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RESEARCH ARTICLE

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Flame retardant investigations on carbon fibre-reinforced polyurethane resin parts for aircraft applications produced by wet compression moulding

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Summary
Epoxy resins are widely used in composite materials for aircraft applications. However, they are difficult to recycle, thus posing an increasing challenge to the aviation sector. By contrast, polyurethane resins (PUR) can be easily chemically recycled by solvolysis, but structural parts made of carbon fibre-reinforced polyurethanes (CF-PURs) are currently not in use in aircraft applications. This is due to a lack of knowledge about the properties of CF-PURs, especially during exposure to higher temperatures and to fire. To increase the recyclability of aircraft parts, for example interior structures like seats, there is a need for CF-PUR components which are able to fulfil the flame retardant regulations as well as the quality and production cycle time requirements of the aviation industry. It was found that a CF-PUR formulation processed by wet compression moulding containing 9 wt% of a phosphorous polyol is able to fulfil these requirements for aviation interior applications.

KEYWORDS
carbon fibres, compression moulding, flame/fire retardancy, thermosetting resin

1 | INTRODUCTION

The use of carbon fibre-reinforced plastics (CFRP) in structural aerospace applications is steadily increasing. About 50 wt%, for example, of the Boeing Dreamliner 787 and the Airbus A350 XWB components already consist of CFRP.[1,2] Main driver for this development are legal requirements like the *Carbon Offsetting and Reduction Scheme for International Aviation* (CORSIA)[3] that aims a carbon neutral growth from 2020 and halved CO_2 emission till 2050 compared to 2005, the technology roadmap of the *International Air Transport Association* (IATA)[4] with focus on weight reduction of aircrafts by the use of composite structures for wing and fuselage as well as economic reasons—reduced weight means lower fuel consumption. The advantage of composites in aerospace structures is their outstanding lightweight potential compared to metal solutions. However, material and production costs for CFRP components are much higher than for comparable metal structures. Current state of the art for the manufacturing of structural aircraft components is the prepreg autoclave process technology, offering high part quality but limited production efficiency. An increasing number of identical parts per aircraft is pushing large-scale production processes such as resin transfer moulding (RTM) and wet compression moulding (WCM) into the aerospace industry improving the production efficiency.

The production of aircraft seating structures is an example for large volume production processes as it consists of several identical components and seating structures are needed multiple times per aircraft.

Within the EU-funded research project Clean Sky 2, an aircraft seating assembly is used as technology demonstrator for the WCM process as well as a technology demonstrator for future challenges within the aerospace industry. One of these challenges is the end-of-life recycling concept for aircraft parts. In the project, the end-of-life recycling concept is addressed by a mono material approach using polyurethane resin (PUR) as the polymer matrix of the WCM parts. In contrast to the epoxy resins usually used in the aviation industry, PUR can be easily chemically recycled by solvolysis and the polyol fraction recovered as well as the carbon fibres from CFRP components. By the combination of PUR-based seating cushions and PUR-based CFRP seating structure parts, the recyclability of the entire aircraft seating structure is feasible.

Processing of PUR systems is already well known and investigated for the RTM process.[5-7] However, the WCM process is used within this project for manufacturing the CFRP seating components as it offers a higher efficiency than the RTM process.[8,9] The processing of PUR materials for CFRP production using the WCM has already been demonstrated.[10]

One key challenge for the use of CFRP with PUR matrix in aerospace structures is their flame resistance. PURs do not fulfil the flame resistance requirements for structural aircraft component and need to be modified by flame retardants. To the best of our knowledge, flame retardants for carbon fibre-reinforced polyurethanes (CF-PURs) are not yet reported in the literature. Therefore, the modification of PUR with 13 flame retardants and the investigation of the associated flame resistance in combination with the processability by WCM are reported in this article.

2 | EXPERIMENTAL PART

2.1 | Materials

For a preliminary study of the intrinsic flame retardancy of neat PUR itself, three different PUR formulations, PUR-1 from Rühl Puromer GmbH, PUR-2 from Henkel AG & Co. KGaA and PUR-3 from BASF Polyurethanes were tested. ACMOS 36-5238 from Acmos Chemie KG was used as external mould release agent. For the CFRP test plates, unidirectional (UD) 50 K carbon fibre non crimp fabric (CF-NCF) from Zoltek Corporation with Panex 35 fibre and 300 gsm aerial weight was used. The 13 tested flame retardants are given in Table 1.

2.2 | Characterization

2.2.1 | Limiting oxygen index test

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 IV ($75 \times 6 \times 3$ mm^3).

2.2.2 | FAR 25.853 test

The Federal Aviation Regulations (FAR) tests were conducted using the UL94 Test Device from WAZAU, Germany, according to FAR, part 25.853, appendix F1, (a)(1)(i).

2.2.3 | Thermogravimetric analysis (TG) coupled with mass spectrometry (TG-MS)

The TG measurements were performed with a TG 209 F1 from Netzsch in a nitrogen atmosphere. The heating rate was 10 K/min and the sample mass was about 10 mg. For the TG-MS measurements, the TG system was coupled to a QMS 403 C Aeolos from Netzsch. To prepare test material, CF-PUR pieces were milled using a cryo-mill from Retsch.

