Scanning electron microscope micrographs were taken by a field emission scanning electron  
29 microscope (FESEM, Zeiss Sigma VP) using a secondary electron detector (SE) to  
30 qualitatively evaluate the distribution of the DCPD and its distribution in the surface layer of  
31 the particleboard.  
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### 33 **Thermogravimetric analysis (TGA)**

34 Thermogravimetric analysis (TGA) was carried out on HA, DCPD and FRC using a Mettler  
35 TC10A/TC15 analyzer (Mettler Toledo, Greifensee, Switzerland). Approximately 10 – 30 mg  
36 of each test samples were analyzed at a heating rate of 10 °C/min in a temperature range of 30  
37 to 800°C under air atmosphere with a flow rate of 20 mL·min<sup>-1</sup>. The experiments were  
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3 performed on sample which was previously acclimatized at a temperature of 20°C and relative  
4 humidity (RH) of 65% until mass constancy.  
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### 8 **Halogen moisture analysis**

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10 Water loss of DCPD sample was determined by exposing the sample for 240s at 200 °C in a  
11 halogen moisture analyzer (Hal. Moisture Analyzer HE73 (230V), Mettler Toledo), simulating  
12 the three-layer particleboard manufacturing conditions.  
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### 16 **Self-Extinguishing time measurements**

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18 The efficacy of the DCPD, FRC and HA was determined by measuring the self-extinguishing  
19 time of the composites in an adapted test setup following ISO 11925-2 (2010)<sup>26</sup> using a burning  
20 chamber (KBK Taurus instruments GmbH, Weimar, Germany) and following the same  
21 procedure as used in Ozyhar et al. 2021.<sup>19</sup> Samples with dimensions of 200 mm x 14.5 mm x  
22 16 mm (thickness) were exposed to a flame for a period of 30 s at an angle of 45°. A total of 12  
23 samples was tested per variant.  
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### 30 **Evaluation of MUF resin curing time**

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32 The influence of the addition of DCPD, FRC and HA on the curing time of the MUF resin was  
33 examined by the rotational rheometry method using an Anton-Paar MCR302 rheometer  
34 equipped with a P-PTD200 temperature-control cell (heating plate) and a disposable PP25  
35 (plate/plate, 25 mm diameter) measuring system. A mixture of 20g of MUF2 with 3% catalyst  
36 (ammonium sulphate-based on solid resin) was prepared by homogenizing at room temperature.  
37 The mixture was then applied immediately onto the measurement plate and the curing time was  
38 recorded following the test protocol shown in Table 1. The procedure was repeated after adding  
39 10% of mineral-based materials to the mixture (based on dry weight of resin).  
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### 50 **Cone calorimetry**

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52 The combustion properties were examined by carrying out cone calorimetry testing using a  
53 Cone Calorimeter apparatus by Dr.-Ing. Goerg Wazau Mess- + Prüfsysteme GmbH, Germany.  
54 The measurements were performed utilizing a heat flux of 50 kW·m<sup>-2</sup>. The experiments were  
55 performed on samples with dimensions of 100mm x 100 mm with the back and edges of the  
56 samples sealed with aluminum foil with a thickness of 0.02 mm.  
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3 Heat release rate (HRR), total heat release rate (THR), smoke production rate (SPR) and total  
4 smoke production (TSP) were determined following the ISO 5660-1 (2015)<sup>27</sup> on samples  
5 containing 20 wt% of DCPD and FRC, HA, respectively.  
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### 10 **Determination of physical and mechanical properties of wood panel**

11 Internal bond strength (IB) and density of the composites were determined for samples  
12 acclimatized under standard climatic conditions (20 °C and 65% RH) following the procedures  
13 described in SN EN 319:1993<sup>28</sup> using a universal testing machine (ZwickRoell Z030,  
14 ZwickRoell, Ulm, Germany). The IB and density were determined for 6 samples per variant  
15 and the moisture content for 10 samples per variant.  
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### 22 **Determination of the density profile**

23 The density profile of the samples was measured with an X-ray density scanner (DAX 5000,  
24 Fagus-GreCon Greten GmbH & Co. KG, Alfeld-Hannover, Germany). Prior to the scanning,  
25 each specimen was measured in width, height and thickness using a digital caliper and weight  
26 using a digital balance to calculate the mean density. The density profile was then automatically  
27 plotted over the mean density.  
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## 33 **Results and discussion**

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36 Similar to the mechanism known for other hydrated minerals,<sup>29</sup> the release of water vapour  
37 from the mineral structure of DCPD is expected to play a role in its fire retardant properties,  
38 along with the known char formation of non-halogenated inorganic phosphorous  
39 compounds.<sup>21,22,30</sup> The release of water vapour has also been suggested as one of the primary  
40 mechanisms contributing to the fire retardancy of the FRC based on a modified calcium  
41 carbonate mineral.<sup>19</sup> Keeping in mind that the FR reaction mechanism of the FRC is a  
42 combination of multiple factors, such as decomposition of active components, the basic nature  
43 of the carrier and the release of water vapour, we have included the FRC as a benchmark FR  
44 in this study. In addition, the effect of a hydroxyapatite (HA)-based mineral, which is a  
45 component of the FRC, was considered. The direct comparison of the effect of DCPD and HA  
46 to the FRC, respectively, is of particular interest, as both represent water-insoluble minerals.  
47 Although DCPD and HA cannot be directly compared with each other due to their different  
48 chemical compositions, they belong to the same group of calcium orthophosphates.<sup>31</sup> The  
49 main factor that was considered when comparing the properties of DCPD and HA to the FRC,  
50 was the effect of adsorbed water, which was not present in HA.  
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## Characterization of the DCPD in relation to its FR potential

With regard to the potential application of DCPD as FR, the total amount of water stored in the FR is of particular interest, as the release of water vapour and the associated dilution of flammable gases is a known mechanism for hydrated minerals contributing to the fire retardancy.<sup>19,32</sup> The expected fire-retardant effect and the efficacy is thus believed to be proportional to the amount of water stored in the FR.

