Correlations Between Measurements of Flame-Retarded High-Density Polyethylene Composites Subjected to Three Conventional Fire Tests

61

Zhi-Sheng Xu, Long Yan, Ding-Li Liu, Tian-Xiao Ni, Jin-Zhi Peng, and Ye Xu

Abstract

The flammability of halogen-containing and halogen-free flame-retarded high-density polyethylene (HDPE) composites was characterized by UL94, limiting oxygen index (LOI), and cone calorimeter tests. Correlations among the data obtained from UL94, LOI, and cone calorimeter tests were analyzed, while the influences of flame-retardant mechanism and burning condition on the correlations were also discussed. Analysis of UL94 rating shows that there is modest correlation between UL94 rating and LOI value in that it is able to differentiate between UL94 HB and V-2/V-0 rating, and no correlations for UL94 rating and cone calorimeter measurements are found due to the differences in flame-retardant mechanisms and burning conditions. The precise correlations are found between LOI value and some cone calorimeter measurements (peak heat release rate and mean heat release rate at 300 s). However, there are weak correlations between LOI value and some measurements (time to ignition, total heat release, mean heat release rate at 180 s, and fire growth rate index) and no correlations for other measurements (mean heat release rate at 60 s and mean heat release rate at 120 s) in cone calorimeter. Meanwhile, there are significantly different fitted equations and coefficients between LOI value and cone parameters for halogen-containing and halogen-free formulations due to the obvious differentiation in flame-retardant mechanisms. The comprehensive discussion of burning conditions could further explain why the correlations among the data obtained from the three fire tests have significant discrepancies and also help to understand why different flame-retardant effectiveness appears in the three fire tests.

Keywords

Correlation analysis • High-density polyethylene (HDPE) • Limiting oxygen index (LOI) • UL94 • Cone calorimeter

61.1 Introduction

Polyethylene (PE) is used more extensively in industry, agriculture, and daily life owing to its good mechanical properties, chemical resistance, low density, low toxicity, excellent electric insulation, and so on [1]. However, the poor fire resistance of polyethylene due to its chemical constitution restricts its application in several areas.

Z.-S. Xu • L. Yan (✉) • D.-L. Liu • T.-X. Ni • J.-Z. Peng • Y. Xu
Institute of Disaster Prevention Science and Safety Technology, Central South University, 22 Shaoshan Road, Changsha 410075, China
e-mail: ylong015@163.com

K. Harada et al. (eds.), *Fire Science and Technology 2015*, DOI 10.1007/978-981-10-0376-9_61

Incorporation of flame retardants has proved to be an effective way to reduce flammability. In order to flame retard polyethylene, inorganic and organic additives were mixed with polyethylene, such as metal hydroxides, halogen-containing compounds, or, in conjunction with antimony trioxide, phosphorous compounds, nitrogen-based compounds, and silicon-based compounds, etc. [2]. The flammability behavior of flame-retarded PE is defined on the basis of several parameters such as heat release rates, spread rates, ignition time, ignition temperature, toxic species emissions, smoke production rates, and so on [3]. These parameters are characterized by the use of usual fire tests including limiting oxygen index (LOI) test, cone calorimeter, UL94 vertical burning test, and so on [4]. The UL94 test and LOI test are widely used as conventional standard fire tests for product development and quality control due to its simplicity, relatively inexpensive equipment and small samples, and good reproducibility [5]. The cone calorimeter has long been a useful tool for basic studies under more realistic conditions. The equipment is relatively expensive, but it is one of the most useful bench-scale tests that attempts to simulate real fire conditions [6].

The fire properties from various fire tests are very dependent on the test conditions, especially the amount of radiant heat from the external source [7]. Indeed, the rating of materials can be reversed in these tests merely by changing the radiant heat conditions [8]. A variety of studies have been conducted to show the correlations between the measurements of various scale flammability tests. Edward Weil [9] showed that the LOI for flame-retardant plastics might be leveled with UL94 rating or cone calorimeter data to some degree, but the LOI was not correlated well with UL94 rating and cone calorimeter data due to the difference of burning conditions and polymers. Lyon [10] and Bundy [11] measured the HRR0 (the heat release rate at zero external heat flux) of various polymers using the cone calorimeter and found that there was good correlation between HRR0 with UL94 rating. Hong [12] showed that the LOI and UL94 rating were not closely related, while HRR was more related to UL94 rating than LOI. In particular, the lower the HRR is, the better is the UL94 rating obtained in styrene resins. Morgan [13] analyzed 18 thermoplastics with different UL94 ratings and explained broad quantitative relationship between UL94 and cone calorimeter. The paper also showed how the cone calorimeter can be used to understand why a material passes or fails a particular UL94 rating. J. M. Cogen [14] found that there were poor correlations between LOI and the main cone calorimeter parameters for halogen-free flame-retarded polyolefin compounds. In fact, the fire property of one material is totally different from that in particular fire risk scenario or in another fire test. For example, low flammability of polymer nanocomposites is only achieved in terms of HRR, but they fail in terms of LOI and UL94 [15].

