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Influence of 3D-Printing on the Flammability Properties of Railway Applications Using Polycarbonate (PC) and Polylactic acid (PLA)

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Summary
Due to limited production numbers, using additive manufacturing for the production of railway components, is proving more economical. Furthermore, strict requirements regarding flammability properties, standardised in EN 45545-2, are applied on trains. This work focuses on the production of transparent components made of Polycarbonate via 3D-printing. The polymer was modified using different flame retardant agents and the influence of the printing parameters, especially the print density, was determined. Polylactic Acid was examined for comparison reasons only. The printed and modified polymers were tested exposing the samples to heat radiation, according to ISO 5660-1 using a Cone Calorimeter, and to a direct flame, according to UL 94.
Processing and printing of the polymer causes thermal stress to the molecules. This may lead to a worsening of the flammability causing a decline of the properties compared to the native Polycarbonate. This was confirmed through both testing methods. Moreover, the additive and the print density both influence the flammability properties depending on the polymer type. In summary print parameters and additivation have to be carefully considered when it comes to the flammability properties of polymers.

Keywords: fire behaviour of material (Polycarbonate, also with additives) after 3D print, Influence of 3D printing on the fire behaviour

1. Introduction

Integration of functionality and design is experiencing more and more importance for railway vehicles. Thus, LED-lightings increasingly replaces conventional tubular fluorescent lamps because of a broader light spectrum, less energy consumption as well as a reduced energy loss through heat radiation. Since modernisation with LED-stripes only requires small numbers of plastic lamp covers, conventional processes for the production are no longer cost-efficient.

Due to small production numbers in the field of railways, especially regarding the aftermarket, modern processing methods commonly known as Additive Manufacturing (AM) seem to be of great interest. AM offers great flexibility for design, reduces production times as well as costs for small quantities and has a high potential to reduce inventory and is therefore known as a disruptive technology[4].

Although AM is known since the early 1980s, only in the last ten years these technologies became common. Today, 3D-printing or FDM (fused deposition modelling) is one of the main AM-processes. Due to its inexpensiveness and the almost unlimited material selection, FDM is highly promising for the production of spare parts for trains and other railed vehicles [1]. Nevertheless, for railway applications the research about the influence of the AM-process on the flammability properties does not exist. This work examined the usability of FDM for the production of LED-lamp covers. The main criteria for this product were the transparency of the material and its flammability properties, which were tested and evaluated accord-

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[4] Disruptive technologies create new markets and processing strategies due to the novel possibilities they offer. Hence, they eventually disrupt already existing markets and conventional production chains.

ing to EN 45545-2 (Fire protection on railway vehicles) via Cone-Calorimeter and UL 94.

Experiments were carried out varying the print density and using Polycarbonate (PC) with different flame retardant agents. Additionally, Polylactic acid (PLA) was used as it can be seen as a reference material that is commonly used for 3D-printing. Next, biopolymers are gaining more and more importance as they are considered as environmental friendly. As so, their flame behaviour is investigated during which the additivation has to be taken into account for an ecological overall view [2, 3]. Toxicological requirements were not taken into consideration and are not part of this paper.

2. Requirements for railway components

According to EN 45545-2:2016, the following requirements apply to materials and components used in railway vehicles (Table 1). Fire testing of polymers is described in general in [4] and detailed for railway applications in [5]. Attempts for globalization of fire testing, regarding railway applications, are further stated in [6].

While phosphorus flame retardants are common as a substitute for halogenic based additives, there are no specific data available for PC, concerning railway applications [7]. Furthermore, flame retardancy affects the design, e. g. the transparency [8].

Nevertheless, for railway applications the research about the influence of the AM-process on the flammability properties does not exist. The subjects of the investigations are not lamp covers or light diffusors but components for luminares, for example plastic and caps, with are required for a luminare. Figure 1 shows examples of 3D printed end caps from an LED luminare, with can vary in size for different applications. While the requirement category R6 applies to large parts (circumference > 0,2 m), R22 applies to smaller parts. If the part can be seen as a small electrotechnical product, it is categorised with R26. The requirement R26 includes small electrotechnical products with low power circuit breakers, overload relays, contactors, contactor relay, switches, control or signalling switches, terminals, fuses [10]. Due to the mentioned fact, that products made in 3D printing technology have not yet been tested for railway requirements, it was decided to determine the fire properties of the selected materials using tests according to

