Cone calorimeter analysis of UL-94 V-rated plastics[‡]

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SUMMARY

Cone calorimeter analysis was conducted on 18 thermoplastics with different UL-94 vertical burn test (V) ratings. Ratings varied from V-0 to no rating (NR), and the types of thermoplastics included were polycarbonate (PC), acrylonitrile–butadiene–styrene (ABS), PC/ABS blends, high-impact polystyrene (HIPS), polypropylene (PP), and poly(vinyl chloride) (PVC). Our analysis of the cone calorimeter data found that there were correlations between UL-94 V rating and some cone calorimeter measurements (peak heat release rate (HRR) average and HRR at 60 s) and no relationship for other measurements (time to ignition and total heat release). However, no precise correlation was found due to significant differences in flame retardant mechanism and polymer fuel energy values. In this paper, we seek to explain further why a broad quantitative relationship between UL-94 V and cone calorimeter remains elusive, and also to show how the cone calorimeter can be used to understand *why* a material passes or fails a particular UL-94 V rating. Copyright © 2006 John Wiley & Sons, Ltd.

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INTRODUCTION

The cone calorimeter (ASTM E-1354/ISO-5660) has long been a useful tool for fire safety engineers and researchers interested in quantitative material flammability analysis. It remains one of the most useful bench-scale tests that attempts to simulate real-world fire conditions [1,2].



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The cone calorimeter brings quantitative analysis to materials flammability research by investigating parameters such as heat release rate (HRR), time to ignition (t_{ig}), total heat release (THR) and mass loss rate (MLR). The HRR measurements can be further interpreted by looking at average HRR, peak HRR and time to peak HRR. The cone calorimeter, if so configured, can also measure and quantify smoke output as well as CO/CO₂ release rates.

A lack of correlation has been observed for cone calorimeter to limiting oxygen index (LOI) measurements [3] and has been claimed anecdotally by many for UL-94, but a recent reference suggests that a relationship exists [4]. This particular reference investigated the relationship between UL-94 and cone calorimeter for two specific flame-retarded systems: glass-filled polyamide-6,6 and high-impact polystyrene (HIPS), which were flame retarded with red phosphorus and red phosphorus/Mg(OH)₂, respectively. UL-94 results were somewhat predicted with the cone calorimeter data: the paper showed inability to differentiate between UL-94 V-0 and V-1 ratings, as well as between V-2 and HB ratings, but could easily differentiate between the broad groupings of V-0/V-1 and V-2/HB.

If one considers how cone calorimeter measures flammability when compared with the LOI and UL-94 fire tests, one should not be surprised by the lack of a strong correlation. LOI [5] is a small-scale test that uses a variable percentage oxygen atmosphere to maintain a candle-like burn, and UL-94 V [6] applies a small calibrated flame twice under the sample (configured vertically) for 10 s followed by a time measurement to extinguishment after each flame application. Cone calorimeter, on the other hand, uses a forced combustion scenario in which radiant heat is projected onto a sample before ignition and during burning of the sample. The sample is usually in a horizontal configuration, thus eliminating any physical effects of polymer burning (dripping away from the flame, for example) that are sometimes used to pass the UL-94 V test, especially under the V-2 rating. Further, the sample in the cone calorimeter exposed to continuous heat during the test while the fire is well ventilated, whereas UL-94 is not a well ventilated fire test. In effect, cone calorimeter measures the material response to a removed fire threat and its time to self-extinction.

When a small/bench-scale test or other flammability test looks at continual fire threat, as does the cone calorimeter, then some good correlations can be seen. There are papers showing a good relationship between flame spread and cone calorimeter HRR for some wire and cable flame spread tests [7,8], and cone calorimeter peak HRR to pyrolysis combustion flow calorimetry heat release capacity measurements [9,10]. Sometimes one or more select measurements provide useful information in regulatory fire scenarios, and one specific example is the Fire Growth Rate index, or FIGRA, which is calculated by dividing the peak HRR by the t_{ig} to give a HRR per unit of time measurement [7,11]. Another technique looks at a parameter called the 'critical HRR' or HRR₀, which is calculated by looking at steady HRR on a particular sample at three different heat fluxes, and then, using the slope of these points to determine the HRR at a zero heat flux [4,9,10]. The HRR₀ has shown good correlation with UL-94 V behaviour for pure polymers, and in this paper we will show how it applies to polymers with flame retardant (FR) additives that have UL-94 V ratings.

The 18 materials discussed in this report were originally tested as part of Flammability Measures of Electronic Enclosures (FMEE) programme run at the National Institute of Standards and Technology Building and Fire Research Laboratory (NIST-BFRL). The FMEE programme studied UL-94 V-rated materials in use today to determine how these materials fared under full-scale fire and constant fire threat conditions. More specifically, how did these materials perform under cone calorimeter conditions or simulated fire scenarios using computer

equipment mockups made from the various UL-94 V-rated polymers? In the first report from the NIST-FMEE programme [12], initial analysis of the cone calorimeter data suggested that quantitative relationships between cone calorimetry and UL-94 V did not exist. Full-scale fire testing data were published, as well as a NIST report which found, as expected, that cone calorimeter data correlated very well with full-scale fire HRR data [13].

The purpose of the FMEE project was to examine the fire safety of existing plastics used for electronic applications, when the fire risk scenario changes from internal ignition (which is addressed by the UL-94V test) to external ignition, a scenario of increasing concern [14-20], especially when non-flame retarded (NFR) polymers are used to meet environmental regulatory needs [21,22]. In the NIST-FMEE study and previous studies, UL-94-rated materials which were V-1 or better did very well in external ignition fire scenarios—they could not easily be ignited with a small candle size flame (ca. 50 W)—whereas igniting materials with less than a V-1 rating led to larger fires [13,15,16,19,21]. However, these studies found that not all materials with the same UL-94 V rating behaved the same in full-scale fire tests. This is not to say that the materials which performed differently are not fire safe for their particular fire scenario. It should also be said that one should not judge the fire safety of one material in one particular fire risk scenario with another fire test that looks at a different scenario. UL-94 V-rated materials are effective at providing fire safety in a local ignition fire scenario, but their safety level is not so clear when these materials are exposed to a more aggressive fire risk scenario. It is important to look at all the data in these studies to make a proper conclusion about the material's contribution to the fire risk outside the scope of the UL-94 test.

