Understanding the influence of melt dripping on UL94 test response in a PA11 system

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ABSTRACT

A commonly used approach in polyamide systems to achieve a V0 rating in Underwriter Laboratories (UL)-94 test involves the exploitation of melt dripping behavior. That is, not allowing the polymer to completely degrade, and thereby, not creating necessary concentration of volatiles for the flame to sustain on the polymer. However, the governing parameters during this process are yet to be well established and quantified. In this work, some of the parameters that influence this process like the heating rate, melt/flame dripping, frequency and size of drips, molecular weight distribution, and the chemical nature of volatiles are considered. For this purpose, this work revisited the role of melamine cyanurate (MC) in polyamide 11 (PA11) from the viewpoint of UL94 flame test. In contrast to studies on PA6 and PA6,6 with MC that have shown a V0 rating due to enhanced melt dripping, only a V2 rating is achieved in UL94 test even with 20 wt% of MC in PA11. Despite a similar chemical structure, the volatiles emitted during the thermal degradation of these polymers are different and plays an important role in determining the behavior of the sample in UL94 test. Besides, it has been shown that at higher heating rates (as in UL94), the role of MC is primarily limited to dilution in the gas phase as opposed to acceleration in thermal decomposition of PA11 at lower heating rates. The consequence of this behavior is also reflected in the differences in the molecular weight distribution of PA11, its MC formulations, and their melt/flame drips collected during the UL94 tests. Within the framework of the tests carried out in this work, it is also found that mass and size of the drips have no correlation to ratings in a UL94 test. The understanding of these parameters has provided some new insights for building a framework on methodologies for designing polymer formulations for UL94 tests.

1. Introduction

Melt (and flame) dripping is an important aspect influencing the flame (and fire) response of a polymeric system. Even in a small-scale flame test like Underwriter Laboratories vertical burning test, UL94, dripping is an important parameter as it can influence the final rating of a polymeric system (see Table S1 in Supplementary Information for the rating criterion) [1]. In this test, a burner flame (flame height of 20 mm) is applied to the bottom of a polymer specimen (dimensions: 125 mm × 12.5 mm with a thickness of ~3.0 mm or 1.6 mm or 0.8 mm) for 10 s in each of the two applications while qualitatively monitoring the flammability characteristics (vertical upward burning and burning time) and dripping behavior (melt and flame drips). However, the melt/flame dripping aspect is also exploited in UL94 tests to quickly remove the burning part of the polymer from the specimen [2,3]. That is, flaming drips can remove the polymer fuel from the burning region and hence

stop further burning of the specimen. On the contrary, from a different perspective, they can become secondary source of ignition, and influence flame propagation and spreading. This can result in a fire hazard as seen in many incidents around the world with aluminum composite panels [4–6]. Another extremity of this behavior is the creation of melt pool from vertically oriented thermoplastic based lining materials [7]. Creation of melt pool from thermoplastic materials depends on factors like the thickness of the specimen, whether surface melting or bulk softening is dominating, ignition behavior, etc.

Though there are significant number of studies using the UL94 test for evaluating the flame response of different polymer formulations, the qualitative nature of the test has been an issue in determining the governing parameters. There have been some efforts to illustrate the temperature variations in the specimen during UL94 test and melt dripping behavior, qualitatively and quantitatively in terms of the frequency of dripping, drip sizes, and mass of the drips [8–17]. For example, Kempel

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et al. [16] have developed a numerical tool based on particle finite element method to estimate the dripping and non-dripping behavior of a polymer [16]. In another recent study, an IR camera capable of providing a temperature profile has been used for understanding the differences in burning behavior of polymers and their respective flame-retardant compositions [17]. The comparison of time required to reach peak temperatures (and cooling) seems to be a better indicator of burning behavior. In a couple of other studies, the frequency and size of melting/flaming drips have been related to the glass transition temperature of the polymer by comparing polymers with varying Tg [18, 19]. In our opinion, though Tg is important, it is not a determining factor and cannot be generalized, particularly when comparing a polymer with varying flame retardants or other high aspect ratio reinforcements or their loadings or even the specimen thickness (thermally thin versus thermally thick). By considering the degradation mechanisms of polymers, it has been shown that polymers undergoing random chain scission form small-sized drips, whereas those degrading by end-group scission and unzipping reactions might result in large-sized drips in a UL94 test [19].

Irrespective of the above findings, knowledge on how the frequency of dripping and drip sizes or their masses influence the UL94 response of a specimen is still limited. More importantly, how this information can be used from the context of improving the formulations to achieve a V0 rating in UL94 test is required. In this work, PA11 system with different loading levels of melamine cyanurate (MC) is chosen for investigating some of these questions. MC is commonly reported to be used alongside polyamides (particularly, PA6 and PA66) for improving the UL94 rating from V2 to V0 by enhancing the melt dripping of the polymer [2,3,20]. Generally, polyamides yield flaming drips in an UL94 test that ignite the surgical cotton placed below the specimen. In the presence of MC, the drips have been observed to be relatively smaller in size, and importantly, extinguished before touching the cotton. In a study on the usage of MC in PA6, by using both oxygen and nitrogen oxide index tests, it has been indirectly noted that MC acts mostly in the condensed-phase in PA6 [21]. In the same study, by using a cup to hold sample during burning (to eliminate the dripping behavior), it has been shown that though condensed phase mechanism dominates, there is a decrease in temperature of volatilization of PA formulation. That is, a reduction in time to ignition. This suggests that MC accelerates the cleaving of the polymer's main chain resulting in a greater reduction of molecular weight as compared to the neat PA. Despite this, with ~12–13 wt% of MC in PA6, Diniz et al. [2] and Zhang et al. [9] have observed a delay in melt dripping from the first to the second flame application relative to neat PA6.

As molecular weight governs the viscosity, and therefore the melt dripping behavior, a few studies have investigated these parameters to have a better understanding. For example, Matzen et al. [8] have investigated the viscosity of the drips collected from neat PA6 and PA6/MC systems after exposing to thermal radiation, and showed a reduction (from ~400 Pa·s to 300 Pa·s in neat PA6 and from ~500 Pa·s to 300 Pa·s in PA6/MC system). The viscosity of the drips was shown to reduce further with increase in temperature. Diniz et al. [2], after exposing the PA6/MC formulations to UL94 tests and analyzing the drips, have found a larger reduction and a narrower distribution of resulting molecular weight in the presence of MC as compared to neat PA6. Besides the above discussed parameters, the rate of generation of volatiles (and so, thermal degradation mechanisms [21–24]) and their chemical nature is also expected to influence the UL94 test response of samples.

