Gradus Vol 3, No 2 (2016) 114-119
ISSN 2064-8014

THERMAL INVESTIGATION OF FLAME RETARDER CONTAINING PET

Dorottya Nagy [1], Balázs Ádám [1] and György Czél [2]*

[1] Pallasz Athéné University, Department of Material Science, Kecskemét
[2] Miskolc University, Department of Polymer Engineering H-3515 Miskolc-Egyetemváros

Keywords:
polyethylene terephthalate,
Termogravimetry,
Differential Scanning Calorimetry,
flame retardant agent,
melamine cyanurate

Article history:
Received 8 Sept 2016
Revised 6 Okt 2016
Accepted 10 Okt 2016

Abstract
PET (polyethylene terephthalate) was modified with a flame retardant (FR) additive, which is melamine derivative (MC). The FR additive was mixed to the original PET material in different quantities. Modified PET samples were investigated by differential scanning calorimetry (DSC) and thermogravimetry (TG). By TG technique the dessolvation and its nature can be measured. With DSC the changes in enthalpy can be investigated, like melting and formation of crystallite fractions. The TG measures were performed in inert (nitrogen) and in oxygen atmosphere, so the effect of oxygen was investigated.
In this paper the materials with different doses of FR additive were compared with each other, and conclusion was made from experiments.

1 Introduction

Flame retardant (FR) additives are developed for stop and slow down the possibility of fire. FR additives can slow down the emergence of the fire so effectively that the fire could be stopped by the firemen and many lives could be saved [1]. As the plastics are used in many applications, expedient to mix FR additives to the polymer melt [2]. Long ago FR additives, which contain halogen, are the most effective, so they were the most popular. The spreading of environmental regulations caused that halogen-free additives are made to protect the environment and avoid the penalty. Many varieties of these additives are available. These contain phosphorus (P), nitrogen (N), sulfur (S), or etc. [3-6]. Sometimes additives contain more elements of these, so the so-called synergistic effect can be reached [1]. This means that the use of more kind of additive in one material is more effective than the sum of the separately use of these.

Many things are made of PET (polyethylene terephthalate) and its manufactured quantity is considerable large. For example bottles, textile materials, technical devices are surely found in our everyday life. So PET is needed to protect from the danger of fire. One of the most dangerous field of use of PET is textile materials, because one wears much of these textiles, and it is hard to shake off in case of fire. New field of FR additives is melamine derivative additive, which is mostly used for polyamide and for polyurethane foams [7]. One of the first combination of these novel melamine based FR additive and PET is made by a group of scientists of Miskolc, who investigated the oxygen index of this material and also measured the rheology properties by torque rheometer [8]. They discovered that more than 5% FR additive gives less degree of linearic results, and more than 15% of it does not give more effective influence.

In this paper, results of the investigation of thermal and themo-oxidative properties of FR containing PET materials are shown. Thermogravimetric method was used to characterize the process of combustion [9]. By DSC other thermal behavior of the material was determined. All process with change of enthalpy can be seen, like melt and formation of crystalline fraction. In the

* Corresponding author. Tel.: +36 30 9666276
E-mail address: nagy.dorottya@gamf.kefo.hu

compounds there are different doses of FR additive, these different compounds were compared and from these experiences conclusions were made.

2 Experimental

2.1 Materials

The melamine based polymer compounds were made of SKYPET BL8050 polyethylene terephthalate and Melapur MC25 by using a Haake Rheomix 3000p type hot chamber mixer equipment [8]. PET material is a polyester, so there are ester-groups in their main chain which influence the combustion properties of the material (Fig. 1).

