


ARTICLE

Intrinsic flame retardancy of poly(lactic acid) bead foams

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Abstract

Linear economy models are no longer acceptable for the plastic industry and a change to a sustainable circular plastic economy must take place. In the field of thermoplastic foams, the biopolymer poly(lactic acid) (PLA) is a suitable alternative for fossil based foams like polystyrene. However, the production of PLA bead foams is still a challenge. In regards to circular plastic economy products, a reduction of the needed polymer additives is aspired to simplify the union of end-of-life plastic streams. Flame retardants (FR) are required in many applications and are often the largest proportion of additives. It turns out that the removal of FRs, for example the removal of the REACH registered FR hexabromocyclododecane for polystyrene foams, requires a great effort. This paper shows that PLA bead foams require no FR to achieve a class E classification for construction products. Therefore, nine PLA types are analyzed by differential scanning calorimetry, thermogravimetric analysis, gel permeation chromatography, and rheotens measurements. From five types, PLA bead foams could be produced with two different densities. In addition, PLA bead foams containing 1.5 wt% alkoxy amine FR were produced. The flammability of the PLA bead foams was investigated by LOI, DIN-4102-1-B2, and cone calorimeter tests.

KEYWORDS

biomaterials, degradation, flame retardance, foams, thermoplastics

1 | INTRODUCTION

The chemical and plastic industry face today dramatic challenges. Linear plastic economy models leading to a global unmanageable accumulation of plastic waste in the ecosystems are no longer socially accepted. Therefore, plastic products are increasingly losing acceptance among consumers and within the society. A transformation from a linear to a circular plastic economy is essential to ensure the future of our world and

restore the acceptance of plastic products among the society.

Together with the implementation of a circular plastic economy, the use of biopolymers is increasingly moving into the focus of the plastic industry. Biopolymers, especially biodegradable polymers produced from renewable resources, are suitable for sustainable circular economy products. Poly(lactic acid) (PLA), polyhydroxyalkanoates (PHAs), polybutylene succinate (PBS), and starch compounds are such biopolymers.¹ They are manufactured

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from renewable resources, are potentially biodegradable and have a large recycling potential due to their thermoplastic processing behavior. From these biopolymers only PLA with a global production capacity of about 0.29 million tonnes in 2019¹ is currently commercially well-developed, cost competitive and readily available.² Large quantities of a specific material are important for a circular economy to ensure a sufficient material flow. Usually the collection of sufficient quantities of end-of-life materials of a specific polymer type and unsuitable recycling technologies are the main restricting aspect regarding the circular economy.

In the application field of thermoplastic foams, PLA is believed to replace polystyrene (PS), polyethylene terephthalate (PET), and polyethylene (PE) in, for example, the packaging industry.²⁻⁴ Today, PLA foams are already used in food packaging applications as a replacement for EPS products.⁵ Forthcoming PLA foams could be used in long-term applications, for example, in the automotive or construction sector. Furthermore, in the medical sector PLA foams can be used as tissue engineering or drug release components.⁶

Besides these already implemented applications, a lot of research is taken out regarding PLA foaming. PLA foams produced by batch foaming technologies^{7,8} and produced by extrusion-foaming technologies^{3,4,9} are discussed in the literature and patents.¹⁰⁻²⁹ A comprehensive overview is provided by Park et al.^{2,30}

Bead foam technology is used to produce low-density products with a complex three-dimensional foam geometry and is well-established for, for example, expanded polystyrene (EPS) products. However, the production of PLA bead foams by conventional bead foam technology is still a great challenge and especially the sintering process of pre-expanded PLA beads to PLA bead foam products causes problems due to the semi-crystallinity of PLA.²

For most application areas, in which a polymeric foam-product is applicable, the flammability of this product is essential. However, so far little is reported in the literature on this topic for PLA foams. For PLA foams produced by batch foaming technologies, Zhai et al.^{7,31} report LOI tests and UL-94 tests on microcellular PLA with phosphorus-containing flame retardants and graphene. LOI values of 18.6 O₂% are reported for pure PLA samples before these samples were foamed (sample thickness: 0.5 mm) and 18.2 O₂% for pure PLA samples after these samples were foamed (sample thickness: 0.8–1.0 mm).⁷ The UL-94 tests is failed by the pure PLA foam.⁷ For PLA foam produced by extrusion foaming, flame-retardant-treated cellulose in combination with an ammonium polyphosphate based intumescent flame retardant system are reported.⁴ The observed LOI value of the pure PLA foam is 20.0 O₂%.⁴ According to the LOI tests, the PLA foam is slightly more flammable than the PLA bulk material.⁴ To the best of our knowledge, the flammability

of PLA bead foams produced by bead foam manufacturing technology² are not reported in the literature.

With regards to circular plastic economy, plastics with a low number of different additives and small amount of these additives are of high interest. It is expected that end-of-life plastics of the same polymer type can be combined more easily. A main objective of flame retardant system development in the field of circular plastic economy is, therefore, the reduction of the required flame retardant amount. The use of intrinsic polymer flame retardant properties is of particular importance in this context. As already shown for polyurethane flexible foams,³² the composition of the polymer matrix influences the flammability of a foam significantly. However, the morphology of a product, especially of foams, is essential for the flammability and burning behavior. Therefore, results of flammability investigations on PLA of different morphologies, for example, on compact PLA samples are not suitable for comparisons or flammability performance predictions. The intrinsic polymer flame retardant properties must be tested on PLA bead foams.

The objective of this paper is to investigate the effects of different PLA polymer matrices on the flammability of bead foams produced from these PLA types. Therefore, the thermal properties as well as the properties of the polymer melt of nine different PLA types were analyzed and the production of bead foams on industrial equipment in a technical scale including the three steps (1) incorporation of a blowing agent by extrusion (2) pre-foaming of polymer beads and (3) sintering of pre-foamed beads to bead foam specimens was investigated. The flammability of the obtained bead foam specimens was tested by limiting oxygen index (LOI), DIN 4102-1 B2, and cone calorimeter tests.