In short, in addition to the aspects like how the size, frequency, and mass of dripping influencing the UL94 rating, the role of other parameters such as thickness of the specimen, nature of volatiles emitted, heating rate, and molecular weight distribution is not clear. Therefore, this work aims to revisit some of these concepts with PA11/MC formulations.

2. Experimental section

2.1. Materials and processing

PA11, PA6 and MC were obtained from commercial sources; PA11 from Arkema (Colombes, France), MC from McKinn International Pte Ltd (Singapore), and Ultramid®B3S NATURA PA6 from BASF (Ludwigshafen, Germany). Before compounding, the required amounts of PA and MC were dried overnight at 70 °C in a SavisLab Thremocenter convection oven (Switzerland, Europe). Compounding was carried out using a twin-screw extruder (Leistriz, Nuremberg, Germany) that has a L/D ratio of 30:1. The temperature profile of the extruder was set between 190 and 210 °C for PA11 based systems, and 230 °C and 260 °C for PA6 with a fixed torque at 150 revolution per minute (rpm). PA11 with 10 wt% MC and PA11 with 20 wt% MC were formulated. The extrudate from the compounder was cut into pellets, dried (at 80 °C in convection oven for 24 hours (h)) and compression molded to a 125 mm × 125 mm x 3 mm. The compression molding was carried out using Carver Hot Press (Savannah, United States) maintained at 230 °C with a molding pressure of 1 bar and a total molding time of 15 minutes (min). The compression molded plates were cut to dimensions of 125 mm × 10 mm x 3.0 (±0.2 mm) for UL94 tests.

2.2. UL94 tests and analysis of drips

Before UL94 testing of the PA formulations, the samples were conditioned at 25 °C at 50% relative humidity (RH) for a minimum of 48 h. The burner with 20 mm flame height was also calibrated with a copper slug prior to the test to achieve a rise in temperature from 100 °C to 700 °C in 44 sseconds (s). During the test, visual observations of the drips, after-flame time, and ignition of cotton were recorded. To determine the size of the drips, a high-speed digital camera (DSC-RXIII, Sony Inc, Tokyo, Japan) was used at 500 frames per second (fps) during both the first and second flame application on the samples in UL94 tests. To measure the size of the drips, post-processing using Adobe Premiere Pro 2021 was carried out on the videos by splitting into 50 fps. The obtained images of the drips were then analyzed with ImageJ software.

To determine the mass of the individual drips, the drips are collected directly into a Petri dish. The mass of the drips was measured using a Mettler Toledo microbalance with a readability of 0.1 mg (Ohio, United States). Drips that were not successfully collected were not considered. A minimum of 3 drips were taken for getting an average value. In the case of samples with flame dripping, the flame was immediately extinguished after collecting in the Petri dish.

2.3. Thermal analysis of samples and drips

Thermal analysis of the UL 94 test exposed samples and obtained drips was performed using a Simultaneous Thermal Analyzer (SDT, TA Instrument, New Castle, United States) to understand the mass loss profiles. The samples were placed in an aluminum crucible and heated to 650 °C, with a heating rate of 10 °C/min in nitrogen. The tests were repeated to ensure repeatability of data. Additionally, Thermogravimetric Analyzer (TA instrument, New Castle, United States) coupled with Fourier Transform Infrared Spectrophotometer (PerkinElmer, Massachusetts, United States) was used on the melt/flame drips to confirm the degradation profiles and the sources of the volatiles. The volatiles were channeled from the Thermogravimetric analyzer into the Fourier Transform Infrared Spectrophotometer, maintained at 300 °C, and at a flow rate of 20 mL/min. The infrared spectra were acquired in the range of 4000 cm^{-1} − 600 cm^{-1} with a resolution of 2 cm^{-1}.

2.4. Molecular weight analysis of polymer formulations and drips

Molecular weight analysis was performed on the formulates samples and the collected drips using Agilent PL Gel Permeation

Chromatography-50 (GPC, California, United States). The drips were dissolved in hexafluroisopropanol (HFIP) purchased from Shanghai Jizhi Biochemical, Shanghai Fengxin, China, and filtered through a 0.22 μm (pore size) PTFE syringe filter (purchased from Tianjin Jinteng Experiment Equipment Co., Ltd, Tianjin, China). 100 μL was injected into Agilent HFIP Eluent with 2 columns in sequence. Poly(methyl methacrylate) with a molecular weight range from 10,000 g/mol – 3,000,000 g/mol was used as GPC standard for calibration.

3. Results and discussion

3.1. Thermal decomposition of PA11 formulations

Thermal decomposition of MC occurs in the temperature range of 300–450 °C with the formation of melamine and cyanuric acid, and their subsequent degradation including sublimation of melamine to some extent [21]. Therefore, heat sink and gas phase dilution effects are expected when MC thermally decomposes. By 450 °C, most of the MC is volatilized (Fig. 1a). Neat PA11, as expected, undergoes a one-step decomposition in the temperature range of 390–500 °C (Fig. 1b). With PA11/MC formulations, thermal decomposition takes place in two steps as compared to a single step seen for neat PA11. The first mass loss occurs between 300 and 400 °C, which is in line with the thermal degradation of MC. However, this step is expected to involve interactions between the thermal degradation products of MC and PA11, and might not be direct dissociation and volatilization of MC independent of PA11.

This is evident when the temperatures corresponding to 5 wt% mass loss for PA11 (~406 °C), and MC (~345 °C) are taken as reference points. At a temperature of ~406 °C, the mass loss of MC by itself and PA11/MC formulations are ~57% (MC), ~17% (with 10% MC) and ~26% (with 20% MC), respectively. While at a temperature of ~345 °C, ~1%, ~10% and ~10% mass loss is seen with PA11, PA11 with 10% MC and PA11 with 20% MC formulations, respectively. The earlier decomposition of PA/MC formulations suggests an increase in the rate of scission of PA11 chains in the presence of cyanuric acid, in line with other studies reported on polyamides/MC formulations [3,9]. Despite the changes in the early stages of decomposition profiles, the peak decomposition temperatures (defined here as T_{max}) of PA11, and its MC-based formulations are similar with values of ~453 °C (for neat PA11), ~442 °C (for PA11 with 10% MC) and 458 °C (PA11 with 20% MC). By 500 °C, all the formulations have lost most of their mass (Fig. 1b). Similar trends were observed in other studies with polyamides [2,9,20]. Table 1 lists the thermal degradation temperatures of $PA6_{87}MC_{13}$ [9] and $PA66_{94}MC_6$ [24] and compares those values with $PA11_{90}MC_{10}$. As evident, all samples show accelerated thermal decomposition relative to their neat polymers. Besides, all PA/MC systems show a similar $T_{5\%}$ and T_{max} irrespective of the temperatures corresponding to their respective neat polymers. The relatively earlier thermal degradation temperatures of MC (and cyanuric acid) could be the reason for the similarity in $T_{5\%}$ values. Ceyda et al. [22] have also reiterated that the role of MC is primarily restricted to the initial stages of degradation of PA6 by studying the molecular weight values between 100 and 600 °C.