TABLE 1 Flame retardants

#	Chemical nature of the flame retardant	Flame retardant	Received from
FR-1	phosphorus polyol (P-Polyol)	Exolit OP 560	Clariant
FR-2	phosphorus polyol (P-Polyol)	Exolit OP 550	Clariant
FR-3	expendable graphite (EG)	GHL PX 90/−2	LUH
FR-4	expendable graphite (EG)	GHL PX 96/−1	LUH
FR-5	expendable graphite (EG)	GHL PX 95 N	LUH
FR-6	melamine cyanurate (MC)	Melapur MC 15	BASF
FR-7	ammonium polyphosphate (APP)	NORD-MIN JLS-APP	NRC
FR-8	6-(3-Oxo-3-butoxypropyl)-6H-dibenzo [c,e][1,2] oxaphosphorin 6-oxide (DOPO-PBE)	DOB 11	metadynea
FR-9	phosphate ester (P-Ester)	ADK STAB FP-600	ADEKA
FR-10	nitrogen/phosphorus-based intumescent system (P/N-Intumescent)	ADK STAB FP-2500S	ADEKA
FR-11	nitrogen/phosphorus-based intumescent system (P/N-Intumescent)	ADK STAB FP-2100JC	ADEKA
FR-12	aluminium hydroxide (ATH)	APYRAL 200SM	Nabaltec
FR-13	aluminium hydroxide (ATH)	APYRAL 20X	Nabaltec

2.3 | Preparation

2.3.1 | Preparation of test samples from neat PUR resins

For the pre-analysis of the three different PURs PUR-1, PUR-2 and PUR-3, neat resin plates were manufactured by using a heated plate mould with a cavity size of 400 × 400 mm^2. The premixed (manually via dissolver) resin was injected by a pressure pot injection system. The plates were cured at 85 °C and for 8 minutes and show a nominal thickness of 2 mm.

2.3.2 | Preparation of test samples for preliminary flame retardant investigations

For flame retardant investigations on fibre-free PUR-1, plates were manufactured by using pressure pot injection into an oil-heated plate mould with cavity size of 30 × 27 × 2 mm^3 at 85 °C and 10 minutes curing time. Flame retardants were premixed with the polyol fraction. After premixing polyol and isocyanate fraction, the reactive mixture was transferred into a pressure pot. The vertical oriented plate mould was filled bottom-up at 1 bar air pressure on the pressure pot and the vent port was open until the resin system had flushed the whole cavity. After 5 seconds flushing time of the mould, the vent port was closed and the air pressure in the pressure pot was raised to 4 bar. The manufacturing setup is shown in Figure 1.

2.3.3 | Wet compression moulding of CFRP test plates

The WCM trials with fibre reinforcements were conducted with a plate mould of 900 × 550 mm^2 cavity size using a Dieffenbacher hydraulic press type DYL630/500 with active parallelism adjustment control. For the CFRP laminates, the fabric material was cut, stacked (6 plys in UD orientation) and transferred into the mould. The target plate thickness was 4 mm and the fibre volume fraction was 50 %. Flame retardants were homogenised within the polyol fraction. The manually mixed resin system was applied centrally on the fabric stack within the mould; see Figure 2. Vacuum was applied during mould closing to ensure the production of a void-free laminate. During curing at 85 °C mould temperature, a press force of 5000 kN was applied. The plates were demoulded after 10 minutes curing time.

3 | RESULTS AND DISCUSSION

3.1 | Selection of the polyurethane resin type

The intrinsic flame resistance of a flame retardant free polymer matrix differs significantly between different polymer types as it is shown, for example, for polyurethane flexible foams.[11] As flame retardants typically deteriorate mechanical properties, a preliminary study of the intrinsic flame resistance of the polymer matrix can be helpful. It is assumed that polymer types with a high intrinsic flame resistance are

FIGURE 1 Left to right: vertical oriented plate mould with inlet port (red) and vent port (blue); pressure pot which can be connected by a replaceable tube to the inlet port of the plate mould; open mould with cured PUR plate; cured PUR plate

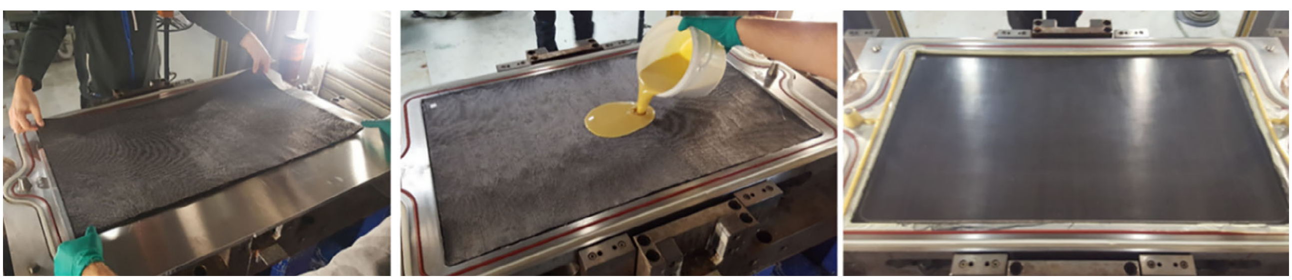

FIGURE 2 Left: transfer of the fabric stack into the mould; middle: manual resin application; right: cured CFRP plate

