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THE ACTIVATION ENERGY OF IGNITION CALCULATION FOR MATERIALS BASED ON PLASTICS

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Abstract

This article deals with the activation energy of ignition calculation of plastics. Two types of polyamide 6 and one type of polypropylene and polyurethane were selected as samples. The samples were tested under isothermal conditions at several temperatures while times to ignition were observed. From the obtained data, activation energy relating to the moment of ignition was calculated for each plastics. The values for individual plastics were different. The highest activation energies (129.5 kJ.mol^{-1} and 106.2 kJ.mol^{-1}) were achieved by polyamides 6, while the lowest was determined for a sample of polyurethane.

Key words

activation energy, thermooxidation, polymers, plastics

INTRODUCTION

Ever since the first industrial scale production of synthetic polymers (plastics) took place in the 1940s, the production, consumption and waste generation rate of plastic solid waste has increased considerably (1).

Nowadays, plastics are used in almost all sectors of industry and services. Figure 1 indicates the approximate market shares consumed by different application sectors for plastics as a whole (2).

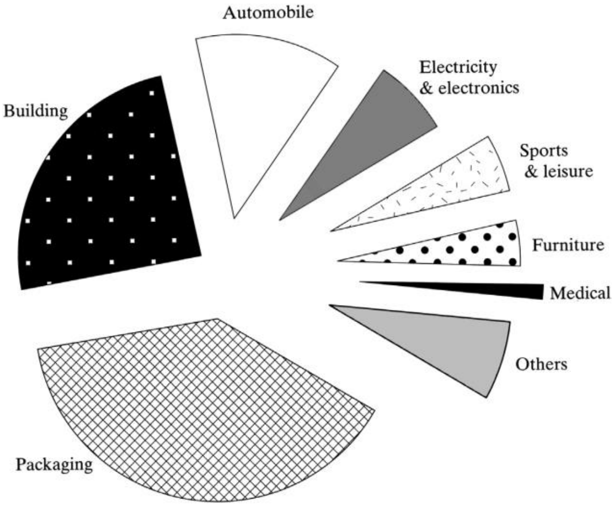

Fig. 1 *Market shares of the seven major plastic application sectors (2)*

Polymeric materials can be regarded as functional hybrid materials that are comprised of a matrix polymer and various kinds of additives, including small volatile and non-volatile molecules and even blended polymers themselves. These additives are used as plasticisers, antioxidants, light stabilizers, flame retardants and other modifiers to enhance the physical and chemical properties of the polymeric materials (3).

Activation energy of the polymeric materials thermooxidation is one of the essential characteristics of materials for the needs of fire protection, as well as in the area of their use as an energy resource.

MATERIAL AND METHODS

According to the standard STN ISO 871:2010, we used hot air furnace. The weight of the samples was 1.001 ± 0.007 g. Measurements were carried out in an air flow at a constant speed of 6 $dm^3.min^{-1}$. Each sample was isothermally heated at five different temperatures. For the purpose of activation energy calculation, the time to ignition was recorded at each measurement. Samples made of four different materials were tested: Mosten EH 501; Slovamid 6 RV2,7; Slovamid 6 GF 15 HI and Ellastolan 1185.

Mosten EH 501 is a block copolymer with the basis of polypropylene with a thermal additive and a nucleating agent. Slovamid 6 RV 2,7 is a spherically shaped granulate made of polyamide 6. Slovamid 6 GF 15 HI is a polymer made of polyamide 6 containing 15 % of glass fibers. Elastollan EH 501 is a thermoplastic elastomer based on polyurethane.

Activation energy

Activation energy can be determined based on the Arrhenius equation. This equation describes the kinetics of reactions. Mostly stated in the general form of:

$$k = A \cdot e^{\frac{E_A}{R \cdot T}}, \qquad [1]$$

where k is the rate constant, A is the frequency factor, EA is the activation energy, R is the universal gas constant and T is the absolute temperature. Logarithm of equation [1] gives a linear relationship. Logarithm of equation [1] gives a linear relationship:

$$\ln k = \ln A - \frac{E_A}{RT} \,. \qquad [2]$$

In the calculations, a similarity with linear algebraic equations of the first order (y=ax+b) can be used. After simplification of the equation, the slope of the curve „$\ln \tau_{\text{ind}}$-1/T“(m) acquires the following form:

$$m = \frac{\Delta(ln[(k)]}{\Delta\left(\frac{1}{T}\right)} = \frac{\Delta(ln[(\tau_{ind})]}{\Delta\left(\frac{1}{T}\right)} = \frac{E_A}{R} \,. \qquad [3]$$

If the expression $\Delta(\ln \tau_{\text{ind}})$ is replaced by the letter b and the expression $\Delta(1/T)$ is replaced by the letters b/a, than it is possible to express the activation energy by the slope of the curve:

$$E_A = -m \cdot R, \text{ [J.mol}^{-1}\text{]} \,. \qquad [4]$$

Balog, Tureková, Slabá also referred to this calculation method in their work which investigated the Determination of the ignition parameters of polymeric materials (4).