In previous studies, halogen-containing flame-retarded low-density polyethylene composites acquired higher LOI value and UL94 rating; meanwhile, they did well in delaying the ignition times and also increased the peak heat release rate and total heat release in cone colorimeter [16]. However, the different or reversed fire response parameters may be acquired among LOI, UL94, and cone calorimeter tests due to the discrepancies of flame-retardant formulations and polymers with various pyrolysis mechanisms [17, 18]. Several papers acquired the correlations among the data obtained from LOI, UL94, and cone calorimeter tests, which also explained how to use the cone calorimeter to understand polymeric material fire performance under other fire tests [8, 13, 14, 19]. Futhermore, the correlations among these tests are varied with the polymers and flame retardants, which are seldom provided in these literatures, especially the correlations for PE mixed with amounts of halogen-containing and halogen-free flame retardants, respectively.

This paper aimed to analyze the correlations among the measurements obtained from LOI, UL94, and cone calorimeter tests for halogen-containing and halogen-free flame-retarded HDPE and investigate the fire response of flame-retarded HDPE based on different flame-retardant mechanisms and fire tests. In addition, it also discussed the influences of flame-retardant mechanism and burning condition on the correlations.

61.2 Experimental Method

61.2.1 Materials

High-density polyethylene pellets (type, HDPE 6098; MFR, 0.9 g/10 min) were purchased from Sinopec Qilu Company Ltd., China. Expandable graphite (EG), red phosphorus (RP), zinc borate (ZnB), aluminum hydroxide (ATH), and magnesium hydroxide (MH) were acquired from the GuangCheng Chemical Co., Ltd., Tianjin, China. Halogenated flame retardants including tetrabromobisphenol A bis(2,3-dibromopropyl ether) (TBAB), decabromodiphenyl oxide (DBDPO), pentabromotoluene (PBT), chlorinated paraffin (CP), and synergistic agent Sb_2O_3 were purchased from Qingdao Haihua Flame-Retardant Material Co., Ltd., China. The halogen-containing flame-retardant system consisted of halogenated flame retardants and Sb_2O_3 with the mass ratio of 3:1.

61.2.2 Sample Preparation

Before the experiment, all materials were dried at 80 °C for 8 h. Formulated HDPE and different flame retardants were mixed at 160 °C for 20 min using lab two-roll mill. Then they were molded into the sample sheets with dimensions of $100 \times 100 \times 4\ mm^3$ for cone calorimeter tests, employing a high-temperature press at 160 °C. The samples were cut into specimens with dimensions of $100 \times 13 \times 4\ mm^3$ for UL94 vertical burning test and $100 \times 6.5 \times 4\ mm^3$ for limiting oxygen index test.

61.2.3 Measurements

Limiting oxygen index (LOI) was measured using an HC-2 oxygen index meter (Jiangning Analysis Instrument Company, China) according to ASTM 2863. In the LOI burning test, the polymer is assessed by the minimum oxygen concentration in nitrogen that will support the combustion of the sample for at least 3 min or for the consumption of 5 cm in length. A vertical burning test was determined to use a CFZ-2-type instrument (Jiangning Analysis Instrument Company, China) according to the UL94 test standard. In the UL94 vertical burning test, the polymer was rated mainly according to the recorded flaming time of the specimen as well as whether the dripping occurs and ignites the cotton placed under the test specimen.

The cone calorimeter test was conducted using an FTT standard device (FTT, UK) according to ISO 5660 at an incident heat flux of 50 kW/m^2. 50 kW/m^2 heat flux represented a medium-scale fire similar to those on their way to full development [13]. In order to avoid overflow and dripping of molten thermoplastics, the aluminum foil used to contain the specimen, the thickness of the aluminum foil was about 10 mm deep, which was larger than that of the specimen. A large number of parameters may be derived from cone calorimeter. Time to ignition (TTI), peak heat release rate (PHRR), total heat release (THR), fire growth rate index (FIGRA), and mean heat release rate at 60 s, 120 s, 180 s, and 300 s, respectively (MHRR60, MHRR120, MHRR180, and MHRR300), for each specimen were obtained. Moreover, FIGRA was calculated from the peak heat release rate divided by the time to peak.

61.2.4 Statistical Analysis

The statistical package for the Social Sciences version 17.0 was used to analyze the correlations. Correlations among UL94 rating, LOI, and cone calorimeter data were analyzed by the use of Pearson, Spearman, and Kendall correlation models. The *P*-value was the result of a hypothesis test; it determined whether there is relevance between two variables. A $P < 0.05$ was considered statistically significant, for $P > 0.05$ was considered no correlation [20]. Among three correlation models, the Pearson correlation model is sensitive only to a linear relationship between two variables (which may exist even if one is a nonlinear function of the other), and the Pearson correlation coefficient ρ_{XY} is defined as the following equations:

$$\rho_{XY} = \frac{\mathrm{cov}(X,Y)}{\sigma_X \sigma_Y} = \frac{E(X-\mu_X)(Y-\mu_Y)}{\sigma_X \sigma_Y} \tag{61.1}$$

where E is the expected value operator, cov means covariance, *X* and *Y* are random variables, and σ_x and σ_y are, respectively, the standard deviations of *X* and *Y*.

