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Quantification of polymer degradation during melt dripping of thermoplastic polymers

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ABSTRACT

This work reports measurement of temperatures of the melting drops in the previously designed and presented melt dripping experiments of thermoplastic polymers. A simple heat transfer model has been used to compute the surface temperatures of the polymer sample at various furnace temperatures and thus the temperatures of the molten drops dripping from the melting surface. The model has been validated by experimental results. The temperatures of the molten drops could help in predicting the degree of degradation in a polymer during melt dripping. By conducting thermogravimetric analysis of both the polymers and their molten drops, a degree of degradation could also be predicted. The values obtained from both approaches have been compared in order to understand the melt dripping/degradation behaviour of polymers.

1. Introduction

Thermoplastic objects are increasingly being used in modern household, workplaces and other consumer product areas. Products range from mattresses, upholstered furniture to moulded objects such as electronic products to fibre-reinforced composites. The commodity and engineering polymers such as polypropylene, polystyrene, polyamide, polycarbonate etc, are highly flammable unless flame retarded. Thermoplastics on heating melt and if held vertically, under the influence of gravity drip. These materials behave in a complex manner when they melt and drip in a burning situation. In addition to the normal form of flame spread over solid surfaces by degradation and flammable volatile gases released in a dynamic loop that leads to the sustainability of fire growth, the downward flow of flaming liquid from melting and dripping polymer may result in a pool fire [1,2]. Thermoplastic materials also tend to deform significantly as they burn. Thus large changes in the geometric shape in burning conditions are common. These two aspects of thermoplastics are difficult to control and need to be understood through laboratory and modelling work [2–7].

In small scale laboratory experiments to measure the flammability of polymers in vertical orientation, namely the limiting oxygen index (LOI) [8], the flame spread test [9], and the UL-94 test [10], only in UL-94 test is the melt dripping behaviour observed and noted. In the latter, based on whether the dripping ignites the cotton placed under the test specimen, the sample is rated 'pass' or 'fail', but no quantitative data is recorded. In the cone calorimetric tests [11] usually the sample is tested in contained horizontal orientation and hence, melt dripping is not an issue. Hence, it is clear that to date no such test method is available where the melt dripping behaviour is quantified. From the published research literature [3,4,6,7,12–14] it can be seen that many researchers, including ourselves [15,16] are attempting to do so, mainly by measuring the mass of the drops of vertically oriented sample exposed to a radiant panel or in the burning mode of the vertical UL-94 test. Most of the reported experimental work [3,4,6,7,13,14] and modelling of the thermal process [5–7,13,14,17,18] has been under fire operating condition, with a limited work on just melt dripping under thermal environment. We have tried to fill this gap.

In our recently published work [15], we studied the melt dripping behaviour of six different commodity polymers: polypropylene (PP), polyamide 6 (PA6), polyester (PET), polycarbonate (PC), polystyrene (PS) and polymethyl methacrylate (PMMA), exposed to convective heat in a purpose built electric furnace. Each polymer was placed in the furnace at four different temperatures, which were selected in the temperature range between the temperature at which melt dripping starts and the temperature at which the sample ignites and starts burning, the information used is given in Table 1. The temperature range of the furnace temperature when polymer starts melting and igniting (T_{D-I}) varied and depended upon the polymer type as is shown in Table 2. Mass loss representing volatilisation and melt dripping as a function of time were recorded. The

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Table 1
Furnace temperature settings for melt dripping experiments.

Polymer	Temp. when dripping starts (°C)	Temp. when sample ignites and starts burning (°C)	Selected furnace temperatures for the melt the dripping test in [Ref. [16]] (°C)	Selected furnace temperatures for the melt drop temperature measurement (°C)
PP	617	735	625, 660,[a] 690, 725	350, 450, 500, 625, 660
PA6	416	639	425, 495, 560,[a] 630	425, 495, 560
PC	504	732	515, 585, 650,[a] 720	515, 585, 650
PET	407	644	415, 490, 565,[a] 635	415, 490, 565, 635
PS	547	622	555, 570, 595,[a] 615	300, 350, 400, 450, 500, 555, 570
PMMA	513	613	520, 550, 575,[a] 600	350, 400, 520, 550