Our hypothesis is to build upon the original NIST-FMEE data to establish that a HRR test can also bring understanding on *how* a material passes a particular small/bench-scale fire test, or *why* the HRR is low for a flame-retarded material *vs* a NFR material. There are several papers which explain how to use the cone calorimeter to understand polymeric material fire performance, sometimes with other small/bench-scale fire tests used on the same material [4,23–26]. However, these papers are polymer and FR additive specific, and do not provide a general discussion of how UL-94 V-rated materials can be better understood with calorimetry. In this paper we hope to elaborate upon the relationship between UL-94 V ratings and HRR to establish further dialogue on this subject, as well as to improve the use of cone calorimeter in developing new FR products for specific fire risk scenarios and more realistic fire scenarios.

EXPERIMENTAL COMMENTARY AND PROCEDURES

The formulations used in this study were chosen based on industry use and FR approach. Industry experts were consulted in choosing a set of 18 formulations which included a variety of resin types, FR levels and FR approaches. Commercial resins were chosen instead of model formulations so that the effects of processing aids and other additives are included in the fire performance results. The compounded formulations were provided by four different manufacturers. The 18 material identification labels used in this study are listed in Table I. The format of the label is: number-resin type-FR type. The resin types include acrylonitrile–butadiene–styrene (ABS), HIPS, polycarbonate (PC), polypropylene (PP), poly(vinyl chloride) (PVC) and a PC/ABS blend. The FR types include brominated (BFR), phosphate (PFR), non-halogenated (NH) and NFR. All experimental procedures (UL-94V and cone calorimeter) can be found in the FMEE report [12] however, since it is crucial to explain the details of the cone calorimeter experiment to better explain the data, some of those details are repeated here.

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UL-94 V testing

The UL-94V results generated by Underwriters Laboratories (UL) for each material are reprinted here from the FMEE project report in Table II [12]. The tests were conducted under the official UL-94 standard, details of which can be found in the appropriate references [6,12]. The uncertainty values in burn time and length listed in Table II represent the standard

PC-NH-1	ABS-BFR-7	PP-BFR-13
HIPS-BFR-2	PC/ABS-8PFR	PP-BFR-14
HIPS-NFR-3	HIPS-BFR-9	PP-NH-15
PC-NFR-4	PC-BFR-10	PVC-NFR-17
PC-BFR-5	PP-BFR-11	HIPS-PFR-18
PC/ABS-NFR-6	PP-NH-12	ABS-PFR-19

Table I. List of materials used in bench-scale tests.

Table II.	Summary	of results	from UL94	testing.	

				Max	Total	Total	Mean total	Mean	
Sample		Thickness	UL-94V	afterflame	$t_1 + t_2$ (s)	$t_1 + t_2$ (s)	after-flame	burn	
identification	Colour	(mm)	rating	time (s)	48 h–23°C	168 h-70°C	time $(t_1 + t_2)$ (s)	length (mm)	Footnotes
PC-NH-1	White	1.6	V-2	18	73	63	13.6 ± 5.1	44 ± 10	2,4
HIPS-BFR-2	Black	1.6	V-0	3	4	5	0.9 ± 1.0	38 ± 13	2
HIPS-NFR-3	White	1.6	NR	35	157	175	33.2 ± 5.4	125 ± 3	4
PC-NFR-4	Clear	1.6	V-2	14	54	85	13.9 ± 6.2	30 ± 5	4
PC-BFR-5	Tan	1.6	V-0	3	6	4	1 ± 1.1	35 ± 6	2
PC/ABS-NFR-6	Black	1.6	NR	35	175	175	35 ± 0.0	104 ± 16	4
ABS-BFR-7	White	1.6	V 0	3	6	1	0.7 ± 1.1	44 ± 11	2
PC/ABS-PFR-8	White	1.6	V-2	15	50	30	8 ± 4.6	60 ± 8	2,4
HIPS-BFR-9	White	1.6	V-2	11	59	52	11.1 ± 6.6	43 ± 13	3,4
PC-BFR-10	Black	1.6	V-0	5	21	10	3.1 ± 1.9	21 ± 6	2,3
PP-BFR-11	White	1.6	V-2	0	0	0	0 ± 0.0	19 ± 7	3,4
PP-NH-12	White	1.6	NR*	31	59	58	11.7 ± 7.6	34 ± 21	2,3,4
PP-BFR-13	White	1.6	V-2	4	13	20	3.3 ± 1.7	24 ± 8	4
PP-BFR-14	White	1.6	V-2	16	5	32	3.7 ± 4.9	23 ± 10	4
PP-NH-15	White	1.6	V-0	5	8	7	1.5 ± 1.6	25 ± 13	2,3
PVC-NFR-17	Black	1.6	V-0	4	12	12	2.4 ± 1.2	26 ± 9	2
HIPS-PFR-18	Black	1.6	V-1	27	106	117	22.3 ± 7.7	59 ± 13	2
ABS-PFR-19	Black	1.6	NR*	35	148	79	22.7 ± 10.2	68 ± 7	2
PC-NH-1	White	3.2	V-0	2	6	4	1 ± 0.8	19 ± 4	2
HIPS-BFR-2	Black	3.2	V-0	2	2	1	0.3 ± 0.7	12 ± 3	2
HIPS-NFR-3	White	3.2	NR	35	175	171	34.6 ± 1.3	52 ± 9	4
PC-NFR-4	Clear	3.2	V-2	15	30	59	8.9 ± 4.1	14 ± 3	4
PC-BFR-5	Tan	3.2	V-0	2	2	4	0.6 ± 0.8	14 ± 2	2
PC/ABS-NFR-6	Black	3.2	NR	35	175	175	35 ± 0.0	45 ± 13	4
ABS-BFR-7	White	3.2	V-0	0	0	0	0 ± 0.0	17 ± 4	2
PC/ABS-PFR-8	White	3.2	_						
HIPS-BFR-9	White	3.2	V-2	11	26	37	6.3 ± 3.8	21 ± 8	2,4
PC-BFR-10	Black	3.2	V-0	2	8	7	1.5 ± 0.5	14 ± 6	2
PP-BFR-11	White	3.2	V-2	0	0	0	0 ± 0.0	14 ± 8	3,4
PP-NH-12	White	3.2	V-0	3	1	3	0.4 ± 1.0	9 ± 5	2
PP-BFR-13	White	3.2	V-2	22	52	29	8.1 ± 6.9	19 ± 4	3,4
PP-BFR-14	White	3.2	V-2	7	18	11	2.9 ± 2.2	19 ± 4	4
PP-NH-15	White	3.2	V-0	0	0	0	0 ± 0.0	9 ± 3	2
PVC-NFR-17	Black	3.2	V-0	2	6	3	0.9 ± 0.9	17 ± 4	2
HIPS-PFR-18	Black	3.2	V-1	27	100	98	19.8 ± 9.1	23 ± 7	2
ABS-PFR-19	Black	3.2	V-1	20	57	63	12 ± 6.6	32 ± 5	2

Footnotes: 2, specimen did not drip; 3, specimen dripped particles which did not ignite cotton; 4, specimen dripped particles which ignited cotton.

