INITIATION PARAMETERS OF GRANULATED SYNTHETIC POLYMERS

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Abstract

Polymeric materials, which are currently very often used in various industries, are often transported and stored in the form of granules before processing. This method has several advantages, but in most studies the test samples are modified to different shapes and dimensions. This paper is therefore focused on the initiation of selected granular plastics. Samples of five polymeric materials were exposed to an external heat flux from 20 kW.m⁻² to 40 kW.m⁻². A spark initiator was used to ignite the released gaseous products of thermal decomposition of the polymer sample. FTP (flow-time product) method was applied to the obtained parameter - time to ignition, from which other initiation parameters were determined. The critical heat flux was determined in the range of 5.0 kW.m⁻² - 11.8 kW.m⁻². Despite the relatively small thickness (4 mm), the samples behaved as thermally thick. During the measurement, thin surface layer melted, and the rest of the polymer remained in its original granulated form. Ignition temperatures were calculated according to the Stefan-Boltzmann's law between 273 °C - 402 °C.

Keywords

Critical heat flux, flow-time product, initiation, initiation temperature

INTRODUCTION

Global plastics production has been growing significantly in the last decades. The most produced plastics include the low and high density polyethylene and polypropylene [1]. About a half of the global plastics production accounts for Asia, followed by Europe. Of the European countries, Germany is the largest processor, and, together with Italy, France, Spain, the United Kingdom and Poland, they accounted for almost 70 % of the European demand in 2017. Most of these plastics were used as packaging (39.7 %), in construction (19.8 %) and in the automotive industry (10.1 %) [2].

Synthetic polymers can differ quite significantly from one another in terms of their thermal decomposition. Table 1 shows the values for oxygen number (LOI), 5 % weight loss temperature and residue at 700 °C in the nitrogen atmosphere.

Table 1 Characterization of thermal decomposition of selected polymers by thermogravimetry at a heating rate of 20 °C.min ⁻¹ [3]			
Polymer	LOI (%)	Temperature at 5 % mass loss (°C)	Residue at 700 °C (N₂) (%)
PMMA	17	344 (N ₂) 305 (air)	0
PE	18	419 (N ₂) 315 (air)	0
PP	18	383 (N ₂) 247 (air)	0
ABS	19	399 (N ₂) 383 (air)	0
PBT	20	380 (N ₂) 379 (air)	4
PET	21	414 (N ₂) 398 (air)	11
PC	27	484 (N ₂) 444 (air)	22

Thermal degradation of polyethylene occurs by random chain scission to form a small amount of monomer via free radicals [4]. Under a nitrogen atmosphere, the polyethylene degrades in one simple step, starting at about 350 °C, while zero weight was measured at 490 °C. However, the degradation curve in the air contains some irregularities. The first step is well definable and starts at a temperature of about 220 °C. The second one, relatively insignificant, occurs at 320 °C, while the third one occurs at 400 °C and continues to above 400 °C. A slight weight gain at 200 °C was also measured when tested in the air [5]. Yu et al. state that the thermal decomposition of polyethylene in helium can be divided into three stages. The first one starts at 340.5 °C, the second one from 390 °C and the final one between 460 °C and 510 °C [6]. Based on the data of macro-thermogravimetric analysis, it is possible to divide the reaction of polyethylene granulate containing 30 % talc into three temperature ranges [7]:

1. Area of a relative stability of the tested material
2. Area of the main thermal decomposition
3. Residue oxidation region

Degradation of polypropylene takes place by a chain radical reaction which leads to chain scission [4]. Its decomposition is described, for example, by Gersten et al. They report that it degrades in a single step in an inert environment with two endothermic peaks. The first occurs during its heating, starting at 430 K and continuing without weight loss up to 481 K. The second peak corresponds to the decomposition reaction. [8] Pyrolysis begins at about 630 K and ends at about 740 K [9]. Also Peterson, Vyazovkin and Wight describe the decomposition of polypropylene in nitrogen in one step, stating a decomposition temperature range between 250 °C and 450 °C. In the air, they initially observed a slight increase in weight at around 180 °C. Thermal oxidation occurs mainly during the first step between 200 °C and 450 °C. A smaller weight loss can then also be measured from 450 °C to 600 °C [5].