[a] Denotes furnace temperature settings of the molten drops of which TGA analyses were conducted

number, diameters and shapes of individual drops were measured and it was found to be influenced by the mechanism of decomposition of each polymer type. Based on these results, the melt dripping of these polymers could be divided in four groups (see Table 2). For PP (Group 1) dripping was very fast and wax like and there was little effect due to set furnace temperature from 625 to 690°C. PA6, PET and PC had very similar melt dripping behaviour and could be grouped together (Group II). In these polymers T_{D-I} was > 200 °C and mass loss occurred in steps, each step corresponding to one drop. 8–12 drops were recorded. The melt dripping behaviour of PS was very different from that of the other polymers. The temperature range between the first melt dripping and igniting of the polymer, $T_{D-I,}$ was 75 °C, which is closer to that shown by the Group 1 polymers. However, the number of drops observed was less being similar to those in Group 2. The melt dripping behaviour of PMMA was very different from all others polymers studied with significantly high volatilisation occurring prior to melt dripping. However, temperature has no effect on either the diameters or the thicknesses of the drops. These different behaviours were related to the mechanism of decomposition of each polymer type [15], also observed and reported by other researchers [2–4,14]. From thermogravimetric analysis and rheology studies of virgin polymers and their molten drops it could be concluded that the melt dripping is a combined effect of physical melting and polymer decomposition, which results in a decrease in the viscosity of the molten drops. However, to assess the degradation, it is important to know the temperatures of the molten drops.

This paper extends this work. A system has been developed to enable the temperature measurement of the melting drops in the melt dripping experiment. A simple heat transfer model has also been used to compute the polymer surface temperatures, at set furnace temperatures, and thus that of the molten drops. This has been validated by experimental results. The temperatures of the molten drops can help in predicting the degree of degradation in a polymer during melt dripping. By conducting thermogravimetric analysis of both the polymers and their molten drops, the degree of degradation can also be predicted. The values obtained from both approaches have been compared to understand the melt dripping behaviour of polymers.

2. Experimental

2.1. Polymer samples

The following six commercially available polymers were sourced in chip form:

Polypropylene (PP), Moplen HP516R, Basel.

Polyamide 6 (PA6), Technyl C 301 Natural, Rhodia, France.

Polyethylene terephthalate (PET, polyester), from Fibre Extrusion Technology, UK.

Polycarbonate (PC), Beyer Makrolon, in form of 4 mm thick sheet.

Polystyrene (PS), Rapid electronics, in form of 2 m 457 × 305 blue plastic sheet (37-3142). Blue pigment less than 1% of total mass, determined via TGA. A 4 mm sheets were prepared by running a thin layer of methyl ethyl ketone (MEK) over one of the surfaces and pressing together and clamping under weight.

Polymethyl methacrylate (PMMA), Vision polymers as 4 mm sheets.

From polymer chips of PP, PA6 and PET plaques were prepared by a melt pressing process. Polymer chips were transformed into 150 mm × 150 mm × ~ 3 mm sized plaques at the melting temperature of the polymer and a pressure of 20 kg/cm^2 for 3 min, followed by sudden cooling. The polymer plaques were then cut into small specimens of 100 mm × 6 mm × 3–4 mm sizes.

2.2. Drop temperature measurements

The details of the melt dripping test rig developed and used for melt dripping experiments have been described elsewhere [15,16]. This essentially consists of a 800 W home-built, movable electric furnace with a bore of 25 mm diameter and 120 mm length. The furnace is managed by a temperature controller with adjustable temperature limit up to 900 °C. Dynamic recording of the mass of the polymer sample (100 × 6 × ~3–4 mm) is made by a digital mass balance connected to a computer. The sample is fixed and a pre-heated furnace is raised on rails via a pulley arrangement until the bottom of sample is in the centre of the furnace. The melting drops are collected on an aluminium foil placed on a conveyer belt

Table 2
Melt dripping behaviour of polymer plaques (size 100 × 6 × 3–4 mm).

Group	Polymer type	T_{D-I}[a] (°C)	No and sizes (diameter, mm) of				Volatilisation[b]
			Number	Size	Mass (mg)	Diameter (mm)	
I	PP	118	>50	Small	3–6	<6	33–42%
II	PA6, PC, PET	>200	<12	Large	20–250	10–17	PA6 = 32–40%; PC = 21–25%; PET = 16–32%
III	PS	75	13–20	Medium	20–100	~10	14–22%
IV	PMMA	100	10–14	Small	<25	5	>40%, Prior to melt dripping

[a] (T_{D-I}) = Temp range between first dripping and igniting.
[b] Volatilisation represents the difference between total mass loss (obtained from digital balance) and total mass of drops (weighing the foil before and after the experiment). The details are given in Ref. [16].

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