

RESEARCH ARTICLE

Intrinsic flame resistance of polyurethane flexible foams: Unexpectedly low flammability without any flame retardant

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Summary

Virgin polyurethane flexible foams are widely assumed to be highly flammable materials. The flammability of three model polyurethane flexible foams suggests that this may not be universally true. Two of them show unexpectedly low flammability in the limiting oxygen index test and pass flammability tests such as FMVSS 302 and FAR 25.853. Cone calorimetric measurements at 25 kW/m² and 50 kW/m² furthermore show a high resistance against ignition and demonstrate the self-extinguishing properties of these two virgin, flame-retardant-free, polyurethane flexible foams.

KEYWORDS

cone calorimetry, FAR 25.853, flame retardant free, flammability, FMVSS 302, LOI, polyurethane flexible foam, TGA

1 | INTRODUCTION

Polyurethane flexible foams (PUR-FFs) are thought to be highly flammable materials. Their “fire safety is only suitable when the material has been fire-retarded appropriately or otherwise protected from the relevant ignition source.”¹ However, results of flammability studies for flame-retardant-free PUR-FFs presented here do not meet this expectation. Virgin PUR-FFs without any flame retardants can be self-extinguishing and meet demanding flammability criteria.

Polyurethane flexible foams consist mainly of two monomer fractions—a polyol fraction and a diisocyanate fraction—as well as smaller quantities of catalysts, stabilizers, and blowing agents. The commercially most common and scientifically most studied PUR-FFs consist of polyether polyols and the diisocyanate toluene diisocyanate (TDI), methylene diphenyl diisocyanate (MDI) or polymeric MDI types. The reported flammability of virgin TDI-based PUR-FFs are as follows: limiting oxygen index (LOI) results in the range of 17.0 O₂% to 20.5 O₂%,^{2–8} underwriter laboratories 94 (UL94) with horizontal burning test failed,^{5,8,9} BS 5852-Crib ignition source 5 test failed,¹⁰ California Technical Bulletin 117 test failed,^{3,4} and ignition in cone calorimeter tests within 15 seconds.^{2–4,9–11} The recorded flammability of virgin MDI-PUR-FFs are LOI results in the range of 17.0 O₂% to 21.3 O₂%,^{12,13} UL94 test failed,¹² BS 5852-Crib ignition source 5 test failed,¹³ and

ignition in the cone calorimeter test within 16 seconds.^{12,14,15} However, due to high melt flow, cold-cured PUR-FFs can pass small-scale flammability tests such as FMVSS 302^{6,7,13,14,16} and California Technical Bulletin 117^{13,16,17} without any flame retardants.¹⁸

Because of the high flammability of PUR-FFs and their widespread use for the cushioning of mattresses and furniture, numerous investigations of flame retardant systems for PUR-FFs have been and are being carried out. Recent review articles present hundreds of research references on this topic.^{1,18–22}

However, intrinsic flame resistance* effects have not been widely studied. Flame retardant effects caused only by the polyol and diisocyanate components are still missing. The results for thermal and flammability studies for three PUR-FF model systems—a TDI-based and two MDI-based PUR-FF, one optimized for aircraft seating cushion material—are reported here.

*“Intrinsic flame resistance” means flame resistance effects produced by the virgin polyurethane polymer. For example, the flame resistance effects of polyurethane polymer modified with a flame retardant (covalently bonded) are not intrinsic because flame resistance effects are induced by the covalently bonded flame retardant. It is a flame resistance caused by the flame retardant. In this context, the incorporation method of the flame retardant—reactively or as an additive—is irrelevant.

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2 | EXPERIMENTAL PROCEDURES

2.1 | Materials

For lab-scale research, the polyols Voranol CP3322 (glycerine-propoxylated-ethoxylated polyether polyol, DOW), Rokopol M6000 (glycerine-propoxylated-ethoxylated polyether polyol, PCC Rokita) and EP 3408/1 (polyether polyols, 30 wt% bio-based polyester polyol, catalysts, stabilizer, water, Rühl Puomer), the catalysts Kosmos 29 (stannous octoate, Evonik), 2-(dimethylamino) ethanol (DMEA, Sigma Aldrich), 2,2'-iminodiethanol (DEOA, Sigma Aldrich), Dabco® NE300 (amine catalyst, Air Products), Dabco® NE1070 (amine catalyst, Air Products) and Dabco® 33-LV (33 wt% triethylene diamine and 67 wt% dipropylene glycol, Air Products), the stabilizer Tegostab® BF 2370 (silicone based, Evonik) and Tegostab® B 4113 (silicone based, Evonik), deionized water and the isocyanate TDI 80 (Alfa Aesar), Desmodur® 2460 M (monomeric diphenylmethane diisocyanate, Covestro), and puronate 939 (MDI based, Rühl Puomer) were used.

2.2 | Preparation of PUR-FFs

All PUR-FFs are synthesized according to the following procedure at lab scale: polyol, catalyst, stabilizer, and water (weighed separately or a premixed catalyst-stabilizer-water solution) were stirred for 55 s at 1200 rpm with an IKA® RW 20 DZM stirrer. Isocyanate was added, and the mixture was stirred for 10 seconds at 2000 rpm. Subsequently the mixture was transferred into a mold (box: 300 × 300 × 300 mm³

or cardboard cylinder: radius: 75 mm, height: 230 mm). The PUR-FF formed instantly, followed by hardening for a minimum of 24 h according to DIN 50014-23/50. The formulations of the TDI-based and MDI-based PUR-FFs used are given in Table 1.