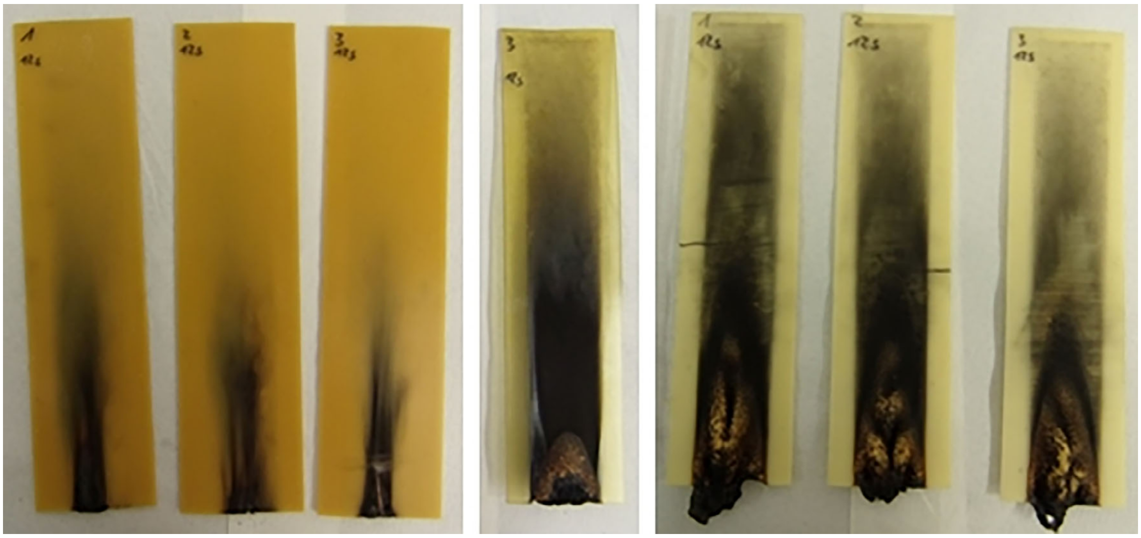

FIGURE 3 12-second FAR 25.853 Part I test results of PUR-1 (left), PUR-2 (middle) and PUR-3 (right)

TABLE 2 FAR 25.853 Part I test result of three polyurethane resins, processed by low pressure injection

#		Flaming time / s	After-burn time / s	Burning drops	After-burn time drops / s	Burn-off length / mm	Test result
PUR-1	1	12	>30[a]	No	0	39	failed
	2	12	>30[a]	No	0	36	failed
	3	12	>30[a]	No	0	32	failed
PUR-2	1	12	>30[a]	No	0	47	failed
PUR-3	1	12	>30[a]	No	0	152	failed
	2	12	>30[a]	No	0	133	failed
	3	12	>30[a]	No	0	126	failed

[a]Test specimens are extinguished manually after 30 seconds after-burn time.

able to pass flammability tests with a lower amount of flame retardant than other types which leads to materials and components with high flame resistance and more suitable mechanical properties. In this study, the flammability of three different neat PUR (PUR-1, PUR-2 and PUR-3) types were tested by the FAR 25.853 Part I method to study the intrinsic flammability of these materials. The test results are shown in Figure 3 and Table 2.

The test criteria of the FAR 25.853 test with a flaming time of 12 seconds or 60 seconds are:

1. 15 seconds average flame time (after-burn time) are not exceeded of all specimens tested;
2. 3 seconds (60-second test) or 5 seconds (12-second test) average drip extinguishing time are not exceeded by all specimens tested;
3. 152 mm (60-second test) or 203 mm (12-second test) average burn length are not exceeded by all specimens tested.

Polymeric materials used in aircraft interiors like CF-PUR have to pass the 60-second FAR 25.853 test. However, none of the PUR samples passed the 60-second FAR 25.853 test. Therefore, the 12-second FAR 25.853 test with manually extinguishing of the test specimens was used to determine the flammability of the PUR samples. Also within the 12-second FAR 25.853 test, none of the PUR types shows self-extinction. To compare the flammability of the three PUR types, the burning specimens were extinguished manually at 30 seconds after-burn time. By the comparison of the burn-off length which corresponds to the flammability behaviour observed during the test, PUR-1 shows with 36 ± 4 mm in comparison to PUR-2 with 47 mm and PUR-3 with 139 ± 13 mm a significant higher flame resistance.

All three PUR resins are methylendiphenyl-isocyanate (MDI)-based resins. However, investigations on just three commercial PUR resin systems are not sufficient to provide any kind of causal analysis which are not in scope of this study. For the flame retardant investigations, PUR-1 was chosen as it shows the highest flame resistance in the 12-second FAR 25.853 test.

3.2 | Preliminary flame retardant evaluation for CF-PUR

The flame retardant effects of 13 flame retardants for CF-PUR were preliminary evaluated by LOI test and 60-second FAR25.853 test

TABLE 3 LOI test results of the preliminary evaluation of flame retardants in PUR-1

#	FR amount / wt%	LOI / O_2%
PUR-1	0	22.5 ± 0.38
PUR-1-FR-1	10.0	28.1 ± 0.30
PUR-1A-FR-1	9.0	29.1 ± 0.38
PUR-1-FR-2	10.0	29.5 ± 0.53
PUR-1-FR-3	15.0	19.5 ± 0.30
PUR-1-FR-4	15.0	22.3 ± 0.38
PUR-1-FR-5	15.0	29.7 ± 0.30
PUR-1-FR-6	15.0	28.3 ± 0.30
PUR-1-FR-7	15.0	23.9 ± 0.38
PUR-1-FR-8	15.0	24.7 ± 0.38
PUR-1-FR-9	15.0	26.2 ± 0.32
PUR-1-FR-10	15.0	27.0 ± 0.48
PUR-1-FR-11	15.0	27.1 ± 0.38
PUR-1-FR-12	25.0	23.5 ± 0.38
PUR-1-FR-13	25.0	26.5 ± 0.38

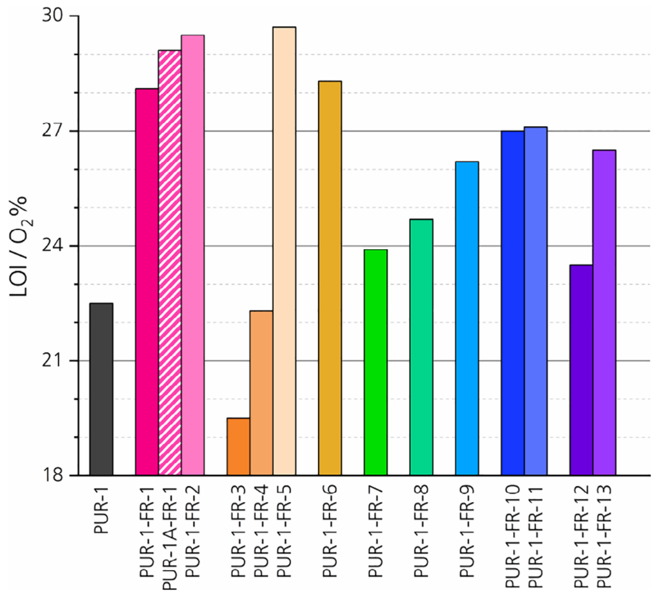

FIGURE 4 LOI test results of the preliminary evaluation of flame retardants in polyurethane resin PUR-1

using fibre-free PUR-1. It was processed in a low pressure injection setup for fibre-free resin plate manufacturing (see Section 2.3.2). The LOI test results are shown in Table 3 and Figure 4.