RESULTS AND EVAULATION

The measured values of the time to ignition corresponding to the required temperatures and the samples are given in Table 1. Time needed for the flame burning to occur decreased with increasing temperature of the furnace. This is a logical consequence of the faster thermal decomposition of the samples. Temperature range was adapted to each sample so that the flame burning was always observed. Melting and evaporating of the samples was minimized. It was also necessary to ensure that the combustion will not occur too soon after inserting the polymer into the furnace. It is obvious that the samples of polyurethane at comparable temperatures ignited in the shortest period of time. On the other hand, the longest time to ignition was measured for the polyamide 6 containing glass fibres.

THE MEASURED RESULTS OF INDIVIDUAL POLYMERS Table 1

Mosten EH 501		**Slovamid 6 RV 2,7**		**Slovamid 6 GF 15 HI**		**Ellastolan 1185**	
Temp. (°C)	Time to ignition (s)	**Temp. (°C)**	Time to ignition (s)	**Temp. (°C)**	Time to ignition (s)	**Temp. (°C)**	Time to ignition (s)
460	123	**510**	72	**510**	103	**480**	30
470	104	**520**	71	**520**	86	**490**	27
480	86	**530**	53	**530**	66	**500**	21
490	65	**540**	34	**540**	52	**510**	19
500	61	**550**	31	**550**	48	**520**	15

Natural logarithm dependency was established from the induction period of the inverse value of the thermodynamic temperature from the measured values based on the mathematical relationship [3]. Subsequently, the dependencies were translated by trend lines. Their directives were finally used to calculate the ignition activation energy of each of the compared polymers. A graphical presentation of those dependencies and their corresponding trend lines are shown in Figures 2, 3, 4 and 5.

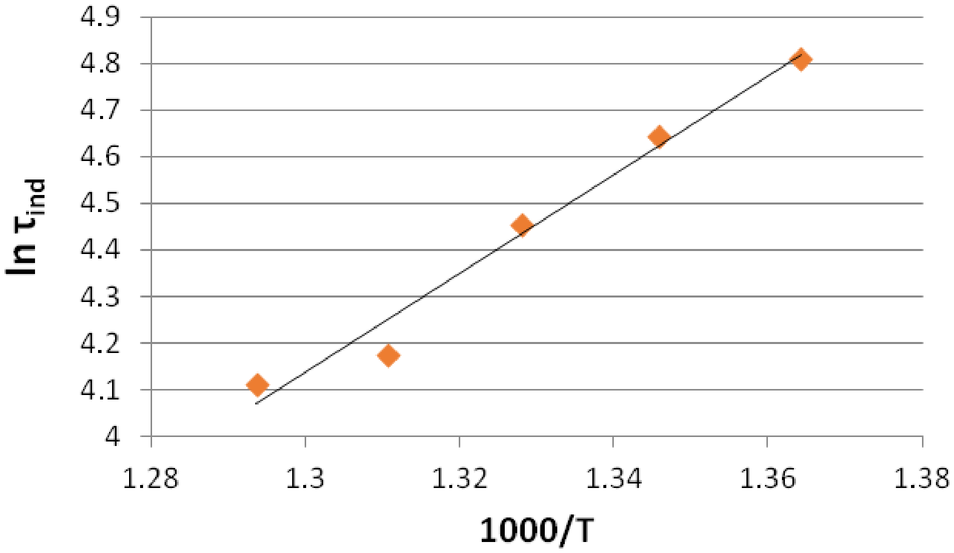

***Fig. 2** A graphical presentation of natural logarithm induction period dependent on the inverse value of the thermodynamic temperature of the sample Mosten EH 501*