Together with two industrial partners—Rühl Puomer (PUR system supplier) and AXYAL (material processor)—a flame-retardant-free MDI-based PUR-FF was optimized (now called AIRCRAFT-PUR-FF) according to industrial needs and an aircraft seat demonstrator was produced. AIRCRAFT-PUR-FF consists of 100 phpp EP 3408/1 including a 5.5 phpp catalyst-stabilizer-solution and 50 phpp puronate 939. The main difference between MDI- and AIRCRAFT-PUR-FF is the polyol fraction. The AIRCRAFT-PUR-FF contains more than one polyether polyol and 30 wt% of a polyester polyol. Due to the polyol mixture, catalysts and stabilizers were adjusted.

Figure 1 is a schematic diagram of the aircraft seating cushions, which consist of three components—headrest, backrest, and bottom cushion—and the complete aircraft seat demonstrator with a seat cover and seat frame. Table 2 includes the mechanical properties of AIRCRAFT-PUR-FF measured by AXYAL. The seating head rest volume is 2.36 L with a weight of 130 g, the seating back rest volume is 8.75 L with a weight of 480 g, and the seating cushion volume is 15 L with a weight of 975 g. The covered PUR cushions were assembled with Velcro® strips on a standard passenger economy class seat. The following were used as cover materials: fabric from LANTAL (Horizons, 2739 LS/560 steel blue), fire blocking layer from IBENA (8033), fasteners from ALFATEX (FR 25-mm hock and loop), and adhesive from COLLANO (BE 11.22). The seat covering was carried out by PMV Industrie (seat upholstery).

TABLE 1 Formulation of TDI- and MDI-PUR-FF

#	TDI-PUR-FF		MDI-PUR-FF	
Polyol	100 phpp ^a	Voranol CP 3322	100 phpp	Rokopol M6000
Diisocyanate	51.2 phpp	TDI 80	49 phpp	Desmodur® 2460 M
Stabilizer	0.8 phpp	Tegostab® BF 2370	0.8 phpp	Tegostab® B 4113
Catalyst	0.2 phpp 0.2 phpp	Kosmos® 29 DMEA	0.6 phpp 0.06 phpp 0.1 phpp 0.6 phpp	Dabco® NE1070 Dabco® NE300 Dabco® 33-LV DEOA
Blowing agent	4.05 phpp	Water	3.0 phpp	Water

^aphpp indicates per hundred parts polyol.



FIGURE 1 Aircraft seating cushions: schematic diagram (left) and aircraft seat demonstrator “green PUR seating cushion” (right) [Colour figure can be viewed at wileyonlinelibrary.com]

TABLE 2 Mechanical properties of the AIRCRAFT-PUR-FF measured by AXIAL

Property		Measurement	
Density [kg/m ³]		55 till 65	
Resistance to compression (with 40% compression) [kPa]		3.5	EN ISO 3386-1
Fatigue by constant load pounding	Loss in thickness at 40% IFD [%]	4.6	NF EN ISO 3385
	Loss in force deflection at 40% IFD [%]	32	
Indentation force deflection (IFD)	At 25% deflection [N]	92.4	EN ISO 2439
	At 40% deflection [N]	144	
	At 65% deflection [N]	330.4	
	Indentation factor (65/25)	3.6	

The comfort of the assembled cushions was evaluated as “good” by PMV Industrie partners. The properties of resistance to fatigue and resistance to compression are comparable to known foams from METZELER (FRM-C65), SKANDIA (DAX-55), GREINER (AW01), and NEOTEX (AIS50) used for aircraft seats and also VIP seats.

2.3 | Characterization

2.3.1 | PUR foaming process

The PUR foaming process was observed with a FOAMAT Type 281 from Format Messtechnik GmbH, Karlsruhe (Germany). The data recording starts with the 10 s stirring step after diisocyanate is added to the polyol mixture. All measurements were performed in a cardboard cylinder (radius: 75 mm, height: 230 mm).

2.3.2 | Attenuated total reflection Fourier transform infrared spectroscopy

For the attenuated total reflection (ATR) Fourier transform infrared (FTIR) spectroscopy, a FTIR spectrometer Nicolet 6700 from Thermo Scientific and a DuraScope diamond ATR unit were used.

2.3.3 | Raman spectroscopy

The Raman spectroscopy was performed with a Bruker RFS 100 Raman spectrometer (Nd:YAG, 1064 nm).

2.3.4 | Density

The PUR foam density was measured with an SI-234 balance from Denver Instruments (USA) on foam cubes (50 × 50 × 25 mm³).

2.3.5 | Air permeability

The air permeability test was carried out by a Textest Instruments FX3300 system from Textest AG, Schwerzenbach (Switzerland) according to DIN EN ISO 7231, 125 Pa and 125 dm³/min air flow on 50 × 50 × 25 mm³ cubes.