The Spearman correlation model is a nonparametric measure which is suitable for data that is not normally distributed. It works better in detecting a nonlinear relationship between two variables. The n raw scores X_i and Y_i are respectively converted to the ranks x_i and y_i, and the Spearman correlation coefficient ρ_s is computed as the following equations:

$$\rho_s = \frac{\sum_i (x_i - \overline{x})(y_i - \overline{y})}{\sqrt{\sum_i (x_i - \overline{x})^2 \sum_i (y_i - \overline{y})^2}} \tag{61.2}$$

The Kendall correlation model is a nonparametric measure. The coefficient has a more intuitive interpretation to analyze the correlation between two variables. The r_k is defined as

$$\gamma_K = \frac{2(C-D)}{n(n-1)} \tag{61.3}$$

where *C* and *D* are, respectively, the number of concordant and discordant pairs.

61.3 Result and Discussion

61.3.1 Compositions and General Trends

The compositions and fire behaviors of HDPE subjected to three fire tests are listed in details shown in Table 61.1. Examination of the formulations indicates that the flame-retarded efficiency has obvious discrepancies depending on the composition of flame retardants and their mechanism of action. For example, the HRR and THR are decreased significantly with lower loading of halogenated flame retardants, while the improvement of LOI and UL94 rating needs higher loading levels in the HDPE. In addition, the relatively low loading of EG could significantly decrease the MHRR and PHRR and increase the LOI value and burning time, but the THR has no obvious change in comparison with THR of pure HDPE due to the longer burning time.

Table 61.1 Compositions and fire properties for flame-retarded HDPE compounds

Parameters	LOI (%)	UL94 rating	TTI (s)	PHRR ($kW \cdot m^{-2}$)	THR ($MJ \cdot m^{-2}$)	MHRR60 ($kW \cdot m^{-2}$)	MHRR120 ($kW \cdot m^{-2}$)	MHRR180 ($kW \cdot m^{-2}$)	MHRR300 ($kW \cdot m^{-2}$)	FIGRA
HDPE	17.2	HB	48	1345.1	158.9	5.8	123.9	314.5	511.3	5.98
7 % DBDPO	19.7	HB	49	1001.4	122.2	11.4	173.1	366.1	386.1	5.41
7 % TBAB	20.3	HB	44	1115.1	142.9	33.2	232.9	414.1	461.1	5.72
7 % MH	19.3	HB	57	1170.7	143.8	3.5	144.1	299.5	455.8	5.57
7 % EG	24	HB	23	267.6	158.2	89.8	161.9	183.2	201.8	4.12
7 % ATH	19.7	HB	31	1024.8	146.5	51.5	204.4	392.6	465.9	4.88
14 % ATH	20.4	HB	33	989.22	141.5	48.8	195.8	355.6	439.4	5.21
14 % RP	22.2	V-0	33	971.2	153.3	21.5	146.7	249.4	445.1	3.96
14 % TBAB	22.2	HB	39	1080.8	123.1	14.6	168.5	330.5	393.9	5.27
14 % PBT	23.7	HB	48	906.6	113.1	3.5	121.6	286.3	365.9	4.65
10 % TBAB/4 % RP	23.2	V-2	32	997.2	118.8	45.3	194.9	358.7	379.2	5.25
10 % PBT/4 % ATH	24.3	HB	35	1039.6	119.7	46.0	212.8	406.5	391.5	5.62
20 % CP	26.5	V-2	40	855.3	133.7	23.9	191.1	325.1	415.5	3.72
20 % EG	26.1	V-2	44	190.0	141.6	54.0	109.5	133.7	151.8	1.19
14 % CP/6 % EG	31.3	V-0	27	248.6	124.9	81.3	134.9	150.7	175.1	4.97
40 % ATH	21.3	HB	39	543.9	142.6	4.6	34.8	112.7	211.4	1.38
35 % ATH/5 % EG	25.3	HB	33	280.9	123.2	36.6	147.2	187.3	206.7	2.01
35 % ATH/5 % RP	24.1	V-2	41	442.5	109.9	9.9	124.6	195.8	251.8	1.38
30 % ATH/5 % EG/5 % RP	29.8	V-0	31	280.3	112.6	14.5	111.2	154.5	180.6	0.73
30 % ATH/5 % EG/5 % ZnB	24.8	HB	31	314.6	139.3	11.1	112.2	158.9	190.3	0.72

Furthermore, as we can see in Table 61.1, EG combined with CP and ATH combined with RP have obvious synergistic effects to improve the flammability in terms of LOI value, UL94 rating, PHRR, THR, TTI, and FIGRA.

In addition, the flame ratings of a sample in three fire tests have notable differences. For example, the 14 % RP flame-retarded HDPE generates UL94 V-0 rating, while the THR are nearly equivalent to the value of pure HDPE. Therefore, regression analysis is performed to assess correlations between the various test parameters by Spearman, Kendall, and Person correlation models, respectively, and quantitative correlations should help to estimate the fire properties of materials. The correlation coefficients and *P*-values will be shown later.

61.3.2 Correlation Analysis Among LOI, UL94, and Cone Calorimeter

61.3.2.1 LOI Versus UL94

The UL94 results shown in Fig. 61.1 plotted the UL94 ratings versus LOI values. It can be easily seen from Fig. 61.1a that the LOI values of V-2- and V-0-rated materials are higher than those of HB materials measured by UL94 test. However, it does not mean that higher LOI value acquires better UL94 rating. For example, halogen-containing flame-retarded HDPE is classified as V-0, but the LOI value is 31.3 which is higher than RP flame-retarded HDPE. From the standard statistical box plotted in Fig. 61.1b, significantly different medians indicate that empirical regimes existed between LOI value and UL94 rating. On the whole, there is no vertical rating in UL94 when LOI <22, and the materials change from V-2 to V-0 classification when LOI >26. To further explore the qualitative correlations between LOI value and UL94 rating, Spearman, Kendall, and Pearson correlation coefficients are listed in Table 61.2.

