

THERMAL ANALYSIS OF POLYOLEFIN AND LIQUID PARAFFIN MIXTURES

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Abstract

The thermal decomposition of the polypropylene and liquid paraffin mixtures with inorganic additives was studied in dynamic conditions. Thus, typical thermal analyses were carried out and thermal decomposition of samples in a specially designed apparatus was also processed. One can observe for samples of sufficiently low mass that thermal analysis allows clear distinction of samples that contain and do not contain liquid paraffin, respectively. Moreover, it is possible to separate two stages of the decomposition process. The relationship between the logarithm of conversion degree and temperature (so called three-parameter model) was used for the description of these processes. Relations between coefficients in three-parameter equation in micro-scale, and characteristic temperatures of thermal decomposition in laboratory scale were observed in spite of meaningful differences in the course of the processes.

Keywords: coupled TG/DTG, decomposition, liquid paraffin, polyolefins, thermal analysis, thermogravimetry

Introduction

Increasing production and consumption of polymers poses many problems in waste management. Consequently, polymer waste recycling attracts more and more attention. Thermal decomposition can be an interesting alternative in this area. Liquid products formed in these processes can be applied as valuable components for fuel production. In this context many investigations concerning polyolefins with catalysts or inorganic additives can be found in [1–4]. Studies in Department of Chemical Technology of Coal and Petroleum [5, 6], which have provided some technological solutions [7, 8], indicated that system containing polyolefin, technological oil and inorganic additive are especially interesting for industrial scale processing.

However, there is a lack in the simple and efficient microscale method that will be suitable for the investigations of these systems. Such a method should allow estimating the influence of the parameters describing waste polymers, oils and additives used in the thermal decomposition process. In this work it was attempted to describe the data obtained from thermal decomposition of the aforementioned systems in the laboratory

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scale and resulted from thermal analysis by using the three-parameter model. This model directly relates conversion degree (α) or to the relative reaction rate (r) to temperature [9, 10], while the so-called single kinetics triplet ($E, A, f(\alpha)$) [11–16] or some alternative approaches [17, 18] are not included.

Experimental

The samples of polypropylene (PP, J-400), liquid paraffin ($M_{av}=410 \text{ g mol}^{-1}$; density 0.878 g cm^{-3} ; iodine number $3.6 \text{ J}_2/100 \text{ g}$) and cracking catalyst G3 were used as raw materials (ratio PP/liquid paraffin was 2:1 and contents of catalyst in samples 2 and 4 equaled 10%).

Thermal decomposition in the laboratory scale and thermogravimetric profiles were registered for the following samples:

- PP (sample 1),
- PP+liquid paraffin (sample 2),
- PP+catalyst G3 (sample 3),
- PP+liquid paraffin+catalyst G3 (sample 4).

Thermal decomposition in laboratory scale was performed in the round-bottom flask heated by heating jacket in the temperature range from the ambient temperature to 430°C (703 K). Heating rate (q) amounted to 3 K min^{-1} . Condensation of liquid products of reaction occurred in water-cooled condenser. In these studies the conversion degree (α) was determined by measuring the quantity of liquid products in contrast to thermogravimetric analysis (it was determined by measuring loss of sample mass).

Introductory thermogravimetric analyses were performed in MOM OD-103 thermal analyser (mass of sample 25–100 mg) due to common using of this apparatus. Thermogravimetric analyses were also performed in the Mettler Toledo TGA/SDTA-851 thermal analyser in the following conditions: platinum crucible, mass of sample about 15 mg, final temperature 800°C (1073 K), heating rate $q=6 \text{ K min}^{-1}$, inert atmosphere of nitrogen flowing at $100 \text{ cm}^3 \text{ min}^{-1}$. Thermogravimetric analyses carried out in MOM OD-103 thermal analyser provided 35–40 measurements points, whereas Mettler Toledo TGA/SDTA-851 thermal analyser provided 300–350 points. These studies showed difficulties in comparing results obtained in different apparatus and conditions.

Modeling of thermal decomposition of polyolefin–liquid paraffin mixtures

A three-parameter relationship between the logarithm of conversion degree (α) and temperature (T) was used for the description of the process. Consequently, it was not necessary to find a kinetic model $g(\alpha)$. The relationship is expressed by equation [9]:

$$\ln\alpha = a_0 - \frac{a_1}{T} - a_2 \ln T, \quad 0 < \alpha \leq 1 \quad (1)$$

where a_0, a_1, a_2 – coefficients of equation; a_2 can be recognized as a characteristic coefficient connected with the rate of thermal decomposition.