The comparison of the thermograms for the DCPD and FRC revealed quite a similarity in terms of the amount of water stored in both FRs (Fig. 1a). The weight loss measured at a temperature of 450 °C, which corresponds mostly to the loss of water (free and adsorbed) reveals an almost equal proportion in both FRs, indicating a water content of slightly above 25 wt%, while HA contained very little water.

Although the total amount of water in both FRs was comparable, the vapour release mechanism appeared fundamentally different (Fig. 1b), as a majority of the moisture within the FRC was released below 150 °C, whereas the water within DCPD was released at higher temperatures between 150 and 250 °C. This can be explained by the different form in which the water is present in the FRs. In the case of the FRC, the water is absorbed by the hygroscopic salt and bound (adsorbed) at the surface of the porous structure of the mineral carrier of the FRC.<sup>19</sup> In contrast, the water in the DCPD is bound within the crystal structure of the hydrated mineral. The lower energy required to release water from the surface of the porous structure of the FRC (adsorbed water) compared to the energy required for dehydration of the DCPD explained the different temperatures at which water was released from FRs (Fig. 1b) and corresponded to data reported in the literature.<sup>33</sup> The significant loss of water from the FRC below 100°C was explained by the initially high relative content of water and the adjustment of the equilibrium humidity between the FRC samples and the dry compressed air used in the TGA instrument.<sup>19</sup>

Despite the fact that both FRs are comparable in terms of the amount of water they initially contained, the exhibited contrasting thermal energy requirements for water vapour release. In addition, water vapour release from the FRC is just one of several fire-retardant mechanisms proposed to contribute to its properties.<sup>19</sup> As one of the objectives of this investigation was to understand the importance of water vapour release as one of the contributing factors in fire retardancy, the FRC was seen as a valid benchmark, as the amount of released water vapour was expected to be similar for both the FRC and the DCPD. In the case of HA, no effect of water vaporisation was expected due to the low water content (Fig. 1a-b).

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3 A significant water loss from both the FRC and DCPD samples was detected by TGA below a  
4 temperature of 250 °C. While the FRC was incorporated into the panel in dry form and is  
5 known to be reabsorb the water reaching its capacity after a 48 h equilibration period <sup>19</sup>, water  
6 loss from DCPD during the manufacturing of the three-layer particleboard could have  
7 occurred. As a consequence, the water would no longer be available in the event of a fire.  
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9 During the manufacturing process, the particleboard was exposed to a temperature of 200 °C  
10 for 240 s, although this temperature is only reached at the surface of the panels. In order to  
11 determine potential water loss during the manufacturing process, halogen moisture analysis  
12 on both the DCPD samples was performed (Fig. 2). The samples were exposed to a constant  
13 temperature of 200 °C for 240 s to accurately simulate the manufacturing conditions, while  
14 being aware that the interior of the panels does not likely reach this temperature within 4 min.  
15 As observed by the change in wt% in Fig. 2, after 240 s the DCPD sample lost only *ca.* 6  
16 wt.% as a result of water evaporation. Considering the total water loss of *ca.* 25 wt.%  
17 according to the TGA analysis (Fig. 1), it was concluded that most of the water remained  
18 bound to the DCPD samples after being exposed to the simulated manufacturing conditions  
19 and would be available in the event of a fire.  
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### 32 **Effect on self-extinguishing and burning behavior**

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34 After the manufacture of three-layer particleboard containing the FRs, the self-extinguishing  
35 and burning behavior of the panels was subsequently investigated. According to the results of  
36 self-extinguishing experiments of three-layer particleboard, DCPD addition indeed had a  
37 positive impact (Fig. 3). These observations were probably related in part to char formation of  
38 the produced polyphosphates upon dehydration of the DCPD sample.<sup>21</sup> Based on the results of  
39 halogen moisture analysis (Fig. 2), we hypothesize that the exposure time to the elevated  
40 temperature (240 s) during composite processing is not sufficient to trigger the release of  
41 substantial amounts of water and thus water vapour release upon dehydration of DCPD plays  
42 an additional role in the FR mechanism. The comparison with HA further corroborates this  
43 hypothesis, as the observed effect of the water-free HA was indeed limited, although HA was  
44 also suspected to form polyphosphate chars, as do other non-halogenated inorganic  
45 phosphorous compounds.<sup>21,22,30,34</sup> Nevertheless, the positive impact of HA on self-  
46 extinguishing time can be explained by the overall change in the ratio of combustible (organic)  
47 to incombustible (inorganic) components in the composite, which has also been demonstrated  
48 for calcium carbonate.<sup>19</sup>  
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3 Overall, the results showed that DCPD is not as effective as a flame retardant compared to the  
4 benchmark FRC when incorporated in three-layer particleboard. At 20 wt% FRC addition, the  
5 composites did not exhibit any notable afterburning and were characterized by immediate  
6 extinction of the flame. Even at rates of 30 wt%, such results were not achieved with the DCPD.  
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8 The better performance of the FRC is not surprising, considering that the effect of the FRC goes  
9 beyond the release of water vapour and is due to a synergistic effect of  $\text{CaCl}_2$  (active agent) and  
10 the inorganic carrier material of the FRC.<sup>19</sup> Nonetheless, the results demonstrated the potential  
11 of DCPD as a functional mineral additive with fire extinguishing properties, although, rates  
12 exceeding 20 wt% are believed to be required.  
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20 The evaluation of the burning behavior of the panels with DCPD was in line with the general  
21 findings observed for the self-extinguishing behavior. The DCPD addition reduced the heat  
22 release and smoke production during combustion compared to the reference and HA at the same  
23 rate of 20 wt%. (Fig. 4). Such a reduction in heat release and smoke production has been  
24 observed in a number of inorganic phosphates, which is often related to char formation and  
25 intumescence.<sup>22,23</sup> However, the performance of the FRC again exceeded those of DCPD and  
26 HA and the decrease in heat release was found to be rather low (Fig. 4a,b). In terms of smoke  
27 development, the DCPD offered clear advantages over the reference and HA in the early stages  
28 of the experiment, as demonstrated by the first shoulder in SPR diagram (Fig. 4c,d). This  
29 indicated a slowdown in the early part of the combustion reaction, most likely by prolonged  
30 ignition due to the release of water vapour.  
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39 Overall, the results demonstrated that the fire-retardant potential of DCPD for application in  
40 MUF-bonded wood composites is quite limited. The data indicated that higher addition  
41 quantities, exceeding those investigated in this study, would likely be required to achieve  
42 sufficient fire retardancy, compared to the FRC based on a modified calcium carbonate. Since  
43 the potential of DCPD is probably limited to the reaction mechanism associated with char  
44 formation and the release of water vapour, after complete dehydration of the DCPD crystal  
45 structure, there is little additional effect. Nevertheless, the use of DCPD as a functional  
46 mineral additive to support the self-extinguishing may be promising, especially if considered  
47 as an extender or in combination with other FRs. Herein, the primary advantage of using a  
48 composition containing DCPD would be its self-extinguishing potential (Fig. 3).  
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## The effect on strength properties