As shown in Table 61.2, only modest correlation is obtained between LOI value and UL94 rating. According to the *P*-values, the Spearman correlation model owns the highest significance level to assess the correlations for non-parametric variables compared to Kendall and Pearson models. Therefore, Spearman correlation model is used to correlate UL94 rating and cone calorimeter data.

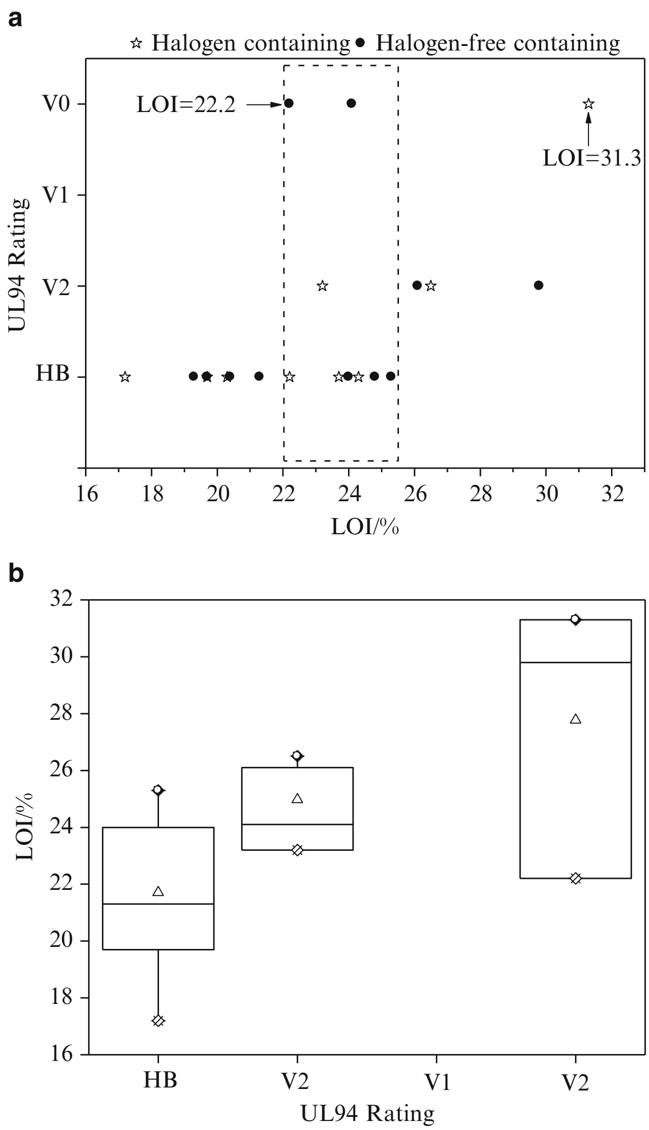

Fig. 61.1 Relationships between LOI value and UL94 rating: (**a**) for the scatter diagram, (**b**) for the standard statistical box

Table 61.2 Correlation coefficients and *P*-values between UL94 rating and LOI value for flame-retarded HDPE

Parameters	Spearman	Kendall	Pearson
Coefficient	0.546	0.446	0.492
P-value	0.013	0.016	0.028

The weak correlations between the results of UL94 test and the LOI test can ascribe to differences between the fire tests as shown in Fig. 61.2.

As seen from Fig. 61.2, there are at least three differences between UL94 test and LOI test. First, the flame spreads upward over the surfaces of the specimen in the UL94 test, while there is downward flame spread in the LOI test. In comparison with upward flame spread, the flame spreads downward where the new pyrolysis area appears or ignition front moves downward. Second, the oxygen concentration in the LOI test is often higher than that in UL94 test. Third, the dropping behavior has different influences on the fire performance in UL94 test and LOI test. Due to the differences of burning conditions, the flame-retardant systems affect the LOI values and UL94 ratings differently. For example, the dropping behavior of halogenated flame-retarded HDPE accelerates heat flux away from the preheating area in LOI and UL94 tests, so the dropping helps to increase the LOI value. However, the dropping behavior failed to improve the UL94 rating due to the dropping that easily ignites the cotton placed under the test specimen [18].