*Only one of the 10 specimens failed V-classification.

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deviation of 10 measurements. In Table II, the UL-94 V ratings for the FR plastics are shown at two different thicknesses, 1.6 mm (1/16 in) and 3.2 mm (1/8 in). These two thicknesses are very common for FR plastics used in electronic enclosures, though sometimes thinner plastics are used, depending upon the device and its architecture. It is not uncommon for a material to have a stronger rating at a higher thickness, as a thicker specimen will generally require more time and heat exposure to reach its ignition temperature or to decompose the part in a uniform manner. In some cases, the FR additive has more time to activate and provide flame retardancy to the material. In a thinner sample, the heat rapidly permeates the sample, which can cause the polymer to degrade faster than the FR can activate. When looking at the burn times, it can be seen that some materials have lower burn times and shorter burn lengths than others that have the same UL-94 V rating at the same thickness. This is due to flame retardancy mechanism differences, as well as differences in base polymer flammability, which are expected in the UL-94 V test. Even without the cone calorimeter data, one can see that for a given rating not all UL-94 V-rated materials are the same.

Cone calorimeter test

Heat release calculations were based on the oxygen consumption principle, which states that for complete combustion of a wide range of fuels, $13.1 (\pm 5\%)$ kJ of energy is produced for every 1 g of oxygen consumed by the fire [27]. The energy value of the base polymers used in this study were within this range, however, the effects of FRs and other additives on this value is unknown.

The cone specimens were 10 ± 0.1 cm in diameter and 1.6 ± 0.1 mm or 3.2 ± 0.1 mm in thickness. The circular samples were used based upon NIST internal data which showed a more uniform heat flux on a circular sample heated with a circular (cone) heater. All of the specimens were conditioned at $50 \pm 5\%$ relative humidity and $23 \pm 3^{\circ}$ C for a minimum of 48 h. The specimens were placed in a round aluminium foil pan with a lip 5 mm above the top surface of the sample. The description of the apparatus and procedures are in accordance with ASTM E1354-02d, with the exception of using round specimens instead of square ones. All data

Material	UL-94 1/8 in	Rating 1/16 in	Peak HRR	Time to ignition	Time to peak HRR	Total HR	Average HRR at 60 s	Average heat combust	FIGRA	Peak HRR (t _{ig})	Average HRR (t _{ig})
PC-NH-1	V-0	V-2	576	193	319	82.2	333	25.56	1.81	2.98	1.73
HIPS-BFR-2	V-0	V-0	304	87	417	1.5	15.58	0.56	0.73	3.49	0.18
HIPS-NFR-3	NR	NR	1108	151	223	116.2	739	33.96	4.97	7.34	4.89
PC-NFR-4	V-2	V-2	734	500	524	56.9	494	18.03	1.40	1.47	0.99
PC-BFR-5	V-0	V-0	321	260	327	73.4	168	23.94	0.98	1.23	0.65
PC/ABS-NFR-6	NR	NR	850	137	190	86.7	506	26.64	4.47	6.20	3.69
ABS-BFR-7	V-0	V-0	459	126	245	44.5	221	13.05	1.87	3.64	1.75
PC/ABS-PFR-8	V-0	V-2	428	154	232	65.1	212	22.75	1.84	2.78	1.38
HIPS-BFR-9	V-2	V-2	930	136	217	63.3	349	19.44	4.29	6.84	2.57
PC-BFR-10	V-0	V-0	225	461	971	69.5	10	21.95	0.23	0.49	0.02
PP-BFR-11	V-2	V-2	1650	221	298	120.8	747	39.81	5.54	7.47	3.38
PP-NH-12	V-0	NR	265	50	403	121.0	30	40.13	0.66	5.30	0.60
PP-BFR-13	V-2	V-2	1689	124	239	134.9	382	45	7.07	13.62	3.08
PP-BFR-14	V-2	V-2	1677	110	229	135.3	348	41.75	7.32	15.25	3.16
PP-NH-15	V-0	V-0	380	140	297	59.7	256	16.81	1.28	2.71	1.83
PVC-NFR-17	V-0	V-0	179	103	117	46.5	127	15.19	1.53	1.74	1.23
HIPS-PFR-18	V-1	V-1	391	98	169	73.3	284	23.99	2.31	3.99	2.90
ABS-PFR-19	V-1	NR	290	99	365	69.8	188	23.38	0.79	2.93	1.90

Table III. Summary cone calorimeter data, 3.2 mm thickness, 30 kW/m^2 heat flux.

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Material	UL-94 1/8 in	Rating 1/16 in	Peak HRR	Time to ignition	Time to peak HRR	Total HR	Average HRR at 60 s	Average heat combust	FIGRA	Peak HRR (t _{ig})	Average HRR (t_{ig})
PC-NH-1	V-0	V-2	531	67	200	79.3	385	23.26	2.66	7.93	5.75
HIPS-BFR-2	V-0	V-0	461	31	89	43.5	283	11.88	5.18	14.87	9.13
HIPS-NFR-3	NR	NR	1265	50	127	116.3	734	33.7	9.96	25.30	14.68
PC-NFR-4	V-2	V-2	703	129	168	71.6	523	22.57	4.18	5.45	4.05
PC-BFR-5	V-0	V-0	343	78	129	69.8	240	21.06	2.66	4.40	3.08
PC/ABS-NFR-6	NR	NR	790	56	94	84.9	530	25.74	8.40	14.11	9.46
ABS-BFR-7	V-0	V-0	395	50	156	39.9	268	11.16	2.53	7.90	5.36
PC/ABS-PFR-8	V-0	V-2	567	53	99	65.5	322	20.8	5.73	10.70	6.08
HIPS-BFR-9	V-2	V-2	760	44	134	57.1	376	16.59	5.67	17.27	8.55
PC-BFR-10	V-0	V-0	214	72	421	70.1	124	22.3	0.51	2.97	1.72
PP-BFR-11	V-2	V-2	2090	62	148	123.3	662	37.97	14.12	33.71	10.68
PP-NH-12	V-0	NR	337	25	259	122.0	101	39.61	1.30	13.48	4.04
PP-BFR-13	V-2	V-2	2206	46	138	130.9	727	44.53	15.99	47.96	15.80
PP-BFR-14	V-2	V-2	2200	35	151	151.8	219	46.15	14.57	62.86	6.26
PP-NH-15	V-0	V-0	487	48	74	59.2	361	16.37	6.58	10.15	7.52
PVC-NFR-17	V-0	V-0	243	23	35	50.5	176	14.37	6.94	10.57	7.65
HIPS-PFR-18	V-1	V-1	445	30	60	75.3	378	24.18	7.42	14.83	12.60
ABS-PFR-19	V-1	NR	293	36	48	67.6	243	22.28	6.10	8.14	6.75