A major drawback associated with the use of FR in wood composites is their negative effect on mechanical properties.<sup>20,35</sup> Therefore, there is often a trade-off between fire retardancy and mechanical properties of wood composites when utilizing FRs. For particulate FRs, the decrease in strength typically arises from the deposition of the FR on the wood particles, which interferes with the inter-particle bonding that, in turn, weakens the mechanical strength.<sup>24</sup> In addition, increasing the amount of FR additive in the composite matrix decreases the amount of wood particles in relation to the FR, reducing the fiber packing and fiber-to-fiber stress transfer, which also directly affects the mechanical properties.<sup>15,36</sup>

The influence of mineral addition on strength is best demonstrated by the decrease in internal bond (IB) strength for composites manufactured with HA and FRC (Fig. 5). The results indicated an almost linear decrease in strength with increasing additive amounts and correlate well with the results reported previously regarding application of calcium carbonate in MDF and particleboard.<sup>15,18</sup> In contrast, the addition of DCPD of up to 30 wt% did not seem to affect the strength of the composite. This is even more astonishing when one considers the nature of the mineral components, which are fine in comparison to the wood particles, which are expected to deposit on the wood particle surfaces and interfere with the inter-particle bonding (Fig. 6).

In this context, the effect of the addition of mineral FR on the density of the particleboard in the outer and inner layer should be emphasized. As can be seen, the addition of the FR results in a notably increased density in the surface layers, by roughly  $300 \text{ kg}\cdot\text{m}^{-3}$  (Fig. 7). Similar results were obtained for the addition of calcium carbonate in the surface layer of particleboard<sup>15</sup> and are attributed to the higher density of the minerals compared to the density of wood.

In contrast to the increased density in the surface layers, the density in the core layer decreases with addition of DCPD, by roughly  $200 \text{ kg}\cdot\text{m}^{-3}$ . This observation can be explained by the manufacturing process of the panels, which are produced in order to achieve the same panel thickness. When using the same amount of material by weight, the material occupies less volume due to the higher density of that material component. While the composite is densified in the surface layer, less volume is occupied in the core layer, which results in lower density. The associated fiber packing and fiber-to-fiber stress transfer was also partly responsible for the decrease in internal bond. Therefore, the decrease in IB strength upon the addition of mineral-based FR is primarily due to the decrease in density in the middle (core) layer. It should further be noted here that the fracture of the specimens almost always

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3 occurred in the core layer. Only in the FRC variants were more fractures observed at the  
4 interface between the core and middle layers.

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6 With regard to the fire-retardant properties, the use of DCPD allows for a significantly higher  
7 amount of FR to be added compared to the FRC, without a substantial impact on the  
8 mechanical properties. This thus allows to achieve self-extinguishing properties, which are  
9 analogous to those of the FRC while maintaining the material's strength, a unique feature that  
10 distinguishes the DCPD from the FRC.  
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### 15 16 **The effect on curing behavior of MUF**