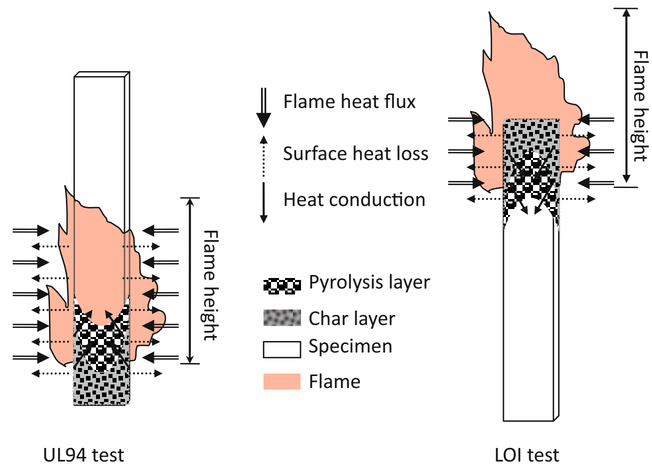

Fig. 61.2 Sketch map of the heat transfer process during UL94 and LOI burning tests

61.3.2.2 UL94 Versus Cone Calorimeter Data

There are no correlations between UL94 rating and some cone calorimeter parameters including TTI, THR, MHRR60, MHRR120, MHRR180, MHRR300, and FIGRA as shown in Table 61.3. Only weak correlation is obtained between UL94 rating and cone PHRR, in which the coefficient has an absolute value of 0.472 as shown in Table 61.3. In an attempt to understand the absence of strong correlations between UL94 ratings and cone calorimeter data, the HDPE composites are grouped by the same UL94 rating as shown in Fig. 61.3.

It can be obviously seen from the plot that in some cases HDPE composites with a UL94 HB rating have very different peak HRRs as shown in Fig. 61.3. For example, the peak HRR of the 7 % EG flame-retarded HDPE is much higher than that of the 40 % ATH or 14 % PBT samples, and the HRR curve shapes are changed with the flame-retardant formulations. Moreover, ATH and EG, both used in HDPE, have obvious synergistic effects in decreasing the PHRR compared to ATH alone with the same HB grade that is rated for UL94 test. The lower PHRR of EG flame-

Table 61.3 Spearman correlation model data between UL94 rating and cone parameters

Parameters	TTI	PHRR	THR	MHRR60	MHRR120	MHRR180	MHRR300	FIGRA
Coefficient	−0.180	−0.472	−0.271	0.189	−0.229	−0.351	−0.329	−0.223
P-value	0.448	0.036	0.248	0.424	0.331	0.129	0.157	0.344

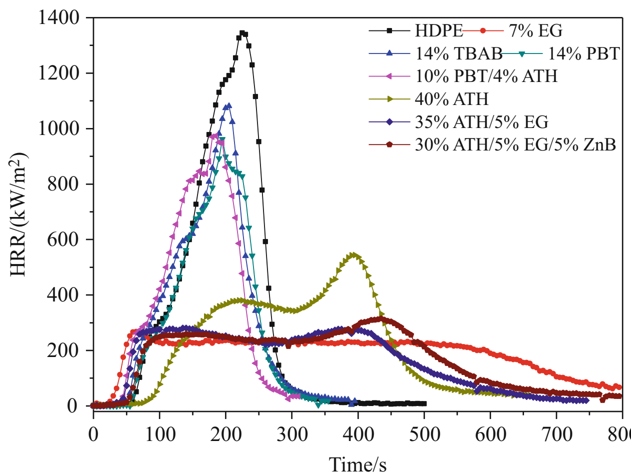

Fig. 61.3 HRR curves for HDPE composites rated UL94 HB

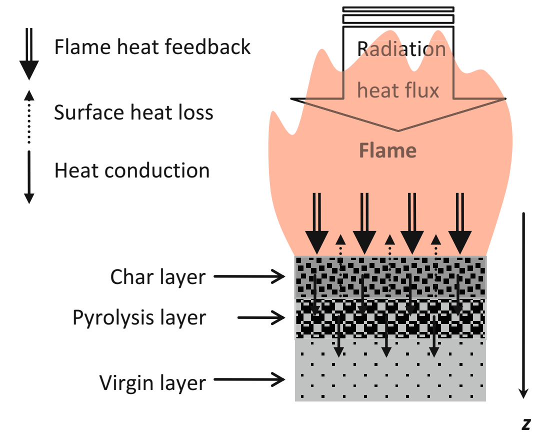

Fig. 61.4 Sketch map of the heat transfer process during cone calorimeter burning

retarded HDPE is due to the formation of a char layer, which limits the amount of mass and heat released for potential combustion [1]. However, HDPE in fire would decompose to produce wax of low molecular weight and trend to form wax-like small-size dripping in the UL94 test [18]. The formation of char could limit the drop behavior in UL94 burning and increase the burning time, and obtain lower UL94 rating [18]. The higher PHRR and lower UL94 rating of 14 % TBAB or 14 % PBT can explain that the addition of halogenated flame retardants releases insufficient halogen atoms to inhibit polymer flammability [2].

These differences in HRR of the same V-rated materials existed in both halogenated and halogen-free samples which can be confirmed in Table 61.1. The data in Fig. 61.3 show that there are no qualitative correlations between the rising of UL94 ratings and the improvement of flame retardancy in cone calorimeter. The differences between the fire tests can illustrate why there are no qualitative correlations between UL94 rating and cone calorimeter data.

The cone calorimeter and UL94 test are very different, while both tests measure flammability so differently as shown in Figs. 61.2 and 61.4, and therefore correlations between the tests are not perfect as shown in Table 61.3.