3.2. UL94 tests and the behavior of PA11 formulations

In general, during the first-flame application in UL94 test, the flame exposed edges of the samples begin to melt and flow to the bottom of the sample due to gravity. This reduces the distance between the sample and the burner from the original ~10 mm–~5 mm. This behavior is schematically shown in Fig. 2a. Hence, the temperature of the flame at these two reference points (that is, at ~10 mm and ~5 mm) from the mouth of the burner is measured. Indeed, as shown in Fig. 2b, there is only a minor difference of ~16 °C between the temperature at 5 mm (928 °C) and 10 mm (944 °C).

Nonetheless, during the flame exposure process, as the temperature is well beyond the decomposition temperature of PA11, pyrolysis of the polymer occurs releasing volatiles. After removing the burner, the oxidation of the flammable volatiles in the gas phase, provides the necessary thermal energy to sustain the flame, and for the combustion cycle to progress. As a result, neat PA11 shows 'no rating' with sustained flaming even after first-flame application (after-flame time of more than 30 s) and with flaming drips that ignited the cotton (shown in Supplementary Information, Fig. S1). In Table 2, the UL94 test ratings and after-flame times of all formulations are reported. Though individual flame drips are seen at the beginning of the after-flame time in neat PA11, with sustained flame on the sample, the frequency of dripping increased significantly. In the presence of MC, irrespective of the loading level, the formulations show a V2 rating due to flame drips igniting the
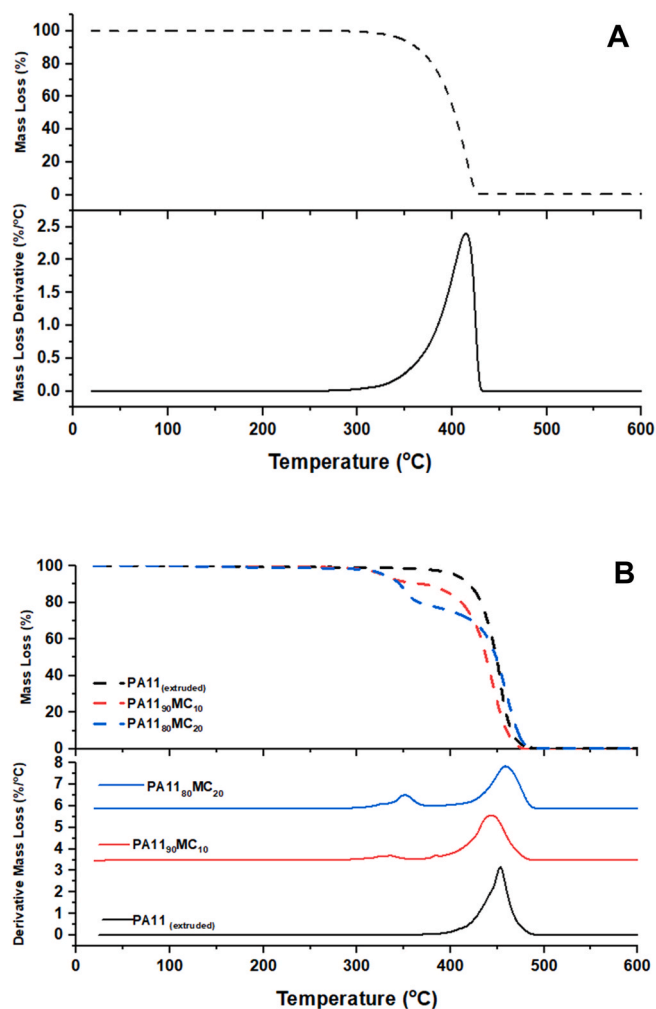

Fig. 1. TG and DTG curves in N_2 for (a) MC; and (b) PA11, $PA11_{90}MC_{10}$ and $PA11_{80}MC_{20}$.

Table 1
TGA data of PA11, PA6, PA6,6 and their respective formulations with MC.

