Study of thermophysical properties of polyamide-based nanocomposites filled with iron nanoparticles

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Abstract. A complex of studies was carried out to study the thermal analysis of the chemical composition of components and compositions based on polyamide filled with iron particles. The paper presents thermogravimetric and other analysis methods of the developed polymer nanocomposites.

1 Introduction

Most often, the behavior of polymer compositions during heating is characterized by two indicators: deformation resistance during heating and short-term loading - deformation heat resistance and chemical resistance during heating - thermal stability. The temperature of the onset of thermal-oxidative degradation of polymer compositions is estimated qualitatively. The main method for determining resistance to thermal degradation is thermogravimetric analysis (TGA) [1]. Samples of polyamide 6 (PA 6) and composites based on them were studied.

2 Objects and methods of research

The development and manufacturing technology of nanocomposite samples based on polyamide are described in [2, 3]. Solutions of iron pentacarbonyl in hexane were used as initial metal-containing compounds. A typical fabrication procedure for core-shell systems was as follows. A liquid (organic) solution of a metal-containing precursor was added dropwise to a suspension of polyamide microgranules in oil heated to 250–300°C with rapid stirring. Then the mixture was left at this temperature for 30 minutes to complete the reaction. After it was cooled to a temperature of 293 K, the resulting precipitate was separated by decantation and filtration and then washed several times with an organic solvent until the oil residue was removed. The size of metal-containing nanoparticles was determined by transmission electron microscopy (TEM) on a JEOL JEM-1011 microscope

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(80 kV). The composite material was dispersed by ultrasound in ethanol to determine the particle size, and a drop of the resulting suspension was applied to a copper grid coated with formvar.

The elemental composition of the nanoparticles was determined by energy-dispersive X-ray spectroscopy (EDS) on a JED-2300 X-ray spectrum analyzer coupled to a microscope.

High-resolution microscopy was performed using a Philips Techai F30 U-Twin (300 kV, FEG cathode) and CM120 Super Twin (120 kV, tungsten/LaB6 cathode) microscopes with an attachment for analysis EDAX (Weizmann Institute of Science).

3 Results and their discussion

Thermal analysis of composites based on polyamide 6 and nanocomposites based on it showed (Table 1) that the composition contained 20 wt % iron nanoparticles.

The study showed [4] that the initial polymer, in our case, polyamide 6, loses mass by 5% of the initial value (T_1) at 623 K, and for a composition based on it, a decrease in mass by 5% is observed at a temperature range of 635–670 K (Table1). Perhaps this is due to a decrease in the magnitude of the mobility of the molecular chains of the polymer during its reinforcement, which, as is known [5], leads to an increase in its thermal and oxidative stability.

Table 1. Heat resistance of polyamide 6 and composites based on it

Materials	Experimental values				Additive
	T_1	T_2	T_3	T_4	T_0
PA 6	625	669	722	775	-
PA 6 + 4.15 mass.% Fe	636	670	738	795	634
PA + 5.19 mass.% Fe	641	671	749	803	641
PA + 14.36 mass.% Fe	664	673	751	810	650
PA + 20 mass.% Fe	671	676	754	813	657

Note. T_1, T_2, T_3, T_4 - temperatures of 5, 10, 20, and 30% weight loss, K

The calculation of additive temperature values at which 5% weight loss (T_1) occurs shows that they are 4-15 degrees lower than the experimental values, table 1, which suggests the formation of chemical crosslinks between the polymer binder and reinforcing particles. The heat resistance increases most intensively at a content of nanoparticles of 14.36 wt. %, after which this growth slows down.

The latter, apparently, can be explained by the violation of the solidity of the samples due to poor impregnation due to the lack of a binder and its high viscosity. Hence, we can conclude that the optimal content of nanoparticles in the composite based on polyamide 6 is 14.36 wt. %.

The study of thermophysical properties shows an increase in the thermal properties of the nanocomposite based on polyamide 6, relative to the original polymer.

