Multiple free-radical-trapping and hydrogen-bonding-enhanced polyurethane foams with long-lasting flam e retardancy, aging resistance, and toughness

Lei He [a], Ming-Jun Chen [b, *], Fu-Rong Zeng [a], Ting Wang [b], Wei-Luo [b], Dan-Xuan Fang [a], Shuai-Qi Guo [a], Cong Deng [a], Hai-Bo Zhao [a,*], Yu-Zhong Wang [a,*]

[a] *The Collaborative Innovation Center for Eco-Friendly and Fire-Safety Polymeric Materials, State Key Laboratory of Polymer Materials Engineering, National Engineering Laboratory of Eco-Friendly Polymeric Materials (Sichuan), College of Chemistry, Sichuan University, Chengdu 610064, China.*

[b] *School of Science, Xihua University, Chengdu, 610039, China.*

***Corresponding Authors**: Tel. & Fax:

E-mail: haibo@scu.edu.cn (Hai-Bo Zhao); cmjchem@126.com (Ming-Jun Chen); yzwang@scu.edu.cn (Yu-Zhong Wang)

Experimental

Synthesis of DBP

Phosphorous-containing polyols (DBP) have been prepared as illustrated in Fig. S1 (a). First, benzaldehyde (10.61 g, 0.1 mol) and 150 mL ethanol were added into a 250 mL four-neck flask equipped with a reflux condenser, nitrogen inlet and stirrer. Subsequently, diethyl phosphite (13.81 g, 0.1 mol) was slowly added into the reaction flask via the dropping funnel at a temperature of 80 °C. After DEP was added, the reaction was continued for 4 h under a nitrogen atmosphere. The product was poured into a rotary evaporator at 60 °C under reduced pressure to obtain a clear liquid by removing ethanol. After cooling down to room temperature, a large amount of white product was precipitated. Then, the product (BP) was separated by suction filtration and dried at 80 °C for 6 h in a vacuum oven. Further synthesis of DBP by transesterification. BP (24.42 g, 0.1 mol) and tetrabutyl titanate (0.12 g) were added to a 100 mL four-neck flask equipped with a reflux condenser, nitrogen inlet and stirrer. Diethanolamine (12.62 g, 0.12 mol) was slowly added into the reaction flask via the dropping funnel at a temperature of 120 °C. The liquid product (DBP) was obtained with continuous agitation for 6 h with reduced pressure to remove by-products. GPC (DMSO): Mn: 1660 g/mol, Mw: 2091 g/mol. The polymer dispersity index (PDI) of DBP is 1.25. the degree of polymerization of DBP (n): 3~4. Hydroxyl content: 157.30 mg KOH/g. Phosphorus content: 9.3 wt%.

Table S1. Formulations of the FPUFs

Samples	DEP-330G (php)	FR (php)	H_2O (php)	DC2525 (php)	GK350D (php)	TEOA (php)	A1 (php)	A33 (php)	NE1070 (php)	MDI-2412 (php)	Density (kg/m^3)
Neat FPUF	100.00	0	0.71	2.00	0.50	4.0	0.40	0.60	0.20	37.16	151
FPUF/2DTAP	100.00	2.00	0.68	2.00	0.50	4.0	0.40	0.60	0.20	36.40	147
FPUF/5DTAP	100.00	5.00	0.66	2.00	0.50	4.0	0.40	0.60	0.20	39.81	152
FPUF/8DTAP	100.00	8.00	0.61	2.00	0.50	4.0	0.40	0.60	0.20	41.35	148
FPUF/8DBP	100.00	8.00	0.65	2.00	0.50	4.0	0.40	0.60	0.20	40.51	150
FPUF/8DMMP	100.00	8.00	0.65	2.00	0.50	4.0	0.40	0.60	0.20	36.72	146
FPUF/8Tinuvin-770	100.00	8.00	0.65	2.00	0.50	4.0	0.40	0.60	0.20	36.72	153
FPUF/5.7DMMP+2.3 Tinuvin-770	100.00	8.00	0.65	2.00	0.50	4.0	0.40	0.60	0.20	36.72	150

FR: flame retardant (DBP, DTAP, DMMP, Tinuvin-770). php: parts per hundred polyether polyols by weight.