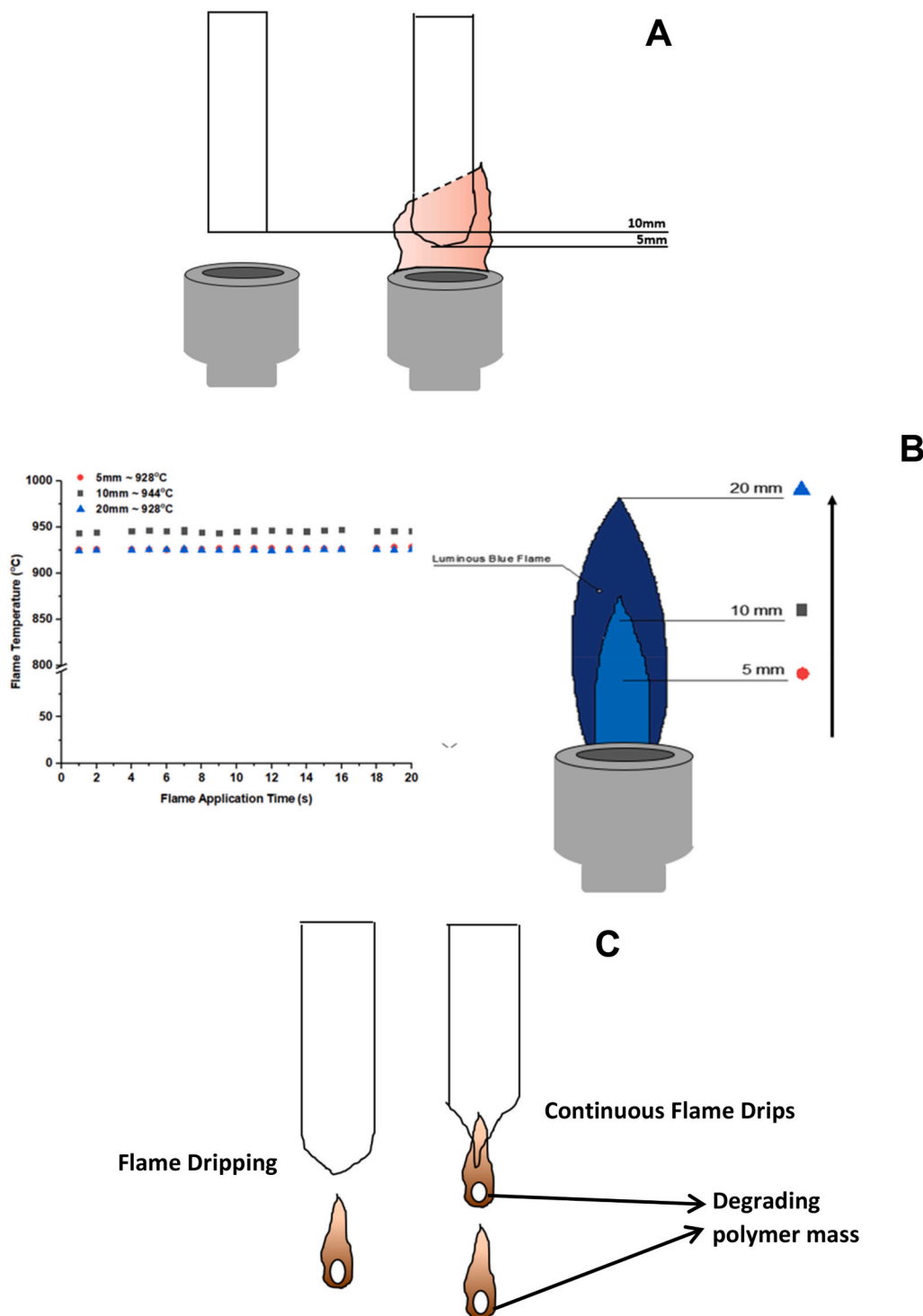| Specimen	$T_{5\%}$	T_{max}	Reference
PA6	421	449	[2]
$PA6_{87}MC_{13}$	332	445	[2]
PA66	403	452	[23]
$PA66_{94}MC_6$	336	457	[23]
PA11	406	453	This work
$PA11_{90}MC_{10}$	329	442	This work

Fig. 2. (a) Behavior of specimens after exposure to flame during a UL94 test; (b) flame temperature at different heights from the mouth of the burner; and (c) schematic showing the differences in the flaming drips seen during the tests.

cotton, despite the absence of sustained flaming on the samples. Flame drips are seen in both flame applications for the sample with 10% of MC, while they are only seen during the second flame application with 20% MC (Fig. S1). However, the frequency of dripping is relatively less as compared to the continuous flame drips seen with neat PA11 (schematically shown in Fig. 2c).

The above observations are somewhat different when compared with other polyamide systems like PA6 and PA66 in the presence of MC. In those studies, as mentioned earlier, only melt dripping is seen.

Considering the similarity in thermal decomposition behavior of different PA systems (Table 1), the observed differences between PA11/MC systems and PA6 or PA66/MC systems in terms of (flame or melt) dripping could be a result of the differences in the chemical nature of the volatiles, and thereby the extent of thermal feedback to the polymer. However, it is important to consider the expected differences in heating rates employed in TGA and UL94 tests. In TGA, the heating rates employed are generally in the range of 5–20 °C/min, whereas in UL94, it is expected to be much higher with direct flame exposure (as the flame

Table 2
UL 94 ratings of neat PA11 and its MC-based formulations (sample thickness ~3.0 ± 0.2 mm).

Formulation PA$_{xx(wt\%)}$MC$_{xx(wt\%)}$	UL94		
	After-flame time		Rating
	(t$_1$)	(t$_2$)	(3.0 ± 0.2 mm)
PA11	>30/>30/>30/>30/>30	–/–/–/–/-	NR
PA11$_{90}$MC$_{10}$	3/4/3/3/4	0/0/0/0/0	V2
PA11$_{80}$MC$_{20}$	0/0/0/0/0	0/0/0/0/0	V2

temperature is in the range of 900–950 °C, Fig. 2b). That is, in UL94 test, rapid volatilization of MC is also expected, particularly in thermally thin samples.

3.3. Analysis of melt/flame drips

To further understand the characteristics of the drips of PA11, PA11$_{90}$MC$_{10}$ and PA11$_{80}$MC$_{20}$, they were collected during each flame application using a Petri dish. In case of the presence of any flame on the drips, it was extinguished immediately after collection. Based on the TGA data of the drips of PA11 based formulations, the thermal decomposition behavior is different to their respective original systems as shown in Fig. 1. The decomposition of MC-based formulations occurs in a single step in between 400 and 500 °C (Fig. 3), which is typical of neat PA11 (Fig. 1). Even in between 300 and 400 °C (where presence of MC should be expected in the sample), the infrared analysis of the volatiles arising from the thermal degradation of the drips contain mainly fractions of aliphatic hydrocarbons. This suggests that most of the MC has rapidly volatilized upon exposure to flame, and the drips are relatively free of MC. Indeed, the temperatures corresponding to 5 wt% mass loss are relatively higher for the drips than their respective original formulations. This behavior is also seen with first drip (indicated with a subscript 'FD') and subsequent drips (indicated as 'OD'), further supporting the above-discussed rapid volatilization of MC. Even the T$_{max}$ of the original samples and their drips are similar. The differences between the first drip and subsequent drips are also not significant in terms of

their T$_{max}$ values. The data is listed in Table 3 for ease of reference.

To get a thorough understanding of the above effects and their consequences on the overall flame retardancy behavior, molecular weight analysis was carried out on the original formulations and the collected drips from UL94 testing. Fig. 4 shows the elution profiles of as-processed PA11 and its MC formulations before UL94. The profiles show a bimodal distribution, with elution times ranging from ~8 to 13 min (relatively higher weight fractions) and ~13–18 min (lower weight fractions). Based on the weight fractions, it is seen that at least ~88 wt% is composed of relatively lower weight fractions in all formulations. Calculated M$_n$, M$_w$ and M$_v$ values based on the profiles are summarized in Table 4. As evident, M$_v$ values range from 16,000 to 25,000 g/mol.