After the differentiation of Eq. (1) one can obtain relative rate of thermal decomposition r , which is given by equation (m_i – initial mass of sample) [10]:

$$r = \frac{d\alpha/dT}{\alpha} T^2 = - \frac{d \ln \alpha}{d(1/T)} = - \frac{DTG}{m_i - TG} T^2 = a_1 - a_2 T \quad (2)$$

Results and discussion

Thermogravimetric analysis

Examples of TG and DTG profiles of the sample 2 are illustrated in Fig. 1. Analysis of TG/DTG profiles registered in MOM OD-103 for the samples containing liquid paraffin (2 and 4) reveals a broadening of DTG band in the lower temperatures, while two separated stages of thermal decomposition were observed for DTG profiles registered in Mettler Toledo TGA/SDTA-851. The first one can be related to the transformation (distillation and decomposition) of liquid paraffin, the second one – to the decomposition of polypropylene. Both stages can be analyzed separately. Thus, it was decided to analyze further data obtained in this thermal analyzer.

The analysis performed after plotting the r vs. T relationship on the basis of Eq. (2) and a_1 and a_2 coefficients from Eq. (1) clearly indicates the ranges in which there is a straight-line plot (Fig. 3). Thus, a linear plot can be observed within a broad range of conversion degree α ($\alpha=0.03$ – 0.99 in the first and $\alpha=0.3$ – 0.99 in the second stage of decomposition). These results indicate that relative rate of reaction (r) is

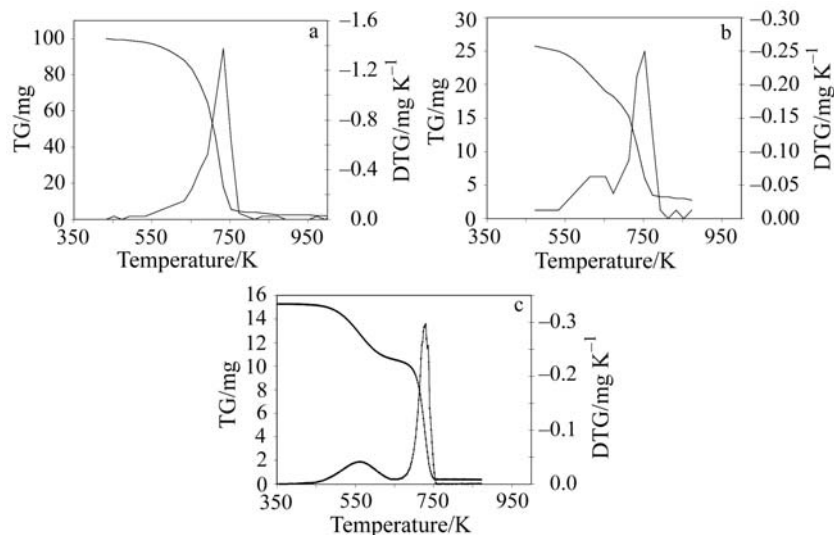


Fig. 1 A comparison of thermogravimetric curves for sample 2 registered in MOM OD-103 thermal analyser a – mass of sample 100 mg, b – mass of sample 25 mg, and in Mettler Toledo TGA/SDTA-851 thermal analyser, c – mass of sample 15 mg

more convenient than typically used analysis of the DTG data (Fig. 1). Basically, we can now describe the thermal decomposition process by establishing the relation between conversion degree (α) and temperature (T) without the knowledge of the reaction mechanism. This is especially important in the case of thermal decomposition of complex samples. Table 2 shows the values of a_2 coefficient and determination coefficient R^2 (square of correlation coefficient).

Table 1 Temperatures T_i , $T_{0.5}$, $T_{0.9}$ of thermal decomposition in laboratory scale

| Sample | T_i /K | $T_{0.5}$ /K | $T_{0.9}$ /K |
|--------|----------|--------------|--------------|
| 1 | 659 | 685 | 715 |
| 2 | 658 | 681 | 689 |
| 3 | 613 | 680 | 703 |
| 4 | 645 | 678 | 695 |

Table 2 Values of a_0 , a_1 and a_2 coefficients in Eq. (1) for samples 1–4 analysed in laboratory scale (R^2 – determination coefficient)

| Sample | a_0 | a_1 | a_2 | R^2 |
|--------|---------|-------------------|--------|--------|
| 1 | 14734.9 | $1.36 \cdot 10^6$ | 1952.3 | 0.9903 |
| 2 | 11595.3 | $1.09 \cdot 10^6$ | 1533.0 | 0.9671 |
| 3 | 21018.5 | $1.92 \cdot 10^6$ | 2788.8 | 0.9874 |
| 4 | 5665.9 | $5.37 \cdot 10^5$ | 747.7 | 0.9768 |

The analysis of the individual a_2 values seems to indicate that physical processes are dominant during the first stage of decomposition ($a_2=57$ and 66). During the second stage ($a_2=776$ – 1710) the influence of chemical reactions is dominating. These conclusions can be confirmed by the analysis of DTA curves, which implies a clear endothermic effect in the range of the polypropylene decomposition, while there is no such effect in the range of liquid paraffin transformation (Fig. 4).