The average LOI of pure PUR-1 is 22.5 O_2%. PUR-1 samples containing flame retardants show a lower flammability which is indicated by a higher LOI value with the exception of the two expandable graphite types FR-3 and FR-4.

PUR-1 samples containing 10 wt% of liquid phosphorus polyol FR-1 or FR-2 were obtained without any test specimen defects and the observed curing behaviour is uncritical. An average LOI of 28.1 O_2% for FR-1 and 29.5 O_2% for FR-2 was observed. As FR-1 and FR-2 are reactive compounds which react with the isocyanate of the PUR formulation, the PUR-1 formulation has to be adapted to ensure the correct stoichiometric mixing ratio of isocyanate, polyol and reactive flame retardant by increasing the proportion of the isocyanate. Also the adapted formulation with 9 wt% of FR-1 “PUR-1A-FR1” showed an uncritical curing behaviour. The measured average LOI of 29.1 O_2% was slightly higher than the LOI of the non-adapted PUR-1 formulation PUR-1-FR-1.

For the processing of PUR containing 15 wt% of solid expandable graphite (EG) FR-3, FR-4, or FR-5, the mixing of the PUR components was problematic due to the high volume of the EG. The mixing behaviour was improved at increasing EG particle sizes from FR-3 (D80: 75 μm) to FR-4 (D80: 150 μm) to FR-5 (D80: 300 μm). The average LOI also increases with higher particle size from 19.5 O_2% to 22.3 O_2% to 29.7 O_2%. However, intense formation of soot was observed for all three expandable graphite types due to the detaching of char layers produced by the expandable graphite.

For PUR-1 containing 15 wt% of solid melamine cyanurate (MC) FR-6, mixing of the polyol fraction with the flame retardant as well as the mixing of the FR-containing polyol fraction with the isocyanate fraction were problematic due to poor homogenisation of the components. However, defect-free specimens were obtained. The average LOI is 28.3 O_2%.

PUR-1 containing 15 wt% of solid ammonium polyphosphate (APP) FR-7 was obtained without any test specimen defects and no problems occurred during the PUR curing. An average LOI of 23.9 O_2% was observed.

PUR-1 containing 15 wt% of liquid DOPO-PBE FR-8 or phosphate ester (P-Ester) FR-9 was obtained without any test specimen defects and no problems occurred during the PUR curing. The high viscosity of both flame retardants is challenging during mixing and dosing. Incorporated in the polyol fraction, FR-8 and FR-9 are processable. The average LOI is 24.7 O_2% for FR-8 and 26.2 O_2% for FR-9.

For PUR-1 containing 15 wt% of solid nitrogen/phosphorus-based intumescent system (P/N-Intumescent) FR-10 or FR-11, mixing problems for the flame retardant with the polyol fraction and the flame retardant-containing polyol fraction with the isocyanate fraction were observed due to conglomerate formation. The test specimens show defects like flame retardant blooming on the surface. The average LOI is 27.0 O_2% for FR-10 and 27.1 O_2% for FR-11.

For FR-12, the high amount of 25 wt% of solid aluminium hydroxide (ATH) caused mixing problems and specimen defects by inhomogeneous particle distribution, thus the amount was reduced to 10 wt%. The inhomogeneous particle distribution was significantly decreased by this measure but was still present. However, 25 wt% of an ATH with a higher particle size (FR-13) were incorporated without any mixing problems or test specimen defects. The average LOI of PUR-1-FR-12 is 23.5 O_2% and 26.5 O_2% for PUR-1-FR-13. It is assumed that the particle size of D90: 0.8 μm of FR-12 compared to

TABLE 4 60-second FAR 25.853 Part I test result of the preliminary evaluation of flame retardants in polyurethane resin PUR-1