The dependence of the mass loss of nanocomposites on temperature for the studied materials showed (Fig. 1) that the decomposition process of composites proceeds as for the initial polymer. In the first interval, for the studied nanocomposites at temperatures of 373–383 K, a decrease in mass by 1.5–2% is observed, which is associated with the loss of moisture. Then, up to T=575 K, the mass of the samples remains almost unchanged.

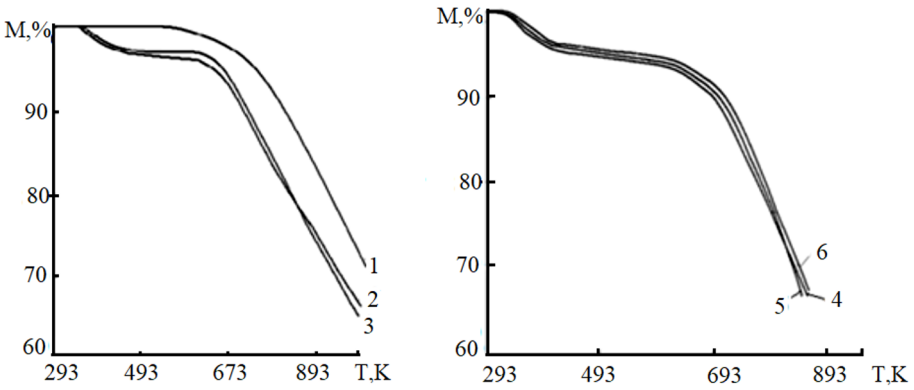

Fig. 1. TG curves of nanocomposites based on polyamide 6 filled with iron nanoparticles containing 4.15 (3); 5.19 (4); 14.36(5); 20 (6) wt. % particles.

The study of thermal properties shown in Fig. 1 shows that after a temperature of 663 K there is a significant loss of mass of both the composition and the polymer, apparently associated with large destruction of the structure; On the DTA curves in the temperature range of 683–873 K, one can see peaks associated with the decomposition of the material; destruction of the material structure fig. 1a.

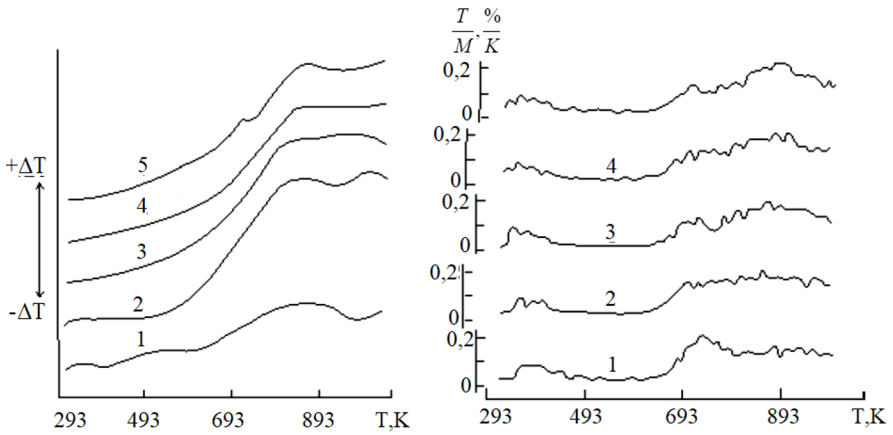

Fig. 2. DTA - (a) and DTG-curves (b) of polyamide 6 (1) and composites based on it containing 4.15 (2); 5.19 (3); 14.36 (4); 20 (5) wt. % particles

To select the most suitable model for describing the thermal degradation of materials based on experimental data obtained using thermophysical analysis, mathematical models were used for various heterostructural thermal processes [6, 7].

