Isothermal crystallization kinetics of flame retardant PET containing melamine based FR

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Abstract. Isothermal crystallization behavior of poly(ethylene terephthalate) (PET) was investigated by differential scanning calorimetry. 1 to 5 wt% halogen-free flame retardant materials were mixed into PET and these samples were examined. Avrami equation was used to analyze the crystallization process. Arrhenius equation was applied to calculate the activation energy of crystallization. It was proven that flame retardant material affects the crystallization.

1. Introduction
The poly(ethylene terephthalate) (PET) is a thermoplastic semi-crystalline polyester having many excellent properties including dimensional stability, chemical resistance, high strength, and stiffness. Therefore, PET is widely used in areas of packaging industry for producing fiber, film, beverage bottles and as engineering plastics in electronics, automotive and construction. [1-3]

However, PET is quite flammable, hence its fire behaviors should be improved to extend its potential application where fire retardant properties are required. [2] Flame retardant (FR) additives are developed to stop or slow down the possibility of a fire. In the past, FR additives, which contained halogen atoms, were the most effective, therefore they were the most popular. Spreading of environmental regulations caused that halogen-free additives were developed to protect the environment. [2, 4]

Another disadvantage of PET that its crystallization is slow. [1, 3, 5, 6] Hence it is difficult to reach high crystallinity using pure material and conventional processing techniques respectively technological settings. Nevertheless, the rate of the crystallization can be improved by nucleating agents. Nucleation is the process when new phases appear. Heterogeneous material with appropriate surface energy can act as a nucleating agent. Among others, nucleation can be controlled by the concentration of the additive. [6]

There are overlaps between the flame retardant and the nucleating additives, such as montmorillonite (MMT), which is often used as a nucleating agent for PET [3, 5] but is also used as a flame retardant for PLA. [7]

In this study, isothermal crystallization of PET containing halogen-free flame retardant additive material has been investigated. Avrami equation was applied to analyze the overall crystallization kinetics and Arrhenius equation was used to calculate the activation energy of the phase transformation.
2. Experimental

2.1. Materials
Matrix material was SKYPET BL8050 PET copolymer. Its density is 1.4 g/cm³, glass transition temperature is 95-98°C and Vicat softening temperature is 78-82°C. [8]

Halogen-free flame retardant was melamine-based Melapur MC25, developed mainly for polyamides and thermoplastic polyurethanes by CIBA. The empirical formula is 1,3,5-triazine, 2,4,6 (1H, 3H, 5H)-trione, and 1,3,5-triazine. Its decomposition temperature is 350°C and the minimum nitrogen content is 65%. [4, 8]

The samples were prepared by the Department of Polymers of the University of Miskolc. The blends were made by a Haake Rheomix 3000p heated chamber mixer. The lowest oxygen index was measured by Polymer-Laboratories unit and the rheological properties of the mixtures were calculated from the mixing torques. [8]

In this study, three samples were tested containing 1, 2, 3, 4 and 5% Melapur. The pure material was not examined in the absence of a sample.

2.2. Method
The thermal behavior of PET was measured by TA Q200 heat-flux DSC instrument, which was calibrated by Indium. The sample weights were about 5 mg. The applied gas during the DSC scan was nitrogen 50 mL/min flowing rate. The temperature range was from 30°C to 300°C.

At first, the sample was heated to 300°C at a heating rate of 20°C/min to eliminate any thermal history. Then the sample was cooled (by the maximum rate of the instrument) to the crystallization temperatures, which were 217, 219, 221, 223°C at 1%, 216, 218, 220, 222°C at 2 and 3%, 219, 221, 223, 225°C at 4%, and 222, 224, 226, 228°C at 5% Melapur content. These temperatures were kept until the end of the crystallization. [10-12]

3. Result and discussion
Determination of the temperatures and the holding times of the isothermal crystallization can be quite difficult, therefore it was necessary to carry out several pre-tests to find the correct data. Due to the different Melapur content, the applied crystallization temperatures were different.

Figure 1 illustrates the DSC curve of the 3% Melapur containing sample during 220°C isothermal crystallization temperature. It has two Y-axes, the thick blue line shows the heat flow, and the thin orange line shows the area percent versus time. The area percent is the relative crystallinity. The time zero (t₀) is that point when the isothermal crystallization starts.

Figure 1. DSC curve of 3% Melapur containing sample, T_c iso: 220°C
The asymmetrical shapes of the heat-flow peak suggest that the growing crystals collide therefore they blockade each other. When the isothermal temperature is increased, the maximum of the heat flow is lower and the time of the crystallization is longer. The change of relative crystallinity at a time can show the rate of the crystallization. The slope of the curve is reduced when the isothermal temperature increases, so it means that the rate of the crystallization becomes slower.

The Avrami equation (1) was used to describe the change of the relative crystallinity with time:

\[ x(t) = 1 - \exp(-Kt^n) \]  

where \( x \) is the relative crystallinity, \( K \) is the rate constant of crystallization, \( t \) is the time and \( n \) is the Avrami exponent. The values \( K \) and \( n \) are considered to be characteristic to the mechanism of crystallization. [10-13]

Figure 2 depicts the relative crystallinity after transformation by Avrami equation. The slope of the linear trend line can show the Avrami exponent, and the rate constant of the crystallization is the intersection of the axis.