#		FR amount / wt%	After-burn time / s	Burning drops	After-burn time drops / s	Burn-off length / mm	Test result
PUR-1	1	0	>15	No	–	–[a]	failed
	2	0	>15	No	–	–[a]	failed
	3	0	>15	No	–	–[a]	failed
PUR-1-FR-1	1	10.0	6	No	–	105	passed
	2	10.0	1	No	–	105	passed
	3	10.0	13	No	–	90	passed
PUR-1A-FR-1	1	9.0	21	No	–	90	failed
	2	9.0	12	No	–	95	passed
	3	9.0	25	No	–	85	failed
PUR-1-FR-2	1	10.0	>15	No	–	–[a]	failed
	2	10.0	>15	No	–	–[a]	failed
	3	10.0	>15	No	–	–[a]	failed
PUR-1-FR-3	1	15.0	>15	No	–	–[a]	failed
	2	15.0	>15	No	–	–[a]	failed
	3	15.0	>15	No	–	–[a]	failed
PUR-1-FR-4	1	15.0	>30	No	–	–[a]	failed
	2	15.0	>30	No	–	–[a]	failed
	3	15.0	>30	No	–	–[a]	failed
PUR-1-FR-5	1	15.0	>30	Yes	>3	–[a]	failed
	2	15.0	19	No	–	100	failed
	3	15.0	>30	No	–	–[a]	failed
PUR-1-FR-6	1	15.0	>30	No	–	–[a]	failed
	2	15.0	15	No	–	100	passed
	3	15.0	>45	No	–	–[a]	failed
PUR-1-FR-7	1	15.0	10	Yes	2	120	passed
	2	15.0	14	Yes	1	140	passed
	3	15.0	18	Yes	0	135	failed
PUR-1-FR-8	1	15.0	>30	No	–	–[a]	failed
	2	15.0	>30	No	–	–[a]	failed
	3	15.0	>30	No	–	–[a]	failed
PUR-1-FR-9	1	15.0	29	No	–	80	failed
	2	15.0	27	No	–	95	failed
	3	15.0	10	No	–	90	passed
PUR-1-FR-10	1	15.0	10	No	–	105	passed
	2	15.0	4	No	–	115	passed
	3	15.0	14	No	–	110	passed
PUR-1-FR-11	1	15.0	14	Yes	0	110	passed
	2	15.0	>30	No	–	–[a]	failed
	3	15.0	>30	No	–	–[a]	failed
PUR-1-FR-12	1	25.0	80	No	0	135	failed
	2	25.0	54	Yes	5	110	failed
	3	25.0	75	No	0	130	failed
PUR-1-FR-13	1	25.0	60	No	–	125	failed
	2	25.0	87	No	–	140	failed
	3	25.0	79	No	–	95	failed

[a]Test specimens are manually extinguished.

TABLE 5 LOI and 60-second FAR 25.853 Part I results of the flame retardant investigations of PUR-1

#	Flame retardant	FR amount / wt%	LOI / O_2%	60-s FAR 25.853 Part I passed
PUR-1-FR-1	P-Polyol	10.0	28.1 ± 0.30	3 of 3
PUR-1-FR-10	P/N-Intumescent	15.0	27.0 ± 0.48	3 of 3
PUR-1-FR-7	APP	15.0	23.9 ± 0.38	2 of 3
PUR-1A-FR-1	P-Polyol	9.0	29.1 ± 0.38	1 of 3
PUR-1-FR-6	MC	15.0	28.3 ± 0.30	1 of 3
PUR-1-FR-9	P-Ester	15.0	26.2 ± 0.32	1 of 3
PUR-1-FR-11	P/N-Intumescent	15.0	27.1 ± 0.38	1 of 3
PUR-1		0	22.5 ± 0.38	0 of 3
PUR-1-FR-2	P-Polyol	10.0	29.5 ± 0.53	0 of 3
PUR-1-FR-3	EG	15.0	19.5 ± 0.30	0 of 3
PUR-1-FR-4	EG	15.0	22.3 ± 0.38	0 of 3
PUR-1-FR-5	EG	15.0	29.7 ± 0.30	0 of 3
PUR-1-FR-8	DOPO-PBE	15.0	24.7 ± 0.38	0 of 3
PUR-1-FR-12	ATH	25.0	23.5 ± 0.38	0 of 3
PUR-1-FR-13	ATH	25.0	26.5 ± 0.38	0 of 3

D90: 80 μm of FR-13 is responsible for the mixing problems of FR-12 which in turn is assumed to be mainly responsible for the observed lower flame retardancy of FR-12.

Beside the LOI test, the FAR 25.853 Part I test with 60 second flame time was performed. The results are shown in Table 4.

The FAR 25.853 Part I test with 60 second flame time was passed by two flame retardants - liquid phosphorus polyol FR-1 incorporated with 10 wt% and solid nitrogen/phosphorus-based intumescent system (P/N-Intumescent) FR-10 incorporated with 15 wt%.

Also PUR-1 with 15 wt% of ammonium polyphosphate (APP) FR-7 had nearly passed the 60-second FAR 25.853 Part I test. Only one of the three specimens showed a slightly too high after-burn time of 18 seconds instead of ≤15 seconds.

From three flame retardants incorporated with 15 wt% - melamine cyanurate (MC) FR-6, phosphate ester (P-Ester) FR-9 and nitrogen/phosphorus-based intumescent system (P/N-Intumescent) FR-11 as well as the adapted PUR-1 formulation with 9 wt% of FR-1, one of three specimens passed the 60-second FAR 25.853 Part I test.

The summarized results of the LOI and 60-second FAR 25.853 Part I test on flame retardant containing PUR-1 are shown in Table 5.

3.3 | Flammability of CF-PUR

For the production of CF-reinforced PUR-1 plates using the WCM process, four FR are selected - FR-1 (liquid) and FR-10 (solid) which passed the 60-second FAR 25.853 Part I test as fibre-free resin plates as well as FR-7 (solid) and FR-9 (liquid) which showed very good processability but did not passes all three FAR 25.853 trials. It is assumed that the CF reinforcement within the structural WCM laminates improves the flame resistance and allows FR-7 and FR-9 to pass the 60-second FAR 25.853 Part I test. The 60-second FAR 25.853 Part I test results are shown in Table 6.

As expected for solid FRs, FR-7 and FR-10 showed a filtration of the solid particles on the surface of the CF-PUR-1 plates; see Figure 5. The flame retardant is thus not homogeneously distributed within the laminate. On the opposite of the resin application side, no particles of the FR are visible. It is expected that the flame resistance is thus higher on the resin application surface. Furthermore, for an industrial application, abrasive flame retardant particles represent a risk for 2K-mixing and injection machines.