Polybutylene terephthalate can also be used at high temperatures. It degrades depending on temperature, environmental properties and photooxidation [4]. In nitrogen, at a heating rate of 10 °C.min⁻¹, it decomposes in one step between 625 K and 700 K. At a temperature of

1000 K, the residue remains equal to 7 % [9]. Arie and Masuda report a temperature range from 300 °C to 450 °C at a heating rate of 5 °C.min⁻¹, but its thermal decomposition is influenced by the partial pressure of water vapour in the atmosphere [10]. In contrast to an inert atmosphere, when tested in oxygen, polybutylene terephthalate decomposes in two stages. The first one is practically the same as in nitrogen, and the second one is caused by the decomposition of the carbon residue in the presence of oxygen [11].

Unlike the thermo-oxidative degradation of other polymers, in the case of polyethylene terephthalate and polybutylene terephthalate, thermal degradation plays an important role especially at the beginning, but polyethylene terephthalate is generally more stable than polybutylene terephthalate [4]. Its thermal decomposition in nitrogen is described by Dhahak et al. as a degradation in one step starting at 350 °C [12]. The initial degradation temperature of polyethylene terephthalate is strongly dependent on the atmosphere in which thermal decomposition occurs. It starts in the air at a heating rate of 10 °C.min⁻¹ from 305 °C, and in nitrogen from 380 °C. The degradation itself is then more significant in the air [13]. Meliflex is a thermoplastic polyolefin used in healthcare [14]. It is transparent, flexible and exhibits high UV resistance [15].

Before processing, polymeric materials are often transported and stored in the form of granules. Form of materials plays an important role during initiation phase of fire. This paper is therefore focused on the initiation parameters of plastics in granular forms.

MATERIALS AND METHODOLOGY OF EXPERIMENT

Samples of five polymers in the form of granules were investigated. Two samples were black, two white and one was milky. The samples were marked P1 - P5. The first four ones were of a known composition, while sample P5 was made of an unspecified type of Meliflex plastics (Table 2).

Table 2 Characterization of samples of polymer granules		
Sample marking	Composition	Bulk density (g.cm⁻³)
P1	Polypropylene, talc 20 %	0.64
P2	Polypropylene 28 %, polybutylene terephthalate 25 %, glass fibres 45 %	0.95
P3	Polyethylene terephthalate	0.90
P4	Polybutylene terephthalate	0.75
P5	Meliflex	0.59

A schematic representation of the measurement is shown in Figure 1. The granules of the measured polymers were poured into an aluminium cone bowl with a free surface area of 265.9 cm² and a height of 4 mm (3). The cones were placed in a sample holder (1), underlain by the mineral wool insulation (2). The external heat flux to the free surface of the samples was provided by a cone heater (5), while a spark initiator (4) located 13 ± 2 mm above the centre of the sample surface was used to initiate the flame combustion of the gaseous decomposition products. The thermal decomposition products were sucked out by the suction bell (6) at a flow rate of 0.024 ± 0.002 m³.s⁻¹. The ambient air temperature during the measurements was from 28 °C to 30 °C, its humidity was between 36 % and 46 %, and the atmospheric pressure was 99.94 kPa - 100.20 kPa.

Figure 1 Measurement scheme: 1 - sample holder; 2 - mineral wool insulation; 3 - sample pan; 4 - spark ignitor; 5 – cone heater; 6 – exhaust hood

Three characteristics were used to describe the initiation: flux-time product (FTP), critical heat flux (q_{cr}) and initiation temperature (T_{ig}).

FTP is used to predict the initiation of combustible material. When its limit value is exceeded, the material ignites. It is possible to use the following relation to calculate FTP [16]:

$$FTP = t_{ig} q_{ef}^n, \quad (1)$$

where t_{ig} is time to initiation, q_{ef} is effective heat flux and n is empirical constant called index of flux-time product. Then:

$$q_{ef} = (q - q_{cr}), \quad (2)$$

where q is heat flux.

The (1) and (2) relationships can then be mathematically adjusted to the following form [16]:

$$q = \frac{(FTP)^{\frac{1}{n}}}{t_{ig}^{\frac{1}{n}}} + q_{cr}. \quad (3)$$

Although the FTP concept was designed to determine the time to initiation in thermally sealed systems, it can also be useful for open systems [17]. Shields, Silcock and Murray state that, for open systems, the flux-time product index is higher, at most equal to one [18].