2 | MATERIALS

Nine different PLA types were studied, see Table 1.

For the PLA bead foam production, a physical blowing agent, a nucleating agent, and Flamestab® NOR116 from BASF SE as flame retardant (FR) were used.

3 | EXPERIMENTAL

3.1 | Bead foam preparation

For the preparation of blowing agent containing beads, a twin-screw extruder ZSE 27 iMAXX from Leistritz was used. Polymer, nucleating agent (talc, 0.4%) and flame retardant are pre-mixed and fed into the extrusion line. There the polymer is melted, the physical blowing agent (2-methylpropane, 5%) is added and all components are homogenized. The mixture was extruded through a multi hole die and the strand

TABLE 1 PLA types which are investigated

#	Type	Producer	MFI (210°C/2.16 kg)
PLA-1	4032 D	NatureWorks LLC	7 g/10 min ³³
PLA-2	4060 D	NatureWorks LLC	8.5 g/10 min
PLA-3	6302 D	NatureWorks LLC	15–20 g/10 min ³⁴
PLA-4	7032 D	NatureWorks LLC	7 g/10 min
PLA-5	8052 D	NatureWorks LLC	14 g/10 min ³⁵
PLA-6	BF2004	Synbra	35.1 g/10 min
PLA-7	BF2005	Synbra	31.9 g/10 min
PLA-8	Luminy L175	Total Corbion	8 g/10 min ³⁶
PLA-9	Luminy LX175	Total Corbion	6 g/10 min ³⁷

was pelletized via an underwater-pelletizer LPUTM from Gala. The blowing agent loaded granules were stored into tightly sealed metal and plastic barrels, to minimize the release of blowing agent from the granules.

The blowing agent containing granules were pre-expanded with an EDVD-150 pre-expander from Erlenbach at 80–100°C steam temperature for 15–80 s, depending on the PLA type and the intended densities. From each polymer type and bead density, 30 L of the produced pre-foamed beads were bottled and stored in a bucked and tightly sealed barrel.

For the production of bead foam specimens, pre-expanded beads were sintered in a wooden form inside an oven or in a heated steel tool. The sintering temperatures were 80–130°C in both cases. The sintering times were 0.5–3 h. The wooden forms were allowed to cool down overnight. The steel tool was actively cooled. Two wooden forms with 200 × 200 × 50 mm³ and 500 × 500 × 50 mm³ were used for the sintering process in the oven. The steel tool has a volume of 1.6 L (220 × 220 × 40 mm³).

For each PLA type and density of the PLA foams, at least three plates with one of the smaller forms (smaller wooden form or steel tool) or one large plate with the larger wooden form were produced. From these plates, the necessary test specimens were cut using a hot wire cutting device.

3.2 | Characterization

3.2.1 | Differential scanning calorimetry

The differential scanning calorimetry (DSC) measurements were performed with a DSC 1 from Mettler Toledo in a nitrogen atmosphere from 0 to 230°C with a heating rate of 10 K/min. The sample mass was about 8.0 mg. From the DSC measurements, the glass transition temperature was determined. For the determination of the melting point (mp) of the crystalline parts, the peak minimum was used. The crystallinity (X_c) of PLA granulates was calculated from the measured melting enthalpy ΔH_m

and enthalpy of crystallization during heating ΔH_c by $[(\Delta H_m - \Delta H_c) / \Delta H_m^0] \cdot 100\%$ with $\Delta H_m^0 = 93 \text{ J/g}$.⁴

3.2.2 | Thermogravimetric analyses

The thermogravimetric analyses (TGA) measurements were performed with a TG 209 F1 Iris from Netzsch in a nitrogen atmosphere. The heating rate was 10 K/min and the sample mass was about 8.0 mg.

3.2.3 | Gel permeation chromatography

The gel permeation chromatography (GPC) measurements were performed with a GPC from PSS with a LC 1100 Agilent with refractive index detector. 1.8–2.5 mg/ml PLA solutions in 1,1,1,3,3,3-hexafluoro-propan-2-ol (HFIP) and a HFIP flow rate of 1.0 ml/min was used. The PLA solutions were prepared by dissolving PLA in HFIP for 24 h. Before the injection, the PLA solution was filtered using 0.45 µm syringe filters.

3.2.4 | Rheotens measurements

The elongation behavior of the polymer melt was studied by a Rheotens test on a melt strand. The Rheotens tests were performed with a high pressure capillary viscometer Rheograph 20 from Göttfert. The used test setup was: punch diameter: 12 mm, nozzle pressure: 65 bar, nozzle diameter: 2 mm, nozzle length: 30 mm, distance between nozzle and rollers: 96 mm and haul-off acceleration: 20 mm/s².

3.2.5 | Melt flow index

The melt flow index (MFI) was measured according to ISO 1133 B at 210°C and with a load of 2.160 kg using a CEAST MF20 melt flow tester from Instron.

3.2.6 | Limiting oxygen index

The limiting oxygen index (LOI) value was measured by using an oxygen index module from FIRE according to DIN EN ISO 4589-2 standardized procedure. The used sample size was type II ($10 \times 10 \times 100 \text{ mm}^3$).

3.2.7 | DIN 4102-1 B2

The DIN 4102-1 test was performed with a test device from WAZAU according to the DIN 4102-19 standard. For each material, three samples with a sample size of $200 \times 90 \times 25\text{--}50 \text{ mm}^3$ were tested.