The elution profiles have clearly changed for the melt/flame drips, whether it is first drip or subsequent drips (Fig. 5) of PA11 and its MC formulations with three broad peaks at different time intervals as compared to their respective original sample profiles. The summarized molecular weight data is also given in Table 4. For the collected drips of PA11, the elution time intervals (and weight fractions) range from ~8 to 11 min (0.06), ~11–14 min (0.22), and 14–20 min (0.78), as compared to ~8–13 min (0.09) and ~13–18 min (0.91) for the original sample. This suggests a clear degradation of the larger fragments after exposure to flame. It is also worth noting the change in Mv values for the different fractions of polymer before and after (drips) flame exposure. As Mv is

Table 3
T$_{5\%}$ and T$_{max}$ of PA11, PA11$_{90}$MC$_{10}$, PA11$_{80}$MC$_{20}$ and their corresponding drips.

Specimen	T$_{5\%}$ (°C)	T$_{max}$ (°C)
PA11	406	453
FFA$_{FD}$	351	451
FFA$_{OD}$	389	450
PA11$_{90}$MC$_{10}$	329	442
FFA$_{FD}$	360	434
2FA$_{FD}$	382	456
2FA$_{OD}$	368	454
PA11$_{80}$MC$_{20}$	328	458
2FA$_{FD}$	380	459
2FA$_{OD}$	373	462
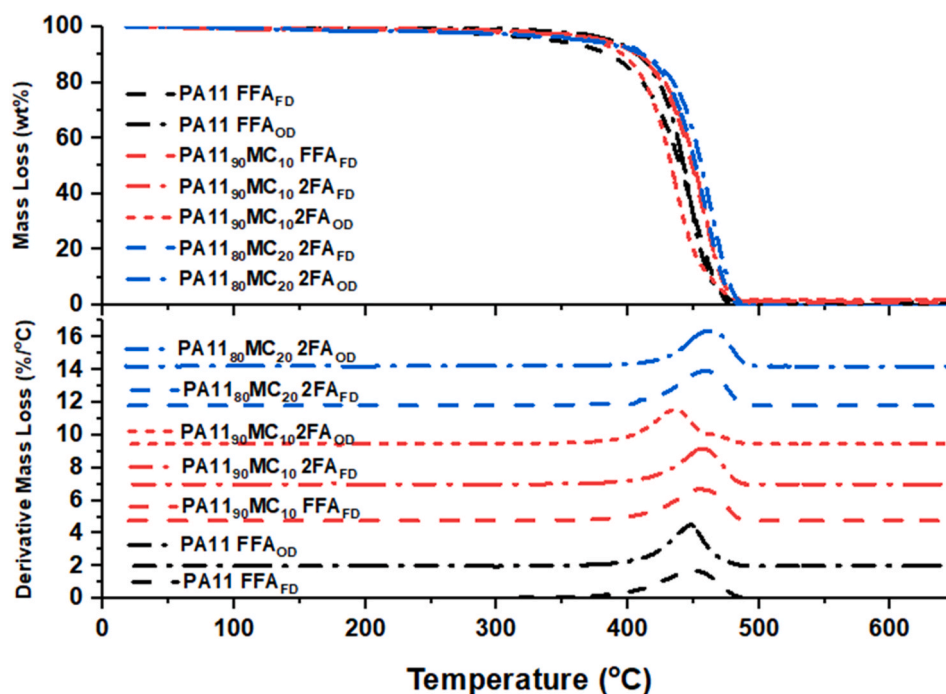
Fig. 3. TG and DTG in N$_2$ of melt/flame drips collected from PA11, PA11$_{90}$MC$_{10}$ and PA11$_{80}$MC$_{20}$ during UL94 test exposure. Take note that for PA11$_{80}$MC$_{20}$ sample, no dripping is seen during the first flame application of 10 s. So, the data of the drips shown here is based on second flame application (2FA$_{FD}$ or 2FA$_{OD}$).
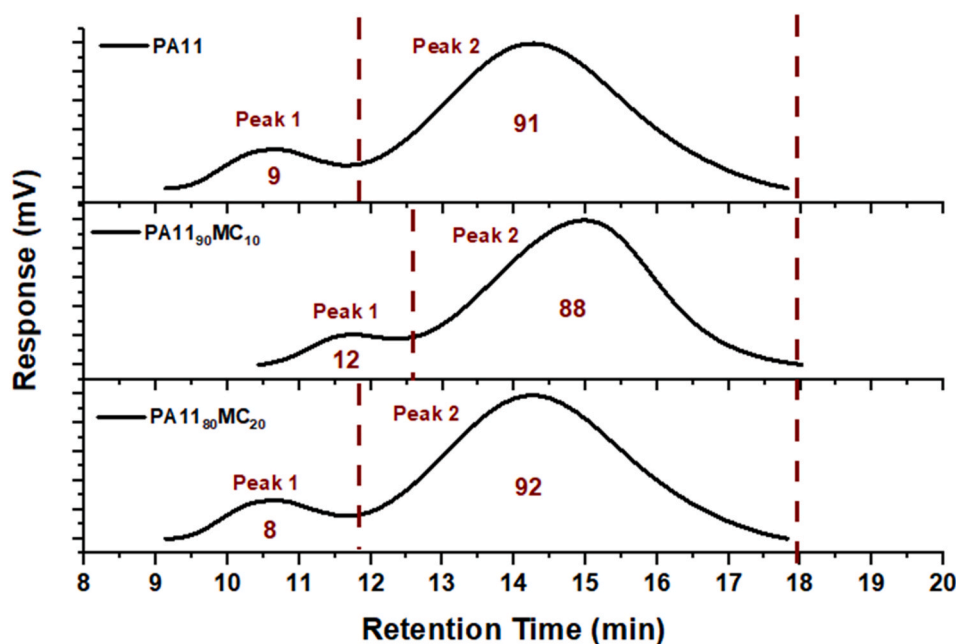
Fig. 4. Elution profiles of neat PA11 and its MC-based formulations (PA11$_{90}$MC$_{10}$ and PA11$_{80}$MC$_{20}$) before the UL94 test. The numbers in maroon color under the curves refer to the area fraction. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table 4

M$_n$, M$_w$ and M$_v$ of PA11, PA11$_{90}$MC$_{10}$ and PA11$_{80}$MC$_{20}$ formulations and their collected drips during UL94 tests based on combined peak values in Figs. 5 and 6, respectively. Individual peak values (relatively higher and lower molecular weight fractions) are given in Supplementary Information (Table S2).