Usually, when assessing the kinetic parameters of the processes of thermal decomposition of polymers in a certain temperature range, difficulties may arise that are associated with conflicting data, based on which kinetic equations are built that can characterize various solid-state transformations occurring in the structure of the polymer and the composition based on it. Based on the study of literature [8 - 10], we can say that there is a well-established stereotype of the description of the above processes with the choice as a criterion for evaluating the chemical-technological process of thermal decomposition of the polymer; this is the degree of conversion α, which is determined by the formula [9]:

$$\alpha = \frac{(G_0 - G)}{(G_0 - G_1)} \qquad (1)$$

where G_o is the initial weight of the samples, G is the weight of the samples at the investigated temperature, G_1 is the final weight of the sample.

The time dependence of the degree of conversion can be described by the following differential equation:

$$\frac{d\alpha}{d\tau} = k\, f\,(\alpha) \qquad (2)$$

where τ is time; k is a constant that determines the reaction rate; f(α) is an algebraic function that can be used to describe the mechanism of the thermal process.

The dependence of the reaction rate constant on temperature is described by the well-known Arrhenius equation [8]:

$$k = Ze^{-\frac{E_{akm}}{RT}} \qquad (3)$$

where R is the universal gas constant equal to 8.31 J/mol K; Z is a pre-exponential factor; E_{act} is the apparent activation energy, kJ/mol.

Taking into account dependence (2), equation (1) can be represented as:

$$\frac{d\alpha}{d\tau} = Ze^{-\frac{E_{akm}}{RT}} f(\alpha) \qquad (4)$$

Two methods are known when describing the kinetic analysis of a nonisothermal dependence obtained with gradual heating: integral and differential. We applied the Coates-Redfern method [11], described by integral kinetic equations, allowing us to investigate a nonisothermal reaction in a very short time interval as an isothermal. After integration and logarithm, the kinetic dependence (3) takes the form [12]:

$$\lg\frac{k'(\alpha)}{T^2} = \lg\frac{ZR}{dT/d\tau \cdot E_{akm}}\left(1 - \frac{2RT}{E_{akm}}\right) - \left(\frac{E_{akm}}{2.3RT}\right) \qquad (5)$$

$$\text{Where } k'(\alpha) = \int_0^n \frac{d}{df(\alpha)};\ k'(\alpha) = \frac{(1-\alpha)^{1-n} - 1}{n-1}\ at\ n \neq 1; \qquad (6)$$

$$k'(\alpha) = -\ln(1-\alpha)\ \ where\ n = 1\ \ \ (where\, n - reaction\, order)$$

In our study, the equation describes the mechanism in heterostructural materials.

Based on the experimental data on α and T, the dependence k`(α) was calculated as the one that best describes the process with the real reaction rate [9].

Determination of the expected mechanism and kinetic parameters of thermal degradation processes for the studied nanocomposites was calculated using the integral kinetic equations of various mechanisms.

The coefficient of correction of the direct dependence of r on S in the selected equations in the coordinates of the Arrhenius equation and the minimum of the function in our case served in the choice of a mathematical model:

$$S = f\{\alpha(\tau), \Delta T(\tau), \Delta T(\tau), E_{act}, Z\} \qquad (7)$$

$$S = \sqrt{\sum_{i=1}^{m} \frac{(\alpha_{\exp} - \alpha_{rac})^2}{m}} \qquad (8)$$

where m is the amount of experimental data; T is temperature; E_{act} activation energy; Z is a pre-exponential factor.

The final parameters of thermal destruction of nanocomposites were calculated, such as activation energy, pre-exponential coefficient, correlation coefficient, etc., which are given in Table 2.

High correlation coefficient values were obtained according to the equations (7–11, 15–16), which served as the main criterion for choosing them with a minimum C index. Analysis of the data in Table 2 showed that the most suitable for describing the process of thermal destruction of nanocomposites based on polyamide 6 corresponds to equation (7, 8), which describes the nucleation process. As is known [13], during the thermal destruction of polymers containing aromatic nuclei in the chain, the main stage is the nucleation of a chain of molecules. This is also confirmed by calculations since Eq. (7) describes the process of random nucleation: polyamide undergoes monomolecular transformations, resulting in radicals forming from valence-saturated molecules.