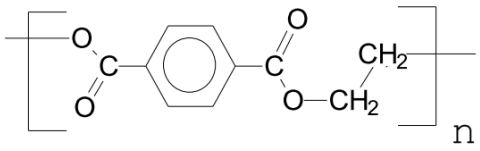

Figure 1. Structural formula of PET [8]

Moreover aromatic groups are in the chain which results stiffened structure and increased melting point and other properties. Without FR additive PET can be used only up to 65°C and typically burns easily. Its density is 1,4 g/cm^3, the glass transition temperature is about 95-98°C. Vicat A softening point is in the range 74-85°C. The intrinsic viscosity is 0,8 dL/g.

Melapur MC25 flame retardant agent is a new halogen-free FR additive containing nitrogen. It is adduct of 1,3,5-triazine,2,4,6(1H, 3H, 5H)-trion and 1,3,5-triazine (1:1) molecules (Fig.2).

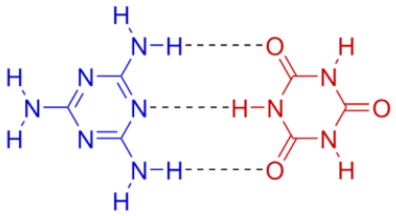

Figure 2. Structural formula of Melapur MC25 [8]

Nitrogen content is minimum 65%. There are strong H-bonds between the molecules leading to a stiffer structure. The decomposition temperature of Melapur is 350°C. This FR additive is effective not only because it increases flame retardancy, but decreases smoke density. In our research the quantity of FR additive in the PET was 1 to 5%.

2.2 Methods

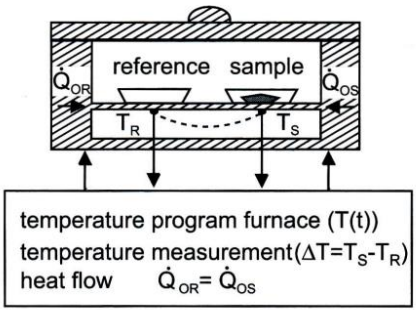

Figure 3. Heat –flux DSC [10]

DSC method measures the change of enthalpy of materials. Thermal Analysis TA Q200 heat-flux DSC (Fig. 3) was used with ISO-11357-1 standard [10]. The specimen and the reference sample are in one furnace. Sample masses were between 3-5 mg. Sample holder was aluminum pan. Reference was an empty pan. The measurement was carried out in nitrogen (inert) atmosphere with 50 mL/min flow rate. The temperature program was heating-cooling-heating from 30°C starting temperature, up to 300°C final temperature with 20°C/min heating rate.

Thermogravimetry equipment determines the change in mass of a sample as a function of time or temperature [10]. The used apparatus was Thermal Analysis TA Q50 thermobalance with a standard of ISO 11358 (Fig. 4.).

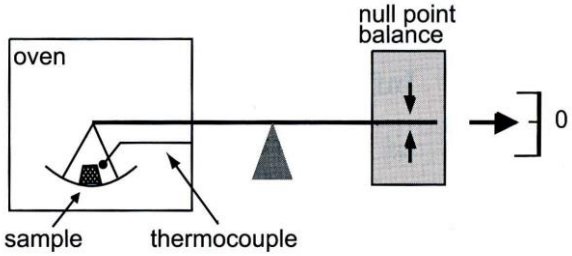

Figure 4. Horizontal thermobalance

By the method of horizontal thermobalance the pan with the sample does not move. The temperature of the sample is measured directly. During the measurement 5-10 mg sample is heated from 30°C to 800°C by 20°C/min heating rate. The purging gas was nitrogen and oxygen.

3 Results and Discussion

TG curves measured in nitrogen are shown in Fig. 5. It can be seen clearly that increasing the FR content the thermal stability of the material decreases. Starting temperatures of decomposition are in the range of 320-340 °C. The degradation reaction mechanism changes in the function of FR content. According to the curves, the FR material decomposes earlier than the PET. The residue of the materials are almost identical (7-8%).