Results and discussion

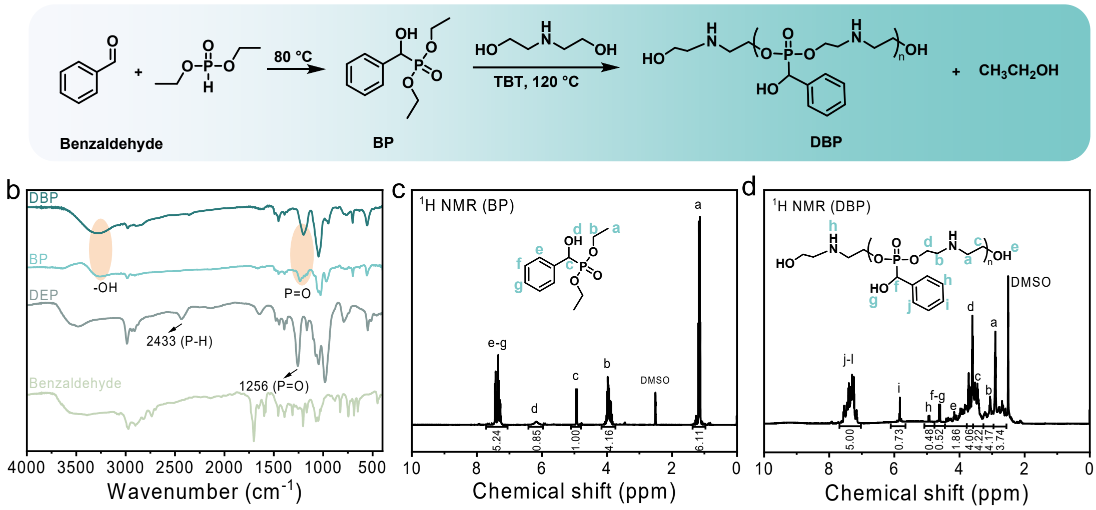

Fig. S1. (a) The synthesis route of DBP. (b) FTIR and (c, d) ^{1}H NMR of BP and DBP.

Table S2. Mechanical performance of neat FPUF and flame retardant FPUFs.

Samples	Tensile strength (kPa)	Elongation at break (%)	Toughness (kJ/m^3)	Tear strength (N/m)	75% compression set (%)
Neat FPUF	49 ± 4	50 ± 5	19 ± 4	129 ± 6	2.84
FPUF/2DTAP	78 ± 3	67 ± 4	32 ± 3	154 ± 8	2.90
FPUF/5DTAP	83 ± 7	74 ± 6	40 ± 4	180 ± 8	2.78
FPUF/8DTAP	91 ± 6	69 ± 3	42 ± 2	188 ± 5	2.60
FPUF/8DBP	80 ± 4	106 ± 3	41 ± 3	215 ± 7	2.80
FPUF/8DMMP	49 ± 2	77 ± 5	25 ± 2	177 ± 5	1.51
FPUF/8Tinuvin-770	54 ± 4	71 ± 2	22 ± 4	169 ± 4	4.19
FPUF/5.7DMMP+2.3Tinuvin-770	51 ± 4	72 ± 5	26 ± 2	172 ± 4	4.47

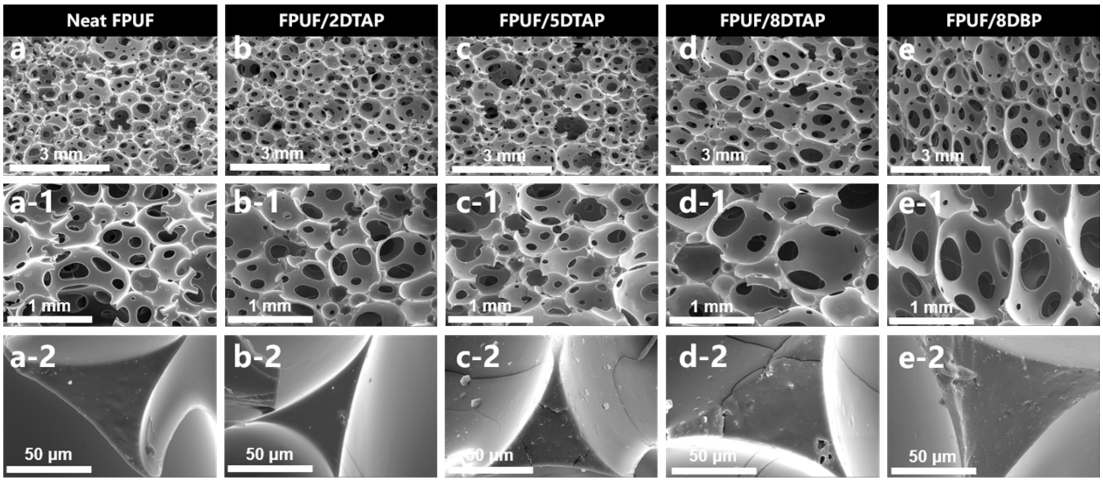

Fig. S2. The SEM images of fractured surface of neat FPUF (a, a-1, a-2), FPUF/2DTAP (b, b-1, b-2), FPUF/5DTAP (c, c-1, c-2), FPUF/8DTAP (d, d-1, d-2), and FPUF/8DBP (e, e-1, e-2).