Table 1

Requirements for railway materials for which tests according to ISO 5660-1 or EN 60695-11-10 apply (excerpt from EN 45545-2: 2016)

Requirement category	Test method	Parameter	Hazard Level		
			HL 1	HL 2	HL 3
R6	ISO 5660-1 (50 kW/m²)	MARHE [kW/m²]	≤ 90	≤ 90	≤ 60
R22	ISO 4589-2	Oxygen Index [%]	≥ 28	≥ 28	≥ 32
R26	EN 60695-11-10	Vertical Small Flame Test	V0	V0	V0

Fig. 1: 3D-printed plastic end caps from LED lighting from railway vehicles (Picture: Horvath HEH-LED)

ISO 5660-1 (at a radiation intensity of 50 kW / m²) [9] and UL 94 [11].

Summarised, R6 is essentially tested via Cone-Calorimeter according to ISO 5660-1, using a conical heater with a heat radiation intensity of 50 kW/m². To pass this test the Maximum Average Rate of Heat Emission (MARHE) must be equal or less than 90 kW/m² (HL 1 and HL 2) or 60 kW/m² (HL 3), respectively [10].

As can be seen in Figure 2 the MARHE-value is the maximum of the ARHE (Average Rate of Heat Emission), while ARHE is calculated by summarizing and averaging all HRR-values, starting with the ignition of the sample. The Hazard Level (HL) is defined by the operation and the design of the railway vehicle and is standardized in EN 45545 part 1 and 2. While small electronic components must pass the Vertical Small Flame Test (ÖVE/ÖNORM EN 60 695-11-10), reaching V0 as test result. The test procedures, according to UL 94 and ÖVE/ÖNORM EN 60 695-11-10 are equivalent [11, 12].

3. Properties and processing of polymers

Regarding the given requirements, materials that are used in railway vehicles must often withstand flame impingement and radiation. While flame retardant agents exist for both types separately, there are hardly any solutions known that can improve flame retardancy for direct flame impingement as well as exposure to thermal radiation. Hence, a printable Polycarbonate type (provided by Covestro AG) was chosen for the projected light application, as PC offers a good intrinsic flame retardancy, is self-extinguishing after ignition, has a high impact resistance and a good optical, glasslike, transparency. Furthermore, PC has a good resistance to UV-light and a relatively high maximum operating temperature of around 130°C. Hence, PC is a common material for light applications [13].

According to the product data sheet, the chosen PC only fulfils V2 according to UL 94. Therefore, two different halogen-free flame retardant masterbatches (provided by Gabriel-Chemie GmbH) were used to improve the burning behaviour of the polymer. Both masterbatches, FR 1 and FR 2, are suitable for extrusion and injection moulding and do not influence the optical transparency. According to the producer they are suitable for PC to achieve V0 via UL 94. The effectiveness of flame retardancy for radiation is not stated.

Polylactic acid on the other hand is a biobased and biodegradable polymer with good mechanical properties. It is used as a standard material for FDM and was tested in comparison to PC. The flame retardancy of PLA was not improved by additivation.

4. Extrusion of Polycarbonate

Preparation of the test samples were done using a laboratory extruder (25 mm screw diameter), which was used for blending the PC with the masterbatches. The material was pre-dried for at least six hours at 110°C and processed at a low melt temperature of 215°C. The extruded filament was than cooled and cut to granulate or winded for the following 3D-printing. The diameter of the strands was adjusted to 1,75 mm. Figure 3 shows the process schematically. The processed materials are given in Table 2.