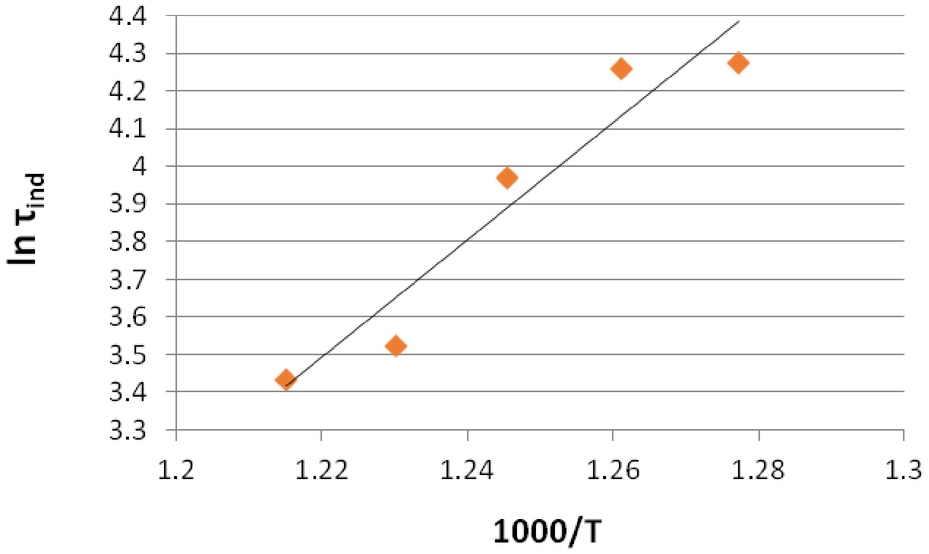

***Fig. 3** A graphical presentation of natural logarithm induction period dependent on the inverse value of the thermodynamic temperature of the sample Slovamid 6 RV 2,7*

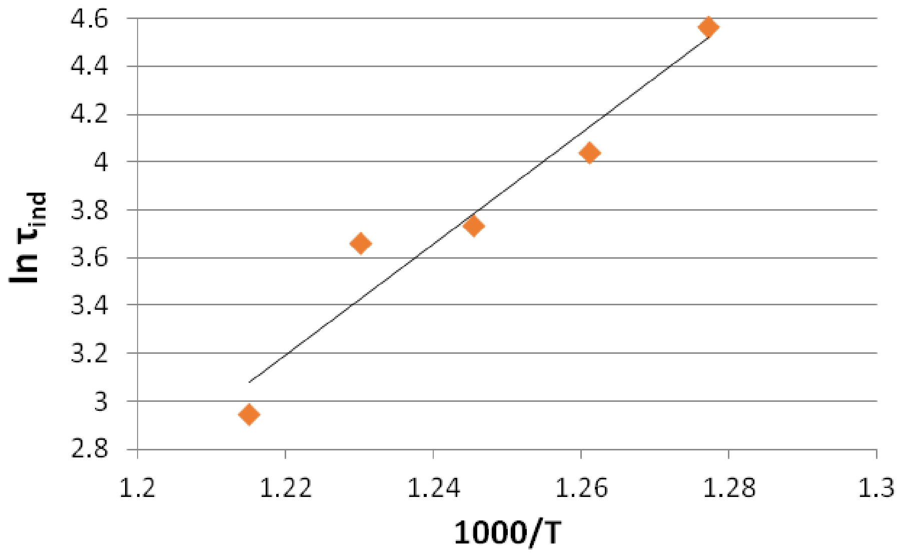

Fig. 4 *A graphical presentation of natural logarithm induction period dependent on the inverse value of the thermodynamic temperature of the sample Slovamid 6 GF 15 HI*