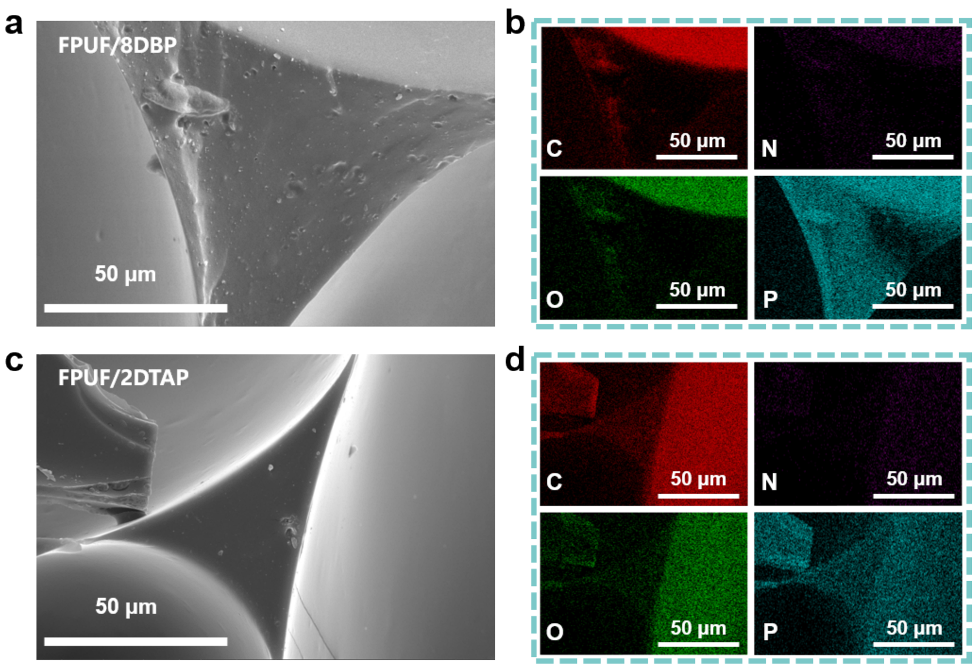

Fig. S3. The SEM images of fractured surface of neat FPUF (a, a-1, a-2), FPUF/2DTAP (b, b-1, b-2), FPUF/5DTAP (c, c-1, c-2), FPUF/8DTAP (d, d-1, d-2), and FPUF/8DBP (e, e-1, e-2).

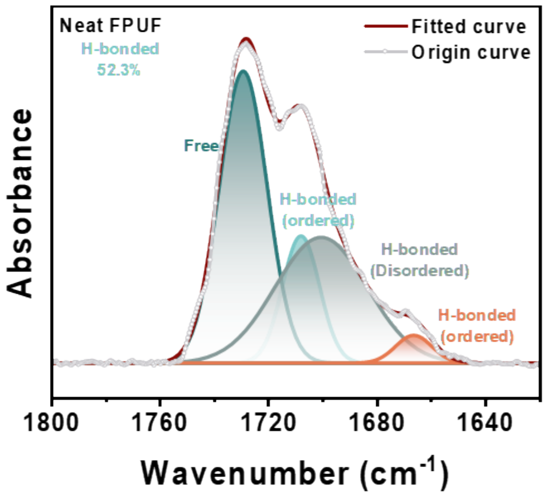

Fig. S4. FT-IR spectra of the neat FPUF in the C=O stretching vibration region.

Table S3. Summary of the assignment of the deconvoluted subpeaks in the FTIR C=O absorption bands for neat FPUF, FPUF/8DTAP and FPUF/8DBP.

Assignment		Wavenumber (cm^{-1})			Area (%)		
		Neat FPUF	FPUF/8DTAP	FPUF/8DBP	Neat FPUF	FPUF/8DTAP	FPUF/8DBP
υ (C=O) urethaneamide ester	Free	1729	1730	1730	47.7	35.9	40.7
	H-bonded (Ordered)	1708	1710	1709	14.4	36.2	56.2
υ (C=O) amide	H-bonded (Disordered)	1699	1691	1686	37.8	24.3	2.6
	H-bonded (Ordered)	1666	1658	1667	1.6	1.1	0.5
Total degree of H-bonded		-	-	-	52.3	64.1	59.3

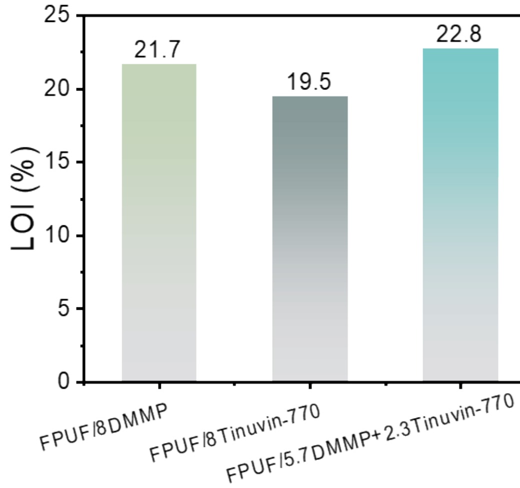

Fig. S5. LOI bar graph of FPUF/8DMMP, FPUF/8Tinuvin-770 and FPUF/5.7DMMP+2.3Tinuvin-770.