The liquid flame retardants FR-1 and FR-9 were processed without visible defects or inhomogeneity. Within the 60-second FAR 25.853 Part I test, test samples from four different flame retardant free CF-PUR-1 plates failed. All test samples from three different plates of the adapted PUR-1 formulation containing 9 wt% of FR-1 passed the 60-second FAR 25.853 Part I test. Also CF-PUR-1 with 15 wt% of the solid FR-10 passed the 60-second FAR 25.853 Part I test, even though a particle filtration during production was observed. CF-PUR-1 containing 15 wt% of FR-7 or FR-9 did not pass the 60-second FAR 25.853 Part I test, in accordance with the preliminary tests on fibre-free PUR-1. This indicates that the replacement of 50 wt% of the PUR matrix by carbon fibres is not sufficient to increase the flame resistance significantly to pass the aviation requirements. However, it is assumed that flame retardant formulations for CF-PUR aviation components can be developed based on preliminary studies on fibre-free PUR resins.

TABLE 6 60-second FAR 25.853 Part I test result of CF-reinforced PUR-1 containing FR (I, II, III and IV indicates different plates from which samples are taken)

#		FR amount / wt%	After-burn time / s	Burning drops	After-burn time drops / s	Burn-off length / mm	Test result
CF-PUR-1 I	1	0	36	No	–	29	failed
	2	0	48	No	–	27	failed
	3	0	39	No	–	31	failed
CF-PUR-1 II	1	0	59	No	–	34	failed
	2	0	46	No	–	30	failed
	3	0	72	No	–	40	failed
CF-PUR-1 III	1	0	60	No	–	33	failed
	2	0	40	No	–	25	failed
	3	0	45	No	–	25	failed
CF-PUR-1 IV	1	0	39	No	–	25	failed
	2	0	48	No	–	24	failed
	3	0	53	No	–	25	failed
CF-PUR-1A-FR-1 I	1	9.0	14	No	–	40	passed
	2	9.0	8	No	–	31	passed
	3	9.0	5	No	–	26	passed
CF-PUR-1A-FR-1 II	1	9.0	2	No	–	10	passed
	2	9.0	4	No	–	15	passed
	3	9.0	3	No	–	13	passed
CF-PUR-1A-FR-1 III	1	9.0	6	No	–	10	passed
	2	9.0	8	No	–	15	passed
	3	9.0	7	No	–	12	passed
CF-PUR-1-FR-7[a]	1	15.0	**16**	No	–	31	failed
	2	15.0	**16**	No	–	33	failed
	3	15.0	3	No	–	50	passed
CF-PUR-1-FR-9[a]	1	15.0	13	No	–	21	passed
	2	15.0	**29**	No	–	24	failed
	3	15.0	**19**	No	–	18	failed
CF-PUR-1-FR-10	1	15.0	3	No	–	34	passed
	2	15.0	3	No	–	35	passed
	3	15.0	7	No	–	35	passed

[a]CF-free PUR containing 15 wt% of FR-7 or FR-9 failed the 60-second FAR 25.853 Part I test.

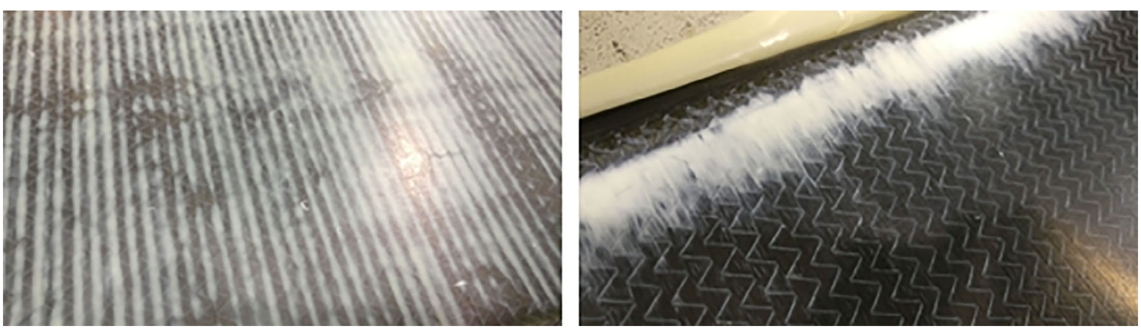

FIGURE 5 Left: CF-PUR-1 containing 15 wt% FR-7; right: CF-PUR-1 containing 15 wt% FR-10

TABLE 7 TG results of CF-PUR-1 containing FR-1, FR-7, FR-9 or FR-10

#	T_{onset} / °C	Mass loss / %	$T_{1\%\ mass\ loss}$ / °C	$T_{5\%\ mass\ loss}$ / °C	Residue at 995°C / %
CF-PUR-1	293	34.6 (27.5°C-600°C)	255	296	63.8
	292	34.6 (27.5°C-600°C)	253	295	63.4
CF-PUR-1-FR-1	290	30.4 (27.5°C-600°C)	240	292	66.5
	290	31.0 (27.5°C-600°C)	242	293	67.3
CF-PUR-1A-FR-1	296	26.6 (27.5°C-600°C)	268	302	71.3
	296	26.7 (27.5°C-600°C)	272	304	71.2
CF-PUR-1-FR-7	272 440 (774)	26.7 (27.5°C-600°C)	253	277	69.5
	273 428 (778)	26.9 (27.5°C-600°C)	253	278	69.3
CF-PUR-1-FR-9	297	30.0 (27.5°C-600°C)	271	303	67.8
	296	30.0 (27.5°C-600°C)	268	301	67.8
CF-PUR-1-FR-10	278	33.1 (27.5°C-600°C)	250	280	63.0
	277	32.9 (27.5°C-600°C)	250	279	63.5

Note: From each material, two samples were analysed under nitrogen atmosphere with a heating rate of 10 K/min.

3.4 | Thermal behaviour of CF-PUR

The thermal behaviour of CF-PUR-1 produced by WCM containing FR-1, FR-7, FR-9 or FR-10 was studied by TG measurements. The results are shown in Table 7 and Figure 6.