Specimen	Summation of all peaks		
	Mn (g/mol)	Mw (g/mol)	Mv (g/mol)
Neat PA11 and its MC formulations			
PA11	8402	17894	16425
PA11$_{90}$MC$_{10}$	11301	31211	26590
PA11$_{80}$MC$_{20}$	6684	18226	16780
Melt/flame drips			
PA11 FFA$_{FD}$	45	17877	10863
PA11 FFAO$_D$	64	19204	12520
PA11$_{90}$MC$_{10}$ FFA$_{FD}$	249	19831	13353
PA11$_{90}$MC$_{10}$ 2FA$_{FD}$	815	30054	20694
PA11$_{90}$MC$_{10}$ 2FA$_{OD}$	864	34485	23755
PA11$_{80}$MC$_{20}$ 2FA$_{FD}$	112	15594	10270
PA11$_{80}$MC$_{20}$2FA$_{OD}$	188	14687	9949

one of the key parameters that dominates the dripping phenomenon, the drastic reduction in M$_v$ after flame exposure clearly illustrates why PA11 shows continuous dripping behavior.

Further, melt/flame drips of PA with MC formulations have higher combined M$_n$, M$_w$ and M$_v$ values than neat PA. This reiterates the findings described above in terms of heating rate effects. That is, during the flame exposure, firstly, degradation products of MC volatilize rapidly providing heat sink and a reduction of heat feedback that slows the degradation of polymer. This differs with the TGA data (Fig. 1) showing accelerated decomposition of PA11 in the presence of MC (because of rapid chain scission that promotes dripping). In fact, many Lyon and Walters [25] have used pyrolysis flow combustion calorimeter (PCFC) on different polymers at different heating rates of up to 5 K/s and have shown that maximum specific heat release rate value is directly proportional to heating rate. For example, in Ref. [25], it has been seen that for polyethylene, the maximum specific heat release rate value changes from ~1.6 kW/g to ~7.5 kW/g with a change of heating rate from 1 K/s to 5 K/s, respectively. This clearly articulates the rapid rate of release of volatiles with heating rate.

3.4. Mass and size analysis of drips

The mass and size of the drips obtained in UL94 tests from different samples are summarized in Fig. 6 to understand if any correlations exist between these parameters and UL94 ratings from the context of this work. Regardless of the influence MC has on PA11, the sizes of the drips are relatively larger for first drips in all samples as compared to their respective subsequent drips. This is understandable as with time of flame exposure, melt viscosity is expected to drop (due to enhanced chain scission), and thus the size of drips. This is also true even for PA11/MC formulations. However, MC is expected to contribute towards dilution and heat sink effects reducing the heat feedback to the system. This could be a reason why relatively higher mass is seen in the drips of MC formulations as compared to PA11. More importantly, there seems to be no evident correlation in the current study between these drip parameters (mass and/or size) and UL94 rating of the formulations tested (PA11: NR versus PA11$_{90}$MC$_{10}$/PA11$_{80}$MC$_{20}$: V2).

3.5. Chemical nature of volatiles

As discussed earlier, thermal degradation temperatures of the polymers, rate of release of flammable volatiles, molecular weight distribution of the polymers and the obtained distribution during the flame exposure period are some parameters affecting the UL94 ratings. Apart from these, chemical nature of volatiles should also be considered. Even for a polystyrene (PS) system, it has been reported that the initial rate of volatilization is higher for low molecular weight PS in comparison with higher molecular weight systems, at least for the first 30 wt% [20]. That is, despite the similarity of the chemical nature of volatiles, the differences in the rate of release of volatiles could be significant in providing the necessary thermal feedback to the polymer and sustaining the flame on the sample.