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18 In view of the favorable mechanical properties of particleboard with 20 and 30 wt% DCPD,  
19 other factors affecting strength development were considered, in addition to the structural  
20 reasons discussed above. The influence of the addition of FR on resin hardening is another  
21 important factor that can affect strength development in the composite. Previous studies have  
22 shown that the addition of calcium carbonate delays the curing reaction of UF,<sup>16</sup> although its  
23 effect on strength development of the composite remains uncertain. Nonetheless, in the search  
24 of a potential explanation of the different strength characteristics for composites with different  
25 FRs (Fig. 5), we compared the curing behavior of the MUF in the presence of each FR sample  
26 via rotational rheometry (Fig. 8). Therein, increased viscosity of the resin and the curve slope  
27 is correlated with the curing reaction time and rate, respectively.  
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29 Notably, the addition of HA and FRC slowed down the curing reaction of the resin, as  
30 demonstrated by the increase in viscosity and, thus curing time compared to the reference  
31 MUF resin without additives. The longer time required to reach the same viscosity as the  
32 reference MUF with addition of HA and FRC indicated slower curing of the resin and thus  
33 demonstrated the adverse effect on the curing reaction. While we could not directly correlate  
34 the delayed and/or incomplete curing of the resin with the strength development in the  
35 composite due to the role of fiber-fiber interfacial interactions discussed above, the observed  
36 linear decrease in strength for particleboards with increasing addition of HA and FRC (Fig.5)  
37 could have also been affected by insufficient resin curing.  
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39 On the contrary, the addition of DCPD did not have an effect on the curing of the resin. The  
40 MUF samples with DCPD were characterized by the same curing time as the samples without  
41 addition of the FR. Interestingly, the addition of DCPD seemed to compensate for the adverse  
42 effect of FRC as demonstrated by the curing time of the MUF with a 50/50 mixture of  
43 DCPD/FRC. This indicated that diluting the FRC with DCPD promoted the curing reaction of  
44 the resin when compared to the FRC alone. This could be a result of the low pH of the DCPD,  
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3 which, when combined with the FRC, lowered the overall pH and promoted the curing  
4 reaction. With a pH between pH 3.60-4.50, DCPD can be considered as acidic<sup>37</sup> and therefore  
5 advantageous in reducing the pH when combined with the FRC. UF resins require acidic  
6 curing conditions, with pH values of around pH = 4 considered the optimum condition.<sup>38-40</sup>  
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8 While we hesitate to directly correlate the difference in the curing reaction obtained in this  
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10 experiment using DCPD with the strength development of the composite, based on the  
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12 observed results, the application of DCPD can be considered advantageous in terms of the  
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14 curing of the resin. The exceptionally good mechanical properties of the panels containing  
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16 DCPD compared to those with FRC and HA and the fact that the addition of DCPD did not  
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18 seem to affect the curing behavior of the MUF highlights its potential as an extender with fire  
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20 retardant properties for application in UF-based systems. Finally, we propose that the use of  
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22 DCPD in combination with other FR additives could potentially compensate for their adverse  
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24 effects on wood composite mechanical properties.  
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## 26 27 **Conclusions**

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29 Herein, the efficacy of DCPD as a mineral-based fire retardant for application in particleboard  
30 was presented. The fire-retardant potential of DCPD was demonstrated through self-  
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32 extinguishing experiments and cone calorimetry, which revealed its limitations with regard to  
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34 the high application rates necessary to achieve sufficient fire retardant behavior. Application  
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36 rates exceeding 20-30 wt% were shown to be necessary in order to achieve a fire retardancy  
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38 comparable to that of 10 wt% of FRC, the benchmark in this study. Contrary to the application  
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40 of FRC, the use of DCPD seemed to have no impact on the mechanical properties of the  
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42 composite, as evidenced by internal bond strength, allowing for up to 30 wt% of DCPD in the  
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44 outer layer of particleboard. Confirmed by the results of the MUF curing experiments, which  
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46 demonstrated that DCPD addition had no influence on curing of the resin, the exceptional  
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48 position of the DCPD and its potential for applications in acid curing urea formaldehyde (UF)-  
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50 based systems was confirmed. Depending on the desired level of fire retardancy, it remains  
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52 open as to whether DCPD can be used as the sole FR in wood panels. More likely, DCPD can  
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54 contribute to improving fire retardancy by using it as an extender for other fire retardants, such  
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56 as the FRC.<sup>17</sup> Based on the minimal impact on the mechanical properties and the curing  
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58 reactions, the DCPD may be a promising extender for applications in UF/MUF-bonded  
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60 composite systems utilizing fire retardant mineral-based additives.

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## *Conflict of Interest:*

The authors declare that they have no conflict of interest.

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## Tables

**Table 1** Test protocol for rotational rheometry method used to determine influence of FR addition on curing behaviour of MUF

	Stage 1	Stage 2	Stage 3
Temperature [C°]	40	40-130 (linear ramp-up)	130
Duration step [s]	10	40	Until complete curing of resin
Share rate [s <sup>-1</sup> ]	10		

For Peer Review

## Figure Captions

**Fig. 1** a) Thermograms and b) 1st derivative thermograms (DTG) for HA, DCPD, FRC

**Fig. 2** Halogen moisture analysis of the DCPD sample

**Fig. 3** Fire extinguishing potential of DCPD at addition quantities of 10-, 20- and 30 wt% in the outer layer of three-layer particleboard in comparison to addition of FRC and HA exemplified by the self-extinguishing time following previous exposure to flame. Whiskers show minimum and maximum values, red plus shows outliers, diamonds in box displays arithmetic mean value, box boundaries display 25th percentile and 75th percentile.