Table IV. Summary cone calorimeter data, 3.2 mm thickness, 50 kW/m^2 heat flux.

Table V. Summary cone calorimeter data, 3.2 mm thickness, 90 kW/m^2 heat flux.

Material	UL-94 1/8 in	Rating 1/16 in	Peak HRR	Time to ignition	Time to peak HRR	Total HR	Average HRR at 60 s	Average heat combust	FIGRA	Peak HRR (t_{ig})	Average HRR (t_{ig})
PC-NH-1	V-0	V-2	532	17	33	61.2	388	16.96	16.12	31.29	22.82
HIPS-BFR-2	V-0	V-0	566	9	43	41.2	388	10.9	13.16	62.89	43.11
HIPS-NFR-3	NR	NR	1623	16	70	111.3	1051	31.8	23.19	101.44	65.69
PC-NFR-4	V-2	V-2	984	40	67	74.1	644	22.31	14.69	24.60	16.10
PC-BFR-5	V-0	V-0	437	24	60	67.9	311	20.26	7.28	18.21	12.96
PC/ABS-NFR-6	NR	NR	762	21	49	79.2	530	22.74	15.55	36.29	25.24
ABS-BFR-7	V-0	V-0	515	17	43	42.6	411	11.6	11.98	30.29	24.18
PC/ABS-PFR-8	V-0	V-2	611	23	56	62.6	361	19.75	10.91	26.57	15.70
HIPS-BFR-9	V-2	V-2	827	17	62	48.8	562	13.81	13.34	48.65	33.06
PC-BFR-10	V-0	V-0	258	16	63	74.5	219	20.86	4.10	16.13	13.69
PP-BFR-11	V-2	V-2	2391	20	95	118.0	1136	36.03	25.17	119.55	56.80
PP-NH-12	V-0	NR	392	0	201	123.3	214	38.37	1.95	39.20	21.40
PP-BFR-13	V-2	V-2	2529	12	85	122.0	1169	42.04	29.75	210.75	97.42
PP-BFR-14	V-2	V-2	2581	16	90	138.8	1025	41.4	28.68	161.31	64.06
PP-NH-15	V-0	V-0	530	19	32	60.1	371	16.9	16.56	27.89	19.53
PVC-NFR-17	V-0	V-0	305	11	21	45.5	231	11.56	14.52	27.73	21.00
HIPS-PFR-18	V-1	V-1	639	9	38	65.2	463	20.53	16.82	71.00	51.44
ABS-PFR-19	V-1	NR	454	11	33	59.9	319	19.47	13.76	41.27	29.00

collected with the cone calorimeter (Tables III–V) have a standard combined uncertainty of approximately $\pm 10\%$. It is important to note that experimental conditions for cone calorimeter testing are essential in understanding of the data, since the experimental conditions greatly affect the results of the test, as well as possible interpretation [28,29].

RESULTS AND DISCUSSION

The 18 materials were tested under three different heat fluxes, 30, 50 and 90 kW/m^2 . These heat fluxes were chosen based upon input from project sponsors and interest in obtaining the critical

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Figure 1. HRR curves for no rating, not flame retardant (NFR) and V-2-rated materials.



Figure 2. HRR curves for UL-94 V-1-rated materials.

HRR (HRR₀) [10]. There is some guidance in ISO 5660-1 on choosing a heat flux for cone calorimeter experimentation, but no guidance on which heat flux may correlate to a particular regulatory fire test that is not calorimetry based, such as UL94. [30]. Lower heat fluxes $(25-35 \text{ kW/m}^2)$ represent small fires, 50 kW/m^2 heat flux represents a medium-scale fire similar to those on their way to full development, and heat fluxes of 90 kW/m^2 have been observed in fully developed room fires near flashover. Some materials, especially the PC samples, were

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Figure 3. HRR for UL-94 V-0-rated materials (3.2 mm thickness only).



Figure 4. HRR for materials rated UL-94 V-0 at 1.6 and 3.2 mm thicknesses.

difficult to ignite at 30 kW/m^2 due to the higher onset of decomposition temperature for these materials. It should be noted again that the UL-94 burner flame only impinges on the lower part of the sample while the cone calorimeter heat affects a much larger surface area. The exact nature of the FRs and their respective formulations with each of the polymer samples tested in this paper is proprietary. Therefore, the data in this paper cannot infer structure–property

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relationships exactly, but it can still reveal how a particular UL-94 V-rated material behaves under various simulated fire conditions.

$50 \, kW/m^2$ heat flux data

The majority of the data collected by cone calorimeter was under a heat flux of 50 kW/m^2 since this heat flux gave consistent burning behaviour for the materials tested and presented a data set tuned to the focused interest of the NIST-FMEE project. Initial analysis of cone calorimeter behaviour done by grouping materials by UL94 V rating and base polymer type was found to be qualitative through investigation of HRR curves. In Figures 1–4, all of the materials are grouped by UL-94 V rating.