2.3.6 | Thermogravimetric analysis

The measurements were performed with a thermogravimetric analyzer TG 209 F1 Iris ASC from Netzsch in nitrogen and synthetic air (80 % nitrogen and 20 % oxygen) as atmospheres. The heating rate was 10 K/min, and the sample mass was 7.00 ± 0.03 mg.

2.3.7 | Limiting oxygen index

The LOI value was measured by using an oxygen index module from FIRE on sheets measuring 140 × 52 × 10 mm³ (sample type: V), stabilized by a U-profile holder, according to DIN EN ISO 4589-2 standardized procedure.

2.3.8 | Federal Aviation Regulations 25.853 Part I test

The Federal Aviation Regulations (FAR) tests were conducted by using the UL94 Test Device from WAZAU, Berlin (Germany) according to FAR 25.853, Appendix F, Part I, (a)(1)(i) and (a)(1)(ii) with 60 s ((a)(1)(i)) and 12 s ((a)(1)(ii)) flame exposures (flame height is 38 mm). The sample bodies were 280 × 75 × 13 mm³.

2.3.9 | FAR 25.853 Part II test

The flammability of covered seat cushions was tested by Centro de Tecnologías Aeronauticas CTA, Miñano Mayor (Spain) according to FAR 25.853 Appendix F, Part II.

2.3.10 | Small burner test FMVSS 302

The FMVSS 302 test was carried out in a test device from WAZAU according to DIN 75200. The sample bodies were 200 × 100 × 13 mm³.

2.3.11 | Cone calorimetry

The measurements were conducted on a cone calorimeter from FTT Fire Testing Technology Ltd., East Grinstead (UK) by using the ISO 5660-1 standard. All samples were conditioned for at least 24 hours at 23 °C and 50 % relative humidity and were tested with 25 kW/m² or 50 kW/m² heat flux. A sample size of 100 × 100 × 40 mm³ was chosen. The samples were covered with an aluminum foil to keep molten polymer inside the sample holder.

3 | RESULTS AND DISCUSSION

3.1 | PUR foaming process

Figure 2 shows the rise profile of all three PUR-FFs. The PUR-FF masses introduced are calculated on the basis of 100 g polyol. To compensate for

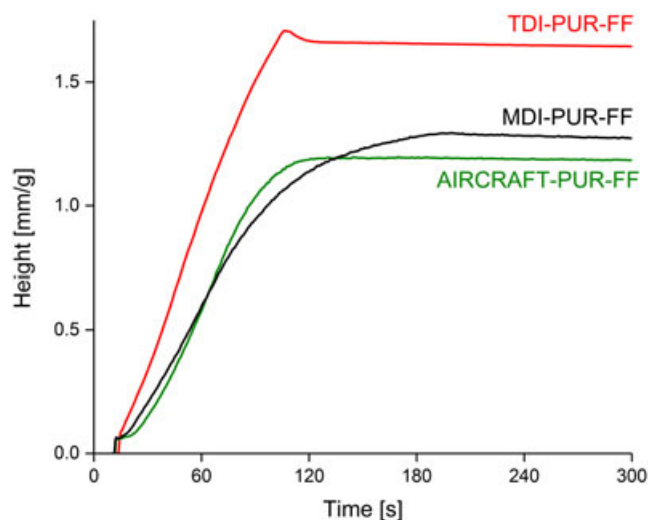


FIGURE 2 Rise profile of PUR-FF normalized to the total foam mass introduced [Colour figure can be viewed at wileyonlinelibrary.com]

the different total masses of the three PUR-FF formulations, the rise heights are normalized to each total PUR-FF mass introduced.

Table 3 shows foaming parameters of the PUR-FF. The cream time (time until the PUR rise begins) was calculated as onset time. The TDI-PUR-FF rises immediately after the 10 s diisocyanate-polyol-stirring process was finished, and the mixture was poured into the mold. Both MDI-based PUR-FF rise with a slight delay and slower rising rates are observed. The end of the free rise is determined through the maximum rise height.

Like polyol and diisocyanate components, the density affects the flammability of PUR-FFs.²³ In this study, the density influence will be not discussed for two reasons. First, of the three PUR-FFs, MDI-PUR-FF shows by far the best flame resistance. However, the foam density of the MDI-PUR-FF is higher than that of the TDI-PUR-FF but lower than that of the AIRCRAFT-PUR-FF. If density is the main reason for the observed flame resistance, the highest flame resistance would be expected for TDI- or AIRCRAFT-PUR-FF, not for the MDI-PUR-FF. Second, reported flammability measurements¹⁵ (cone calorimeter tests and FAR 25.853 Part I) of a similar virgin MDI-based PUR-FF (polyether polyol and polymeric MDI with a mixing ratio polyol:diisocyanate of 100:48; water blown) with a density of 46.5 kg/m³ burns much better than MDI-PUR-FF or AIRCRAFT-PUR-FF. For this reason, density is not considered to be the key reason for the observed high flame resistance and will be not discussed in this study.