The sketch map of the heat transfer process in cone calorimeter is shown in Fig. 61.4. The heating process can be simplified as one-dimensional heat transfer in the direction normal to the exposed surface [8]. For general charring materials, a char layer is formed after decompositions of the specimen top surface. Beneath the char layer, it is usually argued that there are two layers included, the pyrolysis layer and the virgin layer. These three layers are approximately parallel to the top surface. During the burning process, the char layer not only protects the inner polymer from being directly heated by the external heat flux but also enhances the surface heat loss; what is more, the existing char layer could weaken the heat flux into the pyrolysis layer and decrease the pyrolysis rate [15]. For example, 20 % EG sample with existing char layer during burning, rated V-2, obtains the lower peak HRR and longer TTI compared to 20 % CP sample without formation of a char layer. (Fig. 61.5).

Conclusively, one can see that there are at least four differences between the cone calorimeter and UL94 test; the discrepancies are reasonable to illustrate the weak correlations among data obtained from two fire tests. First, the polymer plate in the cone calorimeter is exposed to the heat flux from one direction and burns mainly at the top surface, while the specimen in the UL94 test is heated from three directions and burns at all surfaces in the bottom end. Second, the heat flux subjected by the specimen in the cone calorimeter test is lower than the one commonly used in the UL94 test [8]. So, the specimen in the UL94 is easier to be ignited than that in the cone calorimeter test. Third, the flame spreads upward over the surfaces of the specimen in the UL94 test, while there is no flame spread in the cone calorimeter test. Fourth, the dropping behavior existed in UL94, while cone calorimeter test eliminates the influence of the dropping behavior on the flame retardancy. In some cases, RP samples use dripping, which can improve UL94 rating

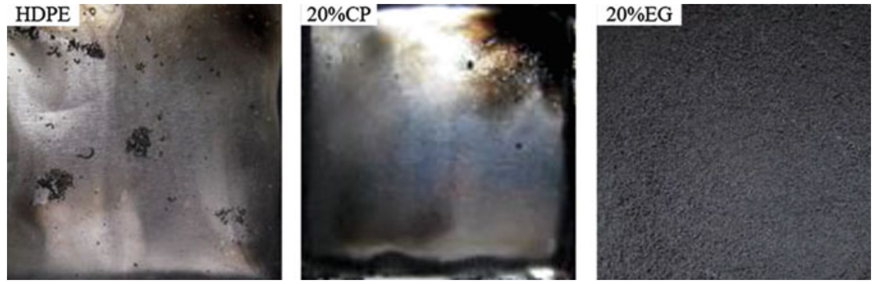

Fig. 61.5 Appearance of the fire residues of the HDPE composites after cone calorimeter test

Table 61.4 Pearson correlation coefficients and *P*-values between LOI value and cone parameters

Parameters	TTI	PHRR	THR	MHRR60	MHRR120	MHRR180	MHRR300	FIGRA
Pearson coefficient	−0.494	−0.757	−0.480	0.368	−0.206	−0.563	−0.778	−0.498
P-value	0.027	0.0001	0.032	0.111	0.383	0.009	0.0001	0.025

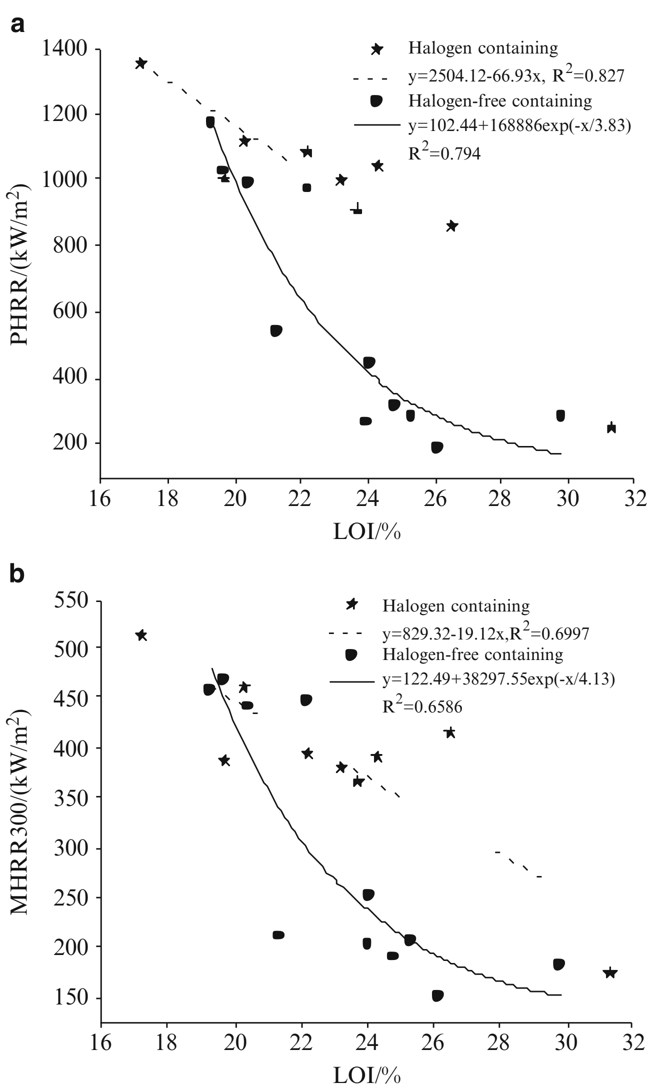

Fig. 61.6 Relationships of LOI value plotted against (**a**) the PHRR and (**b**) the MHRR300

obviously than decrease HRR, as a primary mechanism of flame retardancy in UL94 test [3, 18].