3.2.8 | Cone calorimeter ISO 5660-1

Cone calorimeter measurements were taken using a ISO 5660-1 device from WAZAU. The sample size was $100 \times 100 \times 50 \text{ mm}^3$, with three samples tested for each material. The samples were wrapped in aluminium foil and positioned horizontally at a distance of 25 mm from the cone base heater plate, where a heat flux of 35 kW/m^2 was applied. The data were recorded in increments of 1 s.

4 | RESULTS AND DISCUSSION

4.1 | Characterization of the PLA granulates

The thermal properties of the nine PLA granules were studied by DSC and TGA. The results are shown in Table 2.

For all nine studied PLA types, the glass transition temperature with $58 \pm 3^\circ\text{C}$ and the T_{onset} temperature of the first thermal decomposition with $341 \pm 4^\circ\text{C}$ are identical. Based on the melting point, the nine PLA types are classified in three categories. PLA types with:

1. a melting point of $150\text{--}160^\circ\text{C}$ (PLA-5, PLA-6, PLA-7, PLA-9)
2. a melting point of $170\text{--}180^\circ\text{C}$ (PLA-1, PLA-4, PLA-8)
3. no melting point/amorphous (PLA-2, PLA-3)

The four PLA types of category "mp: $150\text{--}160^\circ\text{C}$ " show a crystallinity of 34.0%–37.3% with exception of PLA-7 with shows a crystallinity of only 25.8%. The re-crystallization tendency after the first heating and cooling cycle of the DSC measurement of these PLA-types is weak with 0.0%–1.3%. Compared to category "mp: $150\text{--}160^\circ\text{C}$ ", the three PLA types of category "mp: $170\text{--}180^\circ\text{C}$ " show a higher crystallinity of 42.6%–51.4% and a higher re-crystallization tendency of 1.8%–2.4%.

The molecular weights of the nine PLA granules were measured by GPC and the viscosity of the molten polymers were analyzed by Rheotens measurements. The results are shown in Table 3.

The two PLA types of the category "amorphous" are a PLA type (PLA-3) with lower molecular mass of $2.68 \cdot 10^5 \text{ g/mol}$ and a lower melt viscosity of 0.026 N at 185°C and a PLA type (PLA-2) with a higher molecular mass of $3.17 \cdot 10^5 \text{ g/mol}$ and a higher melt viscosity of 0.044 N at 185°C .

Category "mp: $170\text{--}180^\circ\text{C}$ " contains three PLA types with a molecular mass of $2.26 \cdot 10^5$ to $2.64 \cdot 10^5 \text{ g/mol}$ and two PLA types (PLA-1, PLA-4) with a higher melt viscosity of 0.033 N to 0.048 N at 185°C and one PLA type (PLA-8) with a lower melt viscosity of 0.022 N at 185°C .

The molecular masses of the PLA types of category "mp: $150\text{--}160^\circ\text{C}$ " are similar with $2.44 \cdot 10^5$ to $2.64 \cdot 10^5 \text{ g/mol}$. Three of them (PLA-6, PLA-7, PLA-9) show very low melt viscosities of 0.004 N to 0.006 N at 185°C and PLA-5 shows a higher melt viscosity of 0.048 N at 185°C .

Each category with regard to the melting point contains PLA types with a high melt viscosity and PLA types with a low melt viscosity.

#	$T_g/^\circ\text{C}$	Mp/ $^\circ\text{C}$	$X_c/\%$, 1th heating	$X_c/\%$, 2nd heating	$T_{\text{onset}}/^\circ\text{C}$
PLA-1	61	171	42.8	2.4	340
PLA-2	56	amorphous	—	—	340
PLA-3	57	amorphous	—	—	338
PLA-4	61	170	42.6	1.8	338
PLA-5	60	155	34.6	1.3	338
PLA-6	59	155	34.0	0.3	344
PLA-7	59	151	25.8	0.0	345
PLA-8	60	180	51.4	2.4	343
PLA-9	60	158	37.3	0.0	344

TABLE 2 Thermal properties of PLA granulates measured by differential scanning calorimetry and thermogravimetric analyses

TABLE 3 Properties of PLA granules measured by gel permeation chromatography and Rheotens

#	GPC		Rheotens: pull-off forces/N				
	M_w /g/mol	D	170°C	175°C	180°C	185°C	190°C
PLA-1	$2.49 \cdot 10^5$	2.055	—	—	0.050	0.033	0.035
PLA-2	$3.17 \cdot 10^5$	2.175	—	—	0.053	0.044	0.035
PLA-3	$2.68 \cdot 10^5$	2.035	0.044	0.030	0.035	0.026	0.021
PLA-4	$2.64 \cdot 10^5$	2.069	—	—	0.063	0.048	0.040
PLA-5	$2.44 \cdot 10^5$	2.112	0.050	0.038	0.031	0.048	0.040
PLA-6	$2.50 \cdot 10^5$	2.180	0.024	0.018	0.016	0.005	—
PLA-7	$2.64 \cdot 10^5$	2.232	0.033	0.011	0.020	0.004	—
PLA-8	$2.26 \cdot 10^5$	2.184	—	—	0.075	0.022	0.014
PLA-9	$2.57 \cdot 10^5$	2.260	0.024	0.021	0.018	0.006	—

**FIGURE 1** From left to right: PLA granule, PLA blowing agent containing granule, pre-expanded PLA beads and sintered PLA bead foam plate [Color figure can be viewed at wileyonlinelibrary.com]

4.2 | Bead foam formation using different PLA types

Bead production and bead foams of eight different PLA types were studied by the preparation of blowing agent containing PLA granules, the pre-foaming of these granules to PLA beads and the sintering of the PLA beads to PLA bead foams. An illustration of the obtained material is given in Figure 1.

The density of the PLA bead foam specimens with no flame retardant (FR) and with 1.5 wt% FR are shown in Table 4.