The initiation temperature can be calculated based on the Stefan-Boltzmann's law. When introducing the simplification that the test sample will behave as a perfectly black body, the emissivity value will be equal to one, and therefore the relation can be used:

$$T_{ig} = \left(\frac{q_{cr}}{\sigma} \right)^{\frac{1}{4}} - 273,15, \quad (4)$$

where σ is the Stefan-Boltzmann's constant.

Thickness of the sample is assessed in terms of initiation parameters, by so-called thermal thickness (δ_p). If the depth of penetration of heat waves into the material is less than its physical thickness, then it is a thermally thick material in which further increase in physical thickness does not affect the time to initiation under the given conditions. However, for thinner samples, the effect of thickness on time to initiation can be expected, while the substrate on which the sample is placed can also play an important role [18].

The thermal thickness of the material thus depends on its physical thickness and the depth of penetration of heat waves inside the sample. In general, thermal thickness of a material is determined based on the relationship [20]:

$$\delta_P = A \sqrt{\frac{\lambda t_{ig}}{\rho C_p}}, \quad (5)$$

where A is constant, λ is thermal conductivity, ρ is density, and C_p is specific heat capacity.

The depth of penetration of heat waves into the polymer can be calculated as [19]:

$$\delta_P = 0,14 \frac{\rho}{q}. \quad (6)$$

However, equation (6) applies to the autoignition and not to pilot ignition of the polymeric material. Another possibility to determine the thermal thickness is to compare the determining coefficients for the dependences compiled according to equation (3) for different n.

Based on the work of Mikkol and Wichman, it can be stated that thermally thin materials have $n = 1$ and thermally thick materials $n = 2$ [21].

ATTAINED RESULTS AND DISCUSSION

From the obtained time to initiation values, linear dependences of the n^{th} root of the time to initiation and the external heat flux were constructed for $n = 1.0 - 2.0$, in steps of 0.1. Subsequently, the dependence with the highest determination coefficient was selected for each sample. Graphs of these functions are shown in Figure 2.

Table 3 Comparison of the initiation characteristics of the measured granules with the values reported for polymers in the literature

Sample	n (-)	R ² (-)	q _{cr} (kW.m ⁻²)	FTP (s.kWn.m ⁻²ⁿ)	T _{ig} (°C)	Source
Polyethylene	-	-	13 ^a 15 ^b	-	363 ^a 380 ^b	[22]
Polypropylene	-	-	11 ^a 11-15 ^b	-	338 ^a 330- 370 ^b	[22]
Polybutyl terephthalate	-	-	8 ^a 10-20 ^b	-	213 ^a 382 ^b	[22]
Polyethylene terephthalate	-	-	12 ^a 10-19 ^b	-	324 ^a 407 ^b	[22]
Polyethylene	2.0 ^c	0.9540 ^c	10.7 ^c	49018 ^c	363 ^b	[23]
Polypropylene	1.9 ^c	0.9979 ^c	4.3 ^c	45846 ^c	334 ^b	[23]
Polypropylene	1.3 ^c	0.9986 ^c	8.0 ^c	3724 ^c	314- 332 ^b	[24]
Polyethylene	1.2 ^c	0.9965 ^c	15.8 ^c	4976 ^c	454 ^c	[25]
Polypropylene	1.1 ^c	0.9927 ^c	10.7 ^c	2526 ^c	332- 345 ^b 386 ^c	[25]
Acrylonitrile-butadiene-styrene	1.8 ^a	-	7.1 ^a	19241 ^a	322 ^c	[16]
P1	1.9	0.9977	5.0	20239	273	
P2	2.0	0.9704	11.8	24149	402	
P3	2.0	0.9831	6.3	94470	304	
P4	2.0	0.9854	5.9	72442	295	
P5	1.4	0.9962	10.0	3157	375	

^a Calculated value

^b Measured value

^c Calculated on the basis of data from other authors

P1

P2

P3

P4

P5

Figure 2 Dependences of the external heat flux and the corresponding power of time to the initiation of measured samples

Critical heat flux and a flux-time product were determined for each sample from the resulting trend line equations. Subsequently, the critical heat flux was used to calculate the initiation temperature according to Equation (4). Their values, together with the relevant coefficients n and the determination coefficients are shown below Table 3.