Pure CF-PUR-1 starts to decompose at a T_{onset} of about 292 °C with a mass loss of 34.6 % till 600 °C. The carbon fibre mass content is assumed to be about 65 %. At 995 °C, a residue of 64 % - 63 % remains.

CF-PUR-1 containing 9 wt% of FR-1 as well as the adapted PUR-1A formulation containing 9 wt% of FR-1 starts to decompose in the decomposition range of pure CF-PUR-1. However, the observed mass losses of the flame retardant containing formulations decrease. A mass loss till 600 °C of 30.7 ± 0.3 % is observed for CF-PUR-1-FR-1 and a mass loss of 26.7 ± 0.1 % is observed for CF-PUR-1A-FR-1. At 995 °C, a residue of 66.9 ± 0.4 % for CF-PUR-1-FR-1 and 71.3 ± 0.1 % for CF-PUR-1A-FR-1 remains, respectively. Due to this observation, the formation of a thermally stable char seems to be a major flame retardant effect of FR-1. Besides the increased char formation, no significant influence of FR-1 on the thermal decomposition of CF-PUR-1 is observed.

CF-PUR-1-FR-10 which also passes the 60-second FAR 25.853 Part I test shows a different behaviour. The T_{onset} of about 277 °C is 15 °C below the decomposition of pure CF-PUR-1 and the mass loss till 600 °C with 33.0 ± 0.1 % is only 1.5 % lower than the mass loss of pure CF-PUR-1. However, the char formed by the nitrogen/phosphorus-based intumescent system FR-10 seems to be protective enough to pass the FAR 25.853 test.

CF-PUR-1 containing FR-9 fails the FAR 25.853 test but shows with a T_{onset} of about 297 °C, a mass loss till 600 °C of 30 % and a residue amount at 995 °C of 67.8 % - a similar behaviour as CF-PUR-1 containing FR-1.

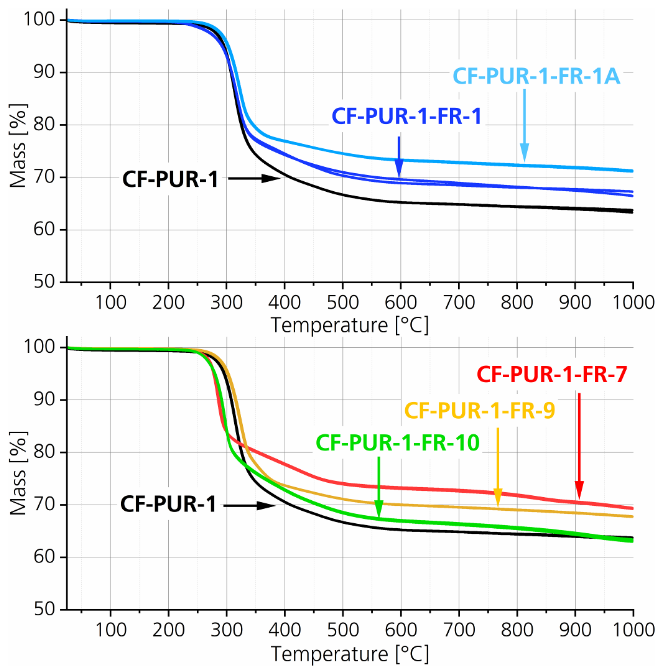

FIGURE 6 TG curves of CF-PUR-1 containing FR-1, FR-7, FR-9 or FR-10

CF-PUR-1 containing FR-7, which also failed the FAR 25.853 test, decomposes at a T_{onset} of 273 °C. Beside the main decomposition step, two additional slight decomposition steps are observed at about 434 °C and 776 °C. The mass loss till 600 °C is 26.8 ± 0.1 % and the residue amount at 995 °C is 69.4 %.

Based on the results of CF-PUR-1 containing FR-1, FR-7 or FR-9, it is assumed that an effective FR for CF-PUR should not decrease the thermal decomposition temperature of the polymer matrix and should

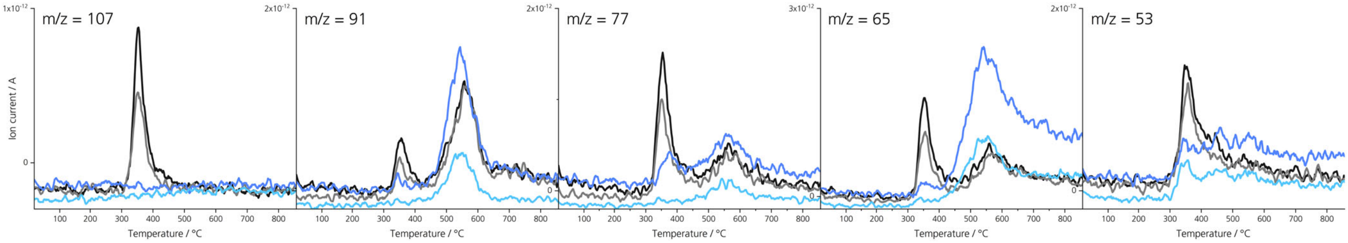

FIGURE 7 TG-MS results for m/z-Indicators of MDI (MS signals smoothed); black signals: CF-PUR-1 (two measurements), blue signals: CF-PUR-1-FR-1 (two measurements)