According to the three PLA type classes with regard to the melting point, a clear tendency with regard to the pre-foaming of the blowing agent containing beads and the sintering of the pre-foamed beads is observed.

PLA types with a melting point of 170–180°C (PLA-1, PLA-4, PLA-8) can be pre-foamed. However, these PLA

TABLE 4 Density in g/L of the bead foam specimens with no flame retardant (FR) and 1.5 wt% FR

	PLA-1	PLA-3	PLA-4	PLA-5	PLA-6	PLA-7	PLA-8	PLA-9
No FR, Low density/g/L	Sintering problems	30	Sintering problems	34	40	39	Sintering problems	34
No FR, High density/g/L		53		52	77	75–81		53
1.5 wt.% FR, Low density/g/L	Sintering problems	37	Sintering problems	26	33–35	31	Sintering problems	32–34
1.5 wt.% FR, High density/g/L		58		50	55	48		60

types show problems within the thermal sintering of the pre-foamed beads, due to the high melting point.

From the amorphous PLA type (PLA-3), PLA bead foam specimens are obtained. Pre-forming and sintering of the beads shows no problems. To study the influence of the density of the PLA bead foam specimens on the flammability, specimens with a low density of 30–37 g/L and specimens with a high density of 53–58 g/L were produced. The addition of 1.5 wt% of FR increases slightly the density of the obtained PLA bead foam specimens.

From all the semi-crystalline PLA types with a lower melting point of 150–160°C (PLA-5, PLA-6, PLA-7, PLA-9) PLA bead foam specimens can be produced. Compared with the amorphous bead foams, foams of these semi-crystalline PLA types show less efficient sintering which increases the susceptibility to damage. For each PLA type, PLA bead foam specimens with a low and a high density were produced. For formulations without a FR, low density PLA bead foam specimens with a density of 34–40 g/L and specimens with a higher density of about 52 g/L (PLA-5, PLA-9) and 75–81 g/L (PLA-6, PLA-7) are obtained. The addition of 1.5 wt% FR decreases the density of the obtained PLA bead foam specimens with the exception of the high density PLA-9 specimen.

Due to the obtained result, semi-crystalline PLA types with a lower melting point of 150–160°C and amorphous PLA types seem to be the preferred materials for realizing PLA bead foam products.

4.3 | Flame retardant properties

The flame retardant properties of the PLA bead foam specimens were studied by the limiting oxygen index (LOI) test and the DIN 4102–1 B2 test, which is, in a similar version as EN ISO 11925-2, commonly used for the classification of isolation materials like thermoplastic foams used as construction products. The LOI and DIN 4102–1 B2 test results are shown in Table 5.

For each of the five PLA types, PLA formulations without and with 1.5 wt% FR were prepared, and two different foam densities were studied for each PLA

TABLE 5 Limiting oxygen index and DIN 4102–1 B2 test results of PLA bead foam specimens of PLA-3, PLA-5, PLA-6, PLA-7, and PLA-9

#	FR/wt%	Density/g/L	LOI/O ₂ %	DIN 4102–1 B2
PLA-3	0.0	30	25.7 ± 0.48	fail
		53	23.1 ± 0.38	fail
	1.5	37	24.8 ± 0.27	pass
		58	23.1 ± 0.38	fail
PLA-5	0.0	34	29.0 ± 0.40	pass
		52	30.0 ± 0.40	pass
	1.5	26	34.5 ± 0.40	pass
		50	32.6 ± 0.38	pass
PLA-6	0.0	40	30.4 ± 0.38	pass
		77	27.8 ± 0.27	pass
	1.5	33–35	31.8 ± 0.27	pass
		55	28.8 ± 0.27	pass
PLA-7	0.0	39	32.8 ± 0.27	pass
		75–81	28.3 ± 0.27	pass
	1.5	31	34.1 ± 0.38	pass
		48	31.1 ± 0.38	pass
PLA-9	0.0	34	32.3 ± 0.27	pass
		53	27.3 ± 0.27	pass
	1.5	32–34	32.8 ± 0.27	pass
		60	30.3 ± 0.48	pass

formulation. Figure 2 shows the LOI test results of all 20 samples.

For all ten PLA formulations, with the exception of FR-free PLA-5, the foams with lower density show higher LOI values which correspond with a higher flame resistance of the foams. Of the foams with lower densities, PLA-3 shows the lowest LOI with 25.7 O₂%. The LOIs of PLA-6, PLA-7, and PLA-9 are about 30–33 O₂%. For these four foams, the LOI difference (Δ LOI) between low density foam and high density foam (density difference: Δ density) of the same PLA type are in the range of 2.6 O₂% to 5.0 O₂% by a Δ density range of –19 to –40 g/L.

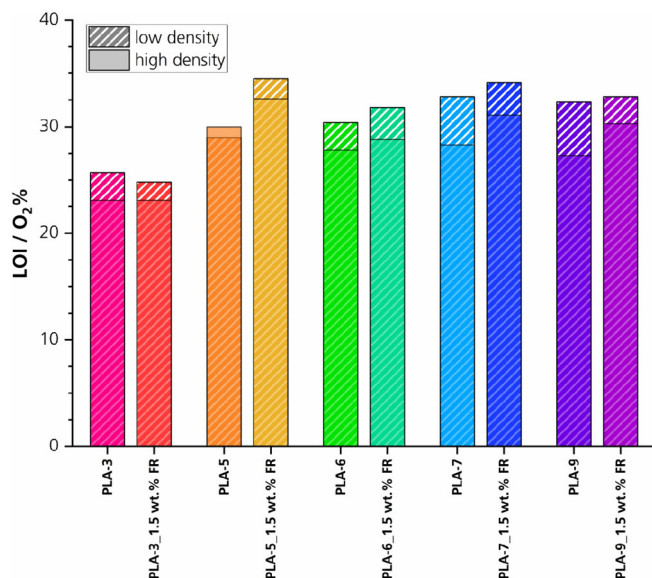


FIGURE 2 Limiting oxygen index test results of 20 PLA bead foam specimens (five PLA types; PLA formulations without and with 1.5 wt% FR for each PLA type; two different densities for each PLA formulation) [Color figure can be viewed at wileyonlinelibrary.com]

A correlation between ΔLOI and $\Delta\text{density}$ is not observed. In contrast, PLA-5 shows a ΔLOI : $-1.0\text{ O}_2\%$ by a $\Delta\text{density}$ of -18 g/L .