ATR-FTIR and Raman spectroscopy were used for the chemical characterization of the PUR-FFs. Figure 3 shows the spectra of the three PUR-FFs. Basic literature for spectroscopy²⁴ helps to identify

important vibration signals of PUR-FF, and investigations into PUR with FTIR spectroscopy²⁵⁻²⁷ and Raman spectroscopy²⁸⁻³² are also reported. The ATR-FTIR spectra of all three PUR-FFs show that the isocyanate (—NCO) absorption band at about 2230 cm⁻¹ is barely present. This confirms that the reaction of the diisocyanate groups was almost complete during the polymerization. To distinguish TDI-based and MDI-based PUR-FF, the main differences in ATR-FTIR and Raman spectra are important: The ATR-FTIR spectra (Figure 3) show four main differences at 1598 cm⁻¹ (aromatic $\nu(\text{C}=\text{C})$), 1510 cm⁻¹ ($\nu(\text{N}-\text{H})$ and $\nu(\text{C}-\text{N})$ of —NHCOO), 1412 cm⁻¹ ($\nu(\text{C}-\text{N})$ of —NHCOO), and 1306 cm⁻¹ ($\nu(\text{C}-\text{C})$). All four signals are more intense in the spectra of the MDI-based PUR-FFs. For the Raman spectra of the three foams (Figure 3), seven main differences can be observed at 3059 cm⁻¹ (aromatic $\nu(\text{C}-\text{H})$), 1615 cm⁻¹ (aromatic $\nu(\text{C}=\text{C})$), 1379 cm⁻¹ (urethane bond), 1266 cm⁻¹ ($\nu(\text{C}-\text{N})$ and $\delta(\text{N}-\text{H})$), 1182 cm⁻¹ ($\nu(\text{C}-\text{O}-\text{C})$ and $\delta(\text{C}-\text{C}-\text{C})$), 902 cm⁻¹ (aromatic $\nu(\text{C}=\text{C})$), and 639 cm⁻¹ (aromatic $\nu(\text{C}=\text{C})$).

3.2 | Thermal behavior and flammability

3.2.1 | TGA

Figure 4 shows the TGA curves of the three PUR-FFs, and Table 4 shows the assigned signal interpretation. In nitrogen atmosphere, TDI-PUR-FF and AIRCRAFT-PUR-FF show a similar thermal decomposition behavior. Two decomposition steps—the start of thermal decomposition (urethane bond decomposition^{33,34}) at 264 ± 4 °C and the second decomposition step (polyol degrading^{33,34}) at 366 ± 11 °C—are

TABLE 3 PUR foaming parameter, raw density, and air permeability of PUR-FF

Material	TDI-PUR-FF	MDI-PUR-FF	AIRCRAFT-PUR-FF
Cream time [s]	<14	21	29
Free rise time [s]	107	200	121
Free rise height [mm/g]	1.70	1.29	1.19
Rise height after 300 s [mm/g]	1.64	1.27	1.18
Density prediction ^a [kg/m ³]	34 + 2	44 + 3	48 + 3
Density (foam core) [kg/m ³]	30 ± 0.8	44 ± 2.4	50 ± 1.2
Air permeability [dm ³ /s]	1.7 ± 0.07	2.7 ± 0.28	1.5 ± 0.21

^aBased on the rise height after 300 s, the density of the PUR-FF was predicted by using a cylindrical model for the foam and a model based on a cylinder with a spherical cap 20 mm high and with a radius of 75 mm.

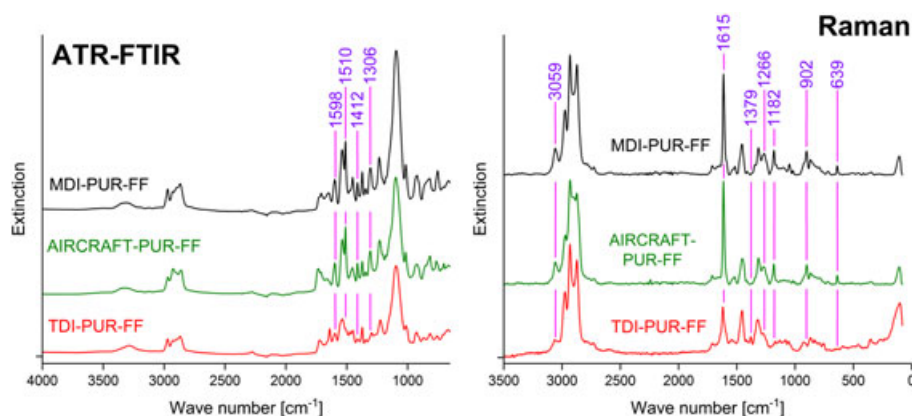


FIGURE 3 (left) ATR-FTIR and (right) Raman spectra of PUR-FFs [Colour figure can be viewed at wileyonlinelibrary.com]