61.3.2.3 LOI Versus Cone Calorimeter Data

The Pearson correlation coefficients between LOI value and cone calorimeter results are listed in Table 61.4. As shown in Table 61.4, some strong correlations existed between LOI value and some cone calorimeter data (Pearson = −0.76 for peak HRR and Pearson = −0.78 for MHRR300) and weak correlations for some measurements (Pearson = −0.49 for TTI, Pearson = −0.48 for THR, Pearson = −0.56 for MHRR180, and Pearson = −0.50 for FIGRA), while no correlations existed for other measurements (MHRR60 and MHRR120). In an attempt to understand the strong correlations between LOI and cone calorimeter data (MHRR300 and PHRR) for halogen-containing and halogen-free flame-retardant system, the LOI plotted against the PHRR and MHRR300 are shown, respectively, in Fig. 61.6.

A correlation is deemed statistically significant when it has an R^2 >0.4 [9]. In the case of halogen-containing flame-retardant system, the statistically significant linear correlations are observed between LOI value and cone parameters: cone PHRR (R^2 = 0.83) and cone MHRR300 (R^2 = 0.70). In the case of halogen-free flame-retardant system, it is noted that plotting LOI values and cone calorimeter data tends to suggest functional relationships having the shape of equilateral hyperbola. The statistically significant correlations are found between LOI values and some cone parameters (R^2 = 0.79 for cone PHRR and R^2 = 0.66 for MHRR300). Considering the fitted equations and R^2 coefficients, it is justifiable to use the LOI value as proxy for assessing the data of PHRR and MHRR300 in cone calorimeter test for halogen-free and halogen-containing flame-retardant systems, respectively.

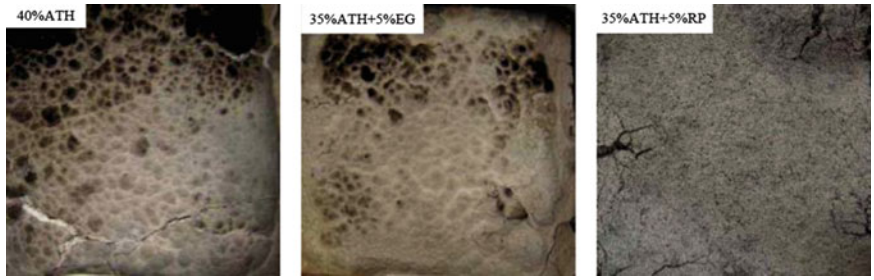

Fig. 61.7 Photographs of the fire residues of the HDPE composites after cone calorimeter test

Furthermore, it can be seen that the fitted equations and coefficients are very different for halogen-containing and halogen-free flame-retardant systems (Fig. 61.6). To be specific, the strong linear correlations are observed between LOI value and cone parameters (PHRR and MHRR300) for halogen-containing composites, while the precise nonlinear correlations are observed for halogen-free composites. So, it is reasonable that the flame-retardant formulations have great influence on the correlations due to the difference of flame-retardant mechanisms. In general, ATH, MH, and ZnB as mineral flame retardants can influence the polymer's fire performance by absorbing energy, releasing nonflammable molecules, and also promoting the formation of a protective ceramic [2]. RP is active both in the gas and the condensed phase, which helps to form an intact char layer (Fig. 61.7). In addition, halogen flame retardants are mainly active in the gas phase, while the halogen-free flame retardants are primarily active in the condensed phase by formation of a protective layer (Figs. 61.5 and 61.7).

The comprehensive comparison of burning conditions provides a deeper understanding of the discrepancies about correlations between the LOI and cone calorimeter tests. It can help to explain the fire performance discrepancies of different flame-retardant formulations in the fire tests. On the basis of Figs. 61.2 and 61.4, it seems that there are at least two discrepancies between the LOI and cone calorimeter tests. First, the heat transfer in the LOI test is considered a three-dimensional heat transfer process, while the cone calorimeter test is considered a one-dimensional heat transfer process. Second, no dropping behavior and flame spread existed in the cone calorimeter, where the dropping behavior helps to improve the LOI value for halogen-containing flame-retardant systems.

Considering the differences of heat transfer process, heat flux, dropping behavior, and flame spread between LOI test and cone calorimeter test, it might be reasonable that quantitative correlations are not perfect between LOI values and some measurements (TTI, TTI, MHRR60, and MHRR120, MHRR180, and FIGRA) in cone calorimeter. However, strong correlations can be seen between LOI and some cone parameters, namely, MHRR300 and PHRR. It is greatly ascribed to the MHRR300 and PHRR approximate to the heat release of maintaining combustion in the LOI test.

61.4 Conclusions

The flammability of halogen-containing and halogen-free flame-retarded HDPE was studied by means of LOI test, UL94 vertical burning test, and cone calorimeter test. Due to the significant discrepancies of the burning conditions and flame-retardant mechanisms, there are significant differences in the measure of flammability in both tests. Correlation analysis of the measurements found that the Spearman correlation model which is used to assess the correlations between the measurements of three fire tests has the higher statistically significant level in comparison with Pearson and Kendall correlation models. The analysis of correlations between UL94 rating and LOI values, one can found that there are weak correlations between UL94 ratings and LOI values, and that it is able to differentiate between UL94 HB and V-2/V-0 rating. However, no correlations for UL94 rating and cone calorimeter measurements are found due to the significant differences in flame-retardant formulations and test conditions. From the HRR curves of same V-rated materials, one can see that there are significant discrepancies of HRR curves for different flame-retardant formulations, and no correlations are found between V rating and HRR curves.