![Figure 2. Transformed 2% Melapur containing sample, \( T_{c, \text{iso}} \): 216°C](image)

Table 1 [13] summarizes the meaning of the Avrami exponent, and Table 2 summarizes the results derived from Avrami analysis after the isothermal crystallization on every sample.

| Dimension of growth | Geometry     | \( n \) | athermal nucleation | thermal nucleation |
|---------------------|--------------|--------|--------------------|--------------------|
| 1                   | Fibrillar    | 1      | 1                  | 2                  |
| 2                   | Lamellar     | 2      | 3                  |                    |
| 3                   | Spherulitic  | 3      | 4                  |                    |
Table 2. The result of Avrami analysis

| Melapur [%] | T_{c iso} [°C] | 1/T_{c iso} [K] | n [-] | ln K [-] |
|-------------|----------------|-----------------|-------|----------|
| 1           |                |                 |       |          |
| 217         | 0,002040816    | 2,2018          | -0,2724 |         |
| 219         | 0,00203252     | 2,4824          | -1,5506 |         |
| 221         | 0,002024291    | 2,4716          | -2,5898 |         |
| 223         | 0,002016129    | 2,6108          | -4,0716 |         |
| 2           |                |                 |       |          |
| 216         | 0,00204499     | 2,9116          | -2,5883 |         |
| 218         | 0,00203666     | 2,8038          | -3,4537 |         |
| 220         | 0,002028398    | 2,8465          | -4,5441 |         |
| 222         | 0,002020202    | 2,9335          | -5,8772 |         |
| 3           |                |                 |       |          |
| 216         | 0,00204499     | 2,6754          | -1,3356 |         |
| 218         | 0,00203666     | 2,624           | -2,1421 |         |
| 220         | 0,002028398    | 2,5564          | -3,0631 |         |
| 222         | 0,002020202    | 2,6553          | -4,3383 |         |
| 4           |                |                 |       |          |
| 219         | 0,00203252     | 2,9534          | -1,746 |         |
| 221         | 0,002024291    | 2,7758          | -2,7534 |         |
| 223         | 0,002016129    | 2,6555          | -3,735 |         |
| 225         | 0,002008032    | 2,5944          | -4,6402 |         |
| 5           |                |                 |       |          |
| 222         | 0,002020202    | 2,9848          | -2,2447 |         |
| 224         | 0,002012072    | 2,767           | -3,169 |         |
| 226         | 0,002004008    | 2,8404          | -4,5505 |         |
| 228         | 0,001996008    | 2,797           | -5,6602 |         |

Figure 3 shows the changing of the Avrami exponent. Despite the fact that the crystallization temperature was changed, there was no significant difference between the n values of the measurements, this suggests that the nucleation is probable athermic.

![Figure 3. Avrami exponent as a function of T_{c iso} and Melapur content](image-url)
All \( n \) values are between 2 and 3, suggest that the geometry can be changed from 2 dimensions to 3, nevertheless the transformation is not complete. The 1\% Melapur containing sample is different from the others, its points are mainly below than 2.6 while the points of 2, 3, 4 and 5\% Melapur containing samples are preferably larger than 2.6. [9-13]

Figure 4 shows the altering of the rate constant of the crystallization as a function of reciprocal isothermal crystallization temperature, in Kelvin.

The activation energy of the crystallization process was determined from the rate constant by the Arrhenius equation (2):

\[
K = A \exp\left(-\frac{E_a}{RT}\right)
\]

where \( K \) is the rate of crystallization, \( A \) is a pre-exponential constant, \( T \) is the crystallization temperature, \( R \) is the universal gas constant and \( E_a \) is the activation energy of crystallization. The activation energy can be calculated from the slope of the rate constants curves. [10-13]

Figure 5 shows the varying of activation energy as a function of Melapur content. It can be seen, that increasing Melapur content from 1\% to 4\% decreases the activation energy of crystallization, as a consequence, the crystallization becomes easier. However, the activation energy of the 5\% sample began to increase again. At present, the reason for the difference is not known, therefore further investigation is needed.
4. Conclusion
1, 2, 3, 4 and 5 wt% halogen-free flame retardant materials were mixed into PET then isothermal crystallization behavior was investigated by DSC. Avrami equation was used to describe the crystallization process, and Arrhenius equation was applied to calculate the activation energy of crystallization. Increasing the amount of the flame retardant Melapur material changes the crystallization process. All values of Avrami exponents are between 2 and 3, suggesting that the geometry can be changed from 2 dimensions to 3, but the transformation is not complete. The sample containing 1% Melapur was the lowest, separated a bit from the rest. The values of 2, 3, 4 and 5% were similar. From the Avrami exponents, it became apparent that nucleation was athermic. The activation energy between 1% and 4% has steadily decreased, resulting that the crystallization has become easier. The activation energy of 5% was larger and this requires further testing.

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