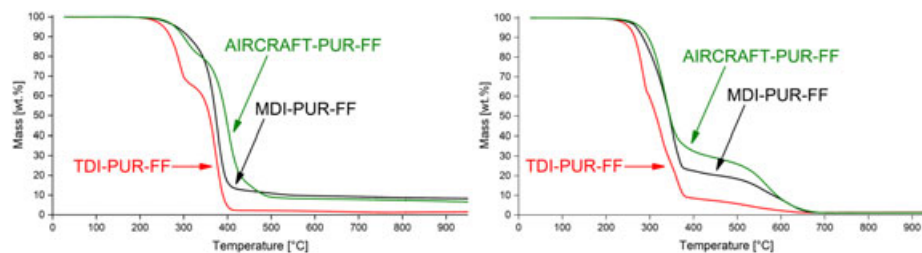


FIGURE 4 TGA curves of PUR-FF in nitrogen atmosphere (left) and synthetic air (right) atmosphere [Colour figure can be viewed at wileyonlinelibrary.com]

TABLE 4 TGA results of PUR-FF

	TGA	Onset [°C]	Weight Loss [%]	Mass at 998 °C [%]
TDI-PUR-FF	N ₂	260	34.6	1.6
		355	63.1	
	Syn. air	260	39.3	1.4
		308	33.6	
		355	18.7	
MDI-PUR-FF	N ₂	343	87.5	8.2
		294	79.9	1.2
	Syn. air	509	19.0	
		296	70.6	1.2
		526	28.4	
AIRCRAFT-PUR-FF	N ₂	267	19.9	6.4
		377	71.8	
	Syn. air	296	70.6	1.2
		526	28.4	
		526	28.4	

observed. The two decomposition steps of MDI-PUR-FF are not observed separately. In nitrogen atmosphere, MDI-PUR-FF decomposes at 343 °C. The decomposition is complete at about 435 ± 10 °C (TDI- and MDI-PUR-FF) and about 530 °C (AIRCRAFT-PUR-FF). For both MDI-based PUR-FFs, low char formation (MDI-PUR-FF: 8 %; AIRCRAFT-PUR-FF: 6 %) is observed. For TDI-PUR-FF, no char formation is measured. In a synthetic air atmosphere, two main decomposition steps—the start of thermal decomposition (urethane bond decomposition and polyol degrading with char formation³³) at 278 ± 18 °C and the second decomposition step (char decomposition³³) at 501 ± 25 °C—are also observed. The AIRCRAFT-PUR-FF shows the largest char formation (about 29 %) compared with MDI-PUR-FF (about 20 %) and TDI-PUR-FF (about 9 %). The char of all three PUR-FFs is completely decomposed at roughly 690 °C.

To summarize, the TDI-based PUR-FF decomposes at lower temperatures and with higher overall mass loss (ie, higher release of combustible pyrolysis gases). Based on the TGA results, a higher flammability for TDI-PUR-FF is assumed. However, MDI-PUR-FF and AIRCRAFT-PUR-FF also decompose to a large extent at temperatures between 300 °C and 500 °C. MDI-PUR-FF shows the lowest flammability in the flame retardant tests (see sections 3.2.2 to 3.2.5). However, the thermal decomposition area and char formation in air observed for MDI-PUR-FF are higher than the TGA results for TDI-PUR-FF but lower than the TGA results for AIRCRAFT-PUR-FF. According to these results, the thermal decomposition area and char formation have a low influence on the fire behavior of PUR-FF. The decomposition products and the mechanical behavior

of the decomposing foam have a more significant influence on the PUR-FF flammability.

3.2.2 | LOI

Table 5 shows the LOI results of the PUR-FF samples. The TDI-PUR-FF is much more flammable than both MDI-based PUR-FFs. The LOI value of the MDI-PUR-FF is unexpectedly high for flame-retardant-free PUR-FFs. Typically, LOI values are in the range of 17.0 O₂% to 21.3 O₂%.^{12,13} Both MDI-based PUR-FFs burn with high melt flow, but only the AIRCRAFT-PUR-FF shows burning drops. Surprisingly, the measured LOI value of AIRCRAFT-PUR-FF is nearly the same as in real air (around 21 O₂%). Nevertheless, AIRCRAFT-PUR-FF shows self-extinguishing properties in the flammability tests FAR 25.853 Part I and FMVSS 302 and does not ignite in the 25 kW/m² cone calorimeter test (see section 3.2.5). According to literature, for many other materials and sample sizes, LOI values often have to be much higher than 21 O₂% for self-extinction to be observed in a flammability test in real air. However, the LOI test procedure used—surface flaming on a U-profile supported 140 × 52 × 10 mm³ sample—generates more realistic LOI results: LOI > 21 O₂% indicates self-extinction in atmospheric air. The reliability of this hypothesis still needs to be verified.

3.2.3 | FMVSS 302

The FMVSS 302 horizontal burning test for automotive or similar standard tests and manufacturers' specifications³⁵ has often been criticized.³⁶ However, because literature data and the test are well-known among scientists and manufacturers, the FMVSS 302 test results of the three PUR-FFs are reported in this paper.

In Table 6, the FMVSS 302 test results for PUR-FFs are shown. All three PUR-FFs pass the FMVSS 302 test (test requirements: burn rate ≤ 100 mm/min). The TDI-PUR-FF burns with 89 mm/min. However, the MDI-based materials MDI-PUR-FF and AIRCRAFT-PUR-FF are not ignited by the heat source.