For all PLA formulations with 1.5 wt% FR, the foams with lower density show higher LOIs. The ΔLOIs are in the range of $1.7\text{ O}_2\%$ to $3.0\text{ O}_2\%$ by a $\Delta\text{density}$ range of -17 to -27 g/L . As well as for the FR-free PLA foams, no correlation between ΔLOI and $\Delta\text{density}$ is observed.

In comparison to the FR-free PLA foams of the same density range, the PLA bead foams with 1.5 wt% FR show higher LOIs with the exception of PLA-3. The highest LOI increase with $5.5\text{ O}_2\%$ is observed for lower density PLA-5 foams.

Marosi, Bourbigot et al.⁴ reports a LOI of about $20\text{ O}_2\%$ for foamed PLA type 3052D from NatureWorks LLC which is a semi-crystalline PLA with a melting point of $145\text{--}160^\circ\text{C}$ and a MFI of $14\text{ g}/10\text{ min}$ @ 210°C / 2.16 kg . This PLA foam was produced by an extrusion foaming process using a chain extender (Joncryl ADR4368-C type, BASF SE) and shows a density of approximately 620 g/L .⁴ Zhai et al.⁷ reports a LOI of $18.2\text{ O}_2\%$ for PLA foam produced from PLA resin from Ningbo Huanqiu Co., China by a batch foaming process.

Compared to these results, all FR-free PLA foams of this study show significant higher flame resistance in the LOI test. It is assumed that both the morphology of the foams obtained by different foaming processes and the density of the studied foams are responsible for the lower flame resistance of the PLA foams reported in the

literature. Lab scale foams are susceptible to density inhomogeneities which can lead to a lower flame resistance. Furthermore, foams with a very low or a very high density are known to us for lower flame resistance. As reported in this study, PLA bead foams with a density of about 50 g/L instead of about 30 g/L show lower LOI values. For foams with a very high density of about 600 g/L a further reduction of the LOI value to the LOI range of compact PLA ($18\text{--}22\text{ O}_2\%$) is expected.

The DIN 4102-1 B2 test is passed by all PLA formulations and foam densities of PLA-5, PLA-6, PLA-7, and PLA-9. FR-free PLA-3 foams with lower density and higher density as well as PLA-3 foam with a higher density containing 1.5 wt% FR fail the DIN 4102-1 B2 test. Only the PLA-3 foam with a density of 37 g/L containing 1.5 wt% FR passes the DIN 4102-1 B2 test.

In comparison to the LOI results, PLA bead foams with LOIs above $27.3\text{ O}_2\%$ have to be considered to pass the DIN 4102-1 B2 test. PLA bead foams with LOIs below $25.7\text{ O}_2\%$ have to be considered to fail the DIN 4102-1 B2 test.

Both pure PLA foams reported by Marosi, Bourbigot et al, and Zhai et al show no self-extinguishing effects in the horizontal UL94 test.^{4,7} Compared to these results, all FR-free PLA foams of this study, with the exception of PLA-3, show self-extinction in the DIN 4102-1 B2 test.

In comparison to the previously in chapter 3.1 mentioned PLA classes with regard to the melting point, amorphous PLA types seem to be more flammable as semi-crystalline PLA types with a melting point of $150\text{--}160^\circ\text{C}$ according to the achieved LOI and DIN 4102-1 B2 test results.

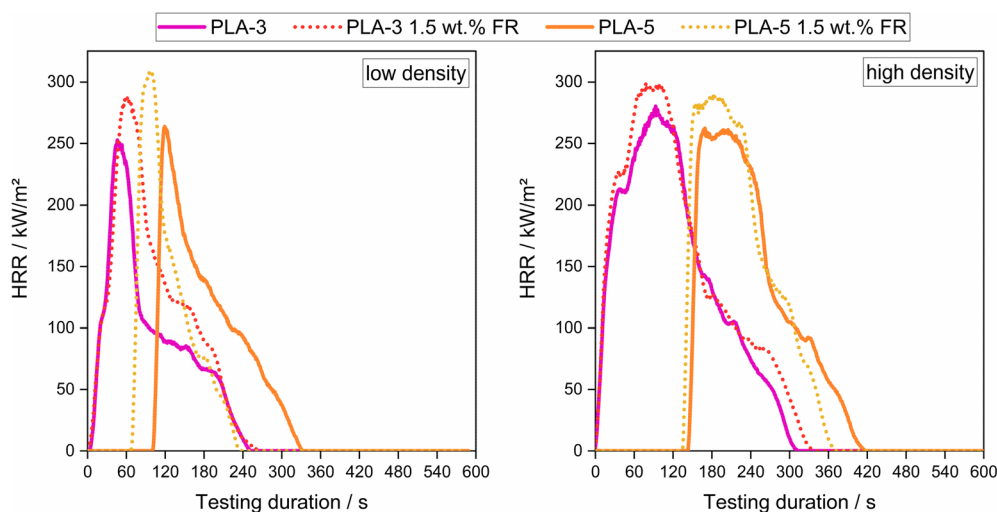
With the use of the cone calorimeter test, it is possible to extract several parameters that give a concise insight into the intensity of a fire. Additionally, these parameters enable the comparison of different materials and their flame retardancy. For the cone calorimeter evaluation, the amorphous PLA type (PLA-3) the semi-crystalline type (PLA-5) were selected for comparison. For each PLA type, a material with high and low density was tested with and without the addition of 1.5 wt% FR. The following readings were evaluated in particular:

- **Relative weight loss** (wt%)
- **TTI**: time to ignition (s)
- **HRR**: heat release rate (kW/m^2)
- **PHRR**: peak heat release rate (kW/m^2)
- **THR**: total heat release (MJ/m^2)
- **FPI**: fire performance index (sm^2/MW)
- **FIGRA**: fire growth rate (W/s)

The results for TTI, PHRR, THR, FPI, and FIGRA are shown in Table 6. Several recorded parameters showed a

TABLE 6 Results obtained by cone calorimetry of bead foam specimens from PLA-3 and PLA-5

#	FR/wt%	Density/g/L	TTI/s	PHRR/kW/m ²	THR/MJ/m ²	FPI/sm ² /MW	FIGRA/W/s
PLA-3	0.0	30	5 ± 1	244 ± 15	23.4 ± 2.6	20.7 ± 5.4	56.7 ± 6.6
		53	2 ± 0	283 ± 3	44.9 ± 1.5	7.1 ± 0.1	79.8 ± 4.2
	1.5	37	4 ± 2	265 ± 34	29.8 ± 1.8	13.9.0 ± 9.8	48.7 ± 2.7
		58	2 ± 0	287 ± 12	50.4 ± 4.9	7.0 ± 0.3	85.9 ± 5.4
PLA-5	0.0	34	99 ± 4	274 ± 10	27.0 ± 1.7	361.6 ± 25.1	20.4 ± 1.0
		52	144 ± 16	267 ± 10	36.8 ± 2.2	539.6 ± 78.4	14.3 ± 1.7
	1.5	26	71 ± 4	303 ± 7	21.2 ± 1.1	234.8 ± 19.6	29.4 ± 2.2
		50	134 ± 7	282 ± 6	41.1 ± 1.6	475.0 ± 27.7	16.1 ± 1.0

FIGURE 3 Heat release rates of bead foams from PLA-3 and PLA-5 with and without 1.5 wt% FR; left: low density bead foams; right: high density bead foams [Color figure can be viewed at wileyonlinelibrary.com]

varying flammability and ignitability for the amorphous and semi-crystalline bead foamed PLA types, which was similarly observed in bulk PLA composites by Jia et al.³⁸

Whilst observing the cone calorimeter measurement it became obvious that the various PLA-3 and PLA-5 specimen respectively manifested similar behaviors. Semi-crystalline PLA-5 specimen are ignited once they were already molten, whereas amorphous specimens of PLA-3 already caught on fire before they melted completely, still in the form of foam. The only exception to this is the low density foam of PLA-3 containing FR, where one of three tested specimen showed late ignition, similar to all semi-crystalline specimens, leading to high standard deviations for that set of specimens. However, every bead foam specimen burned until there was no residue left.

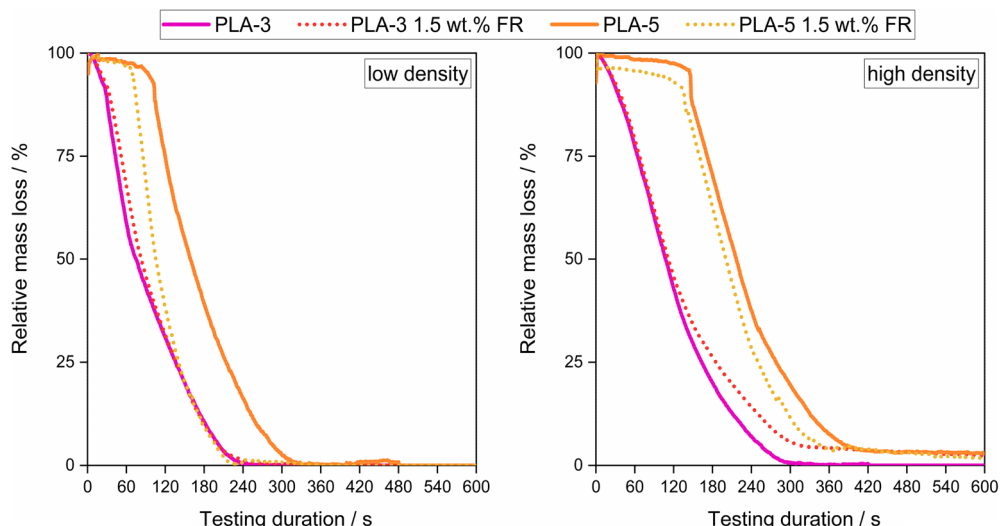
The TTI shows a high ignitability for amorphous PLA bead foams, whereas semi-crystalline foam samples took significantly longer to ignite. A higher density seems to have the second strongest impact upon increasing the TTI, at least for PLA-5 specimen. The amorphous PLA-3 specimens ignited with a TTI of 2–5 s too fast to observe a meaningful difference in value.

The heat release rate (HRR) of the PLA bead foams show a roughly similar shape with a shoulder before and after a heat release peak, see Figure 3. This shape is a typical HRR curve of a deforming material and occurs due to the PLA bead foam melting during measurement.³⁹

Compared to the lower density PLA bead foams, the PLA bead foams with a higher density, amorphous PLA-3, and semi-crystalline PLA-5 alike, show a broad maximum for the heat release rate that coincides with the higher amount of polymer in these foams available for combustion. The addition of 1.5 wt% FR leads to an increase of HRR and PHRR.

