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Polypropylene as a Reference Material for Small Scale Horizontal Rate of Burning Instrument

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Abstract

Controlling the risks associated with the flammability of polymeric materials depends on their flammability tests, as well as the existence of reference materials which are important tools for ensuring the quality of measurement results. In this study, polypropylene (PP) was prepared and tested to be a certified reference material for horizontal burning rate test instrument (UL94) in accordance with ISO guides and standards. Differential scanning calorimetry (DSC) and Thermo gravimetric analysis (TGA) were used to characterize some of the thermal properties like melting point and decomposition temperature of PP. The certified value of the PP burning rate was assigned by analyzing the data obtained through bi-lateral laboratory comparison involving two competent laboratories. The results of the burning rate measurements for the participating laboratories were clearly consistent and harmonic. The certified value and expanded uncertainty were calculated using results of characterization, homogeneity study and stability assessment and were found 19.63 ± 1.2 mm/ min at approximate confidence level of 95 %.

Keywords: Reference material; Bi-lateral laboratory comparison; Polypropylene; UL94 flame chamber; Flammability.

1. Introduction

UL94 flame chamber instrument is used to measure the response of materials, assemblies and products to flame under a prescribed conditions, and in either horizontal or vertical positions [1, 2]. According to the burning behaviour, materials can be classified as HB (horizontal burning) when they are tested in horizontal position following to ASTM D 635 and the burning rate does not exceed 40 mm/min and the thickness of samples between 3 -13 mm [1]. When samples are tested in vertical position according to ASTM D 3801, they can be classified as V2, V1, and V0. The criteria for these classifications are presented in Table 1 [2]. Horizontal and vertical tests are commonly used to measure burning rate of polymeric and construction materials and to evaluate their fire performance [1- 4]. Comparability, reliability and credibility of the measurement results are guaranteed when certified reference materials

(CRMs) are used to ensure traceability of the results to the International System of Units (SI). Quality control in individual laboratories and analytical methods validation are also dependent on CRMs. A standard reference material (SRM) was produced by the National Institute for Standard and Technology (NIST) as well as a reference material (RM) produced by our laboratory at National Institute of Standards (NIS), Egypt, for smoke density measurements [5, 6]. Our research group has also developed a reference material for the flash point measurements [7]. However there is a lack in RMs to assess plastic burn rate in small scale tests.

Polypropylene is a thermoplastic polymer that is used in a wide range of applications. It is produced by one of the most common petrochemical products, propylene monomer and it is characterized by good mechanical properties, and economic price [4]. The aim behind this research work is to ensure appropriate homogeneity and thermal stability of PP

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which affords it to be used as a reference material for the UL94 flame chamber instrument. The certification process of the reference material under study involved characterization, homogeneity study, stability assessment and value assignment [6 – 10]. The prepared RM is expected to be employed to achieve confidence in the rate of burning measurement results and to confirm reproducibility between laboratories.

2. Material and methods

2.1. Material

Polypropylene pellets were provided by Al-Waha Petrochemical Company, Saudi Arabia. The pellets was pressed and molded at 190 ºC for 10 min and at a pressure of 150 kg/cm^2 using an electrically heated hydraulic press, supplied by Mackey Bowley International LTD, UK, to form specimens with dimensions 125 mm x13 mm x 4 mm for UL94 horizontal test. The obtained strips were kept in controlled temperature (25 ± 5 °C) and humidity (50 ±10%).

2.2. Rate of burning measurement

The rate of burning measurements were executed using UL94 instrument (purchased from Fire Testing Technology Ltd, UK) and Forty-five/sixty degree flammability tester, Covmark according to the standard test method ASTM D635 [1].

2.3. Thermal analysis study

DSC and TGA measurements were carried out using DSC50 and TGA50 instruments which were purchased from Shimadzu Company, Japan. The temperature was increasing at heating rate 10 ºC/min, from room temperature to 750 ºC and 650 ºC in TGA and DSC, respectively. The samples were tested under inert atmosphere using high pure nitrogen gas with flow rate 30 mL/min. The samples were placed in platinum crucible and their weights were 6.5 mg.

2.4. Certified value evaluation for PP CRM

The certified value for the rate of burning of PP samples oriented in the horizontal position was calculated from the results of inter-laboratory comparison, involving two laboratories only as there is a lack of competent fire testing laboratories performing the rate of burning measurements in Egypt. The first laboratory is Fire and Explosion Protection Laboratory, NIS, Egypt and the second laboratory is affiliated as Fire Testing Laboratory-Egypt Air Company. These laboratories are accredited according to ISO 17025 [11]. The standard test method ASTM D 635 was used by the participating laboratories to determine the horizontal burning rate.

2.5. Homogeneity study

Twenty test samples were selected using a scheme for random sample selection to do the homogeneity study. They were divided into four groups used for assessment of between groups variability of the candidate material. The within group variability was studied by five replicate measurements per each group.