Levichik [26] has reviewed the thermal degradation mechanisms of PAs and reported that the three main primary chain scission mechanisms in PAs are hydrolysis, homolytic scission, and intramolecular hydrogen transfer. Subsequently, depending on the PA's structure and the experimental conditions used, chain scission mechanisms could vary. Nonetheless, as seen in Table 5, the chemical structure of PA6, PA66 and PA11 are similar, but they yield volatiles of different chemical nature. As
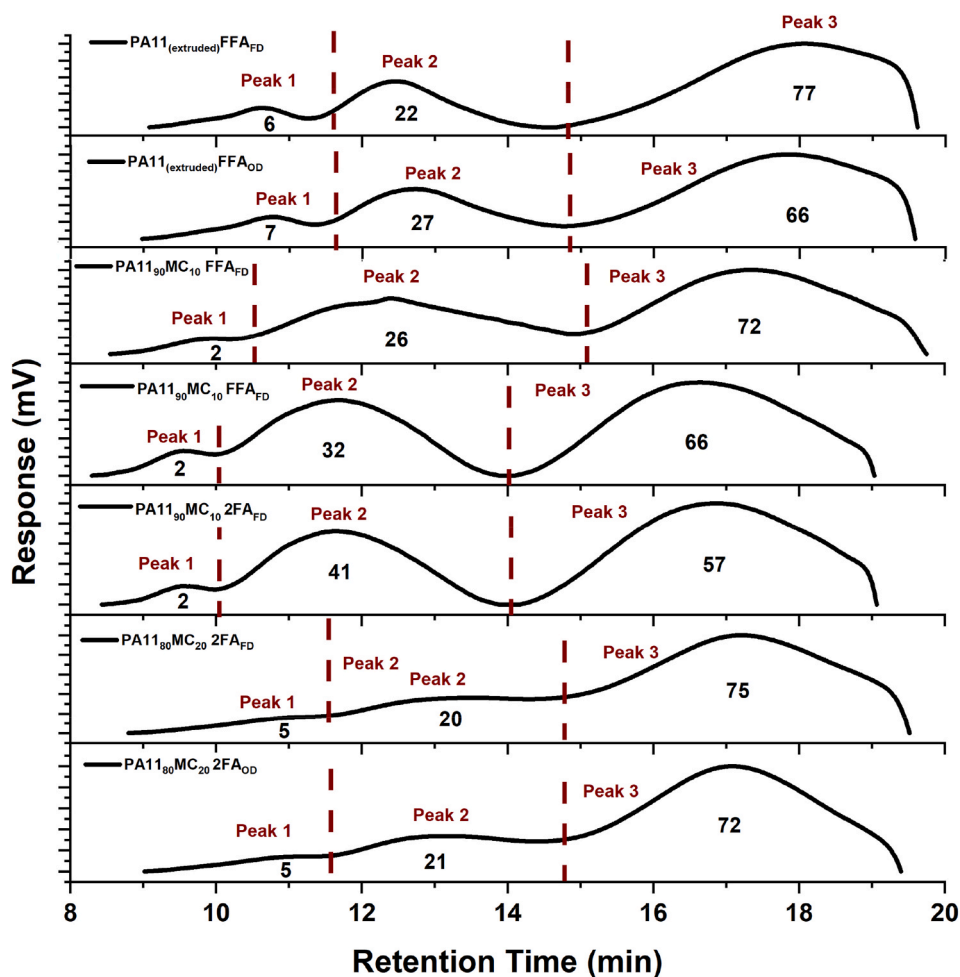
Fig. 5. Elution time of PA11, PA11$_{90}$MC$_{10}$ and PA11$_{80}$MC$_{20}$ drips collected during the UL94 test.
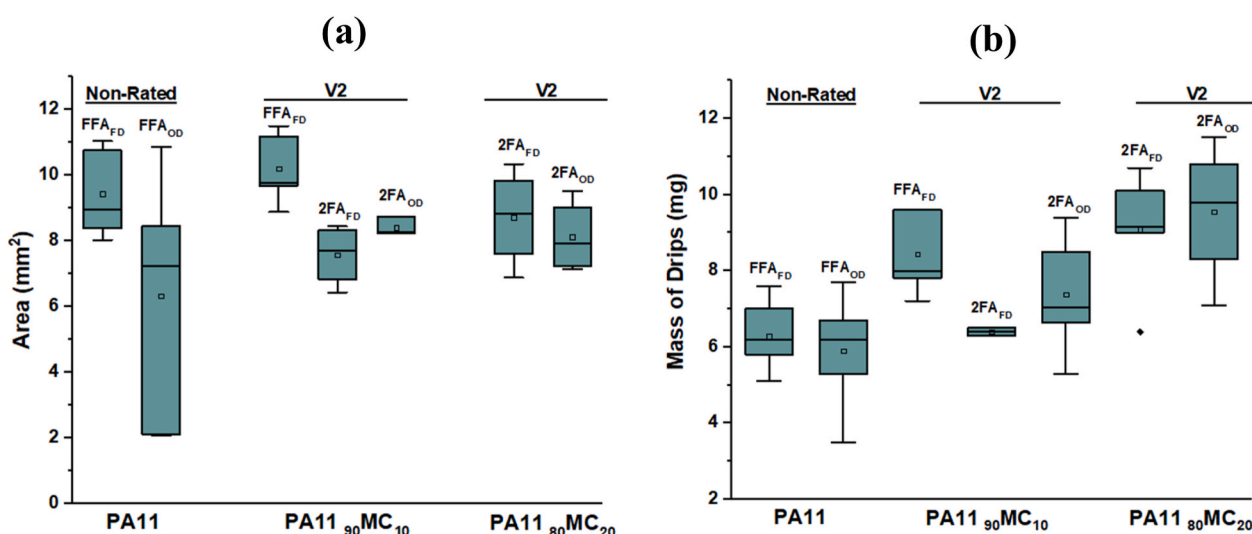
Fig. 6. (a) Size and (b) mass of PA11, PA11$_{90}$MC$_{10}$ and PA11$_{80}$MC$_{20}$ drips.
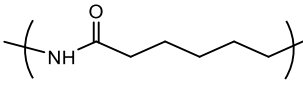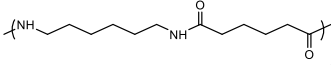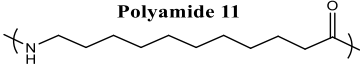
compared to PA6 and PA6,6, the aliphatic hydrocarbon nature of the volatiles emitted by PA11 shows relatively higher total heat release (THR) values as listed in Table 5. This also corroborates with the PCFC observations of Walters and Lyon [27] on approximately 100 polymers. For example, polypropylene (undergoing random chain scission and producing shorter aliphatic hydrocarbon chains) was shown to have a THR of 41.4 kJ/g; while PA6 (undergoing hydrolysis, homolytic scission at the alkyl-amide bonds, and cyclization to produce caprolactam) showed a THR of 24.4 kJ/g. Since both these polymers do not yield any char, the amount of heat generated depends on the chemical nature of the volatiles.

In summary, the melt/flame drip analysis provides valuable

Table 5
Chemical structure of aliphatic PA, corresponding emitted volatiles and the heat released (total heat released per gram).

Chemical structure of aliphatic PA	Nature of volatiles emitted	THR (kJ/g)	Ref
Polyamide 6	Caprolactam	30.8	[28]
Polyamide 6.6	Cyclopentanone	26.4	[29]
Polyamide 11	Aliphatic hydrocarbons	32.4	[30]

information that can help understand the UL94 response of a particular polymer system. This is despite the size and mass of drips having no correlation with the UL ratings. Heating rate plays a critical role, and hence, care should be taken while correlating TGA and UL94 data. Molecular weight distribution of the polymer formulation before the flame exposure and the chemical nature of volatiles released during the exposure process are also critical and influence the UL94 test rating.

4. Conclusions

This study revisited the role of melamine cyanurate in polyamides in achieving a better rating in UL94 flame test. The aspects of melt/flame dripping, frequency and size of drips, molecular weight distribution, heating rate and the chemical nature of volatiles during UL94 test are also considered here.

➢ In the UL94 tests, PA11 showed a non-rating (NR) and sustained flaming. With both 10 wt% and 20 wt% of MC in PA11, only a V2 rating was achieved (flame drips were observed that ignited the cotton placed below the sample).
➢ TGA data has shown that the presence of MC accelerated the decomposition process of PA11. However, correlating with the UL94 tests data, molecular weight analysis of the melt/flame drips obtained in UL94 tests, and chemical nature of the volatiles emitted, it was concluded that TGA data could be misleading as heating rate governs the entire process.
➢ Size and mass of drips of PA11, PA11$_{90}$MC$_{10}$ and PA11$_{80}$MC$_{20}$ were found to have no correlation with UL94 ratings.
➢ Based on the molecular weight analysis of the PA11, its MC formulations, and their melt/flame drips collected during the UL94 tests, it was shown that the elution profiles completely differ between the original samples and their drips. Degradation of the larger fragments was evident justifying the dripping phenomenon.
➢ Based on the relative increase in molecular weights of the drips collected from PA11/MC formulations as compared to PA11, the role of MC in diluting the gas phase (reduction in heat feedback to the sample) was evident.
➢ It was shown that the nature of the volatiles emitted and the molecular weight distribution of polymer, especially the lower molecular weight fraction, were mostly responsible for the thermal feedback to the polymer.

Author statement

Dean Seah: Methodology, Data curation, Writing- Original draft preparation. **Aravind Dasari:** Conceptualization, Supervision, Writing-Reviewing and Editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymertesting.2022.107893.