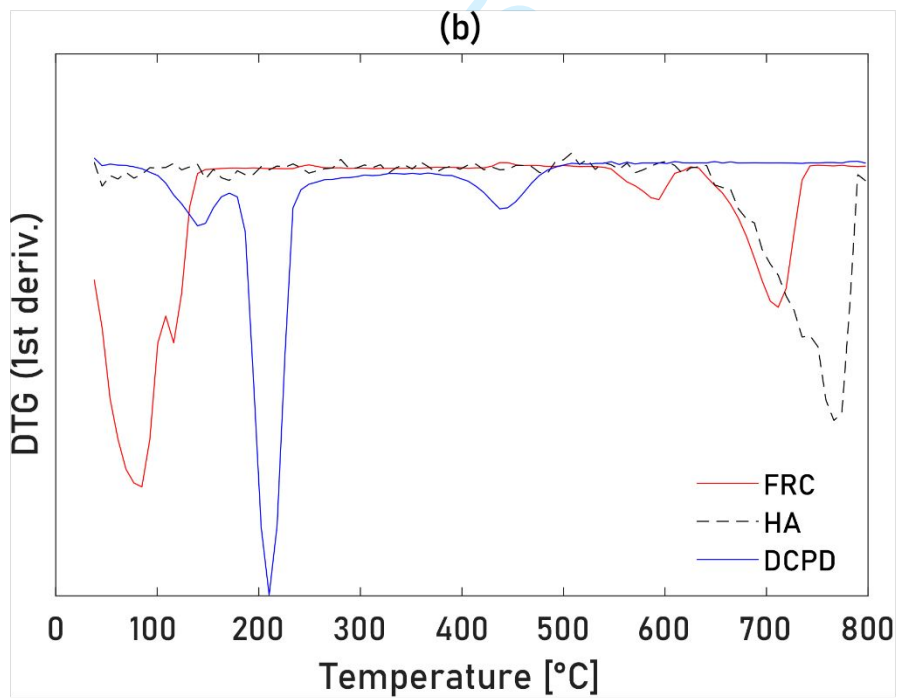
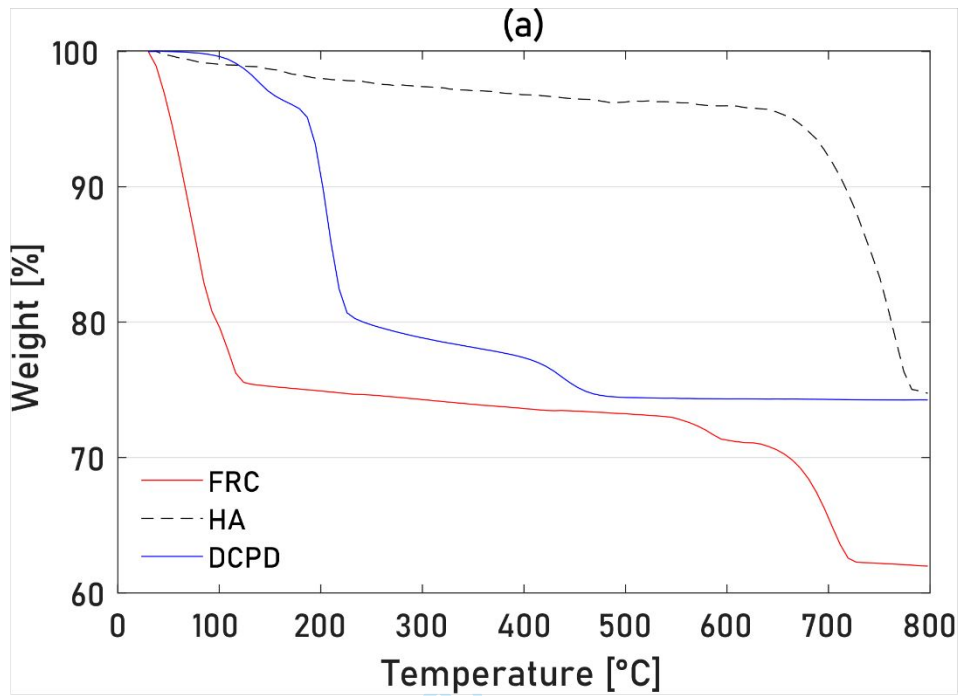
**Fig. 4** a) Heat release rate (HRR); b) total heat release rate (THR); c) smoke production rate (SPR) and d) total smoke production (TSP) determined on three-layer particleboards with 20 wt% of DCPD, FRC and HA in comparison to reference (without any addition).

**Fig. 5** Internal bond (IB) strength determined on three-layer particle with addition of 10-, 20-, and 30 wt% of DCPD in the outer layer of three-layer particleboard in comparison to addition of, HA and FRC. Whiskers show minimum and maximum values, red plus shows outliers, diamonds in box displays arithmetic mean value, box boundaries display 25th percentile and 75th percentile.

**Fig. 6** Scanning electron micrographs (SEM) of a) DCPD particles and b) the cross section of three-layer particleboard with 20 wt% addition of DCPD in outer layer.

**Fig. 7** Comparison of density profiles for three-layer particleboard with 20 wt% DCPD in outer layer and reference board without additive.

**Fig. 8** Curing behavior of MUF as affected by DCPD, FRC, and HA at 10 wt% addition compared to the neat MUF. Each individual curve demonstrates an average value from measurements performed on three individual samples.





