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STUDY OF THE PYROLYSIS PROCESS OF PLASTIC WASTE BY DERIVATOGRAPHIC ANALYSIS METHOD

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The dependance of temperature and time on mass loss, mass loss rate and intensity of endothermic peaks during the pyrolysis process of polyethylene terephthalate (PET-1) polymer at various heating rate (10, 50 °C/min) was studied by derivatography methods. The parameters, as temperature (T) and time (t) of the beginning of destruction, temperature (T) and time (t) of half destruction, mass destruction time (min) at 510⁰C and energy activation of the destruction process were estimated. Furthermore, the melting parameters as ΔH, square peak (mJ) and mass loss rate (Δmdt) are calculated. The obtained results show that as the heating rate increases, the destruction process occurs at higher temperatures, the initiation time of the destruction process decreases, and the activation energy of the decomposition is approximately equal to 58-60 kcal/mol. Two stages of exothermic nature were observed. The first occurs in the temperature range from 377,0 °C to 410.4°C, and the other in the range of 430.0°C to 475.7°C.

Keywords: pyrolysis, mass loss, plastic, thermogravimetric analysis.

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INTRODUCTION

The generation of plastic waste and its negative effects on the environment are increasing. It is known that there is about one ton of plastic waste in every three tons of fish [1]. The analysis conducted in 2017 showed that by 2050, the amount of primary plastic waste, untreated and treated may increase dramatically [2]. Hence, research on the neutralization and recycling of these wastes is a significant scientific and practical issue [3-6]. Currently, despite the development of various methods (mechanical, landfill placement, chemical plasma method) in this field, the pyrolysis method is more promising. Solid residues, liquid compounds and gas products can be obtained, in the pyrolysis method [7-9]. The speed of the process is related to the composition of pyrolyzed plastic masses as well as the temperature. One of the investigation methods of plastic wastes degradation processes is application of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), that gives the information of kinetics and thermal properties of wastes under the effect of heat energy. Despite some research work on thermogravimetric study, there is need to continue the work on pyrolysis processes of plastic waste. Purpose of this work is the study of the thermal conversion process of PET-1 plastic wastes with TGA and DSC analysis methods.

MATERIAL AND METHODS

The Perkin Elmer Simultaneous Thermal Analyzer STA 6000 (USA) was used. The PET samples (5.66-11.76 mg) with dimensions of 0.03-0.06 cm² were taken for analysis. In the device, these samples were heated up to a temperature of 700°C in a nitrogen atmosphere, and appropriate parameters were set. The activation energy was calculated according to Arrhenius equation [10]:

$$\ln \Delta t = -\frac{E}{RT} + C$$

where Δt is the depth of the peak of the DTA curve, which is proportional to the rate constant of the phase transformation at the temperature T . From the dependence $\ln \Delta t - 1/T$. The tangent of the slope of which will be expressed:

$$\operatorname{tg} \varphi = -E/R$$

To graphically determine the activation energy on the initial branch of the peak of the DTA curve, 8-9 points are randomly selected, as shown in Figure 1.

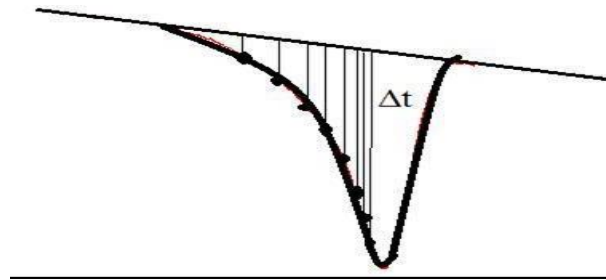


Fig. 1. Initial branch of the peak of the DTA curve

For each of them, using a ruler, measure the distance to the baseline (Δt , mm). For each of them, the temperature (t , °C) is determined by projecting onto the T curve. The data obtained are applied in the form of dots to the figure and an averaged line is drawn in the coordinates $\ln \Delta t - 1/T$, as shown in Figure 2 the tangent of the slope angle of which is used to calculate the activation energy E , kJ / mol.