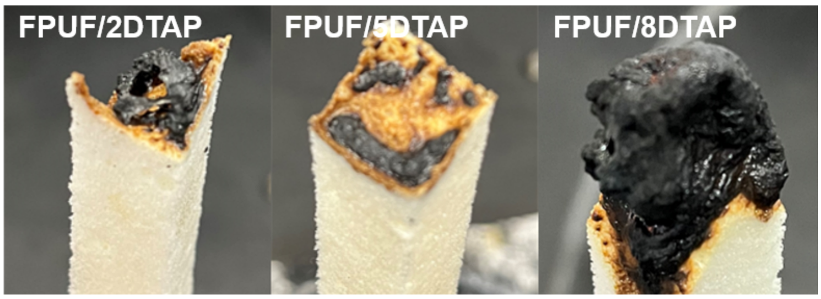

Fig. S6. Digital photos of LOI test for FPUF/2DTAP, FPUF/5DTAP and FPUF/8DTAP.

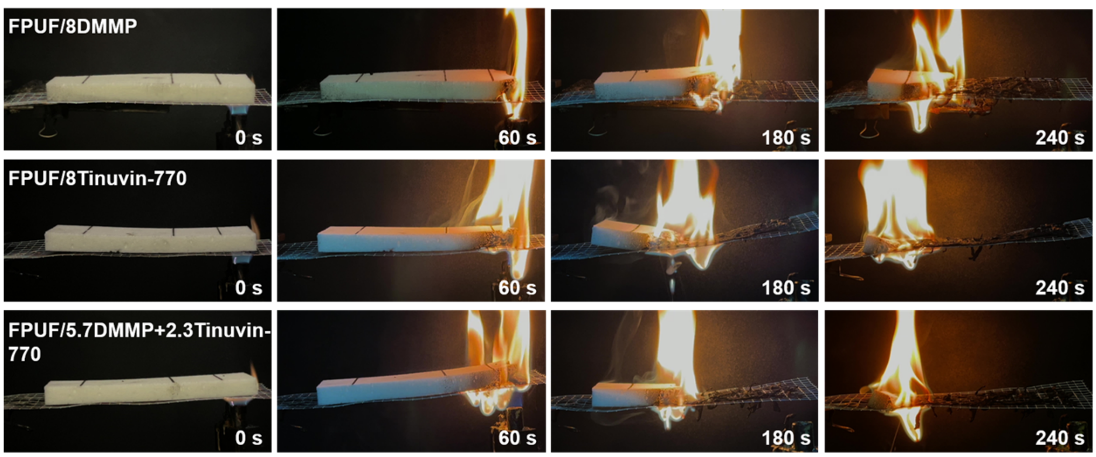

Fig. S7. Digital photos of horizontal combustion test for FPUF/8DMMP, FPUF/8Tinuvin-770 and FPUF/5.7DMMP+2.3Tinuvin-770.

Table S4. Comparisons of DBP and DTAP with other flame retardant FPUFs that can pass the Cal TB 117 vertical burning test in recent reports.

FR Structure	FR content (wt%)	Test results (pass or fail)	ΔTensile strength (%)	ΔEab (%)	Ref.
PTMA	5.8	-	-28.9	-56.7	[15]
HNPN	8.0	-	-38.5	+72.3	[16]
PDEO	6.3	Cal TB Pass	+18.2	-11.6	[24]
DMOP	6.3	Cal TB Pass	+9.3	+2.7	[25]
HAMPP	10.0	-	+29.0	+75.9	[26]
DPM	2.6	Cal TB Pass	+19.7	+58.7	[27]
DOM	2.6	Cal TB Pass	-7.0	+18.2	
DPE	2.6	Cal TB Pass	+9.3	+21.2	
BDMPP	6.4	Cal TB Pass	-3.2	+0.5	[28]
DMMP	6.4	Cal TB Pass	-2.2	+12.6	[29]
D-Mel	6.4	Cal TB Pass	+29.1	-14.0	[30]
D-DICY	6.4	Cal TB Pass	+47.3	-16.3	
D-Urea	6.4	Cal TB Pass	+19.1	-6.0	
TPT	5.0	Cal TB Pass	-18.2	-5.8	[31]
MoS_2-DOPO	5.7	-	-6.0	-15.6	[32]
ZIF-8@$Ti_3C_2T_X$	4.0	-	+52.7	-30.2	[33]

DPPMA	3.3	Cal TB Pass	-4.5	+18.8	[34]
$Ti_3C_2T_X$@BPA@PCL/DH-DOPO	14.2	Cal TB Pass	+25.0	-30.1	[35]
PPN	3.5	Cal TB Pass	+40.0	+14.0	[36]
CMA	12.0	Cal TB Pass	-	-	[43]
EDPPA	6.4	Cal TB Pass	-	-	[44]
EDPPO	12.1	Cal TB Pass	-	-	
EDPMA	12.1	Cal TB Pass	-	-	
TCDP	12.6	Cal TB Pass	-	-	[45]
MPBT	10.0	Cal TB Pass			[46]
DMPMA/TAMPO	12.1	Cal TB Pass	-	-	[34]
DTAP	5.1	Cal TB Pass	+85.7	+38.0	This work
DBP	5.1	Cal TB Fail	+63.3	+112.0	

Table S5. Vertical burning test of neat FPUF and flame retardant FPUFs.