The PHRRs of the amorphous PLA-3 specimens are in the range of 244–287 kW/m² and the PHRRs of the semi-crystalline PLA-5 specimens are in the range of 274–303 kW/m². Thus the PHRR does not show evidence that it is influenced by the crystallinity of the foam beads. In fact, the measurements for the PHRR do not indicate a strong dependency on the availability of flame retardant in the foam either and only a slight dependency on the density of the specimens.

FIGURE 4 Relative mass loss of bead foams from PLA-3 and PLA-5 with and without 1.5 wt% FR; left: low density bead foams; right: high density bead foams [Color figure can be viewed at wileyonlinelibrary.com]



The THR results show as expected that a higher material density and thus more combustible material results in a higher amount of heat released. Overall, the FR containing foams show a slightly higher THR.

FPI indices and FIGRA indices were used to express the fireproofing quality of the PLA bead foams. The FPI was calculated as the quotient of TTI and PHRR^{39,40}:

$$FPI = \frac{TTI}{PHRR}$$

A higher FPI value indicates a higher safety rank of the material.⁴⁰ The FPI of amorphous PLA-3 bead foam specimens is in the range of 7–21 sm²/MW whereas the FPI of semi-crystalline PLA-5 bead foam specimens is in the range of 234–540 sm²/MW. This indicates that amorphous PLA bead foams and semi-crystalline PLA bead foams exhibit a vastly different fireproofing behavior due to the significant differences in TTI. It is assumed that the semi-crystalline parts prevent the PLA bead foam from the immediate ignition as the melting of these parts consumes energy and thus reduces the local rapid pyrolysis and gasification. Instead, the bead foam structure collapses and is retracted from the incineration source in this way.

FIGRA is a devised index trying to assess the complex information of a measurement into a single number.³⁹ Generally, the lower the FIGRA value, the lower the hazard produced by the burning specimen. The FIGRA was calculated as the maximum of the quotient of HRR and corresponding point in time³⁹:

$$FIGRA = \frac{HRR(t)}{t}$$

The FIGRA of amorphous PLA-3 bead foam specimens is in the range of 49–86 W/s whereas the FIGRA of

semi-crystalline PLA-5 bead foam specimens is in the range of 14–30 W/s.

The relative mass loss of each material is shown in Figure 4. An immediate loss of mass upon thermal radiation can be observed for all amorphous PLA-3 bead foams whereas rapid mass loss for semi-crystalline PLA-5 bead foams is delayed until ignition of the specimen. Once the rapid mass loss started, the mass loss rate is generally higher for semi-crystalline PLA-5 than for amorphous PLA-3 bead foams. The mass loss of PLA-5 bead foams shows that the addition of 1.5 wt% FR leads to a premature decomposition. This behavior could not be observed in amorphous samples due to their instant ignition with instant mass loss.

The effect of premature decomposition in the presence of the selected NOR can be explained through the known mechanism of the flame retardant, which accelerates the radical degradation of the polymer and removes the polymer from the incineration source through dripping.^{41–43} However, this flame retardant mechanism cannot be observed in cone calorimeter testing as dripping is not possible.

The cone calorimeter measurements confirmed the observed difference in flammability of PLA bead foams produced from amorphous and semi-crystalline PLA types found by LOI and DIN 4102–1 B2 tests.

5 | CONCLUSIONS

In this paper, the bead foam production performance and the flammability of nine different commercial PLA types were studied with regard to the PLA crystallinity, the foam density and the addition of FR additive.

Effect of the PLA crystallinity: Although PLA types with a melting point of 170–180°C can be pre-foamed,

the thermal sintering of the pre-foamed beads and the production of the bead foam plates were not feasible due to the high melting point. On the contrary, semi-crystalline PLA types with a lower melting point of 150–160°C and amorphous PLA were suitable to produce bead foam plates. Compared with the amorphous bead foams, bead foams of the semi-crystalline PLA types show less efficient sintering which increases the susceptibility to damage. To realize a sintering of the pre-foamed beads, only the surface of the beads must be melted sufficiently. It is assumed that semi-crystalline parts prevent the melting process, which leads to a less efficient sintering of the pre-foamed beads. In flammability test, semi-crystalline bead foams show lower flammability (LOI: 27–33 O₂%) than amorphous ones (LOI: 23–26 O₂%). Cone calorimeter measurements confirmed this observation, proven through an extended time to ignition of semi-crystalline bead foams, resulting in higher FPI and lower FIGRA values. It is assumed that the melting of the semi-crystalline parts has a significant influence and prevents the PLA bead foam structure from immediate ignition and act as heat absorber. All bead foams from semi-crystalline PLA types passed the DIN 4102–1 B2 test.

Effect of the foam density on flammability: PLA bead foam plates with a low density of 30–40 g/L and a high density of 50–80 g/L were analyzed. PLA bead foams with lower density show higher flame resistance. It is assumed that the availability of polymer material in the area adjacent to the flame front, which is lower for foams with a lower density, is responsible for this. To realize the same pyrolysis gas release rate, a larger area of a foam with low density must be heated and pyrolyzed in the same time compared to a foam with high density. The comparatively larger heat flux into the surroundings reduces the heat flux into the polymer matrix and leads to a higher LOI for foams with low density.

Effect of a NOR FR: In comparison to the FR-free PLA bead foams of the same density range, the PLA bead foams with 1.5 wt% FR show higher LOIs. An acceleration of the radical degradation of the polymer and removing the polymer from the incineration source through dripping is assumed as main flame retardant effect of NOR FR on PLA. Low-density PLA bead foams of amorphous PLA containing 1.5 wt% FR passed the DIN 4102–1 B2 test.