2.6. Stability study

Stability assessment was performed on samples kept in ambient conditions (temperature 25 ± 5 °C and humidity 50 ±10%) over 6 months. The measurements were performed at regular time intervals.

3. Results and discussion

3.1. DSC and TGA of PP

DSC data of PP are presented in Figure 1 and Table 2. It is clearly seen that PP has melting point peak at 170.5 ºC. Repeating DSC measurements over a period of six months shows that the temperature at melting point of PP nearly was not changed. This gives indication that the polymer is stable and does not undergo vital changes. On the other hand, TGA and Dr. TGA results presented in Figure 2 shows that pp under study decomposes in one step and it loses 98% of its weight in the temperature range 235 °C-400 °C. The temperature at which maximum degradation for PP takes place (T_{max}) is 381.3 °C as it is clear in Figure 2.

3.2. Characterization

Characterization of the RM for the rate of burning property was conducted based on specific-method approach giving only method specific measured property values by two laboratories based on the ASTM D635 [1]. Results are listed in Table 3. The data obtained were compared according to measurement results and variances. Laboratory means and variances were examined using t- test and F- test, respectively. Both tests proved that there were no significant differences between laboratories. The good agreement between the data obtained from the participant laboratories indicates that the study can be completed to produce a fully certified PP RM.

3.3. Homogeneity study

Homogeneity assessment is always necessary to demonstrate that the degree of homogeneity of a RM concerning the property or properties of interest is appropriate for purpose. To quantify the heterogeneity of PP, the experimental design of the study was fashioned in such a way that the between groups variability and the within group variability can be evaluated [7- 9]. Twenty test samples were randomly picked from a total of one hundred samples. The selected samples were randomly divided in to four groups for between group's variation measurements. Each group included five samples to be tested for within group variance quantification. The measurements were carried out using the standard test method ASTM D635, under repeatability conditions [1].The results are presented

in Table 4. Statistical analysis of the obtained results was carried out using analysis of variance (ANOVA) and the data obtained are shown in Table 5. The value of F calculated was found to be smaller than that of F critical and *P*- value is larger than 0.05. According to these two criteria, it is clear that the material under study has suitable homogeneity [12 – 16].

3.4. Stability study

Stability monitoring of the candidate RM has been started since its processing, test samples were kept under storage at ambient temperature and humidity 25 ±5°C and 50 ±10%. The samples was tested at six different time periods, at each time point five replicates was measured, the mean results are listed in Table 6. The results were examined for outliers using Grubb's test at 95% confidence level (*P* = 0.05). Plotting the results as a time function showed no evidence of deterioration as there were no detected trends at the storage temperature, and throughout the duration of the experiment [13 – 15, 17].

3.5. *Value* assignment

PP burning rate was calculated as the mean of the measurement results obtained from the collaborative study and it was 19.63 mm/min, see Table 3. This value was defined as the certified value. Collaborative study data were statistically evaluated, where Kolmogorov- Smirnov test was used to check the conformity of results to normal distribution, and Grubb's test to detect 'outlying' values in the population of results. The *P*- value was larger than 0.05 which indicates that results is normally distributed and there were no detected outliers at confidence level 95%.

3.6. *Uncertainty estimation*

Expanded uncertainty is derived from the uncertainty components owing to sample inhomogeneity (u*bb*), long term stability (u*s*) and

characterization (u*char*) [18]. The calculated results are tabulated in Table 7.

3.6.1. Uncertainty of homogeneity (u*bb*)

Uncertainty was calculated using equation (1), because it can be clearly seen from the ANOVA results that MS_{within} (mean squares within groups) is larger than that of $MS_{between}$ (mean squares between groups) [8, 10, 15, 19]. The u*bb* value is displayed in Table 7.

$$\mathrm{u}bb = \sqrt{\frac{\mathrm{MS}within}{\mathrm{n}}} \times \sqrt[4]{\frac{2}{v\,\mathrm{MS}witin}} \qquad (1)$$

Where (n) is the number of replicates per group, (v MS_{within}) represents degrees of freedom of MS_{within}.

3.6.2. Uncertainty of stability (u*s*)

The uncertainty in PP stability was estimated as the uncertainty in the regression line slope created by variation of burning rate against time, and multiplied by the time (months)[7, 15, 20]. The value of u*s* is shown in Table 7.

3.6.3. Uncertainty of characterization (u*char*)

The standard error derived from the collaborative practice (s/√n) was used as the best estimate of the characterization uncertainty [7]. The results of u*char* is 0.89 %, see Table 7.