Samples	After flame time (s)		After glow time (s)	Char length (mm)		Test results (pass or fail)
	Average	Maximum	Average	Average	Maximum	
Requirements for pass	≤5.0	≤15.0	≤15.0	≤152.4	≤203.2	Pass
Neat FPUF	83	130	0	No	Burn out	fail
FPUF/2DTAP	45	61	0	200	220	fail
FPUF/5DTAP	10	13	0	140	160	fail
FPUF/8DTAP	1	5	0	100	140	Pass
FPUF/8DBP	15	21	0	130	150	fail

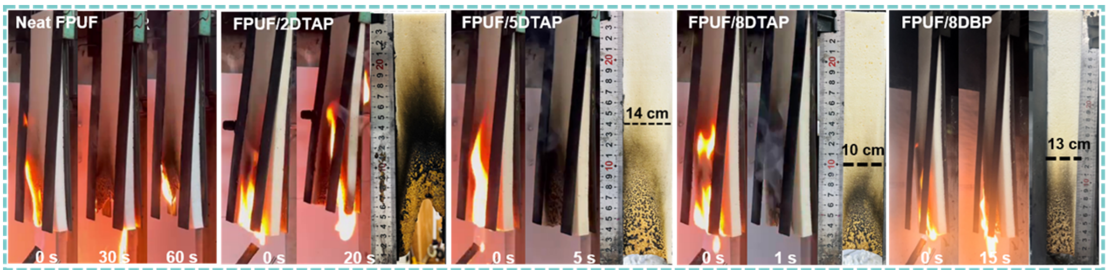

Fig. S8. Digital photos of neat FPUF and flame retardant FPUFs at different ignition time.

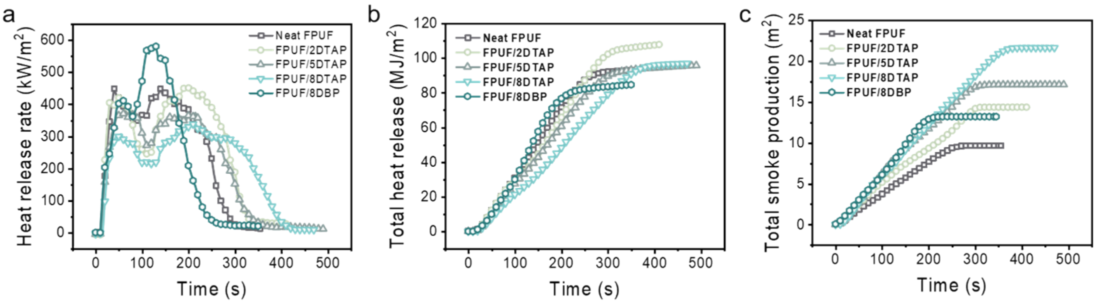

Fig. S9. Heat release rate (a), total heat release (b), and total smoke production (c) as a function of time for neat FPUF and flame retardant FPUFs.

Table S6. Cone calorimeter data for neat FPUF and flame retardant FPUFs [a].

Samples	TTI (s)	t_p (s)	pHRR ($kW{\cdot}m^{-2}$)	FIGRA ($kW{\cdot}m^{-2}\ s^{-1}$)	THR ($MJ{\cdot}m^{-2}$)	Av-EHC ($MJ{\cdot}kg^{-1}$)	TSP (m^2)	Char yield (wt%)
Neat FPUF	8 ± 1	48± 7	441 ± 18	9.2 ± 0.3	96 ± 2	27 ± 2	12 ± 2	1.3 ± 0.2
FPUF/2DTAP	9 ± 1	175 ± 15	458 ± 6	2.6 ± 0.1	105 ± 3	26 ± 1	14 ± 1	6.2 ± 0.3
FPUF/5DTAP	7 ± 2	213 ± 2	386 ± 2	1.8 ± 0.1	93 ± 2	25 ± 2	17 ± 1	8.4 ± 0.2
FPUF/8DTAP	8 ± 1	220 ± 5	347 ± 12	1.6 ± 0.1	99 ± 4	25 ± 1	22 ± 2	9.1 ± 0.4
FPUF/8DBP	6 ± 2	135 ± 5	555 ± 25	4.1 ± 0.2	88 ± 2	23 ± 2	14 ± 2	2.4 ± 0.1

[a] TTI means time to ignition; pHRR represents the peak of heat release rate; t_p denotes time to pHRR; FIGRA is defined as the quotient of pHRR/t_p; THR is total heat release; avEHC denotes the average effective heat of combustion of the volatiles; TSP is total

smoke production.