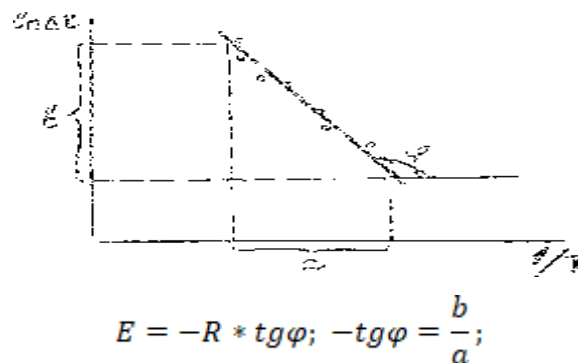


Fig. 2. Dependence $\ln \Delta t$ on $1/T$

The structural formula (Figure 3) and physicochemical properties of PET-1 brand polyethylene terephthalate polymer for research are given in the table 1.

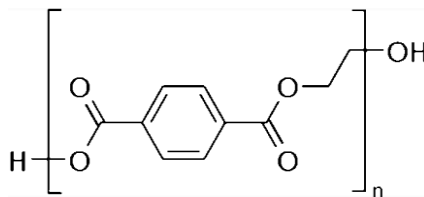


Fig. 3. The structural formula of polyethylene terephthalate polymer PET-1 brand

Table 1.

Physico-chemical properties of polyethylene terephthalate polymer PET-1 brand [11]

Molar mass	10–50 kg/mol, varies
Density	1.38 g/cm ³ , 20 °C 1.370 g/cm ³ , amorphous 1.455 g/cm ³ single crystal
Melting point	> 250 °C -260 °C (280 °C-320 °C)
Boiling point	> 350 °C (decomposes)
Solubility in water	Practically insoluble
log P	0.94540
Thermal conductivity	0.15 to 0.24 W/(m·K)
Refractive index (nD)	1.57–1.58, 1.5750
Heat capacity (C)	1.0 kJ/(kg·K)
Young's modulus, E	2800–3100 MPa
Tensile strength, σ	55–75 MPa
Elastic limit	50–150 %
Notch test	3.6 kJ/m ²
Glass transition temperature, Tg	67–81 °C
Vicat B	82 °C
Linear expansion coefficient, α	$7 \times 10^{-5} \text{ K}^{-1}$
Water absorption (ASTM)	0.16

Apparently, the melting temperature of the polymer is (280°C-320°C) according to some data, and the pyrolysis process of polymers usually occurs around 500°C. As a result of the pyrolysis process, fractions of gas products, liquid products and solid residual products are obtained.

RESULTS AND DISCUSSION

Polymer materials used for water packaging (bottles) were divided into parts with an area of approximately 0.03-0.06 cm² and placed in glass ampoules and pyrolyzed in the range of 20°C-700°C in a nitrogen flow in a brand derivatograph device using standard methodology. The quantity of the substance taken for pyrolysis was in the range of 5-12 mg and prepared samples were pyrolyzed at the rates of 10, 50°C/min, respectively. As a result of the study, polymer mass loss, mass loss rate and endothermic peaks characteristic of thermal transformations were measured in the considered temperature range. The results obtained at different heating rates are given in the following figures (Figure 2 a-b, Figure 3 a-b).