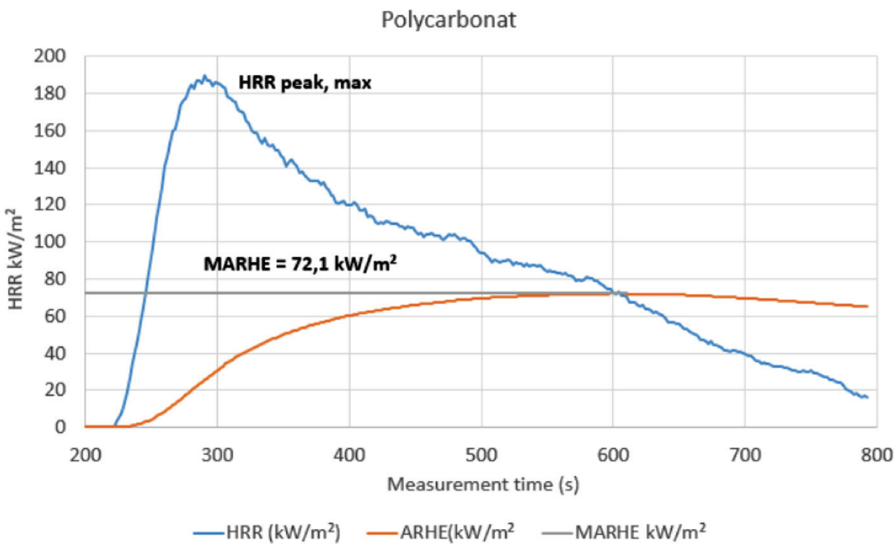

Fig. 2. Heat Release Rate (HRR), Average Rate of Heat Emission (ARHE) and the Maximum Average Rate of Heat Emission (MARHE)

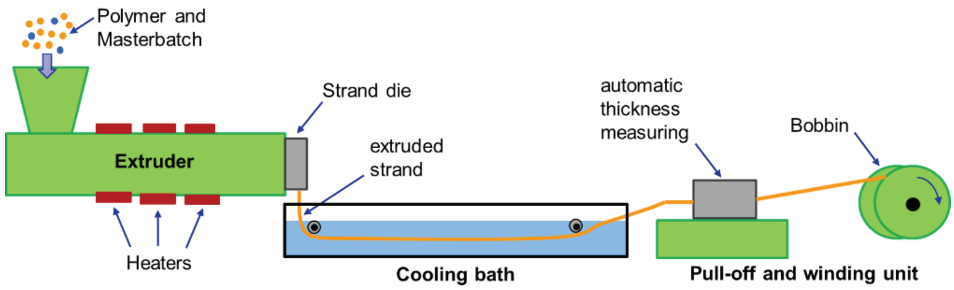

Fig. 3. Schematic processing layout for polymer processing

Table 2

Extruded materials for flammability test

Sample	Composition
PC nature	100% PC
FR 1_3%	97% PC + 3% Masterbatch FR 1
FR 1_5%	95% PC + 5% Masterbatch FR 1
FR 1_20%	80% PC + 20% Masterbatch FR 1
FR 1_30%	70% PC + 30% Masterbatch FR 1
FR 1_35%	65% PC + 35% Masterbatch FR 1
FR 2_3%	97% PC + 3% Masterbatch FR 2
FR 2_5%	95% PC + 5% Masterbatch FR 2
FR 2_20%	80% PC + 20% Masterbatch FR 2
FR 2_30%	70% PC + 30% Masterbatch FR 2
FR 2_35%	65% PC + 35% Masterbatch FR 2

Table 3

Influence of the print density on the sample mass

Print density [%]	Relative sample mass [%]
100	100,0
50	91,2
25	87,2
10	83,2

Fig. 4. Shoulder segment of tensile test specimens with a print density of 50% (a) and 10% (b) made of PLA

5. Printing of test samples

For the printing of the testing samples the pure PC, the extruded PC-blends and the native PLA were used. The PC-samples were printed at a nozzle temperature of 300°C and a bed temperature of 150°C. PLA was processed at 270°C and with a bed temperature of 60°C. Sample size for the Cone Calorimeter was chosen according to ISO 5660-1 with 100 mm times 100 mm and a thickness of 3 mm. The samples for the UL 94 test had a rectangular geometry with 125 mm times 13 mm and a thickness of 3 mm. The print density was varied between 10% and 100%, meaning a reduction of the total material of up to 17% (Table 3). This is due to the fact that only the core volume is reduced by changing the printing density. While the outer layer, with a thickness of 1 mm, was printed without material reduction, the inner core was printed like a diamond shaped honeycomb structure, as shown in Figure 4.

6. Pre-tests with PC-granulate

The first flammability tests were conducted with the Cone Calorimeter, using the granulate itself. This was done for a preliminary screening of the suitable additive percentage that would allow a relevant improvement of the burning behaviour of PC. Tests were carried out with a heating intensity of 50 kW/m² and a sample mass of 30 g, which is equal to the mass of the printed samples.