Thermal decomposition in the laboratory scale

The profiles of the individual processes are illustrated in Fig. 2. The characteristic temperatures of thermal decomposition: initial temperature (T_i), half conversion temperature ($T_{0.5}$) and temperature corresponding to $a=0.9$ ($T_{0.9}$) (Table 1) were determined on the basis of the obtained results.

Analysis of Fig. 2 proves particularly these conclusions reported in previous publications [5, 6] that concern the advantageous influence of the oils on the thermal decomposition of polymers. This effect is achieved through the decrease of the process temperature.

There were difficulties in keeping the same conditions of the process run for each sample during the studies, which resulted from strong energetic effects that are

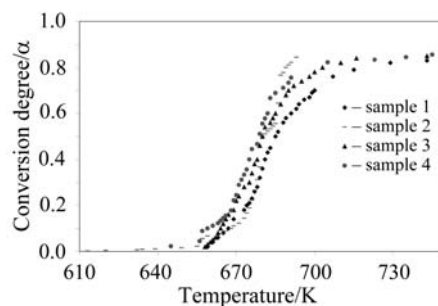


Fig. 2 A comparison of processing curves for samples 1–4

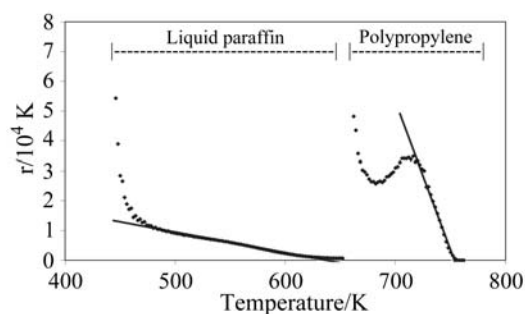


Fig. 3 Relation of relative rate of reaction (r) as a function of temperature (T) for sample 2

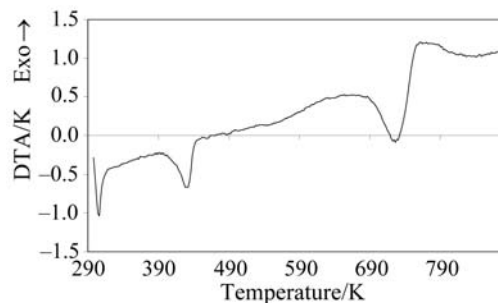


Fig. 4 DTA curve for sample 2 (endothermic peak appeared at 304 K as result of the melting of crystals suspended in liquid paraffin; peak appeared at 430 K corresponds to the melting of polypropylene and that one at 730 K indicates the decomposition of polypropylene)

connected with the processes investigated. Thermostatic heater will be an efficient solution in further studies.

It was found that for samples 1–4 three-parameter Eq. (1) can be used for the description of thermal decomposition of the polypropylene/liquid paraffin systems in the laboratory scale (Table 3). It is very interesting, because there are marked differences in the course of the process in different scales and different ways of conversion degree determination.

Table 3 Values of a_2 coefficient in Eq. (1) and determination coefficient R^2 for samples 1–4 (samples 1 and 3 without liquid paraffin)

| Sample | Stage I | | Stage II | |
|--------|---------|--------|----------|--------|
| | a_2 | R^2 | a_2 | R^2 |
| 1 | – | – | 776 | 0.9705 |
| 2 | 66 | 0.9750 | 1143 | 0.9907 |
| 3 | – | – | 1710 | 0.9832 |
| 4 | 57 | 0.9889 | 1441 | 0.9917 |

The analysis of the processing profiles (Fig. 2) indicates that only a single thermal decomposition stage occurs in such complex systems. Hence, a difference between the samples containing liquid paraffin (2 and 4) and samples without one (1 and 3) disappears. On the other hand, the a_2 parameter in Eq. (1) takes relatively high values.