TABLE 5 LOI measurement results of PUR-FF

Material	LOI [O ₂ %]
TDI-PUR-FF	16.8 ± 0.15
MDI-PUR-FF	25.3 ± 0.32
AIRCRAFT-PUR-FF	21.3 ± 0.19

TABLE 6 FMVSS 302 test results of PUR-FF

Material	Burn rate [mm/min]
TDI-PUR-FF	89 ± 9.0
MDI-PUR-FF	0 (extinguishes)
AIRCRAFT-PUR-FF	0 (extinguishes)

3.2.4 | FAR 25.853 test

To meet the requirements for aviation, PUR-FFs are commercially modified with flame retardants. For example, molded PUR-FFs based on polymeric MDI, polyether polyols, and silicones for aviation seat cushions are reported.¹⁵ The reported silicone-free PUR-FF, the silicone containing PUR-FF, and silicone-PUR-FF formulations with 5 wt.% to 8 wt.% flame retardant additives do not pass the 12 s FAR 25.853 test. To pass the FAR 25.853 12 and 60 s tests, 30 pbw of resorcinol bis(diphenyl phosphate) and 7 pbw of a halogenated phosphate ester, 15 pbw of a halogenated phosphorus ester, or 15 pbw of a halogenated phosphorus ester in combination with 3 pbw of a triol cross linker are incorporated into the foam. None of the three PUR-FF formulations passes the required oil burner test FAR 25.853(c), Appendix F, Part II. FAR 25.853 12 s test results for water-blown PUR-FFs based on polyether polyols and MDI are reported³⁷ but only in combination with FRs. To pass the FAR 25.853 (a)(1)(ii) test approx. 8 wt.% melamine or approx. 8 wt.% expendable graphite in combination with 1.5 wt.% of a liquid phosphor-based FR is needed. Information about the flammability of the pure PUR-FF is not provided.

The FAR 25.853, Appendix F, Part I, (a)(1)(i) and (a)(1)(ii) are 60 s and 12 s vertical Bunsen burner tests (similar to AITM 2.0002 A and AITM 2.0002 B from Airbus). The test requirements of at least three specimens are flame time (average flame must not exceed 15 s), drip

flame time (average drip extinguishing time must not exceed 3 s for the 60 s test or 5 s for the 12 s test), and burn length (burn length must not exceed 152 mm for the 60 s test or 203 mm for the 12 s test). Seat cushion foams must pass the 12 s test. Interior structures like the construction of stowage compartments have to pass the 60 s test. Polyurethane flexible foams that passed the 12 s test were also tested under the more difficult conditions of the 60 s test.

Table 7 shows the results of the 12 s and 60 s FAR 25.853 tests. The TDI-PUR-FF samples already burn completely during the 12 s test. Both MDI-based PUR-FFs pass the 12 s test. The PUR-FF melts and is removed from the heating source (flame) without ignition. The MDI-PUR-FF also passes the 60 s test, whereas the AIRCRAFT-PUR-FF fails the 60 s test due to the ignition of dropping material. Methylene diphenyl diisocyanate PUR-FF and AIRCRAFT-PUR-FF fulfill the aviation requirements.

The FAR 25.853 Part II was performed with a modified 75 kW oil burner and a seat cushion model. Because only AIRCRAFT-PUR-FF was used for the construction of an aircraft seating structure demonstrator, only a seat model consisting of AIRCRAFT-PUR-FF was tested according to FAR 25.853 Part II. The seat model (cushion on: back: 636 × 458 × 54 mm³, bottom: 510 × 459 × 104 mm³) was ignited for 120 s with an oil burner (heat flux: 12.2 W/cm², temperature: 1012 °C) according to FAR 25.853 Appendix F, Part II. The cushions with AIRCRAFT-PUR-FF passed the test. Figure 5 shows the test procedure.

3.2.5 | Cone calorimetry

Cone calorimetric data of the three PUR-FFs at 25 kW/m² and 50 kW/m² are given in Tables 8 and 9. The time to ignite (TTI) is probably the most important element in the 25 kW/m² measurements. The TDI-PUR-FF ignites within the expected time of the first 20 s.

TABLE 7 FAR 25.853 results of PUR-FF for 12 s and 60 s flame exposure

#		TDI-PUR-FF	MDI-PUR-FF	AIRCRAFT-PUR-FF	Jayakody et al. ¹⁵
12 s flame exposure	Flame time [s]	28 ± 5	0	0	70
	Burning drops	Yes	No	No	>5
	Burn length [mm]	>250	152 ± 20	136 ± 11	>203
		Fail	Pass	Pass	Fail
60 s flame exposure	Flame time [s]		0	32 ^a	
	Burning drops		No	Yes ^a	
	Burn length [mm]		172 ± 8	206 ± 32	
			Pass	Fail	

^aJust one of the three samples shows flame time and burning drops.

