Polymer Degradation and Stability 98 (2013) 52–63

Contents lists available at SciVerse ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Development of a novel experimental technique for quantitative study of melt dripping of themoplastic polymers

B.K. Kandola*, D. Price, G.J. Milnes, A. Da Silva

Institute for Materials Research and Innovation, University of Bolton, Deane Road, Bolton BL3 5AB, UK

ARTICLE INFO

Article history:
Received 18 July 2012
Received in revised form
17 October 2012
Accepted 31 October 2012
Available online 9 November 2012

Keywords:
Melt dripping
UL-94
Thermal degradation
Flammability

ABSTRACT

This paper presents a methodology developed to quantitatively record the real-time melt and burn dripping behaviour of thermoplastic polymers. Six different commodity polymers were tested for their melt dripping behaviour exposed to convective heat in a purpose built electric furnace. The number, diameters and shapes of individual drops were measured and found to be influenced by the mechanism of decomposition of each polymer type. By conducting thermogravimetric analysis and measuring the viscosity of both the polymers and their molten drops, it could be established that the melt dripping is a combined effect of physical melting and polymer decomposition, which results in decrease in the viscosity of the molten drops. The effect of fire and heat on melt dripping was also observed in a UL-94 equivalent test where it was observed that the behaviour is quite different from pure melt dripping. Relationships between the glass transition temperature and melt viscosity with melt/flame dripping and burning intensity of these polymers have been observed. These will be studied in detail in a subsequent publication.

1. Introduction

The influence of the melt dripping tendency of thermoplastics on their burning behaviour though well known [1–6], is not completely understood. The melting and flaming drops can either remove the polymer fuel from the burning region and hence stop further burning or can become secondary source of ignition. The first scenario is often exploited in using them in products required to pass simple vertical flame spread test. One such example is the use of polyester fabrics for children nightwear in accordance with BS 5722/EN 1103 [7]. However, if the melting and flaming drips further ignite the polymer or other materials in the vicinity, the fire hazard is increased. The frequency and size of melting/flaming drips have been related to the glass transition temperature [3] and pyrolysis mechanisms of polymers [2]. Polymers pyrolysing through random chain scission, such as PE, are reported to form small-size drips, whereas those pyrolysing by unzipping reactions, such as PMMA result in large-size drips in fires [1]. It is believed that the critical material parameter for melt dripping is viscosity. As the temperature rises, the viscosity of a thermoplastic polymer decreases both by increased mobility of the polymer molecules and degradation of the polymer due to breaking of bonds and leaving shorter polymer chains. Hence, viscosity is a function of both temperature and molecular weight [1]. The addition of flame retardants or other additives influences the viscosity of the pyrolysing melt, and hence, the melt dripping behaviour of the polymer [8,9].

Over the years, many tests to measure the flammability of polymers have been developed, the most commonly used being the limiting oxygen index (LOI) [10], the flame spread test [11], cone calorimetry [12] and the UL-94 test [13]. Out of all these, only in UL-94 test is melt dripping behaviour observed and noted. In this widely used fire test for industrial polymeric materials and products, a Bunsen flame is applied to a small-size specimen for 10 s and the polymer is 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. To date no such test is available where the melt dripping behaviour is quantified, though many researchers have attempted to do so, mainly by measuring the mass of the drops of vertically orientated sample exposed to a radiant panel [1] or in the burning mode of the vertical UL-94 test [2,5,6,8,9,14]. Most of this work has been on the study of fire operating conditions and modelling of the thermal process [4–6,14–16], however, no work has been reported on a quantitative relationship between their melting and burning behaviour.

* Corresponding author. Tel.: +44 1204 903517; fax: +44 1204 399074.
E-mail address: B.Kandola@bolton.ac.uk (B.K. Kandola).

0141-3910/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.polymdegradstab.2012.10.028

This work reports development of an experimental technique to measure the melt dripping behaviour of polymers at a set temperature in an electric furnace. Six polymers, selected based on their mechanism of decomposition were tested to record the real-time melt-dripping behaviour in a furnace. The viscosity of all polymers and their molten drops have been measured. All experiments were repeated in a UL-94 set-up to replicate their melt dripping behaviour in flaming conditions. An attempt has been made to draw relationships between melt viscosity, melt dripping and burning intensity of the polymers.

2. Experimental

2.1. Samples

The following six commercially available polymers were used:

Polypropylene (PP), Moplen HP516R, Basell.

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

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

Polycarbonate (PC), Beyer Makrolon, received as a 4 mm thick sheet.

Polystyrene (PS), supplied by Rapid electronics as 2 m 457 × 305 blue plastic sheet (37–3142). The blue pigment accounts for less than 1% of the mass by TGA. The 4 mm sheets were prepared by running a thin layer of methyl ether ketone (MEK) over the surface and then pressing together and clamping under weight.