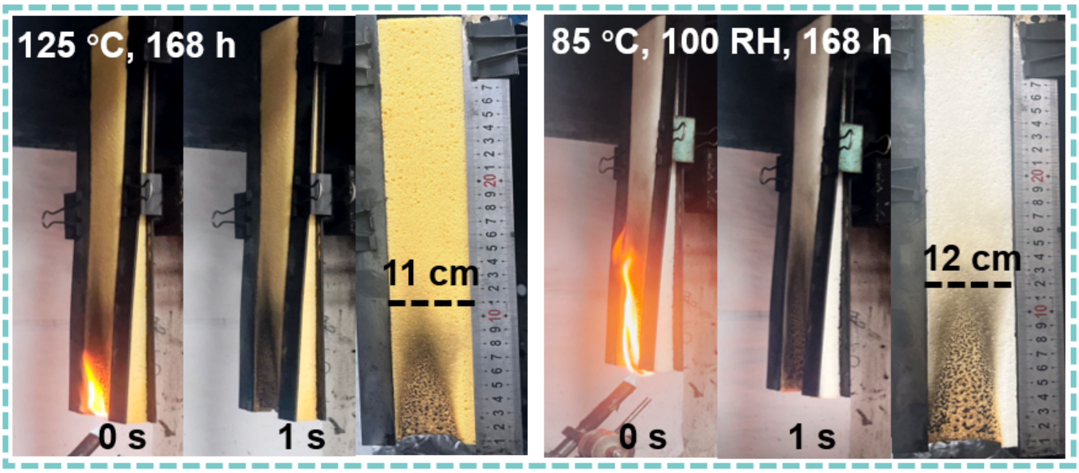

Fig. S10. Digital photos of FPUF/8DTAP at different ignition times after accelerated aging test.

Table S7. Vertical burning test of FPUF/8DTAP after accelerated aging test.

Samples	After flame time (s)		After glow time (s)	Char length (mm)		Test results (pass or fail)
	Average	Maximum	Average	Average	Maximum	
Requirements for pass	≤5.0	≤15.0	≤15.0	≤152.4	≤203.2	Pass
125 °C, 168 h	1	2	0	110	120	Pass
85 °C, 100RH,	2	4	0	120	135	Pass

168 h					

Table S8. LOI test data of neat FPUF and flame-retardant FPUFs after accelerated aging test at 125 °C.

Samples	LOI（%）（0 h）	LOI（%）（24 h）	LOI（%）（72 h）	LOI（%）（120 h）	LOI（%）（168 h）
Neat FPUF	18.5	18.2	18.0	18.0	18.3
FPUF/2DTAP	21.5	21.0	21.1	21.0	21.0
FPUF/5DTAP	22.5	22.5	22.5	22.1	22.0
FPUF/8DTAP	22.0	21.8	21.5	22.0	21.8
FPUF/8DBP	21.0	21.1	21.0	21.2	21.0

Table S9. LOI test data of neat FPUF and flame-retardant FPUFs after accelerated aging test at 85 °C, 100 RH.

Samples	LOI（%）（0 h）	LOI（%）（24 h）	LOI（%）（72 h）	LOI（%）（120 h）	LOI（%）（168 h）
Neat FPUF	18.5	18.3	18.2	18.1	18.4
FPUF/2DTAP	20.5	20.3	20.3	19.8	20.0
FPUF/5DTAP	22.5	22.3	22.0	21.5	21.7
FPUF/8DTAP	22.0	22.1	22.0	21.7	22.0
FPUF/8DBP	21.0	20.9	21.1	21.2	21.0

Table S10. Tensile strength and elongation at break of neat FPUF and flame-retardant FPUFs after accelerated aging test at 125 °C [a].

125 °C	0 h		24 h		72 h		120 h		168 h	
Samples	Ts (kPa)	Eab (%)	Ts (kPa)	Eab (%)	Ts (kPa)	Eab (%)	Ts (kPa)	Eab (%)	Ts (kPa)	Eab (%)
Neat FPUF	49± 4	50 ± 5	46 ± 3	53 ± 2	44 ± 3	56 ± 4	44 ± 2	56 ± 4	43 ± 3	60 ± 4
FPUF/2DTAP	78 ± 3	67 ± 4	69 ± 5	61 ± 2	61 ± 5	55 ± 3	60 ± 4	54 ± 4	63 ± 2	52 ± 1
FPUF/5DTAP	83 ± 7	74 ± 6	68 ± 4	69 ± 2	63 ± 2	65 ± 5	62 ± 4	57 ± 3	62 ± 2	53 ± 2
FPUF/8DTAP	91 ± 6	69 ± 3	77 ± 2	68 ± 4	76 ± 2	65 ± 3	74 ± 3	57 ± 2	75 ± 3	56 ± 4
FPUF/8DBP	80 ± 4	106 ± 3	75 ± 3	99 ± 6	80 ± 5	99 ± 3	65 ± 4	92 ± 3	65 ± 4	80 ± 3

[a] Ts means Tensile strength; Eab represents the Elongation at break.