Table 2. Calculated kinetic parameters of process of thermal degradation of materials

Mathematical model-process	r	$S.10^{-1}$	$Eакт.$,kJ/mol	lgZ
1	2	3	4	5
PA 6				
(7)	1.000	0.032	51.18	0.31
(8)	1.000	0.021	20.55	1.62
(9)	0.995	0.131	71.32	1.94
(10)	0.993	0.130	79.19	2.63
(11)	0.999	0.058	96.75	3.99
(12)	0.999	2.642	43.33	0.22
(13)	0.999	3.681	25.52	-0.96
(14)	0.998	4.072	16.63	-1.52
(15)	0.996	0.131	112.41	4.45
(16)	0.999	0.522	136.35	6.39
(17)	1.000	3.241	168.44	8.50
(18)	0.999	2.593	146.86	6.76
PA 6 + 4.15 mass.% Fe				
(7)	0.996	0.095	52.75	-0.15
(8)	0.994	0.095	26.37	1.84
(9)	0.988	0.180	75.50	1.76
(10)	0.985	0.208	84.74	2.53
(11)	0.977	0.260	98.96	4.30
(12)	0.972	2.171	42.98	0.40
(13)	0.964	2.992	25.32	0.86
(14)	0.953	3.302	16.50	1.43
(15)	0.997	0.034	115.48	3.54
(16)	0.993	0.485	121.74	5.75
(17)	0.986	3.472	159.48	8.42
(18)	0.991	2.761	134.02	6.30

Continuation of Table 2

Mathematical model-process	r	$S.10^{-1}$	$E_{акт.}$,kJ/mol	lgZ
1	2	3	4	5
PA 6 + 5.19 mass.% Fe				
(7)	0.998	0.072	59.83	-0.43
(8)	0.996	0.072	34.85	1.97
(9)	1.000	0.033	76.58	1.38
(10)	0.999	0.053	87.37	2.11
(11)	0.997	0.094	99.48	3.76
(12)	0.996	2.022	40.22	0.12
(13)	0.994	2.793	23.49	-1.02
(14)	0.992	3.082	15.10	1.56
(15)	0.998	0.071	119.73	2.99
(16)	1.000	0.371	124.86	5.09
(17)	0.999	3.542	150.78	7.57
(18)	1.000	2.752	126.57	5.57
PA 6 + 14.36 mass.% Fe				
(7)	0.994	0.106	62.82	-0.95
(8)	0.992	0.106	41.40	-2.25
(9)	0.987	0.123	78.63	0.80
(10)	0.991	0.138	92.16	1.50
(11)	0.988	0.170	101.88	3.13
(12)	0.984	1.861	35.92	-0.21
(13)	0.979	2.562	20.60	-1.24
(14)	0.970	2.822	12.95	-1.72
(15)	0.995	0.105	125.68	1.94
(16)	0.994	0.471	129.47	3.94
(17)	0.992	3.602	134.42	6.54
(18)	0.994	2.791	110.81	4.40
PA 6 + 20 mass.% Fe				
(7)	0.999	0.052	64.21	-0.84
(8)	0.996	0.052	42.08	-2.20
(9)	0.991	0.136	78.10	1.16
(10)	0.988	0.162	98.21	1.99
(11)	0.980	0.215	102.03	3.96
(12)	0.975	1.782	40.99	0.22
(13)	0.967	2.462	23.98	-0.95
(14)	0.957	2.711	15.47	-1.50
(15)	0.999	0.052	128.46	2.15
(16)	0.996	0.362	135.23	4.40
(17)	0.989	3.581	146.48	7.34
(18)	0.994	2.869	118.52	5.05

4 Conclusions

1. A nanocomposite material based on polyamides - PA 6, filled with iron nanoparticles, has been created, which consists of a scientifically based choice of polymer and filler, and a technology for preparing the composition has been developed.

2. Analysis of thermophysical studies showed that for composites based on PA 6, an increase in the degree of filling with iron nanoparticles from 5 to 20 wt. % leads to a decrease in heat capacity by 1.2 times, an increase in thermal conductivity, and thermal diffusivity - by 1.3 times.

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