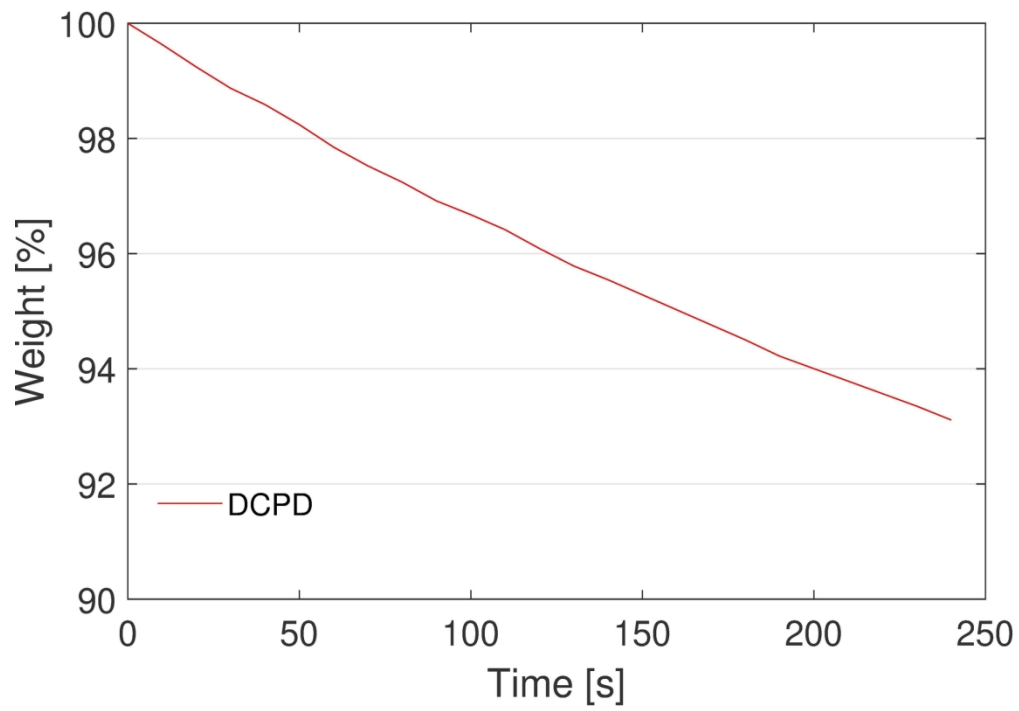


Fig. 2

162x112mm (300 x 300 DPI)

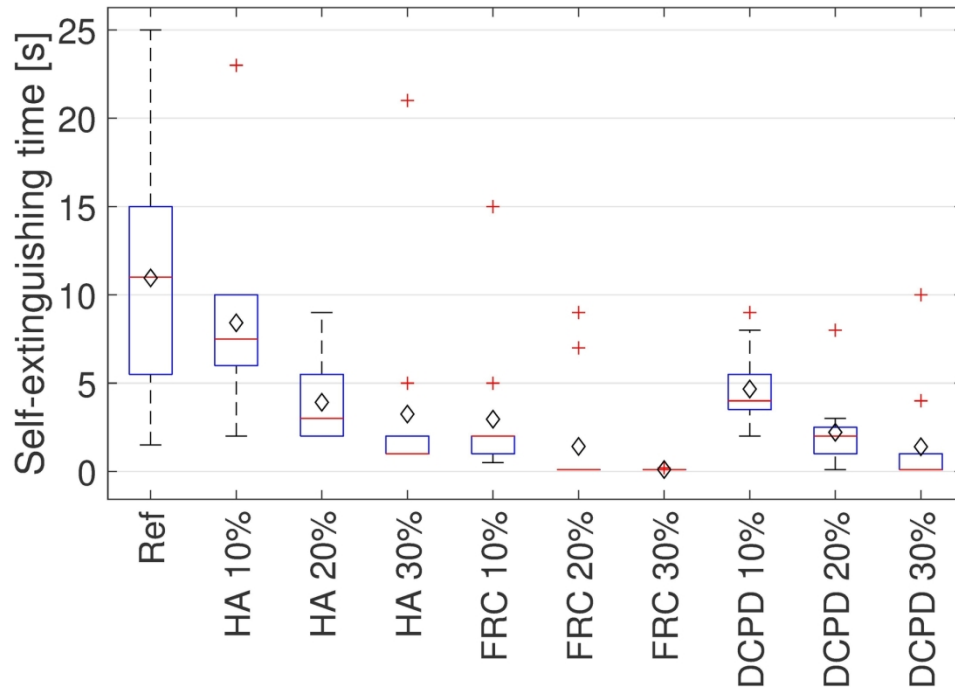
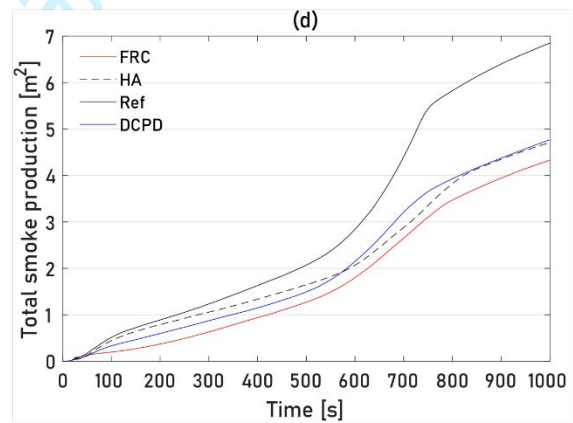
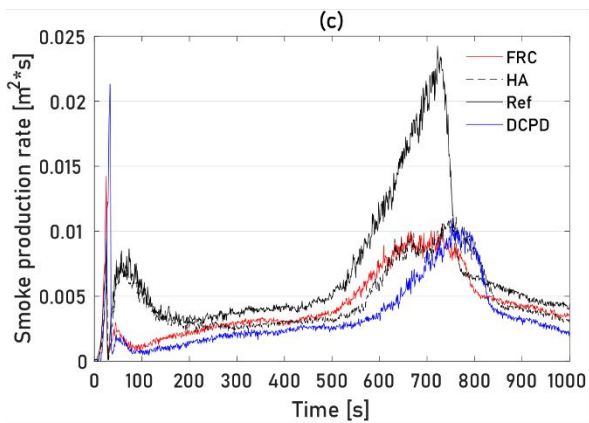
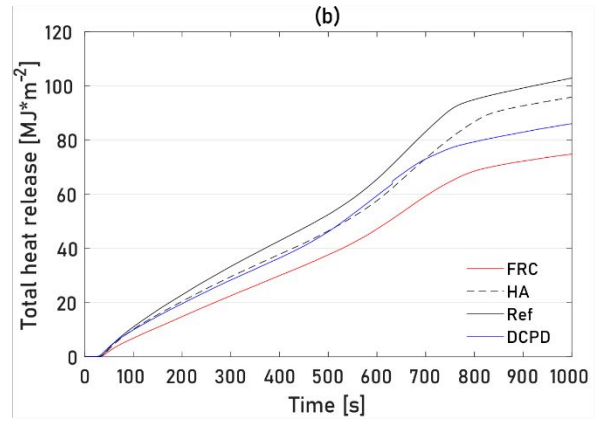
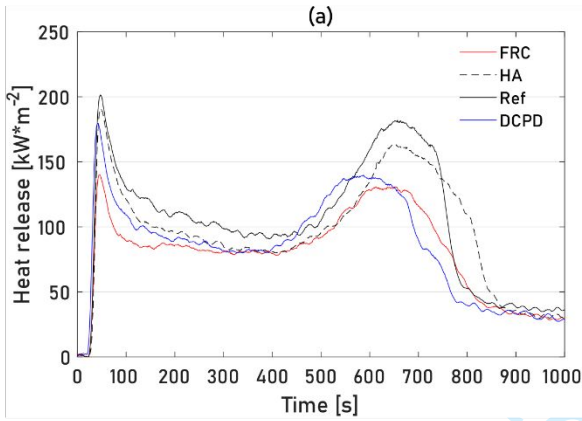