3.6.4. Combined uncertainty (u*c*)

Combined standard uncertainty u*c* was calculated using equation (2).

$$\mathrm{u}c = \sqrt{\mathrm{u}char^2 + \mathrm{u}bb^2 + \mathrm{u}s^2} \qquad (2)$$

3.6.5. Expanded uncertainty (U*e*)

Expanded uncertainty is quantified as two times the combined uncertainty at a confidence level 95% [21- 23].The certified value and associated uncertainty are 19.63 ±1.2 mm/min.

Table 1 Sample classification according to ASTM D3801 [2].

Conditions	V0	V1	V2
The first afterflame time (t_1) and the second afterflame time (t_2) for each single sample	≤ 10 s	≤ 30 s	≤ 30 s
Total afterflame time ($t_1 + t_2$) for five sample	≤ 50 s	≤ 250 s	≤ 250 s
The second afterflame time (t_2) plus afterglow time (t_3) for each single sample ($t_2 + t_3$ for each single specimen)	≤ 30 s	≤ 60 s	≤ 60 s
Continuity of afterflame or afterglow of any sample up to the holding clamp	No	No	No
Ignition of cotton indicator by flaming particles	No	No	Yes

Table 2 Melting point temperature monitoring over 6 months.

Months	0	1	2	3	4	5
Melting point (°C)	170.5	171.3	171.7	170.8	170.1	170.9

Table 3 Linear burning rate results of PP by two competent laboratories.

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| Lab. Name | Rate of burning (mm/min) | |
	NIS lab.[a]	Egypt air lab.[a]
	20.45	18.52
	20.09	18.75
	19.57	20.45
	20	20.45
	20.36	18.75
	19.91	19.57
	19.74	19.07
	19.31	19.15
	19.57	20.09
	18.99	20.65
Average	19.80	19.45
S[b]	0.46	0.71

[a] Both laboratories are accredited according to ISO 17025 [11].
[b] standard deviation.

Table 4 Results of homogeneity study of PP.

| Property | Linear burning rate (mm/min) | | | |
Groups	A1	A2	A3	A4
	20.36	20.00	20.45	18.44
	18.52	20.27	18.60	22.06
	18.37	19.57	20.09	19.65
	21.95	20.27	20.36	20.36
	20.45	18.91	20.55	18.99

Table 5 ANOVA of the homogeneity study.

Property	Sources of variation	SS	df	MS	$F_{Calculated}$	P value	$F_{Critical}$
Linear burning rate(mm/min)	Between groups	0.113	3	0.038	0.029	0.993	3.24
	Within groups	20.922	16	1.308			

Table 6 Results of the stability study expressed as rate of burning (mm/min).

| Storage temperature and humidity | Months | | | | | | Regression | |
	0	1	2	3	4	5	Slope	S
25± 5 ºC	19.34	20.06	19.48	19.40	20.06	19.77	0.059	0.082
50± 10 %								

S: is the standard deviation of slope

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Table 7 Uncertainty evaluation

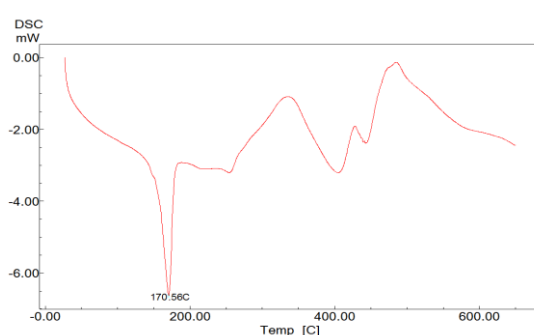| Uncertainty component	Uncertainty value
ubb (%)	1.53
us (%)	2.51
u$char$ (%)	0.89
uc[a] (%)	0.60
Ue[b] (mm/min)	±1.20

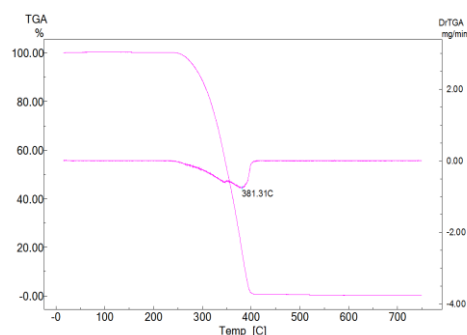[a] Combined uncertainty [b] Expanded uncertinty

Fig. 1. DSC curve of PP.

Fig. 2. TGA and Dr. TGA curves of PP.

4. Conclusion

A reference material for the flammability horizontal test has been developed by our lab (Fire and Explosion Protection lab, NIS, Egypt). The certified value was assigned and calculated from bilateral laboratory comparison in proper compliance with ISO 17034 standard and ISO Guide 35. Statistical analysis of obtained data confirmed that the reference material is sufficiently homogenous and stable. The developed reference material succeeded to meet the horizontal burning classification requirements (HB). The certified value and associated uncertainty are19.63 ±1.2 mm/min.

5. Conflict of interest

There are no conflicts to declare.

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