Polymethyl methacrylate (PMMA), Vision polymers, received as a 4 mm thick sheet.

From polymer chips of PP, PA6 and PET, plaques were prepared by a melt pressing process where chopped polymer chips were transformed into 150 mm × 150 mm × ~ 3 mm sized plaques using high temperature (melting temperature of the polymer) and pressure (20 kg/cm^2) for 3 min, followed by sudden cooling. The polymer plaques were then cut into small specimens of required sizes.

2.2. Development of melt dripping test rig

The experimental set up constructed to investigate the melt dripping behaviour of polymers is shown in Fig. 1(a). The 800 W home-built furnace contains a cylindrical aluminium silicate former, mounted in a casing of perforated mild steel with calcium silicate board end pieces. The furnace tube had a 25 mm bore, and a length of 120 mm. The furnace is managed by an adjustable temperature controller with a temperature limit set to 900 °C. The temperature controller measures the core surface temperature in middle of the furnace via a thermocouple.

Dynamic recording of the mass of the polymer sample is made by a digital mass balance (Ohaus Scout Pro) connected to a computer. The mass of the sample is shown to the nearest 0.001 g. Mass loss data are recorded in real time via the data acquisition software. The scale allows weighing of the polymer sample, located via a thin wire and built-in hook attached to the bottom of the balance. The sample is fixed and the furnace is raised on rails via a pulley arrangement (See Fig. 1(a)), until the bottom of sample is in the centre of the furnace. The temperature is pre-determined and pre-fixed before the furnace is mounted. Since the thermocouple connected to the temperature controller gives the surface temperature of the furnace, it is different from the air temperature in the centre of the furnace. To measure the air temperature in the furnace, a thermocouple embedded in ceramic fibre and hung on a clamp, was inserted at the centre inside the furnace. The temperature of the controller was set to a particular temperature and the furnace left to stabilise for 10 min. Then the temperature of the thermocouple was recorded. By plotting the set furnace temperature vs the temperature in the furnace, the true temperature in the furnace could be noted and used for further tests. It was also noticed that the temperature in the centre of the furnace was different from that near the top surface of the furnace bore due to air convection, amplified by the use of extractor fan above the rig. To minimise this temperature difference, a calcium silicate board sits on top of the furnace. A small hole, drilled in the centre of this board, enables a fine wire and hook bearing the sample to be connected to the balance. Mass retention as a function of time curves are shown in Figs. 2 and 4–9. From these curves the time of the first melt drop, number and mass of drops, and mass of the polymer volatilised could be obtained.

A long strip of aluminium foil placed on a conveyer belt located under the bore of the furnace, collects the drops from the heated sample. The conveyer belt, 52.8 cm long and 15 cm wide moves at a pre-determined uniform speed in x–y (forward and backward) and z – directions as shown in Fig. 3. For this work a constant speed of 11.2 cm/s was used for all polymers, i.e., no experiments were conducted with different speeds. The size and the distance (i.e. time) between the drops were measured by taking a photograph of the aluminium foils, as shown in Fig. 3. These photographed drops were analysed using an image analysis software, ImageJ® (image processing and analysis in Java) to measure the diameter of each drop. For non-spherical drops, an average of both dimensions was taken. Average values for diameters of all drops are reported here. The aluminium foil used to collect the drops is weighed before and after the test. This gives the total mass of the drops. The time when the sample is in position inside the oven was set at zero. Using a video camera the images of falling drops were also taken, which also gave information about their number, size and shape. The number of drops counted from the video images can be verified by

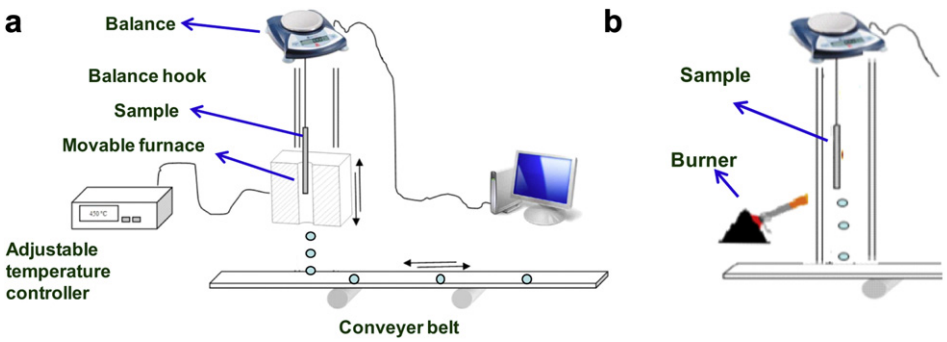

Fig. 1. Schematic of melt dripping experiment in a) furnace and b) UL-94 equivalent test.