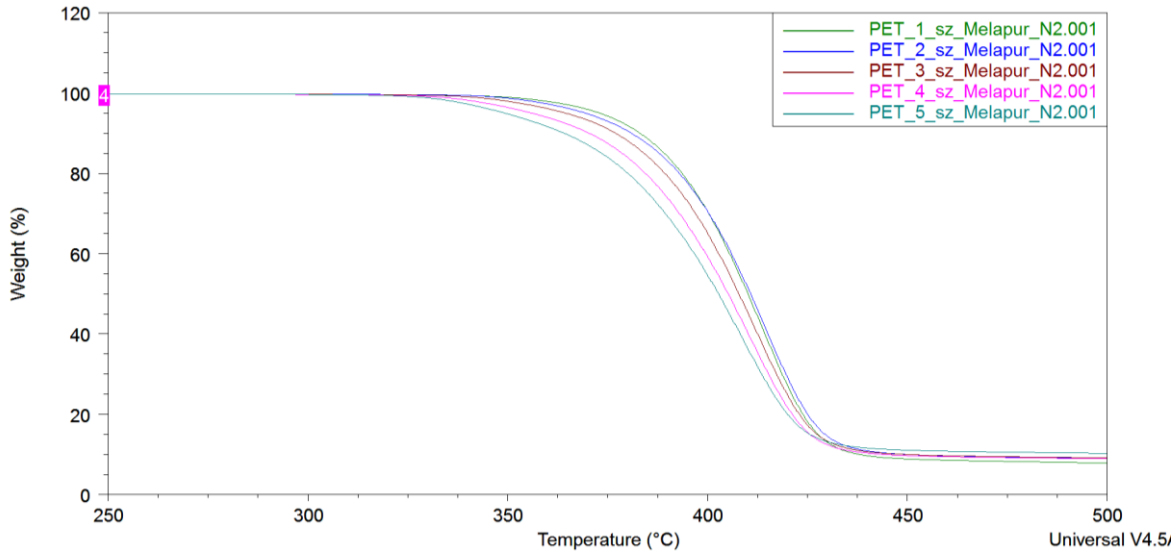

Figure 5. TG curves in nitrogen atmosphere

In oxygen atmosphere all the samples decompose in the same way (Fig. 6.). The degradation reaction starts around 300 °C and the first step finishes around 400 °C. There is a second step between 400 and 500 °C. This step most probably is the decomposition of the charred residue. It is evident from the curves that the degradation reaction is much faster in the presence of oxygen than in nitrogen.