Table S11. Tensile strength and elongation at break of neat FPUF and flame-retardant FPUFs after accelerated aging test at 85 °C, 100 RH [a].

85 °C, 100RH	0 h		24 h		72 h		120 h		168 h	
Samples	Ts (kPa)	Eab (%)	Ts (kPa)	Eab (%)	Ts (kPa)	Eab (%)	Ts (kPa)	Eab (%)	Ts (kPa)	Eab (%)
Neat FPUF	49 ± 4	50 ± 5	44 ± 2	56 ± 3	44 ± 3	54 ± 4	40 ± 4	61± 3	44 ± 2	57 ± 3
FPUF/2DTAP	78 ± 3	67 ± 4	57 ± 2	64 ± 4	64 ± 3	58 ± 4	56 ± 4	68 ± 6	58 ± 6	64 ± 4
FPUF/5DTAP	83 ± 7	74 ± 6	64 ± 5	68 ± 2	65 ± 2	60 ± 2	70 ± 5	78 ± 3	68 ± 6	77 ± 4
FPUF/8DTAP	91 ± 6	69 ± 3	65 ± 2	72 ± 5	68 ± 1	70 ± 3	72 ± 2	76 ± 4	68 ± 3	81 ± 2
FPUF/8DBP	80 ± 4	106 ± 3	88 ± 2	100 ± 4	83 ± 1	94 ± 5	81± 4	93± 2	70 ± 3	89 ± 4

[a] Ts means Tensile strength; Eab represents the Elongation at break.

Table S12. LOI and yellowing index of FPUF/8DMMP, FPUF/8Tinuvin-770 and FPUF/5.7DMMP+2.3Tinuvin-770 after accelerated aging for 168 h.

	Original	85 °C, 100 RH, 168 h		125 °C, 168 h	
Samples	LOI (%)	LOI (%)	Δ Yellowing Index (%)	LOI (%)	Δ Yellowing Index (%)
FPUF/8DMMP	21.7	20.4	4.63	20.1	29.24
FPUF/8Tinuvin-770	19.5	19.0	0.87	18.8	18.32
FPUF/5.7DMMP+2.3Tinuvin-770	22.8	21.2	1.66	21.0	25.24

Table S13. Tensile strength and elongation at break of FPUF/8DMMP, FPUF/8Tinuvin-770 and FPUF/5.7DMMP+2.3Tinuvin-770 after accelerated aging for 168 h.

	Original		85 °C, 100 RH, 168 h		125 °C, 168 h	
Samples	Tensile strength (kPa)	Elongation at break (%)	Tensile strength (kPa)	Elongation at break (%)	Tensile strength (kPa)	Elongation at break (%)

FPUF/8DMMP	49 ± 2	77 ± 5	39 ± 2	81 ± 3	22 ± 2	127 ± 3
FPUF/8Tinuvin-770	54 ± 4	71 ± 2	48 ± 3	82 ± 6	44 ± 3	124 ± 5
FPUF/5.7DMMP+2.3Tinuvin-770	51 ± 4	72 ± 5	50 ± 2	87 ± 4	38 ± 1	120 ± 5

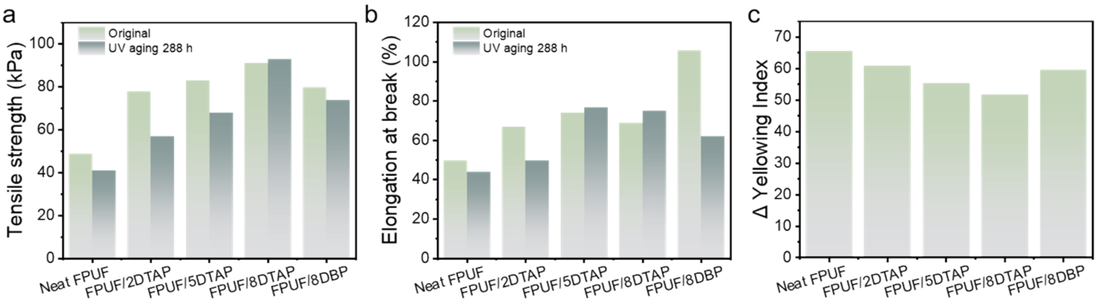

Fig. S11. (a) Tensile strength, (b) elongation at break and (c) yellowing index of neat FPUF and flame-retardant FPUF after UV aging for 288 h.

Table S14. Tensile strength and elongation at break of neat FPUF and flame-retardant FPUFs after UV aging for 288 h.