In the spirit of circular plastic economy, the absence of flame retardant additives improves the recyclability performance of PLA bead foams as PLA production waste and end-of-life PLA bead foams can be combined easily with other PLA production waste and PLA end-of-life material streams. Compared with conventional bead foam products produced from polystyrene or polypropylene, which must contain a flame retardant to achieve the

same flame resistance as PLA bead foams, PLA bead foams represent a more sustainable circular plastic economy solution for bead foam products.

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REFERENCES

- [1] nova-Institute, European Bioplastics-Bioplastics Market Data, **2019**
- [2] M. Nofar, C. B. Park, *Poly lactide Foams: Fundamentals, Manufacturing, and Applications*, William Andrew, Oxford **2018**.
- [3] S. Pilla, S. G. Kim, G. K. Auer, S. Gong, C. B. Park, *Polym. Eng. Sci.* **2009**, *49*, 1653.
- [4] D. Vadas, T. Igricz, J. Sarazin, S. Bourbigot, G. Marosi, K. Bocz, *Polym. Degrad. Stab.* **2018**, *153*, 100.
- [5] S.-T. Lee, *Polymeric Foams: Innovations in Processes, Technologies, and Products*, CRC Press, Boca Raton, London **2016**.
- [6] T. Standau, C. Zhao, S. Murillo Castellón, C. Bonten, V. Altstädt, *Polymers* **2019**, *11*, 306.
- [7] K. Wang, J. Wang, D. Zhao, W. Zhai, *J. Cell. Plast.* **2017**, *53*, 45.
- [8] M. Zhao, X. Ding, J. Mi, H. Zhou, X. Wang, *Polym. Degrad. Stab.* **2017**, *146*, 277.
- [9] M. Keshtkar, M. Nofar, C. B. Park, P. J. Carreau, *Polymer* **2014**, *55*, 4077.
- [10] R.N. Britton, F.A.H. Van Doormalen, J. Noordegraaf, K. Molenveld, G.G.J. Schennink US2010087556A, **2010**.
- [11] J. Noordegraaf, F.P.A. Kuijstermans, J.P.M. De Jong US2011218257, **2011**.
- [12] M. Gebraad, F.P.A. Kuijstermans, J. Noordegraaf US20130087735, **2013**.
- [13] P.F.M. Rensen, J. Noordegraaf, K. Van Den Hoonaard, P.H.J. Van Der Burgt US2013203879, **2013**.
- [14] C.B. Park, M. Nofar US2016039990, **2016**.
- [15] K. Molenveld, J.P.M. De Jong, J. Noordegraaf, K. Van Den Hoonaard, **2017**.
- [16] F. Hirose, K. Okuma JP2007186692, **2006**.
- [17] J. Liu, J. Chen, J. Feng CN101134362, **2007**.
- [18] A. Füßl, B. Sampath, M. Hofmann, I. Bellin, S. Nalawade, K. Hahn, A. Künkel, R. Loos WO2011086030, **2011**.
- [19] J. Lohmann, B.D.S. Sampath, P. Gutmann, A. Künkel, K. Hahn, A. Füßl WO14001119, **2014**.
- [20] J. Lohmann, B.D.S. Sampath, P. Gutmann WO16096481, **2016**.

- [21] B.D.S. Sampath, J. Lohmann, P. Gutmann WO17211660, **2017**.
- [22] K. Takase, T. Kawada, A. Iwamoto US2010086758, **2010**.
- [23] K. Haraguchi, H. Ohta US2006167122, **2006**.
- [24] T. Hirai, K. Nishijima, T. Ochiai US2010136338, **2010**.
- [25] M. Shinohara, M. Oikawa US2013288056, **2013**.
- [26] C. Beal, F. Chivrac, A.-F. Jacob US2015147507, **2015**.
- [27] M. Shinohara, M. Oikawa US2015315351, **2015**.
- [28] M. Shinohara, M. Oikawa US2014235741, **2014**.
- [29] T. Chiba, M. Oikawa US2017029591, **2017**.
- [30] S. Iannace, C. B. Park, *Biofoams: Science and Applications of Bio-Based Cellular and Porous Materials*, Taylor & Francis Inc, Bosa Roca **2016**.
- [31] J. Wang, Q. Ren, W. Zheng, W. Zhai, *Ind. Eng. Chem. Res.* **2014**, 53, 1422.
- [32] C.-C. Höhne, R. Hanich, E. Kroke, *Fire Mater.* **2018**, 42, 394.
- [33] Ingeo™ Biopolymer 4032D Technical Data Sheet, NW4032DGEN_051815V1.
- [34] Ingeo™ Biopolymer 6302D Technical Data Sheet, NW6302D_051815V1.
- [35] Ingeo™ Biopolymer 8052D Technical Data Sheet, NW8052D_051815V1.
- [36] LUMINY® L175 Product Data Sheet, 2019.
- [37] LUMINY® LX175 Product Data Sheet, 2019.
- [38] L. Jia, W.-C. Zhang, B. Tong, R.-J. Yang, *Chin. J. Polym. Sci.* **2018**, 36, 871.
- [39] B. Schartel, T. R. Hull, *Fire Mater.* **2007**, 31, 327.
- [40] G. Gallina, E. Bravin, C. Badalucco, G. Audisio, M. Armanini, A. de Chirico, F. Provasoli, *Fire Mater.* **1998**, 22, 15.
- [41] D. C. O. Marney, L. J. Russell, T. M. Soegeng, V. P. Dowling, *J. Fire Sci.* **2007**, 25, 471.
- [42] D. C. O. Marney, L. J. Russell, T. M. Stark, *Polym. Degrad. Stab.* **2008**, 93, 714.
- [43] C.-E. Wilén, R. Pfaendner, in *Polymer Green Flame Retardants: A Comprehensive Guide to Additives and their Applications* (Eds: C. D. Papaspyrides, P. Kiliaris), Elsevier, Amsterdam **2014**, p. 267.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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