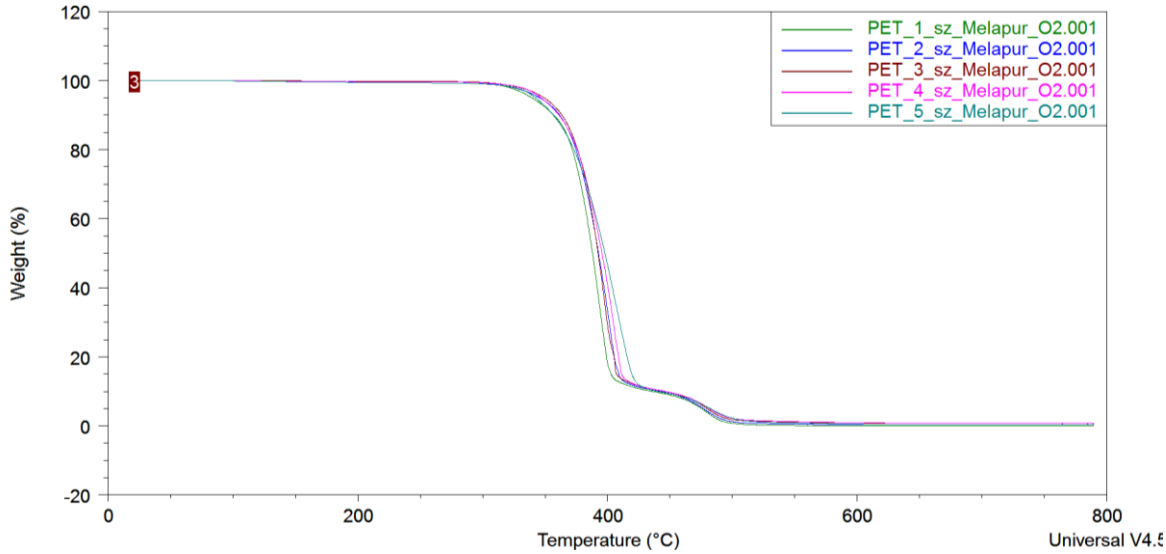

Figure 6. TG curves in oxygen atmosphere

Melting properties of the FR containing PET are almost identical (Fig. 7.). Melting range of the materials is 230-250 °C.

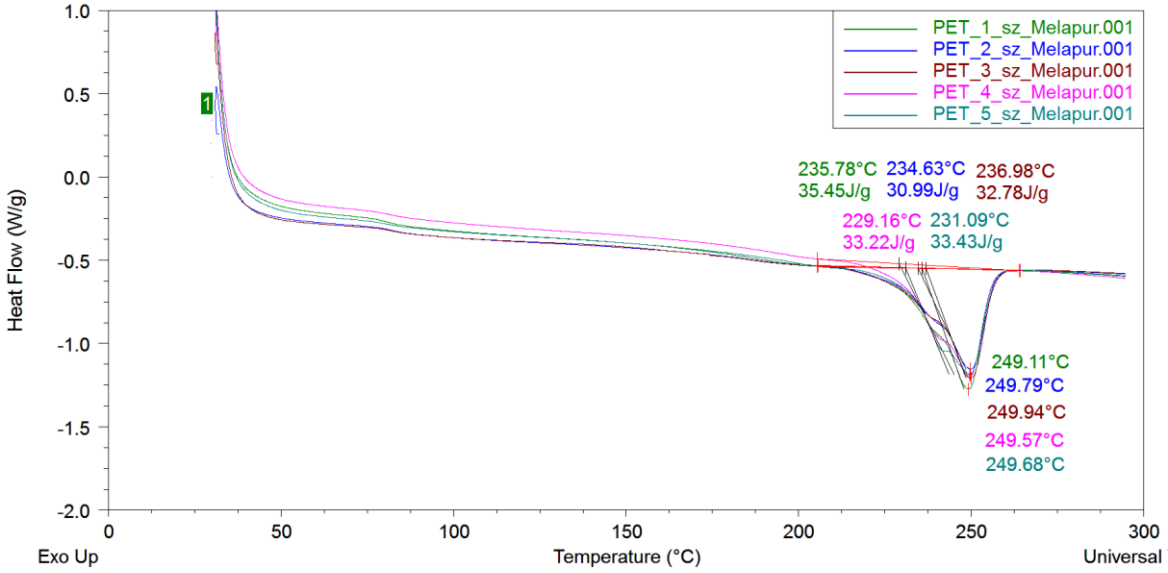

Figure 7. Melting curves of PET compounds

The crystallization ranges of the materials show a little shift, however the change is not significant (Fig. 8). This change in the crystallization temperatures indicates that FR material might be having weak nucleation effect.