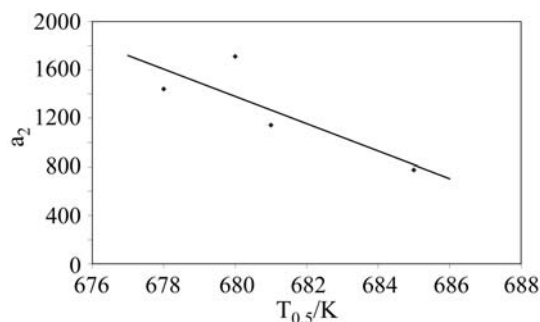
Analysis of results obtained in different scales

Relations between coefficients in Eq. (1) in micro-scale, and characteristic temperatures of thermal decomposition in laboratory scale were observed, in spite of meaningful differences in the course of the processes, and different methods of conversion degree determination. Figure 5 shows relation a_2 vs. $T_{0.5}$. In the case of a_2 vs. T_i occurs similar relation, where a_2 applies to micro-scale, whereas T_i and $T_{0.5}$ are concerned in laboratory scale.

In work [19] relations between the a_0 , a_1 and a_2 coefficients in Eq. (1) were analyzed for chemical compounds, which decomposition occurs in accordance with equations with stoichiometric coefficient (ν) at gaseous products of reaction:



where A , B , C – chemical compounds, and indices s and g – solid and gaseous state, respectively.

**Fig. 5** Relation between (a_2) in micro-scale and half conversion temperature ($T_{0.5}$) in laboratory scale

In the case of reaction (3) for variable heating rate there are new possibilities of interpretation of Eq. (3), among which relation containing thermodynamic nature component and dimensionless temperature difference simplex is interesting:

$$r = \frac{\Delta H}{\nu R} \frac{T_f - T}{T_f - T_r}, \quad T_f = \frac{a_1}{a_2}, \quad a_2 > 0 \quad (4)$$

ΔH – average enthalpy of process, J mol^{-1} , T_f – temperature corresponded to $r=0$, K, T_r – experimentally determined temperature of intersection of linear relation with parallel-line, $r=\Delta H/\nu R=\text{const.}$ when $a_2=0$, K, $R=8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ – universal gas constant.

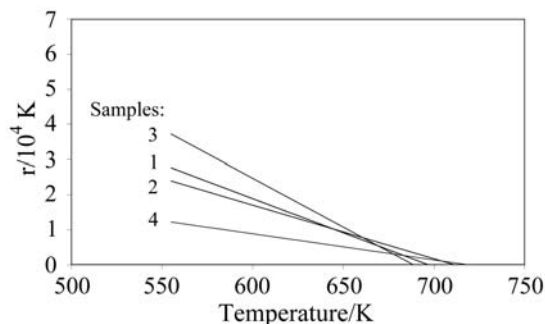


Fig. 6 Relationship r vs. T for samples 1–4 analyzed in the laboratory scale

In the case of analyzed one-, two- and three-component mixtures composed from: polyolefins, liquid paraffin and catalysts it was observed that for constant heating rate $q=\text{const.}$ the linear plots of r vs. T (2) intersect almost in one point, at temperature T_r (Fig. 6). This effect is connected with differences in initial compositions of samples, as distinct from [19], where the decomposition of selected chemical compounds was analyzed for $q=\text{var.}$ Therefore, Eq. (4) is given in form with allowing for experimentally determined point of intersection with coordinates $[T_r, r_{\text{eq}}]$:

$$r = r_{\text{exp}} \frac{T_f - T}{T_f - T_r} \quad (5)$$

where r_{exp} – relative rate of reaction in point of straight-lines intersection, K.

On the basis of this consideration one can draw the conclusion that using a three-parameter equation allows to avoid difficulties connected with complicated thermodynamic considerations in the case of complex mixtures. It also allows to describe thermal decomposition without analyzing the thermal decomposition mechanism.

Conclusions

Thermogravimetric analysis seems to be a promising method for the analysis of polypropylene/liquid paraffin systems. A clear advantage is the fact that such analysis clearly distinguishes samples that contain liquid paraffin from these that do not contain. Thermal decomposition occurs in two stages, while the process occurs in one

stage in the laboratory scale. A three-parameter equation that relates the logarithm of conversion degree to temperature (1) can be applied to describe the data obtained both in laboratory scale and thermogravimetric analysis. This allows to connect directly the conversion degree (α) and temperature (T) without analyzing the thermal decomposition mechanism or generating mass integral $g(\alpha)$. Relations between coefficients in Eq. (1) in micro-scale, and characteristic temperatures of thermal decomposition in laboratory scale were observed. Thus, the experimental relation between data obtained in different scales were found in spite of meaningful differences in the course of the processes. Therefore, there is a possibility to the practical application of the method that could be used for the evaluation of the influence of the waste materials recycled during thermal decomposition. It would also enable a more complete control over industrial scale processing. The prediction of such processing will be possible without the necessity to execute experiments in a larger scale.

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