References

[1] Standard for Tests for Flammability of Plastic Materials for Parts in Devices and Appliances, Underwriter Laboratories, 2013.
[2] A. Turski Silva Diniz, C. Huth, B. Schartel, Dripping and decomposition under fire: melamine cyanurate vs. glass fibres in polyamide 6, Polym, Degrad. Stab. 171 (2020), 109048.
[3] S.V. Levchik, A.I. Balabanovich, G.F. Levchik, L. Costa, Effect of melamine and its salts on combustion and thermal decomposition of polyamide 6, Fire, Mater 21 (1997) 75–83.
[4] S.T. McKenna, N. Jones, G. Peck, K. Dickens, W. Pawelec, S. Oradei, S. Harris, A. A. Stec, T.R. Hull, Fire behaviour of modern façade materials–Understanding the Grenfell Tower fire, J. Hazard Mater. 268 (2019) 115–123.
[5] T. Byrnes, L. Angel, K. Hunt, T. Flynn, Review of techniques for identifying the chemical composition of Aluminium Composite Cladding cores, Electron. J. Struct. Eng. 19 (2019) 14–22.
[6] J. Torero, Grenfell Tower Public Inquiry, Phase 1 Report, Expert Report), 2018.
[7] J. Sherratt, The Effect of Thermoplastics Melt Flow Behaviour on the Dynamics of Fire Growth, PhD Doctoral Thesis, The Univeristy of Edinburgh, 2001. http://hdl.handle.net/1842/4788.
[8] M. Matzen, B. Kandola, C. Huth, B. Schartel, Influence of flame retardants on the melt dripping behaviour of thermoplastic polymers, Mater 8 (2015) 5621–5646.
[9] J. Zhang, M. Lewin, E. Pearce, M. Zammarano, and J. W. Gilman, Flame retarding polyamide 6 with melamine cyanurate and layered silicates, Polym. Adv. Technol. 19 (20008) 928-936.
[10] B. Kandola, D. Price, G. Milnes, A. Da Silva, Development of a novel experimental technique for quantitative study of melt dripping of themoplastic polymers, Polym. Degrad. Stabil. 98 (2013) 52–63.
[11] Y. Wang, J. Jow, K. Su, J. Zhang, Dripping behavior of burning polymers under UL94 vertical test conditions, J. Fire Sci. 30 (2012) 477–501.
[12] P. Joseph, S. Tretsiakova-McNally, Melt-flow behaviours of thermoplastic materials under fire conditions: recent experimental studies and some theoretical approaches, Mater 8 (2015) 8793–8803.
[13] J. Zhang, T. Shields, G. Silcock, Effect of melting behaviour on upward flame spread of thermoplastics, Fire Mater. 21 (1997) 1–6.

[14] C. Hu, G. Fontaine, P. Tranchard, T. Delaunay, M. Collinet, S. Marcille, S. Bourbigot, In-situ investigation of temperature evolution of drippings via an optimized UL-94 instrumentation: application to flame retarded polybutylene succinate, Polym. Degrad. Stabil. 155 (2018) 145–152.

[15] R. Dupretz, G. Fontaine, S. Duquesne, S. Bourbigot, Instrumentation of UL-94 test: understanding of mechanisms involved in fire retardancy of polymers, Polym. Adv. Technol. 26 (2015) 865–873, 2015.

[16] F. Kempel, B. Schartel, J.M. Marti, K.M. Butler, R. Rossi, S.R. Idelsohn, E. Oñate, A. Hoffman, Modelling the vertical UL 94 test: competition and collaboration between melt dripping, gasification and combustion, Fire Mater. 39 (2015) 570–584.

[17] B. Spieß, E. Metzsch-Zilligen, R. Pfaendner, Mechanistic evaulation of flame retardants during UL94 standard testing, via IR-camera, Polym. Test. 103 (2021), 107320.

[18] Y. Wang, F. Zhang, X. Chen, Y. Jin, J. Zhang, Burning and dripping behaviors of polymers under the UL94 vertical burning test conditions, Fire Mater. 34 (2010) 203–215.

[19] W. Tao, J. Li, Melamine cyanurate tailored by base and its multi effects on flame retardancy of polyamide 6, Appl. Surf. Sci. 456 (2018) 751–762.

[20] A. Casu, G. Camino, M. De Giorgi, D. Flath, V. Morone, R. Zenoni, Fire-retardant mechanistic aspects of melamine cyanurate in polyamide copolymer, Polym. Degrad. Stabil. 58 (1997) 297–302.

[21] L. Costa, G. Camino, Thermal behaviour of melamine, J. Therm. Anal. 34 (1988) 423–429.

[22] C. Isbasar, J. Hacaloglu, Investigation of thermal degradation characteristics of polyamide-6 containing melamine or melamine cyanurate via direct pyrolysis mass spectrometry, J. Anal. Appl. Pyrolysis 98 (2012) 221–230.

[23] Y. Li, K. Liu, R. Xiao, Preparation and characterization of flame-retarded polyamide 66 with melamine cyanurate by in situ polymerization, Macromol. Res. 25 (2018) 779–785.

[24] Y. Nagasawa, M. Hotta, K. Ozaw, Fast thermolysis/FT-IR studies of fire-retardant melamine-cyanurate and melamine-cyanurate containing polymer, J. Anal. Appl. Pyrolysis 33 (1995) 253–267.

[25] R.E. Lyon, R.N. Walters, Pyrolysis combustion flow calorimetry, J. Anal. Appl. Pyrolysis 71 (2004) 27–46.

[26] S.V. Levchik, E.D. Weil, M. Lewin, Thermal decomposition of aliphatic nylons, Polym. Int. 48 (1999) 532–557.

[27] R.N. Walters, R.E. Lyon, Molar group contributions to polymer flammability, J. Appl. Polym. Sci. 87 (2003) 548–563.

[28] A. Tewarson, Generation of heat and chemical compounds in fires, in: Philip J. DiNenno (Ed.), Section 3 – 4, SFPE Handbook of Fire Protection Engineering, 2002, pp. 3–82.

[29] B. Schartel, K.H. Pawlowski, R.E. Lyon, Pyrolysis combustion flow calorimeter: a tool to assess flame retarded PC/ABS materials? Thermochim. Acta 462 (2007) 1–14.

[30] A. Cayla, F. Rault, S. Giraud, F. Salaün, R. Sonnier, L. Dumazert, Influence of ammonium polyphosphate/lignin ratio on thermal and fire behavior of biobased thermoplastic: the case of polyamide 11, Mater 12 (2019) 1146.