Fig. 3

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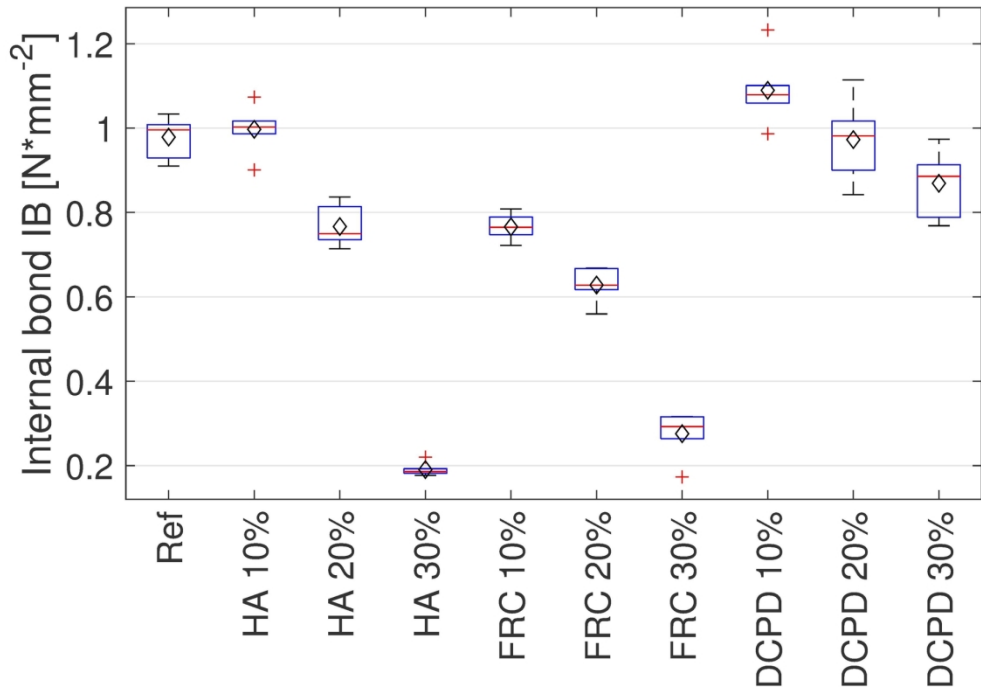
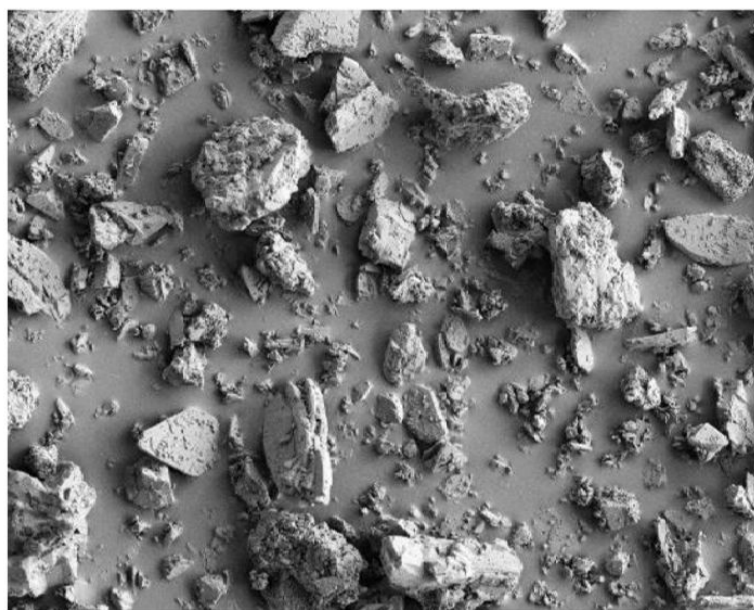