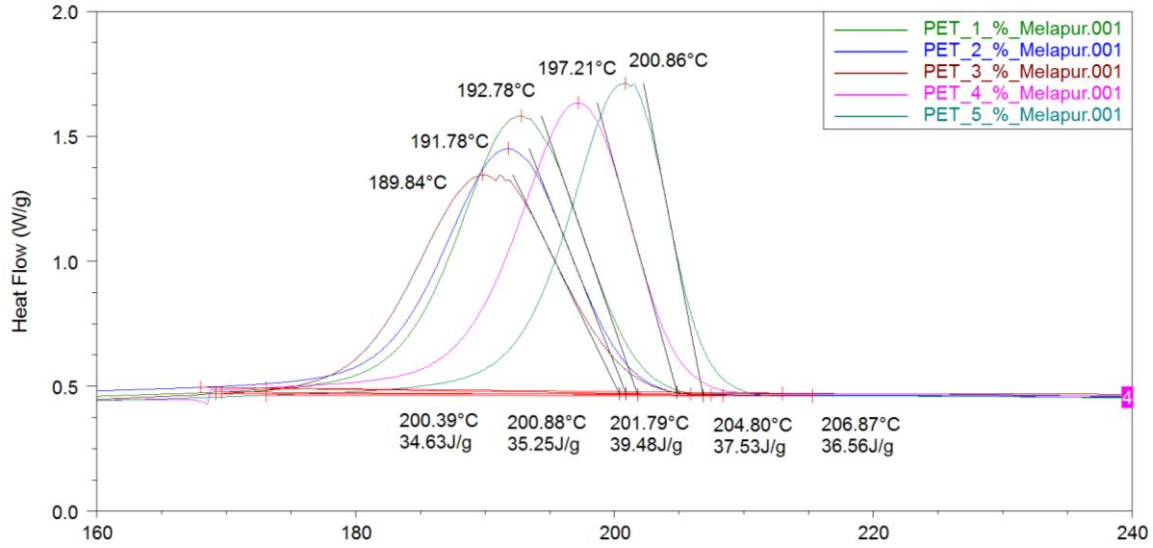

Figure 8. Crystallisation curves of PET compounds

4 Conclusions

PET materials containing 1-5% melamine cyanurate flame retarding material were investigated by thermogravimetry and differential scanning calorimetry. TG measurements were performed in nitrogen and oxygen atmosphere. The materials completely decompose in oxygen atmosphere, while in nitrogen there is around 7-8% charred residue. FR content influences the decomposition temperature of the compounds. Higher is the FR content, lower is the starting temperature of the decomposition. FR content does not influence the melting properties of the material There is a slight chance that the additive has some nucleation effect.

References

[1] Dr. Pál Károlyné, Dr. Macskásy Hugó: “A műanyagok éghetősége”, Műszaki Könyvkiadó, Budapest, 1980
[2] Rudolf Pfaender: “How will additives shape the future of plastics?”, Polymer Degradation and Stability 91, 2249-2256, 2006.
[3] Zhao, Huang, Xiong, Wang: “A novel halogen-free flame retardant for glass-fiber-reinforced poly(ethylene terephthalate)”, Polymer Degradation and Stability 93, 1188-1193, 2008
[4] Lim, Bee and comp.: “A review of application of ammonium polyphosphate asintumescent flame retardant in thermoplastic composites”, Composites Part B 84, 155-174, 2016
[5] Ike van der Veen, Jacob de Boer: “Phosphorous flame retardants: Properties, production, environmental occurrence, toxicity and analysis”, Chemosphere 88, 1119-1153, 2012
[6] Huang, Gerber and comp.: “Formation of a flame retardant-cyclodextrin inclusion compound and its application as a flame retardant for poly(ethylene terephthalate)”, Polymer Degradation and Stability 71, 279-284, 2001
[7] Thirumal and comp.: “Halogen-free flame retardant PUF: Effect of melamine compounds on mechanical, thermal and flame retardant properties”, Polymer Degradation and Stability 95, 1138-1145, 2010
[8] Gy. Czel, A. Kelemen, D. Solyom: Flame retardant polyethylene terephthalate fibers added with melamine based FR additive, Materials Science Forum Vol. 659, pp. 135-140, 2010
[9] I. Martin-Gullón, M. Esperanza, R. Font: Kinetic model for the pyrolysis and combustion of poly-(ethylene terephthalate) (PET), Journal of Analytical and Applied Pyrolysis 58-59, 635-650, 2001
[10] Ehrenstein, Gottfried W., Riedel, Gabriela, and Trawiel, Pia: Thermal Analysis of Plastics Theory and Practice, Carl Hanser Verlag GmbH & Co. KG, 2004