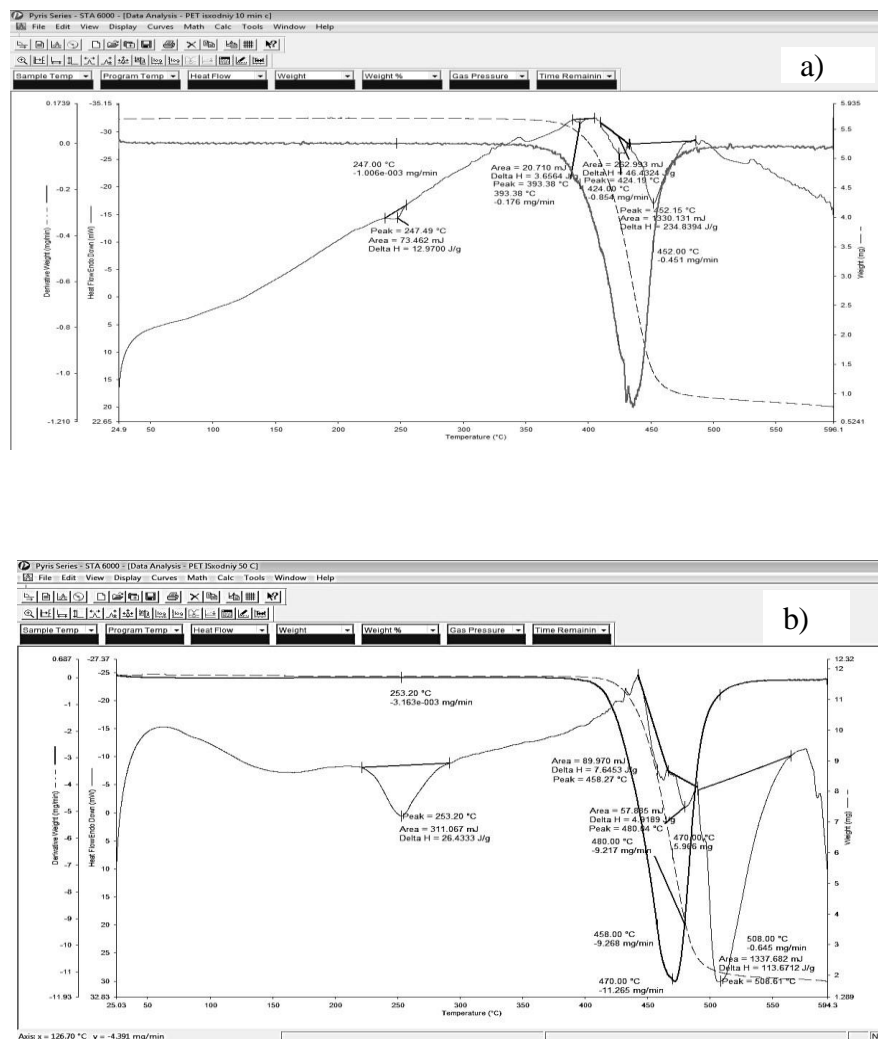
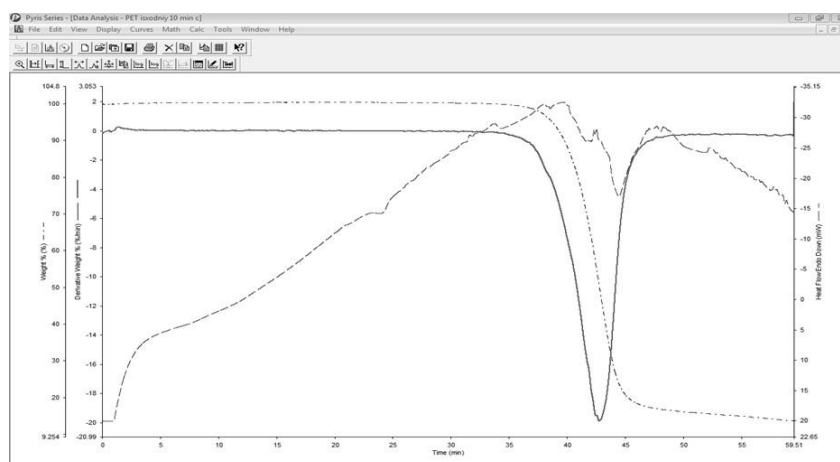
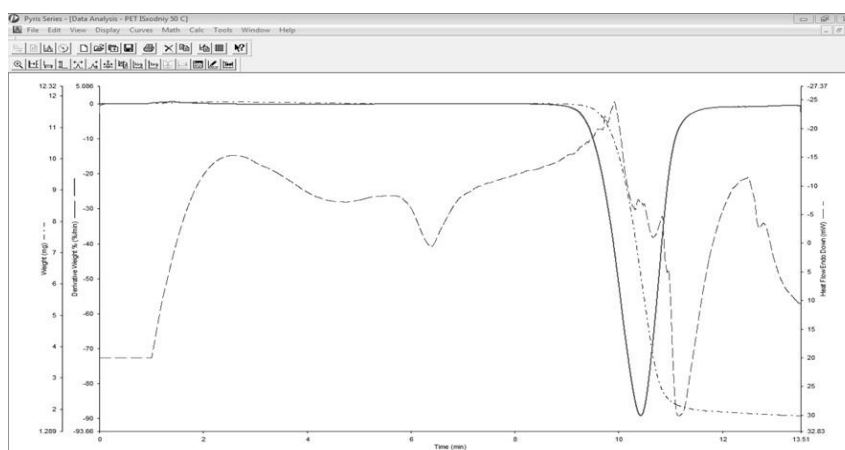