As shown in Figure 5, adding the flame retardant FR 1 to the PC causes an earlier ignition of the material. The overall released energy was reduced, which is indicated by the area underneath the curve and the MARHE, respectively. The obtained Heat Release Rates (HRR) and MARHE values are given in Table 4. It is also noticeable that, by adding up to 30% of the flame retardants, the released energy was lowered. But, by adding more than 30% the HRR rose again.

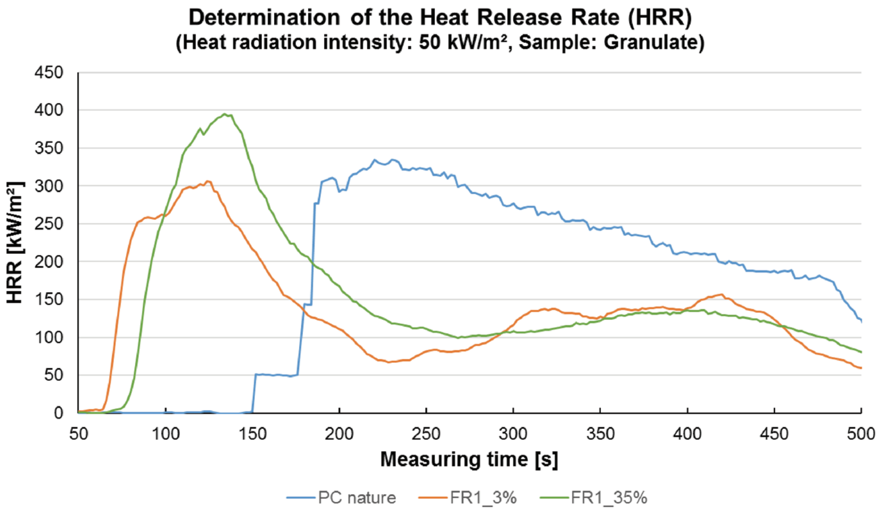

Fig. 5. Influence of the additive content on the Heat Release Rate of PC

Table 4

Results of the flammability tests (ISO 5660-1) using PC-granulat

Sample	Ignition-time [s]	HRR_{peak} [kW/m²]	MARHE [kW/m²]
PC nature	179	335	162
FR 1_3%	56	306	144
FR 1_5%	52	269	157
FR 1_20%	47	291	148
FR 1_30%	59	352	134
FR 1_35%	66	395	163
FR 2_3%	55	341	150
FR 2_5%	51	283	145
FR 2_20%	54	286	135
FR 2_30%	81	261	94
FR 2_35%	60	336	135
FR 2_100%	60	288	131

Figure 6 shows that the masterbatch FR 2 was generally more effective than FR 1, whereas with 3% masterbatch this effect cannot be seen. The pure flame retardant masterbatch FR 2 showed a higher MARHE than the PC-batch with only 30% which came as a surprise. This may be caused by some synergistic effects of the additive.

7. Testing of printed samples

Compared to granulate the printed samples were expected to show a better flame retardancy, due to the closed surface. The granulate also offers a larger surface area and is not tightly packed. Hence, more oxygen was supposed to react with the granulated polymer, worsening the flammability properties. This theory was proven, which can be seen in Figure 7.