In Figure 1, the base polymers with NFR materials and the samples with V-2 ratings are shown. It is obvious from the plot that in some cases materials with a UL-94 V-2 rating (which are considered more flame retardant than NFR materials) have higher peak HRR than the NFR samples. For example, the peak HRR for the V-2 PP materials (PP-BFR-11, -13, -14) is much higher than the HIPS-NFR-3 sample and is very different when compared with PC-NFR-4. This is to be expected as PP has a much higher net heat of combustion than HIPS or PC based upon its chemical structure. PP decomposes to give aliphatic hydrocarbons, while HIPS and PC give off aromatic hydrocarbons. Certainly both hydrocarbons are flammable, but more heat energy is needed to decompose and combust aromatic hydrocarbons fully. This is seen in the average heat of combustion for these samples in Table IV. PC has an extra advantage: with every repeat unit, carbon dioxide is released upon burning, which yields a substantially lower HRR for the base polymer, and the remaining organic structure has a propensity to char, which limits the amount of mass released for potential combustion. These results have been explained in terms of chemical structure elsewhere [31], and the observations are explained by looking at the molar contribution of chemical structures to polymer flammability, as published by Lyon and Walters [9].

In Figure 2, the two UL-94 V-1 resins are shown. The curves show that the ABS sample has a much lower peak HRR than the HIPS sample. HIPS and ABS are roughly the same in peak HRR content, with ABS being slightly lower [32], so a contributing factor to the lower peak HRR may be the differences in the base resin. However, differences in FR chemistry between these two FR samples may account for the HRR difference. More specifically, the PFRs may be undergoing different chemical reactions in the presence of HIPS and ABS. The materials have similar average heat of combustion (Table IV), with the ABS sample slightly lower. A co-charring polymer (polyphenylene oxide) which is commonly added to phosphorus-containing styrenic FR systems may also be playing a role [33–35].

There were many materials in this study with a UL-94 V-0 rating, but not all of these materials were able to obtain this rating at 3.2 and 1.6 mm thicknesses. The samples were organized based upon the ability to generate UL-94 V-0 at one thickness (3.2 mm) or two thicknesses (3.2 and 1.6 mm). In the UL-94 V test, ratings are given at particular thicknesses, and in general thinner samples are more flammable (less resistant to sustained ignition). Therefore, a material rated V-0 at 1.6 and 3.2 mm would be considered more FR than a material rated V-0 at 3.2 mm only. For clarification, the HRR data in Figures 3 and 4, and throughout the paper, are for cone calorimeter samples 3.2 mm in thickness. In Figures 3 and 4, one can see that there are significant differences between polymer types, with no obvious relationship between the V-rating and HRR curves. Because the polymer chemical structure greatly affects

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ABS (BFR, PFR) HRR Curves

Figure 5. HRR for 3.2 mm ABS FR samples.



Figure 6. HRR for 3.2 mm HIPS samples.

the HRR measurement, the materials were reorganized based on polymer type rather than UL-94 V rating. When this was done (Figures 5–9), some trends began to appear.

One might expect to observe lower peak HRR in materials with better UL-94V ratings. However, this was not the case for ABS-BFR-7 and ABS-PFR-19 (Figure 5). This was more

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Figure 7. HRR for PC samples.



Figure 8. HRR for PC/ABS samples.

surprising since the average heat of combustion was much lower for ABS-BFR-7 than ABS-PFR-19 (Table IV). The brominated FR, rated V-0, had a higher peak HRR than the V-1-rated material. While we do not know the exact chemistry of the phosphorus FR used in sample #19, we do know that BFRs inhibit gas-phase combustion chemistry, effectively lowering the amount

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Figure 9. HRR for PP FR samples.

of oxygen consumed and heat generated. While the peak HRR of the BFR sample is higher than that of the PFR system, the BFR is inhibiting heat release/complete combustion of polymer decomposition products, as seen in the delay to peak HRR for this material relative to the PFR sample. The PFR system has a lower peak HRR, but a much longer burn time which suggests a more condensed phase (or char forming) mechanism of flame retardancy as reflected in the higher average heat of combustion for this sample (Table IV). This type of flame retardancy (char forming) is difficult to achieve in styrenics, so it is possible that while peak HRR is low due to char-forming behaviour, the char may not be durable/non-porous enough to prevent fuel release and subsequent flame propagation in a UL-94 fire test, hence its UL-94 V-1 rating.

Figure 6 shows the HIPS samples, and a more obvious trend in HRR behaviour in regards to UL-94 V rating. As peak HRR is decreased, UL-94 V rating improves. The difference between UL-94 V-1 and V-0 is subtle, and the only major differences are the time to peak HRR, THR and heats of combustion (Table IV). This suggests that if peak HRR had been a little more delayed in HIPS-PFR-18, and if the sample had shown a reduction in THR as well as in heat of combustion, a V-0 may have been achieved for this material. This small difference has been seen by others in a study of NHFR HIPS samples comparing a V-1 with a V-0 resin [35]. With the V-2 resin, peak HRR is reduced just enough to provide some extinguishing behaviour not seen in the base polymer, but the change in THR and average heat of combustion is quite different between HIPS-BFR-9 and HIPS-NFR-3, with the V-2-rated material having much lower values in this area. At first glance this suggests that THR could be useful in differentiating between non-ratable materials and those with V-2 ratings, but our later statistical analysis in this paper (Table VII) suggests that this is not the case and other factors like peak HRR and average HRR (Figures 21–23) are probably more indicative.

In Figure 7, similar behaviour to that seen with the HIPS samples is observed: the FRs lower peak HRR and THR when compared with the base PC polymer. Time to peak HRR was not

always prolonged with these samples, as the FR samples have much earlier t_{ig} values than the base PC. For the material that is V-2 at 3.2 mm, the peak HRR is only slightly reduced. Base PC is inherently V-2 rated, and can be made V-0 rated by using an additive (such as charring salt or fibrillar polytetrafluoroethylene) to inhibit dripping. The V-0 PC-NH-1 probably has just enough FR to pass the V-0 rating, while the V-0 PC-BFR-5 and PC-BFR-10 have much more robust flame retardancy, yielding significantly lower peak HRR with a very prolonged time to peak HRR for the PC-BFR-10 sample. Average heat of combustion (Table IV) were little changed amongst these samples, so we assume that the significant differences in HRR behaviour must be due to other physical decomposition/FR mechanisms between four samples.