Fig. 2. Temperature dependence of mass loss, mass loss rate and intensity of endothermic peaks during the pyrolysis process of PET 1 polymer, a-10⁰ C/min, b-50⁰ C/min



a)



b)

Fig. 3. Time dependence of mass loss, mass loss rate and intensity of peaks during the pyrolysis process of PET 1 polymer. a-10 °C/min, b-50 °C/min.

Table 2 a.

Values of parameters calculated from derivatographic dependencies

Heat rate, °C/min	Initial mass, mg	Left mass, mg	Conversion, %
10	5,66	4.892	86,36
50	11,76	9,97	84,77

Table 2 b.

Values of parameters calculated from derivatographic dependencies (continuation)

Heat rate °C/min	10	50
Temperature of beginning of destruction, °C	395,5	416,58
Time of beginning of destruction, min	38,731	9,43
Temperature of half destruction, °C	435,52	470.3
Time of half destruction, min	42,7	10,4
Destruction at 510 °C, %	16	17,6
Mass destruction time at 510 °C, min	49,3	11,21
E _a kkal/mol	58,1	59,8

As can be seen from the table (2 a, 2 b), the temperature of the start of destruction changes from 395°C to 416°C as the heating rate increases. As the heating rate increases, the decomposition process takes less time. Thus, the decomposition time at the heating rate of 10 °C/min is 38,7 min, but at 50 °C/min. 9,43 min at the heating rate. The half-destruction temperature also increases from 435°C to 470°C as the heating rate increases. Time of half destruction decreases from 42,7 min to 10,4 min as the heating rate increases. Destruction time at 510°C is 49,3 min at 10°C/min, that decreases up to 11,2 min at 50 °C/min. The activation energy values were calculated from the mass reduction curve at both heating rates based on the Arrhenius equation, and these values were 58,1 kcal/mol at a heating rate of 10 °C/min, and 59,8 kcal/mol at a heating rate of 50°C/min. The melting and destruction processes are listed in the table 3.

Table 3.

Melting and destruction processes

ΔT Δt	Melting, Peak 1				Destruction, Peak 1				Destruction, Peak 2				Destruction, Peak 3			
	dm/dt, mg/sec	T, °C	Area, mJ	H, J/gr	dm/dt, mg/sec	T, °C	Area, mJ	ΔH, J/gr	dm/dt, mg/sec	T, °C	Area, mJ	ΔH, J/gr	dm/dt, mg/sec	T, °C	Area, mJ	ΔH, J/gr
10 °C / min	1,97 E-03	247,0	73,4	13,0	0,2	393,4	20,7	3,7	0,85	424	252,9	46,4	0,5	452,2	1330,1	234,8
50 °C / min	3,16 E-003	253,0	311,0	26,0	9,3	458,0	90	7,6	9,217	480	57,9	4,9	0,6	508	1227,7	113,7