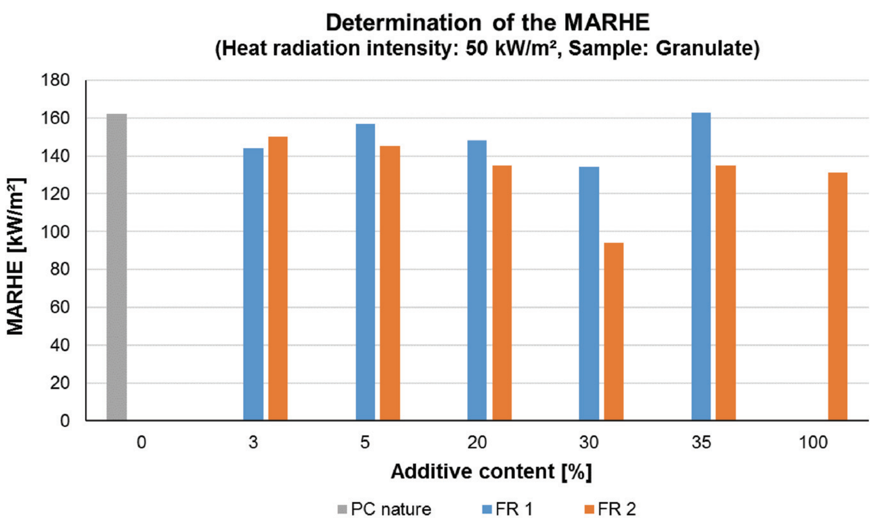

Fig. 6. Influence of the additive content on the MARHE of PC

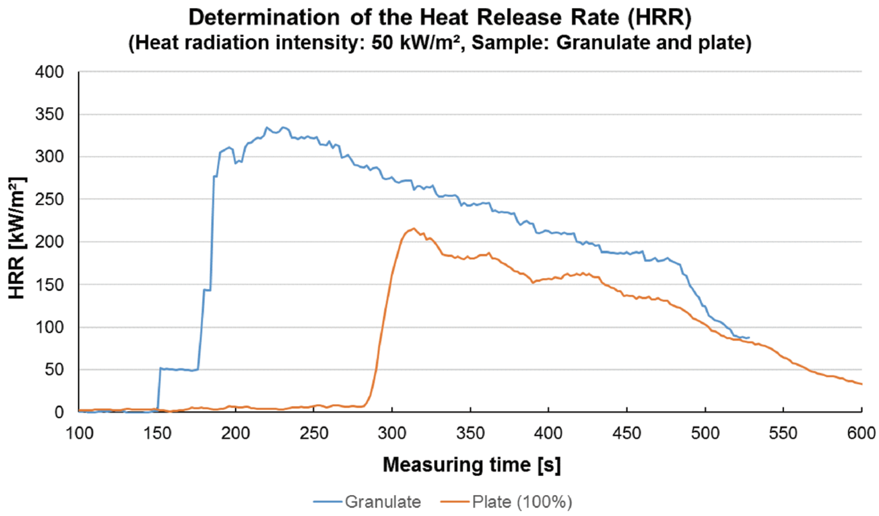

Fig. 7. Influence of the sample type (granulate vs. printed plate) of PC

If the HRR-curve of the granulate is compared to the 3D-printed plate, with a density of 100%; it is noticeable that the plate ignites after nearly twice the time than the granulate. Moreover, the MARHE of the granulate is more than twice as large as the MARHE of the 3D-printed plate (Table 5).

Table 5

Comparison of the MARHE of granulate and printed

Sample	Print density [%]	MARHE [kW/m²]
Granulate	–	162
Plate	100	72

Regarding the print density, Figure 8 shows the effect on the MARHE of pure PC. The values are given in Table 6.

Table 6

Influence of the print density on the MARHE of PC

Material	Print density [%]	MARHE [kW/m²]
PC nature	25	61 ± 3
	50	71 ± 5
	100	72 ± 1

While the reduction of the print density led to a reduction of the MARHE, the result of the PC-sample with a print density of 50% stands out. Not only does the plate with a print density of 25% ignite earlier, but the measurement error of the 50% sample is significantly larger. A possible explanation for these observations is the difference in the sample mass and therefore in the amount of air that is enclosed in the printed plates. While a reduction of the sample mass would

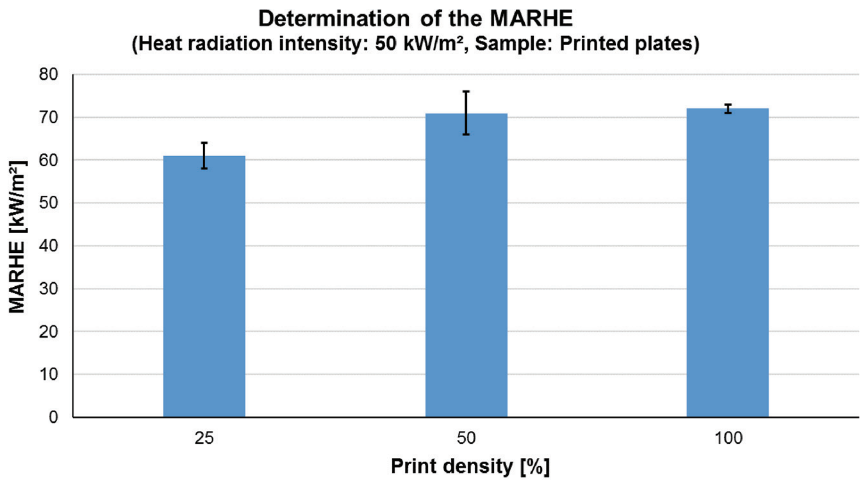

Fig. 8. Influence of the print density on the MARHE of PC-printed samples

cause a lower MARHE, more enclosed air would promote the burning. Obviously, at a print density of 50% both effects seem to compensate each other, resulting in an unchanged MARHE of PC, but in a higher variance, compared to a print density of 100%.