The HRR trend observed for the PC and HIPS samples is seen again in the case of PC/ABS in Figure 8, where the FR sample lowers peak HRR and delays time to peak HRR. Unlike the HIPS and PC/ABS samples, the FR sample has a delayed t_{ig} . PFR additives used in PC/ABS formulations can act as both vapour-phase and condensed-phase (char-forming) FR [36], and this combination mechanism may be responsible for the delayed t_{ig} . More specifically, the PFR chars the PC phase rapidly and delays the release of flammable products. Another possible explanation for the delay in t_{ig} is that the two PC/ABS samples do not have the same ratio of PC to ABS. It may be that in the FR system there is more PC than ABS, and this would account for the delay in t_{ig} as PC has a higher onset of decomposition temperature and a delayed t_{ig} compared with ABS (compare Figure 7, sample PC-NFR-4 with Figure 8). Unfortunately, we do not know the exact ratio of PC to ABS in these materials due to their proprietary nature, and therefore the exact reasons for the differences in observed flammability in these samples are unknown.

In Figure 9, there are some obvious differences in HRR when comparing V-rated materials. The V-2 samples are all practically the same; they have similar peak HRR, THR, t_{ig} , and time to peak HRR values. It is noted that V-2 materials, especially these PP samples, use dripping as a primary mechanism of flame retardancy; they drip away from the flame. As expected, they had a much higher peak HRR than the V-0-rated materials since dripping is more important for these materials than lowering HRR. In effect, the cone calorimeter (in the standard horizontal configuration) cannot account for the effect of dripping on HRR, so flame retardancy associated with this physical phenomena cannot be easily quantified. However, if such a material was prevented from dripping away from a flame source, then the high HRR would be of some concern in a fire risk scenario.

For the NH samples the HRR curves for the V-0 materials are very different. PP-NH-15 is V-0 rated at both 3.2 and 1.6 mm, while PP-NH-12 is not. While peak HRR values for PP-NH-12 and PP-NH-15 are very similar, the HRR curve shapes, THR value, time to peak HRR and average heat of combustion are very different. PP-NH-12 has almost the same THR as the V-2 resins, and it burns for a very long time, slowly rising to peak HRR and then slowly burning until all flammable material is consumed, and the flame extinguishes. PP-NH-15, on the other hand, rises to peak HRR fairly quickly, but then extinguishes quickly as well with a much lower THR than any of the other PP samples tested. It was observed that PP-NH-12 had an intumescent char that formed during the cone calorimeter test, and PP-NH-15 had a white powdery char at the end of the test. While we cannot determine the exact NHFR system in each of these samples, we can assume that PP-NH-12 is an intumescent FR system, and PP-NH-15 is likely a mineral filler (such as aluminium or magnesium hydroxide) system. Keeping these possible FR additives in mind, we can explain some of the phenomena observed. Intumescent chars rapidly preventing

additional heat and fuel release [37]. In the case of PP-NH-12, we have an intumescent char that keeps HRR low by slowing the rate of fuel release, and eventually the fuel is completely consumed. For PP-NH-15, high amounts of mineral filler (50–70 wt%) [38] are required to obtain flame retardancy, so most of the reduction in THR is due to the replacement of highly flammable fuel with non-flammable mineral filler, which also decomposes endothermically to release water and cool the remaining PP. The significant reduction in flammable mass results in lowered peak HRR as well as a material that can obtain V-0 ratings even at a lower thickness (1.6 mm). This assumption also fits with the average heat of combustion in that a water-release FR would keep HRR low, while lowering the heat of combustion *via* water release under fire conditions.

The data in Figures 5–9 suggest a qualitative general trend in improving UL-94V flame retardancy. Lower peak HRR and delayed time to peak HRR appear to be general qualities of a UL-94 V-0-rated material. V-2-rated materials have similar HRR curve shapes to that of their NFR base polymers but with lowered peak HRR. The one exception to this observation would be for PP, since no base PP (non-FR) was tested in this study. V-1-rated materials are somewhere in between with significant lowering of peak HRR but a little delay in time to peak HRR. While this trend can be seen regardless of base polymer type, some exceptions were observed. It should be noted that it is difficult to compare different polymers with the same UL-94 V rating since the fuel energy values of the decomposing polymers are completely different. This becomes important when examining THR and heats of combustion as contributing factors, as these will depend on the FR type.

$30-50-90 \, kW/m^2$ heat flux data and HRR_0 calculations

In a recent publication [10] Lyon proposed that by looking at the steady burning behaviour of a polymer under different heat fluxes, it would be possible to determine the peak HRR in an unforced ignition scenario, thereby better simulating the conditions of the UL94 test. Lyon



Figure 10. HRR curves for PC-NH-1 and HIPS-BFR-2.

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Figure 11. HRR curves for HIPS-NFR-3 and PC-NFR-4.



Figure 12. HRR curves for PC-BFR-5 and PC/ABS-NFR-6.

proposed that by taking the HRR values during steady burning under different heat fluxes, one could plot a line of HRR values whose slope intersects at heat flux of 0 kW/m^2 , to give the 'critical HRR' or HRR₀. This HRR₀ value was measured for a wide range of pure polymers, and it was found that some of these values correlated very well with UL-94 V ratings. In Figures

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Figure 13. HRR curves for ABS-BFR-7 and PC/ABS-PFR-8.



Figure 14. HRR curves for HIPS-BFR-9 and PC-BFR-10.

10–18, the HRR curves collected at 30, 50 and 90 kW/m^2 heat flux for each sample are shown, and the data are summarized in Table III. An example of the method for determining HRR₀ is shown in Figure 19 for two different materials. In general, one can see that as heat flux is increased, the HRR curve shifts to earlier times and the peak HRR increases, though again there

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Figure 15. HRR curves for PP-BFR-11 and PP-NH-12.



Figure 16. HRR curves for PP-BFR-13 and PP-BFR-14.

were exceptions. For example, the HRR curve for HIPS-BFR-2 (Figure 10) is very similar at 50 and 90 kW/m² heat flux, but is completely different at 30 kW/m^2 heat flux. At 30 kW/m^2 , there is a short ignition around 90 s, followed by a 300 s delay until HRR rises again and the sample burns itself out. This suggests that at low heat fluxes, the BFR is very effective in preventing ignition, but at higher heat fluxes, the polymer pyrolyzes at a rate equal to or faster than the rate

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Figure 17. HRR curves for PP-NH-15 and PP-NFR-17.