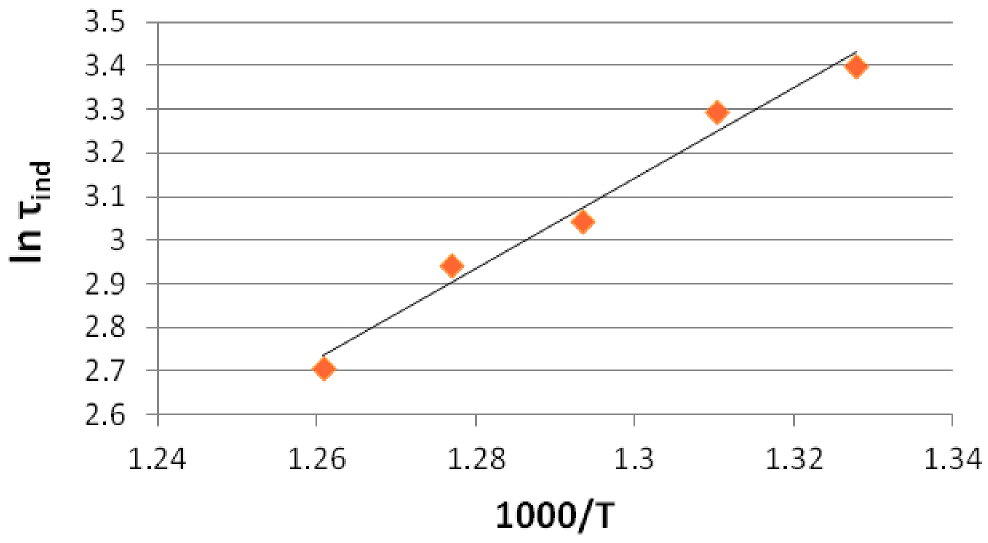

Fig. 5 *A graphical presentation of natural logarithm induction period dependent on the inverse value of the thermodynamic temperature of the sample Elastollan 1185*

The activation energies as well as the squares of correlation coefficients are shown in Table 2. During all measurement, the samples which achieved lower values of the time to ignition also achieved lower activation energies. The lowest activation energy was calculated for polyurethane and, on the other hand, the highest one was calculated for polyamid 6 containing glass fibres. Squares of correlation coefficients ranged from 0.9204 in the case of Slovamid 6 RV 2,7 to 0.9794 for Elastollane 1185.

ACTIVATION ENERGIES AND SQUARES OF CORRELATION COEFFICIENTS OF TESTED POLYMERS Table 2

Sample	Activation energy (kJ.mol^{-1})	R^2
Mosten EH 501	102.634	0.9771
Slovamid 6 RV2,7	129.515	0.9204
Slovamid 6 GF 15 HI	193.783	0.9363
Elastollan 1185	86.216	0.9794

DISCUSSION

Zong et al. in their work reported that the value of activation energy for polyamide 6 of the first reaction phase was determined at 171 kJ.mol^{-1}, and, for polyamid 6 with the addition of organophilic montmorillonite, the activation energy was 184 kJ.mol^{-1}. Further the authors suggested that the oxygen plays an important role in the stabilization process of Polyamide 6 with organophilic montmorillonite by oxidation of the clay surface (5). These results are in between the values determined for the ignition of both types of polyamide 6. It can be assumed that the activation energy of the tested samples was affected by their composition. Polyamide 6 containing glass fibres had a higher activation energy, and therefore we may consider that they have a similar effect as organophilic montmorillonite mentioned in Zong´s study.

Chan and Balke determined the activation energy of the first reaction phase degradation of polypropylene in the air at 100.1 kJ.mol^{-1} (6). This value almost exactly matches the activation energy of sample Mosten EH 501. Virtually identical activation energy of thermal decomposition of polypropylene in the air (102 kJ.mol^{-1}) reported Quick, Fast and Matisová-Vavreková (7).

In the Gopalakrishnan´s and Sujatha´s study, the activation energy of the first phase thermooxidation of polyurethanes is determined according to the method and type of samples from 48.1 kJ.mol^{-1} to 99.1 kJ.mol^{-1} (8). Balog, Tureková a Slabá reported that the activation energy for thermooxidation of polyurethane using the same method as in this study was 90.7 kJ.mol^{-1} (4). The ignition activation energy of Elastollanu 1185 correlated with activation energies in mentioned articles.

CONCLUSION

Samples of selected plastic materials were isothermally heated at different speeds in a hot air furnace and the time needed to the ignition was measured. From the measured results, the following conclusions can be drawn:

- The induction period decreases with increasing temperature;
- The polyurethane sample ignited in the shortest period of time;
- The longest induction period from all the samples was reached by the polyamid 6 containing glass fibres.

Subsequently, the activation energies of ignition were calculated for each of the tested polymers. Samples which ignited after longer period of time at a comparable temperature achieved lower activation energies. The lowest activation energy (86.2 kJ.mol^{-1}) was calculated for the sample of thermoplastic elastomer on the basis of polyurethane (Elastolan 1185) and the highest activation energy (193.8 kJ.mol^{-1}) was calculated for the of polyamidu 6 containing 15 % of glass fibers (Slovamid 6 GF 15 HI). The results are in agreement with those reported by other authors.

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