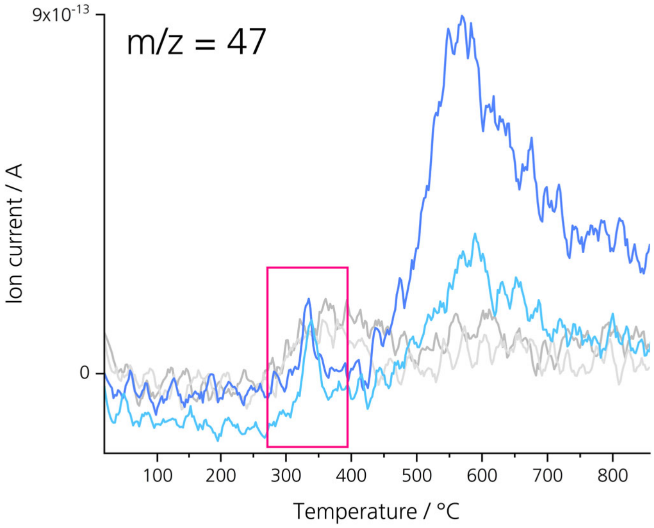

FIGURE 8 TG-MS results for m/z-Indicators of the PO radical (MS signal smoothed); grey signals: CF-PUR-1 (two measurements), blue signals: CF-PUR-1-FR-1 (two measurements)

produce a significant amount of thermally stable char. However, the results of CF-PUR-1-FR-10 show that also FRs which decrease the thermal decomposition temperature of the polymer matrix and produce only low amount of char are sufficiently effective FRs.

Additionally, CF-PUR-1 and CF-PUR-1-FR-1 were analysed by TG-MS. Two effects are observed which are shown in Figures 7 and 8.

Figure 7 shows the TG-MS results of typically m/z-Indicators for MDI in form of MDI fragments at 107 ($MePhNH_2^+$), 91 ($MePh^+$), 77 (Ph^+), 65 ($C_5H_5^+$) and 53 ($C_4H_5^+$). Whereas CF-PUR-1 shows significant signals of MDI fragments at about 300 °C to 400 °C, CF-PUR-1-FR-1 shows no or very weak signals in this area. It is assumed that FR-1 inhibits the thermal release of MDI fragments into the gas phase. This reduces the amount of burnable pyrolysis gases in the initial thermal decomposition phase which leads to a reduced flammability.

Figure 8 shows the TG-MS results of the m/z-Indicator of the PO radical at m/z = 47. At about 300 °C to 400 °C, CF-PUR-1-FR-1 shows a weak MS signal. However, for CF-PUR-1 no significant MS signal is observed in this area. This observation leads to the assumption that probably PO radicals are released during the initial thermal decomposition phase, which are known as efficient gas phase active flame retardant species.

4 | CONCLUSIONS

The research objective of this investigation was to identify flame retardants for CF-PURs which fulfil the requirements for aircraft interior applications. Initially, the flammability of three different MDI-based PURs was studied using the 12-second FAR 25.853 Part I test. None of the three PURs showed self-extinguishing effects. However, the burning behaviour of the resins - represented by the burn-off length - varied significantly. The lowest burn-off length, which corresponds to the highest flame resistance, was achieved by PUR-1 (36 ± 4 mm). The burn-off length of PUR-2 (47 mm) and PUR-3 (139 ± 13 mm) was significantly higher, corresponding to a higher flammability. PUR-1 was therefore used for the further tests. This investigation shows the importance of identifying a polymer matrix with high flame resistance before flame retardant formulations are developed. Polymers with high flame resistance lead to benefits in the material processing of thermosets as a lower amount of flame retardant is required which leads to a lower influence on the viscosity of the uncured material. Additionally, mechanical properties of cured or moulded materials are less affected by the flame retardant.

Thirteen flame retardants were tested in PUR-1 using the LOI and 60-second FAR 25.853 Part I test. Two flame retardants - the phosphorous-containing polyol FR-1 (Exolit OP 560) with 10 wt% and a phosphorous-nitrogen based intumescent flame retardant FR-10 (ADK STAB FP-2500S) with 15 wt% - passed the 60-second FAR 25.853 Part I test. No correlation was found between the LOI results and the test samples which passed or failed the 60-second FAR 25.853 Part I test. Besides the flame retardant effect, the manufacturing properties were evaluated. Based on both the manufacturing and flame retardant properties, four flame retardants were chosen and incorporated into CF-PUR with a fibre volume fraction of 50 %. CF-PUR-1 with 10 wt% of FR-1 or 15 wt% of FR-10, and an adapted CF-PUR-1 formulation with 9 wt% of FR-1 fulfil the 60-second FAR 25.853 Part I test requirements. CF-PUR-1 with 15 wt% of FR-7 (NORD-MIN JLS-APP) or 15 wt% of FR-9 (ADK STAB FP-600) fail the 60-second FAR 25.853 Part I test. Based on this observation it is assumed that preliminary flame retardant investigations on fibre-free PUR are able to predict the performance of flame retardants in CF-PUR whose production is many times more complex and expensive. The influence of CFs on the flame retardant performance of CF-PUR, by reducing the quantity of burnable polymer, seems to be minor. The flammability of CF-PUR is mainly attributable to the PUR polymer matrix. It is assumed that the formation of thermally stable char by the flame retarded polymer matrix is the main flame retardant effect. This thermally stable char protects the polymer matrix as well as the CFs. Additionally, the CFs stabilise the thermally stable char which enhances the flame retardant effect.

However, solid flame retardants are filtered out by the carbon fabric material in the WCM process. Consequently, only CF-PURs containing the liquid FR-1 fulfil both flame retardant and product performance requirements. With 9 wt% of FR-1 in an adapted CF-PUR-1 formulation, a CF-PUR material processable by WCM was developed which could replace epoxy resins in the aviation interior and significantly increase the recyclability of aircraft parts. The actual recyclability is the subject of current investigations.

The flame retardant effects of FR-1 were studied by TG and TG-MS. The measurements indicated that FR-1 promotes the formation of thermally stable char and inhibits the release of burnable MDI fragments. Additionally, the release of PO radicals by FR-1 is assumed. These are known as efficient gas phase active flame retardant species.

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