In conclusion, the result obtained with granulate using FR 2 was more effective than using FR 1 when printed (see Figure 6). An overall reduction of the MARHE, caused by a lower print density, was not verified as there were no significant differences between FR 2_30% with a print density of 25% and 50% (Table 7, Figure 9).

Table 7

Influence of the print density on the MARHE of PC

Material	Print density [%]	Time to ignition [s]	MARHE [kW/m²]
PC nature	25	370 ± 35	61 ± 3
	50	288 ± 64	71 ± 5
	100	246 ± 24	72 ± 1
FR 2_30%	25	64 ± 15	134 ± 9
	50	70 ± 8	170 ± 29
PLA nature	25	24 ± 0	192 ± 21
	50	35 ± 1	195 ± 25
	100	29 ± 1	202 ± 4

A change of the print density does not affect the flammability of PLA either. As it is shown in Figure 9, the MARHE of PLA was not reduced at lower print densities. Consequently, the influence of the print density on each material has to be analysed separately and conclusions based on other polymers are not permissible.

As it can be stated, the flame retardant masterbatch caused a worsening of the flame retardancy of PC. While the 3D-printed plates made of pure PC would pass the limit of EN 45545-2 for HL 1 and HL 2, the PC-batch containing FR 2 showed two times higher MARHE results. Hence, the flame retardant acts contrary to expectations as seen in the results using granulate instead of 3D-printed plates. Thus, it has to be stated that flame retardants may act differently, depending on the processing history and sample shape, respectively.

8. Comparison to UL 94

While it is well known that flame retardant agents act differently depending if the material is exposed to an open flame or to heat radiation, UL 94 tests were carried out for comparison reasons [14]. The results of the tests are given in Table 8. While the pure Polycarbonate fulfils the criteria for a V0-rating, this is only true with a print density lower or equal to 50%. Furthermore, FR 1 and FR 2 seem to worsen the flammability when tested with an open flame. While an additive content of 2% FR 2 does not influence the UL 94-rating of PC, an additivation of 5% causes the material to fail to reach a V0-rating. Additionally, if 30% FR 1 is added to PC, no rating according to UL 94 was reached. Only at a print density of 50% a V1-rating is possible. The test specimens of both PC-blends are shown in Figure 10. The UL 94-results are comparable to the data obtained via Cone Calorimeter. Likewise, it seems that the flammability of printed materials, tested by UL 94, is also influenced by the printing parameters in a complex way.

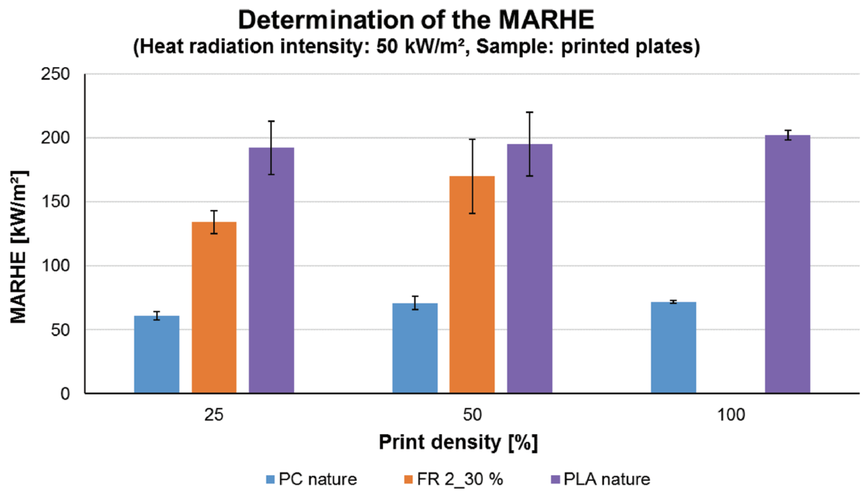

Fig. 9. Influence of the print density on the MARHE of PC and PLA

Table 8

Influence of the print density to flammability of nature and modified PC

Material	Print density [%]	Overall burning time [s]	Evaluation
PC nature	25	6	V0
	50	4	V0
	100	13	V1
FR 1_30%	25	36	failed
	50	32	V1
FR 2_2%	25	13	V1
	50	8	V0
FR 2_5%	25	10	V1
	50	15	V1