Figure 18. HRR curves for HIPS-NH-18 and ABS-NH-19.

of brominated FR/Br · release, hence the earlier sustained ignition at higher heat flux. The most dramatic difference in HRR behaviour is for the PC samples, in particular PC-NFR-4 and PC-BFR-10 (Figures 12 and 14). With these two samples there is a major difference in t_{ig} values when going from 30 to 50 kW/m^2 heat flux. This can be explained by the higher onset of decomposition temperature for PC in comparison with the other polymers. It

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Figure 19. Example HRR₀ calculations using peak HRR at three heat fluxes.



Figure 20. Cone calorimeter unforced, zero flux, peak heat release rate from the intercept of the plot of peak HRR *vs* incident flux.

should be noted that others have observed changes in HRR behaviour as a function of heat flux and sample thickness, both with pure polymers and with a limited sample set of FR polymers [28,29] (Table V).

In calculating the HRR_{0} , one can see that selecting a point of steady burning behaviour in each sample is not an easy task. This technique has uncertainty associated with it due to the

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large variance in the shape of the HRR curves (as seen in Figures 10-18), and the difficulty in selecting an appropriate steady burning HRR value in these samples. In order to understand the differences in the shapes of the HRR curves, it is useful to describe the dominant physical mechanisms that can affect the fire growth in the cone calorimeter. The nearly uniform heat flux from the cone-shaped heater raises the surface temperature of the fuel until it pyrolyzes and ignites. Additional heat from the flame feeds back to the surface and increases the fuel MLR and thus the HRR (assuming the fire is well ventilated). In some cases, a balance is reached when the heat of gasification of the fuel is equal to the net heat flux at the fuel surface. This 'steady burning' is observed for simple fuels such as PMMA at a thickness of 25mm. For many materials steady burning is never achieved for a number of possible reasons. A material that chars, melts or intumesces may never reach a steady state because the physical properties of the fuel are changing throughout the test. A thin sample may never reach steady burning because the fuel supply is exhausted before the peak HRR is reached. Since it is difficult to state which samples are thermally thick and which are thermally thin, we assume them to be thermally thin based upon our understanding of polymer behaviour in the cone calorimeter as described above. Therefore, we used peak HRR where a steady burning HRR was not present to calculate the HRR₀ values (Table VI) which are shown in Figure 20. The uncertainty bars in Figure 20 represent the standard deviation of the intercept from the linear fit of the data.

Even for materials that exhibit a period of steady burning, a late peak in the HRR can make the data difficult to interpret. This late peak (seen in samples #7 and #15 at 30 kW/m^2) could be caused by an increase in the pyrolysis rate as the back side of the sample increases in temperature. It is unclear if the HRR behaviour late in the cone test is relevant to the UL94 performance due to the way the heat flux is applied and the difference in time scale for the two tests (UL94 total exposure time is 20 s *versus* several minutes for a typical cone test). This adds further uncertainty to the HRR₀ calculations.

Sample identification	Peak HR	R (kW/m ²)	HRR0	(kW/m^2)
Irradiation (kW/m ²)	30	50	90	0
PC-NH-1	576	531	532	582
HIPS-BFR-2	304	461	566	210
HIPS-NFR-3	1108	1265	1623	843
PC-NFR-4	734	703	984	548
PC-BFR-5	321	343	437	254
PC/ABS-NFR-6	850	790	762	878
ABS-BFR-7	459	395	515	387
PC/ABS-PFR-8	428	567	611	378
HIPS-BFR-9	930	760	827	909
PC-BFR-10	225	214	258	197
PP-BFR-11	1650	2090	2391	1383
PP-NH-12	265	337	392	217
PP-BFR-13	1689	2206	2529	1396
PP-BFR-14	1677	2200	2581	1344
PP-NH-15	380	487	530	336
PVC-NFR-17	179	243	305	128
HIPS-PFR-18	391	445	639	252
ABS-PFR-19	290	293	454	180

Table VI. HRR₀ calculation data (Figures 11–19).

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With the above assumptions in mind, one can see that the majority of V-1 and V-0-rated materials have HRR_0 below 400 kW/m^2 , but the PC-NH-1 is an exception to this. Some V-0 materials have a higher HRR_0 than the V-1-rated materials, and the difference between V-2 and NR is much harder to determine, as there are V-2 materials with much higher HRR_0 values than the NR, or NFR materials. Some of the observations can be explained by the differences in heat release for the base polymers, as we know that PP has an inherently higher peak HRR than HIPS, ABS, PC/ABS, PC or PVC. This at least explains why a V-2 PP has a higher peak HRR than a V-2 HIPS or V-2 PC result. However, this hypothesis about base polymer flammability breaks down when looking at the V-1 and V-0 results, where it appears that the effectiveness of the FR at reducing peak HRR is more important.

Statistical analysis of cone calorimeter data by UL-94 V rating

After completing a qualitative analysis, efforts were undertaken to attempt a quantitative correlation through statistical analysis. All the data, including some additional parameters, from the three different heat fluxes are summarized in Tables III–V. Some additional composite



Figure 21. Relationships between UL-94 V rating and 30 kW/m² heat flux cone calorimeter data.

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	Peak HRR	Time to ignition	Time to peak HRR	Total HR	Average HRR at 60 s	Average Heat combustion	FIGRA	Peak HRR (T_{ig})	Average HRR (T_{ig})
30 kW/m ² stats									
Correlation coefficient <i>P</i> -value	0.76 0.0003	0.09 0.7310	$-0.37 \\ 0.1260$	0.47 0.0465	0.85 0.0000	0.51 0.0317	0.71 0.0009	0.65 0.0034	$0.80 \\ 0.0001$
50 kW/m ² stats									
Correlation coefficient <i>P</i> -value	$0.74 \\ 0.0004$	0.09 0.7126	$-0.04 \\ 0.8741$	0.56 0.0150	0.67 0.0023	0.59 0.0103	0.68 0.0019	0.60 0.0091	0.60 0.0085
90 kW/m ²									
Correlation coefficient <i>P</i> -value	$\begin{array}{c} 0.80\\ 0.0001 \end{array}$	0.14 0.5694	0.45 0.0624	0.49 0.0373	0.81 0.0000	0.57 0.0134	0.64 0.0039	0.59 0.0107	0.65 0.0036

Table VII. Spearman correlation model data.

Spearman correlation model results for UL94 ranking vs. Cone parameter ranking (3.2 mm samples only).



Figure 22. Relationships between UL-94 V rating and 50 kW/m² heat flux cone calorimeter data.