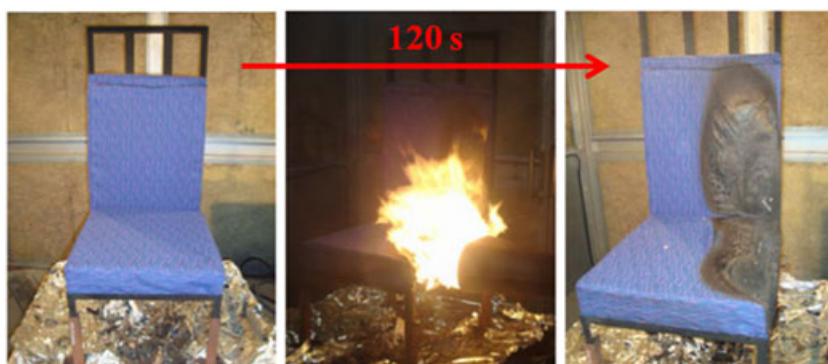


FIGURE 5 Test setup for oil burn test FAR 25.853 Appendix F, Part II before (left), during (center), and after (right) test [Colour figure can be viewed at wileyonlinelibrary.com]

TABLE 8 Cone calorimetry results for PUR-FFs at 25 kW/m² (100 × 100 × 40 mm³)

#	TDI-PUR-FF			MDI-PUR-FF			AIRCRAFT-PUR-FF			Jayakody et al. ^{a15}
	1	2	3	1	2	3	1	2	3	
TTI [s]	7	16	7	–	172	684	–	282	–	16
Peak HRR [kW/m ²]	370	408	454	19	366	556	8	416	11	412
Ave. HRR [kW/m ²]	207	226	246	3	187	186	2	229	3	225
THR [MJ/m ²]	36.4	33.6	40.4	5.2	21.0	25.4	4.0	42.1	2.5	57.4
Ave. HOC [MJ/kg]	26.8	25.4	21.0	4.3	27.1	27.2	2.6	26.8	1.8	25.0
Ave. SEA [m ² /kg]	196	180	140	973	371	400	973	569	920	413
Ave. MLR [g/s m ²]	11.0	13.2	13.5	0.7	12.4	16.1	1.0	13.0	1.7	11.3
Initial mass [g]	12.63	11.75	13.68	14.59	15.16	14.30	18.89	19.12	19.66	24.55
Residue [wt%]	4.1	1.0	0	28.6	54.9	42.7	32.6	30.4	38.3	6.6
Ave. CO [kg/kg]	0.021	0.019	0.016	0.033	0.029	0.030	0.052	0.042	0.041	0.018
Ave. CO ₂ [kg/kg]	1.93	1.83	1.52	0.03	1.88	1.89	0.09	1.78	0.13	1.38
TSR [m ² /m ²]	270	237	270	1178	287	371	1400	891	1260	
MARHE [kW/m ²]	253	260	296	4	18	32	3	99	4	

^aMeasurement setup was similar (100 × 100 × 50 mm³ foam specimens).

TABLE 9 Cone calorimetry results for PUR-FFs at 50 kW/m² (100 × 100 × 40 mm³)

#	MDI-PUR-FF		AIRCRAFT-PUR-FF	
	1	2	1	2
TTI [s]	50	42	29	5
Peak HRR [kW/m ²]	577	656	569	605
Ave. HRR [kW/m ²]	336	357	319	357
THR [MJ/m ²]	34.4	35.1	49.9	44.3
Ave. HOC [MJ/kg]	25.6	26.1	25.4	24.9
Ave. SEA [m ² /kg]	391	402	577	568
Ave. MLR [g/s m ²]	17.8	19.3	17.5	18.7
Initial mass [g]	13.20	13.13	18.77	16.18
Residue [wt%]	3.0	2.5	0.0	3.0
Ave. CO [kg/kg]	0.033	0.031	0.037	0.034
Ave. CO ₂ [kg/kg]	1.78	1.82	1.73	1.72
TSR [m ² /m ²]	522	538	1137	1012
MARHE [kW/m ²]	250	276	321	367

Similar behavior has been observed for MDI-based PUR-FF; see the reference from the literature.¹⁵ However, MDI- and AIRCRAFT-PUR-FF show quite different flammability. The MDI-PUR-FF ignites in two of three measurements but, in these cases, even after more than 11 min. The AIRCRAFT-PUR-FF ignites in one of three measurements. For both MDI- and AIRCRAFT-PUR-FFs, the same progress of the measurement is observed. Both foams melt completely within the first minutes. The molten polymer decomposes slowly and could be ignited if there are surface defects due to the sample holder (the foam is covered with an aluminum foil on the lateral sides and on the bottom). If the PUR-FF does ignite, the polymer pyrolyzes, releasing less smoke, but the heat release rate and the amount of the burning product CO₂ are much higher.

Both MDI- and AIRCRAFT-PUR-FF ignite in the 50 kW/m² cone calorimetric measurement. However, the MDI-PUR-FF takes 40 s to 50 s to ignite, which is clearly longer than expected for a flame-

retardant-free PUR-FF. Based on the 50 kW/m² tests, MDI-PUR-FF shows significantly better flame resistance than AIRCRAFT-PUR-FF. The average TTI of MDI-PUR-FF (46 s) is more than twice the average TTI of AIRCRAFT-PUR-FF (17 s).

Both 25 kW/m² and 50 kW/m² cone calorimetric measurements showed that MDI- and AIRCRAFT-PUR-FFs are not as easy to ignite as previously shown in the literature.