9. Conclusions

Pre-tests using granulate for the flammability tests with the Cone Calorimeter proved the effectiveness of the flame retardant masterbatches FR 1 and FR 2. While the granulate contains a significant amount of air between the individual particles, the ignition time is shortened if compared with printed specimens (Figure 7). Furthermore, the Heat Release Rate is higher if granulate is tested (see Table 5). This may be caused by the additional thermal stress during filament extrusion and printing.

While a 50% reduction of the print density does cause a total mass loss of only 9% for the printed samples (Table 3), the MARHE was lowered significantly for Polycarbonate. At a print density of 25% the MARHE was reduced by 15% compared to a dense printed sample (Table 6).

Reducing the print density causes a higher standard deviation which was especially noticeable for Polycarbonate with a high content of flame retardant (30% FR 2) shown in Table 7 and Figure 8.

Tests according to UL 94 showed a complex influence of the printing density on the flammability properties. While a high print density causes pure PC to lose its V0 rating this influence was reversed when using flame retardants. Hence, a higher print density causes better burning behaviour for the flame retardant materials.

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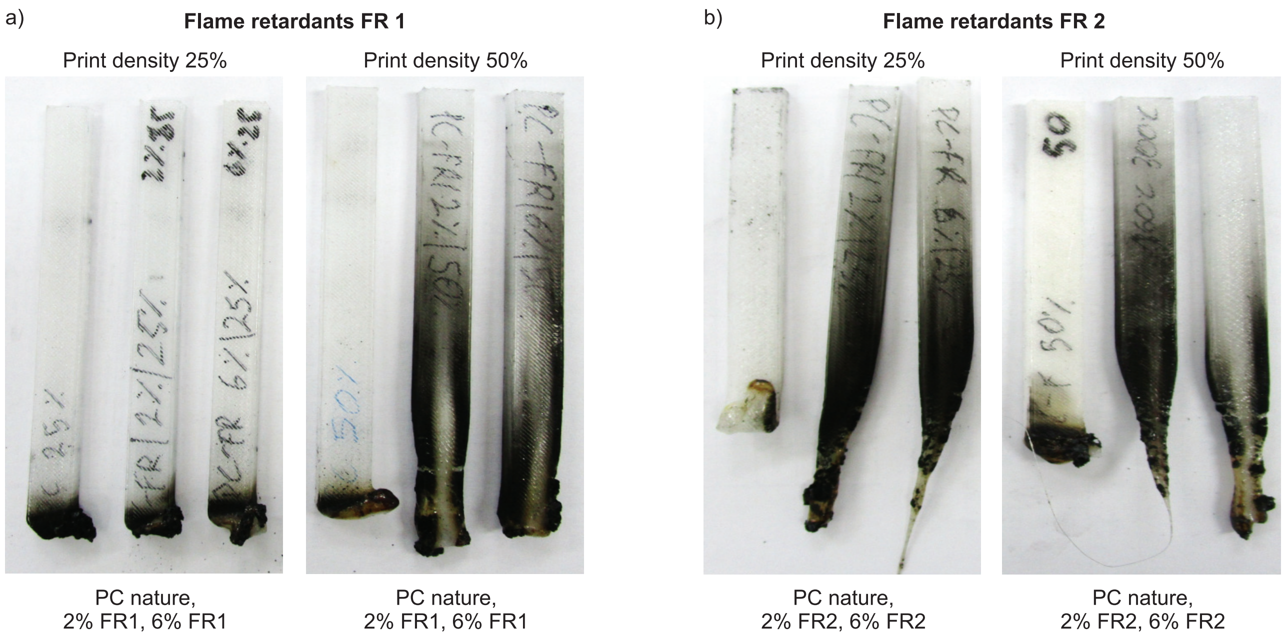

Fig. 10. UL 94-specimens after testing of PC blended with FR 1 (a) and FR 2 (b)

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