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data such as FIGRA, Peak HRR/ T_{ig} and Avg HRR at $60 \text{ s}/T_{ig}$ were also included in these tables. The last two parameters can be seen in the previously cited paper which looked at the relationship between UL-94 and cone calorimeter [4]. A Spearman correlation model (Table VII) was then used for these parameters. The *p*-value in Table VII is the result of a hypothesis test to determine whether a correlation exists (if we can statistically prove it is not zero). The main assumptions are that the model is valid and that the sample number is large enough to draw meaningful conclusions. If the *p*-value is greater than 0.05, no correlation exists. For example the t_{ig} is clearly independent (zero correlation) of the UL94 ranking. The total HR has a very weak but still non-zero correlation. Some of the composite indices (FIGRA, Peak and Avg HRR divided by T_{ig}) seem to have some correlation.

In Figures 21–23, some of the parameters are chosen for visual comparison using a standard statistical box plot. Side-by-side comparison of two notched box plots provides a graphical way to determine which groups have significantly different medians. When this is done, some trends appear.



Figure 23. Relationships between UL-94 V rating and 90 kW/m^2 heat flux cone calorimeter data.

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At 30 kW/m² heat flux, Avg HRR at 60 s seems to be a strong indicator of UL-94 V rating, followed by Peak HRR as a secondary indicator. FIGRA is only able to differentiate between the broad categories of V-0/V-1 and V-2/NR. At 50 and 90 kW/m² heat flux, Avg HRR at 60 s is not a strong indicator, but it can differentiate between V-0/V-1 and V-2/NR, as can peak HRR to some extent. At 50 and 90 kW/m² heat flux, FIGRA now cannot differentiate between V-1/V-2/NR now, but perhaps can hint at V-0 performance under 50 kW/m² heat flux and just barely at 90 kW/m² heat flux. Under no heat flux condition does T_{ig} correlate with UL-94 V rating.

CONCLUSIONS

In this paper we have shown the HRR data on various UL-94 V-rated plastics tested by cone calorimetry. Through qualitative analysis of HRR curves, trends of fire behaviour can be seen which point to important parameters in achieving a particular UL-94 V rating. However, upon quantitative analysis, only at very low heat flux (30 kW/m²) we are able to achieve some sort of correlation between cone calorimeter measurement (namely Avg HRR at 60 s and peak HRR to a lesser degree) and UL-94 V rating. At higher heat fluxes the quantitative relationship breaks down. To some extent, our results match the conclusion of the previous paper on the correlations between UL-94 V-0/V-1 or V-2/NR ratings. Our hypothesis at this time is that a universal model between UL-94 and cone cannot be established due to major differences in heat release values for polymer degradation products and FR mechanisms. Instead, one must look for relationships/predictions in a polymer type and may be even more narrowly in a FR type, to develop a more quantitative relationship between these two tests.

Returning to the commentary about qualitative interpretation of HRR curves, the cone calorimeter data have been useful in explaining how various materials obtain their UL-94V ratings, perhaps enabling a more general relationship between the two tests. In general, lowering peak HRR and delaying time to peak HRR after ignition appear to be important phenomena for gaining higher UL-94V ratings. While this trend seems to be useful across multiple samples, different FR types and base polymers sometimes deviate from this generalization, and it is this level of deviation that leads us to conclude again that one cannot compare the HRR results between one base polymer and another in regards to UL-94V rating and expect to find a similar result.

Regarding heat flux effects on the cone calorimeter performance of the materials in this paper, it should be noted again that we are not stating that the heat fluxes used to generate the data in this paper correlate exactly with UL-94 V conditions, although the 30 kW/m^2 heat flux data did correlate the closest to UL-94 V rating. Rather, the data collected helps determine how these materials behave at higher heat fluxes which represent full-scale/well-developed fires, as well as *why* these materials have their particular UL-94 V rating.

When investigating the HRR₀ of these materials, it was difficult to determine a unique value when the specimens never reached steady burning. Further, there are samples that give a much different shaped HRR curve at one heat flux compared with another, which increase the uncertainty in the HRR₀ calculation. Despite this higher level of uncertainty, the HRR₀ showed some trends in relation to UL-94 V rating that could not be discerned from HRR curve alone. Again, there were outliers in the data, but materials having a HRR₀ less than 400 kW/m² showed a strong tendency to produce UL-94 V-0 or V-1 ratings. Our results suggest that for

thermally thin samples, the HRR_0 model may not be an effective tool in comparing flammability performance in the UL-94V test.

Finally, in regards to cone calorimeter analysis of UL-94 V-rated materials, there is a practical matter to consider when comparing the UL-94V with the cone calorimeter, and that is the amount of material needed for testing. UL-94V consumes far less polymeric material than cone calorimetry, and collecting data for the HRR_0 require a factor-of-three increase in material to obtain the necessary results. However, the uncertainty from the cone calorimeter test is less than that of the UL-94 V test. Anecdotal evidence from numerous operators of UL-94 tests and suppliers of UL-94 V-rated resins strongly suggests that the current UL-94 V test is prone to erratic results. This is because the UL-94 V test operator has to 'follow' the plastic with the Bunsen burner flame during the test, and maintaining a steady ignition source on a moving/curling/ dripping thermoplastic can be difficult; two operators can find different UL-94V ratings even when working with the same polymer FR formulation. 'Round robin' testing between different labs with the same FR material and using the same operator for each UL-94V test can alleviate some of these problems, but not all of them [39]. The HRR_0 method, or even just cone calorimetry at a single heat flux, may become a more useful technique for quality control in the UL-94 V test, especially if there is interest in determining how the resin contributes to fire risk outside the UL-94V test scenario. Rather than collecting full-scale fire data, calculating HRR₀ could yield more reproducible and meaningful data to the regulator and the FR researcher/supplier.

In conclusion, the cone calorimeter and UL-94V are very different tests; while both tests measure flammability, they do so differently, and therefore quantitative correlation between the two tests is not perfect. However, some relationships can be seen, namely Avg HRR at 60 s and peak HRR at low heat flux. Through qualitative analysis, combined with numerical interpretation of THR and average heat of combustion, the cone calorimeter test can reveal FR polymer behaviour, explaining how various V-ratings are obtained, and also showing that not all V-rated materials perform the same in full-scale fires. The HRR₀ shows some promise at better differentiation between sample types, but it does have some practical hurdles for the researcher, as well as uncertainties in HRR₀ calculation due to the chaotic nature of polymer combustion and irregular HRR curves.

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