The obtained results show that as the heating rate increases, the decomposition process occurs at higher temperatures, the initiation time of the decomposition process decreases, and the activation energy of the decomposition is approximately equal to 58-60 kcal/mol. Melting temperature is 249-253 °C, enthalpy (ΔH) is about 28-30 J/gr. The area of the peak corresponding to the melting process increases as the heating rate increases. At a heating rate of 50 °C/min, the melting peak area is 358.4 mJ. Two stages of exothermic nature were observed. The first occurs in the temperature range from 377.0 °C to 410.4 °C, and the other in the range of 430.0 °C to 475.7 °C. Initial decomposition can be broadly seen as a two-stage thermal degradation process consisting of primary decomposition and secondary reactions. During the primary steps of decomposition weak aliphatic bonds (non-aromatics) are broken. The secondary phase of pyrolytic, thermal decomposition results in CH_4 and other n-alkanes.

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PLASTİK TULLANTILARIN PİROLİZ PROSESİNİN DERİVATOQRAFİK ANALİZ ÜSULU İLƏ ÖYRƏNİLMƏSİ

E.V. Mirzəzadə, N.İ. Vəlimatova, Ü.A. Quliyeva, M.Ə. Qurbanov

Polietilentereftalat (PET-1) polimerinin müxtəlif qızdırma sürətlərində (10, 50 °C/dəq) piroliz prosesi zamanı temperatur və vaxt kütlə itkisindən, kütlə itkisi sürətindən və endotermik piklərin intensivliyindən asılı olaraq derivatoqrafiya üsulları ilə tədqiq edilmişdir. Parametrlər, temperatur (T) və destruksiyanın başlama vaxtı (t), yarımdstruksiya temperaturu (T) və vaxt (t), 510°C-də kütlə-



nin destruksiya vaxtı (dəq) və destruksiya prosesinin aktivasiya enerjisi hesablanmışdır. Bundan əlavə, ΔH , kvadrat pik (mJ) və kütlə itkisi dərəcəsi ($\Delta m/dt$) kimi ərimə parametrləri hesablanır. Alınan nəticələr göstərir ki, qızdırma sürəti artdıqca, daha yüksək temperaturda destruksiya prosesi baş verir, destruksiya prosesinin başlama vaxtı azalır və parçalanmanın aktivləşmə enerjisi təxminən 58-60 kkal/mol-a bərabər olur. İki ekzotermik təbiətli mərhələ müşahidə edilmişdir. Birincisi 377,0°C ilə 410,4°C arasında, digəri isə 430,0 °C ilə 475,7°C arasında olan temperatur intervalında baş verir.

Açar sözlər: *piroliz, kütlə itkisi, plastik, termoqravimetrik analiz.*

ИССЛЕДОВАНИЕ ПРОЦЕССА ПИРОЛИЗА ПЛАСТИКОВЫХ ОТХОДОВ МЕТОДОМ ДЕРИВАТОГРАФИЧЕСКОГО АНАЛИЗА

Э.В. Мирзазада, Н.И. Валиматова, У.А. Кулиева, М.А. Курбанов

Методами дериватографии исследована зависимость температуры и времени от потери массы, скорость потери массы и интенсивность эндотермических пиков в процессе пиролиза полимера полиэтилентерефталата (ПЭТФ-1) при различной скорости нагрева (10, 50 °C/мин). Оценивались такие параметры, как температура (Т) и время (t) начала деструкции, температура (Т) и время полудеструкции (t), время массовой деструкции (мин) при 510°C и энергия активации процесса деструкции. Кроме того, рассчитываются такие параметры плавления, как ΔH , квадрат пика (мДж) и скорость потери массы ($\Delta m/dt$). Полученные результаты показывают, что с увеличением скорости нагрева процесс деструкции протекает при более высоких температурах, время инициации процесса деструкции уменьшается, а энергия активации распада примерно равна 58-60 ккал/моль. Наблюдались две стадии экзотермического характера. Первый происходит в интервале температур от 377,0°C до 410,4°C, а другой - в интервале от 430,0°C до 475,7°C.

Ключевые слова: *пиролиз, потеря массы, пластик, термогравиметрический анализ.*