The lowest critical heat flux was determined for granulate P1 and the highest for granulate P2. Their values were 5.0 kW.m^{-2} and 11.8 kW.m^{-2} respectively, which is similar to the values determined from measurements by other authors (Table 3). The variance of FTP values is significantly wider, which is due to its dependence on the exponent n . The lowest value was reached by the sample P5 with $n = 1.4$, the highest by the samples P2, P3 and P4 with $n = 2$. Initiation temperatures ranged from $273 \text{ }^{\circ}\text{C}$ to $402 \text{ }^{\circ}\text{C}$. These values should be considered as indicative and slightly lower than they would be during direct measurement, as the emissivity

in the molten state was not known. Nevertheless, these values are similar to those given by other authors.

Equation (6) was used to determine the thermal thickness of the granules, substituting the bulk density of the granulate instead of the density of the polymer itself. The results are shown in Table 4. The heat flux for which the heat thickness of the materials was calculated is given by a numerical value in the index. It is obvious that at a heat flux of 20 kW.m^{-2} the real thickness of the measured samples is greater than the limit for thermally thin samples. When heat fluxes of 35 kW.m^{-2} and 40 kW.m^{-2} were used, it was already possible to consider all samples as thermally thin. From this point of view, the thickness of the sample during the measurement is at the interface of thermally thin and thermally coarse materials at the used heat fluxes. However, these values refer to the autoignition of the sample and not to its pilot ignition. For this reason, it is more advantageous to determine their thermal thickness based on the dependences in Figure 2.

Table 4 Thermal thickness of measured granules for used heat fluxes					
Sample	δ_{P20}^a (mm)	δ_{P25}^b (mm)	δ_{P30}^c (mm)	δ_{P35}^d (mm)	δ_{P40}^e (mm)
P1	4.5	3.6	3.0	2.6	2.2
P2	6.6	5.3	4.4	3.8	3.3
P3	6.3	5.1	4.2	3.6	3.2
P4	5.2	4.2	3.5	3.0	2.6
P5	4.2	3.3	2.8	2.4	2.1

^a external heat flux of 20 kW.m^{-2}

^b external heat flux of 25 kW.m^{-2}

^c external heat flux of 30 kW.m^{-2}

^d external heat flux of 35 kW.m^{-2}

^e external heat flux of 40 kW.m^{-2}

The values of the coefficient n indicate that most samples behaved as thermally thick rather than thermally thin materials. Given the physical thickness of the samples, this is quite a surprising finding. Since all samples melted owing to the elevated temperature, one sample was extinguished and cooled immediately after initiation. Three layers can be observed in its cross-section in Figure 3:

1. A thin layer of degraded material on the surface of the sample
2. A layer of molten material
3. A layer of original material

It is clear from this composition that the temperature profile in the cross section of the sample at the time of initiation was not constant. Thus, the temperature inside the sample varied quite significantly and, despite the small physical thickness, it could not be a thermally thin material. The probable explanation is its form. The granulate is composed of grains between which there are spaces filled with air. Such a structure has a significantly higher insulating capacity than the compact polymer and thus impairs the penetration of heat waves into the interior of the sample.

Figure 3 Detail of the sample after measurement: 1 - layer of degraded material; 2 - layer of molten material; 3 - layer of raw material

CONCLUSION

The estimated time to initiation of combustible materials can be calculated using the critical heat flux and flux-time product. Both of these initiation characteristics can be obtained by measuring the initiation time at different external heat fluxes. For the purposes of this paper, five polymeric materials in the form of granules were exposed to these heat fluxes. The highest critical heat flux was determined on the basis of the FTP method for a polymer containing a mixture of polyethylene, polybutylene terephthalate and glass fibers - 11.8 kW.m^{-2} . This material can be considered the safest in terms of fire protection. In contrast, the lowest critical heat flux (5.0 kW.m^{-2}) was calculated for a polypropylene-based polymer.

FTP ranged from 3157 to 94470. This significant variance is caused by the exponent n , which characterizes the thermal thickness of the sample and varied with the individual granules. The samples behaved as thermally thick material during testing, which is probably due to air gaps between the polymer granules. Under thermal loading, the upper layer of material melts and the layers below it remain in their original form due to insulation.

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