UV aging	Original		UV aging 288 h	
Samples	Tensile strength (kPa)	Elongation at break (%)	Tensile strength (kPa)	Elongation at break (%)
Neat FPUF	49 ± 4	50 ± 5	41 ± 6	44 ± 4
FPUF/2DTAP	78 ± 3	67 ± 4	57 ± 4	50 ± 1

FPUF/5DTAP	83 ± 7	74 ± 6	68 ± 3	77 ± 4
FPUF/8DTAP	91 ± 6	69 ± 3	93 ± 2	75 ± 5
FPUF/8DBP	80 ± 4	106 ± 3	74 ± 3	62 ± 2

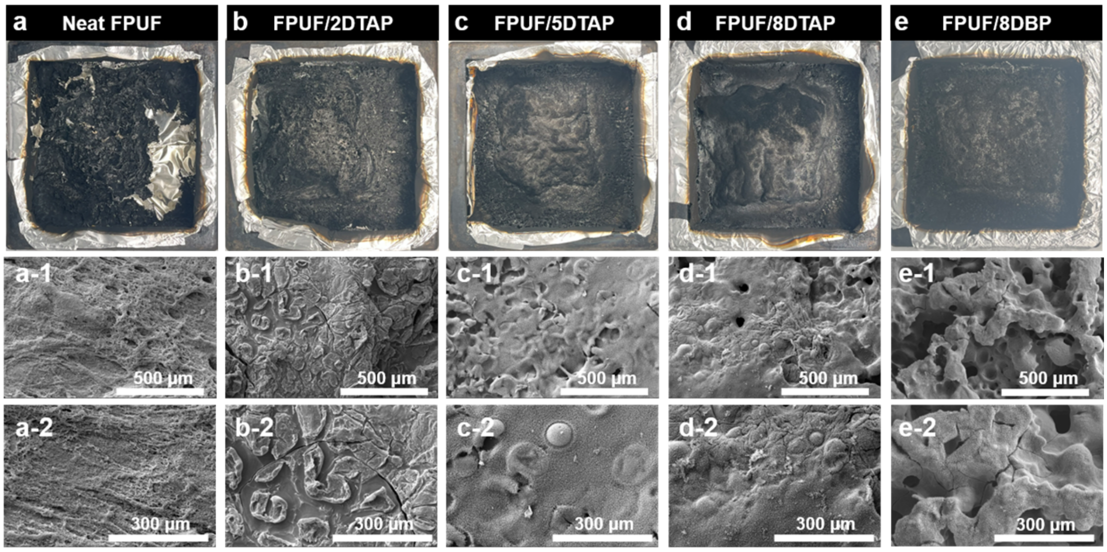

Fig. S12. Digital images of the char residues of (a) neat FPUF, (b) FPUF/2DTAP, (c) FPUF/5DTAP, (d) FPUF/8DTAP and (e) FPUF/8DBP after cone calorimeter test. SEM microphotographs of the external surfaces of (a-1, a-2) neat FPUF, (b-1, b-2) FPUF/2DTAP, (c-1, c-2) FPUF/5DTAP, (d-1, d-2) FPUF/8DTAP and (e-1, e-2) FPUF/8DBP.

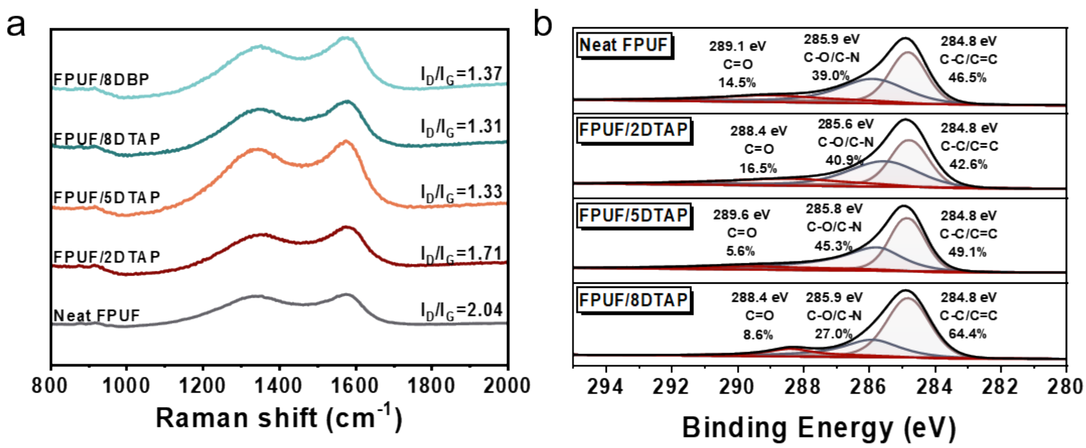

Fig. S13. (a) Raman spectra and (b) C_{1s} spectra of char residues after cone test for neat FPUF and flame-retardant FPUFs.