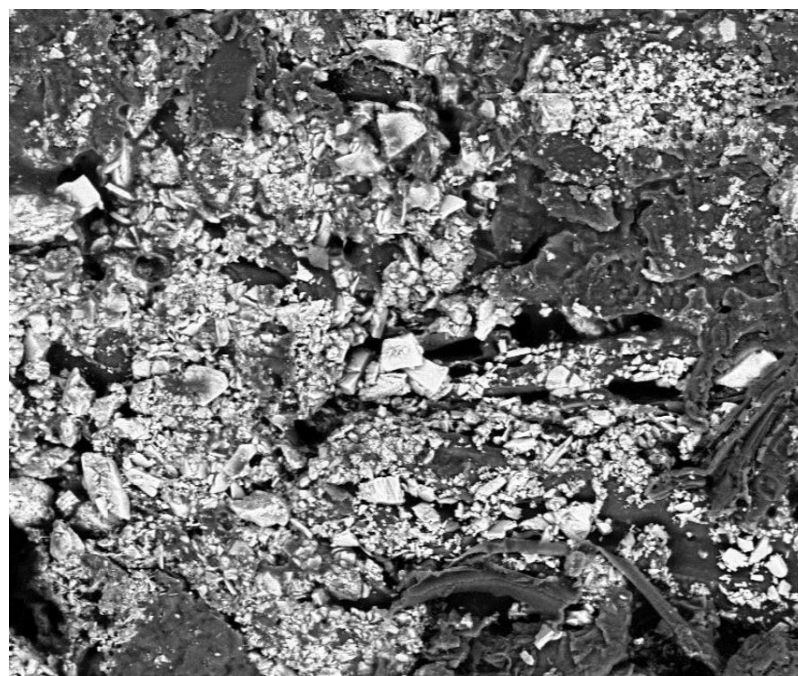
Fig. 5

162x119mm (300 x 300 DPI)



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**Fig 6**

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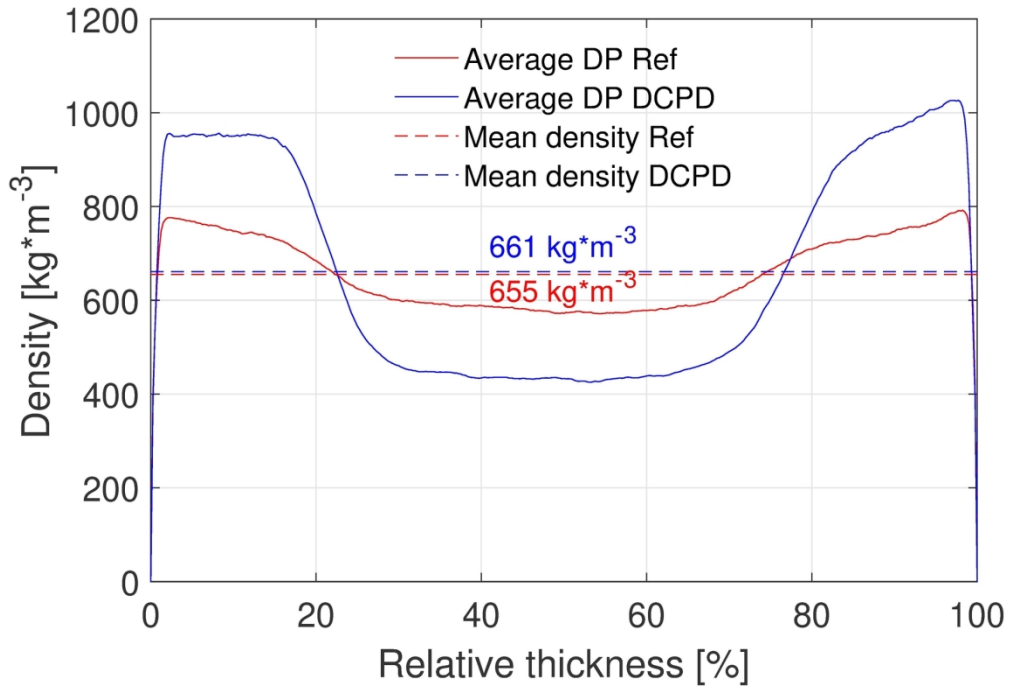


Fig. 7

166x112mm (300 x 300 DPI)

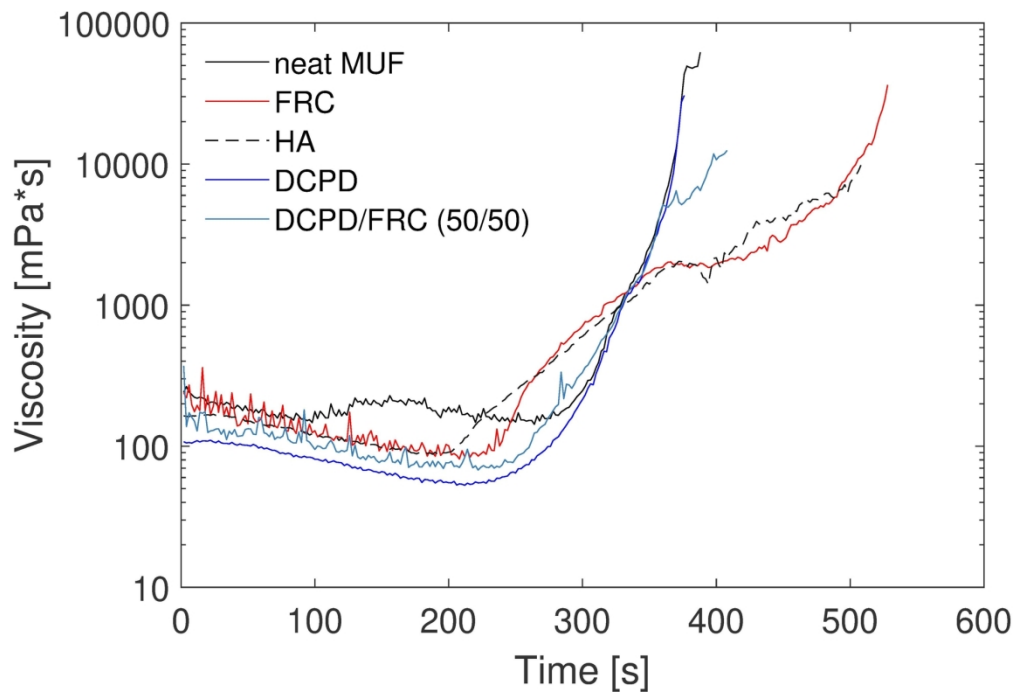


Fig. 8

165x112mm (300 x 300 DPI)