4 | CONCLUSION

The flammability of two virgin water-blown polyether-polyol-based TDI- or MDI-PUR-FFs and one polyether-polyester-polyol-based MDI-PUR-FF were compared. Both MDI-based PUR-FFs show an unexpectedly high flame resistance in flammability tests such as LOI, FMVSS 302, and FAR 25.853. To identify flame retardant effects, TGA and cone calorimetry measurements were carried out.

During the TGA measurements, the main decomposition of all three PUR-FFs was observed between 200 °C and 500 °C. The TDI-PUR-FF decomposes at lower temperatures while producing more pyrolysis gases. However, both MDI-based PUR-FFs also produce large amounts of pyrolysis gases in this temperature range. Flame retardant effects are not obvious.

Instead, cone calorimetry measurements provide indications for the observed flame resistance of the MDI-based PUR-FFs: The TDI-PUR-FF combusts and the pyrolysis gases are ignited in the first seconds. The MDI-based PUR-FFs also combust, but pyrolysis gases are not ignited. Obviously, the chemical nature of the PUR structure is essential for the flammability of PUR-FFs. At first glance, the diisocyanate, TDI, or MDI is responsible for the flame resistance. However, MDI-based PUR-FFs are known,¹⁵ which burn as well as the TDI-PUR-FF. Methylene diphenyl diisocyanate is therefore one but not the only reason for the flame resistance of the MDI-based PUR-FFs. Also, the polyols used have a significant influence on the flammability. This becomes clear through the investigations of the two MDI-based PUR-FFs: MDI- and AIRCRAFT-PUR-FF.

MDI-PUR-FF shows a significantly higher flame resistance than AIRCRAFT-PUR-FF. The main differences between MDI- and AIRCRAFT-PUR-FF are the polyol fraction. Methylene diphenyl diisocyanate PUR-FF consists of polyether-polyol, whereas the polyol fraction of AIRCRAFT-PUR-FF among polyether polyols also includes 30 wt% of a polyester polyol. This results in several assumptions for the observed differences in flame resistance:

1. Chemical nature: The chemical composition of the polyol fraction is the most variable part of a PUR-FF and will be the first part to be optimized in industrial application development. About flame retardancy, the chemical composition of the polyols determines which, at which temperature, and how fast liquid and gaseous products are produced during pyrolysis. For example, (a) for the same number of monomers, polyether polyols based on propylene oxide carry a higher fuel load than ethylene-oxide-based polyols due to the methyl side chain. (b) For the same carbon atom number and the same molecule constitution, polyester polyols have a lower fuel load than polyether polyols due to higher oxidized carbon (carboxyl group). However, the weakness of carboxyl groups against nucleophiles in the condensed phase or the higher viscosity of the polyester pyrolysis melt, caused by hydrogen bond interactions, can negatively affect the flammability of polyester-polyol-based PUR-FF. (c) If the polyol tends to char, flame-resistant effects based on the retraction mechanism are less efficient.
2. Physical nature: The morphology of the condensed phase (solid foam and liquid pyrolysis products) during the thermal decomposition influences mainly the flammability at the time of inflammation. During the thermal decomposition, the foam retracts from the heat source and liquid pyrolysis products are produced. If liquefaction and retraction are fast enough, the pyrolysis of the liquid decomposition products and the associated production of burnable gases are disturbed. If the burnable gas production is too low, the foam cannot be ignited and does not burn on its own. The retraction ability of a foam depends on the foam density (foam density determines the polymer mass that has to retract from the temperature-critical volume around the heat source), on the pore structure of the foam (PUR-FFs have an open cell structure and therefore capillary actions), and mainly on the viscosity of the liquid pyrolysis products. The viscosity of these products depends on the viscosity of the polyol fraction. However, the viscosity of a liquid is also temperature dependent. The thermal stability of the PUR-FF polymer matrix, which determines the formation temperature of the liquid pyrolysis products and the heat capacity of the liquid polyol fraction, is therefore not negligible.

It is a challenge to alter the chemical composition, eg, the polyol fraction of a PUR-FF, without major changes in PUR-FF morphology, especially if the PUR-FF is bimodal (one diisocyanate and one polyol). However, for a reliable analysis of the phenomenon reported here, a stepwise change of just one possible flame retardant mechanism must be carried out. This will form part of future studies.

Starting from the TGA and cone calorimetry, the results of the flammability test LOI, FMVSS 302, and FAR 25.853 are comprehensible. The MDI-based PUR-FFs decompose under the production of a

liquid pyrolysis melt. This pyrolysis melt retreats from the flame zone. The produced pyrolysis gases burn badly, and therefore, neither MDI-based PUR-FFs are able to burn by themselves. If the decomposition zone of the PUR-FF is retracted far enough or the igniting flame is removed, the thermal decomposition stops and the materials pass the flammability tests.

Together with industrial partners, an aircraft seating structure demonstrator using the AIRCRAFT-PUR-FF as a seating cushion material, which meets fire safety as well as mechanical application requirements, was manufactured.

Until now, the reasons for the flame resistance of virgin PUR-FFs are not fully understood; especially the influence of the chemical structures of the diisocyanate fraction and polyol fraction is unknown. Nevertheless, the potential of virgin, flame-retardant-free PUR-FFs with respect to flame retardancy are presented here, which is so far underestimated in the scientific community.

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