Focusing on the correlations between LOI value and cone calorimeter parameters, there are obvious differences. The good correlations are found between LOI values with PHRR (P-value $= -0.76$) and MHRR300 (P-value $= -0.78$) in the cone calorimeter. In addition, there are weak correlations between LOI values and some measurements (TTI, TTI, MHRR180, and FIGRA) and no correlations between other measurements (MHRR60 and MHRR120) in cone calorimeter. Considering the differentiation of flame-retardant mechanisms, the fitted equations and coefficients between LOI values and cone parameters (PHRR and MHRR300) are obviously different for halogen-containing and halogen-free flame-retarded HDPE, respectively. The strong linear correlations are observed between LOI values and cone parameters ($R^2 = 0.83$ for PHRR and $R^2 = 0.70$ for MHRR300) for halogen-containing composites, while the precise nonlinear correlations are found between LOI values and cone parameters ($R^2 = 0.79$ for cone PHRR and $R^2 = 0.66$ for MHRR300) for halogen-free composites.

In conclusion, the three fire tests are very different tests, so the quantitative correlations among data obtained from the three tests are not perfect. Multi-scale methods should be employed to estimate fire properties of flame-retarded materials. The comprehensive discussion of burning conditions could further explain why the correlations among the data obtained from the three fire tests have significant discrepancies and can also help to understand why different flame-retardant effectiveness appears in the three fire tests.

Acknowledgment The authors are grateful for the financial support by the Hunan Provincial Innovation Foundation for Postgraduate (No. CX2014B071).

References

1. Jun Z, Kui-jiang J, Yan-zhi X (2005) Polymer combustion and fire-retardant technology. Chemical Industry Press, Beijing, pp 118–120
2. Laoutid F, Bonnaud L, Alexandre M, Lopez-Cuesta JM, Dubois P (2009) New prospects in flame retardant polymer materials: from fundamentals to nanocomposites. Mater Sci Eng R Rep 63 (3):100–125
3. Bourbigot S, Duquesne S (2007) Fire retardant polymers: recent developments and opportunities. J Mater Chem 17:2283–2300
4. Kiliaris P, Papaspyrides CD (2010) Polymer/layered silicate (clay) nanocomposites: an overview of flame retardancy. Prog Polym Sci 35:902–958
5. Rothon R (ed) (2003) Particulate-filled polymer composites. iSmithers Rapra Publishing, Shrewsbury, pp. 264–268
6. Babrauskas V, Peacock RD (1992) Heat release rate: the single most important variable in fire hazard. Fire Saf J 18(3):255–272
7. Lyon RE, Janssens ML (2005) Polymer flammability, DOT/FAA/AR-05/14, FAA, USA
8. Wang Y, Zhang J (2012) Influences of specimen size and heating mode on the ignitability of polymeric materials in typical small-scale fire test conditions. Fire Mater 36(3):231–240
9. Weil ED, Patel NG, Said MM et al (1992) Oxygen index: correlations to other fire tests. Fire Mater 16(4):159–167
10. Lyon RE, (2003) Fire & flammability, Sweden: symposium on fire safe electronics. pp 62–63
11. Bundy M, Ohlemiller T (2005) Fire performance of flame retarded polymers used in consumer electronics. Proceedings of Fire and Materials, pp 85–97
12. Hong S, Yang J, Ahn S, Mun Y, Lee G (2004) Flame retardant performance of various UL94 classified materials exposed to external ignition sources. Fire Mater 28(1):25–31
13. Morgan AB, Bundy M (2007) Cone calorimeter analysis of UL-94 V-rated plastics. Fire Mater 31(4):257–283
14. Cogen JM, Lin TS, Lyon RE (2009) Correlations between pyrolysis combustion flow calorimetry and conventional flammability tests with halogen-free flame retardant polyolefin compounds. Fire Mater 33(1):33–50
15. Zhang J, Bai M, Wang Y et al (2012) Featured structures of fire residue of high-impact polystyrene/organically modified montmorillonite nanocomposites during burning. Fire Mater 36(8):661–670
16. Long Y, Jun Z, Zhisheng X (2013) The flame retardancy and correlations between the alcohol blow lamp test and other three fire tests of LDPE used in mine. Eng Plast Appl 41(11):78–81 (in Chinese)
17. Schartel B, Braun U (2003) Comprehensive fire behaviour assessment of polymeric materials based on cone calorimeter investigations. e-Polymers 3(1):177–190
18. Wang Y, Zhang F, Chen X et al (2010) Burning and dripping behaviors of polymers under the UL94 vertical burning test conditions. Fire Mater 34(4):203–215
19. Schartel B, Hull TR (2007) Development of fire-retarded materials – interpretation of cone calorimeter data. Fire Mater 31(5):327–354
20. Xu Q, Majlingova A, Zachar M et al (2012) Correlation analysis of cone calorimetry test data assessment of the procedure with tests of different polymers. J Therm Anal Calorim 110(1):65–70