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MELTING AND THERMODESTRUCTION PROCESSES IN THE POLY(ETHYLENE)-NANOCRYSTALLINE NICKEL SYSTEM

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Abstract

Composite materials (CM) based on poly(ethylene) (PE) and nanocrystalline nickel (Ni) have been produced. The effect of the content of nanocrystalline Ni and processes of structure formation of its particles on a melting temperature (T_m), interval of melting, true melting heat (ΔH_m), degree of crystallinity (χ) as well as characteristics of CM thermodestruction have been determined by DTA and thermogravimetry techniques. It was found that these characteristics are changed non-linearly when the content of nanocrystalline Ni increases. The most efficient influence of Ni on the above mentioned characteristics was observed for its low content (0.01 volume part of Ni). It was shown that a formation of a branched multifractal cluster of nickel above a percolation threshold favored a decrease in T_m, ΔH_m, χ of filled PE and a majority of thermal characteristics of CM thermodestruction as well.

Keywords: composites, melting, nanocrystalline nickel, poly(ethylene), thermodestruction

Introduction

Lately, an increased interest has been observed in the preparation and investigation of properties of metal-polymer composite materials (CM) with nano-sized particles as well as a nanocrystalline structure of functional components [1, 2]. The great attention to those materials is due to their practical usage in radio-technique, radioelectronics, microelectronics, catalysis. The composites with nano-sized metallic particles are known [1–3] to be used in registrating elements of devices, devices having a high density of information record, miniature sensors of indication of gas-like compounds.

One of the promising components to produce such materials and articles is a nanocrystalline nickel (Ni). Previously [3], we showed that its application in CM on the basis of poly(ethylene) (PE) made it possible to increase an electric conductance of CM samples (in comparison to similar compositions that contain a polycrystalline Ni) and allowed to decrease a percolation threshold (θ_c) in the PE–Ni system.

In order to work out an optimum technological regimen for producing these materials and their successful usage, along with data on mechanical and electric proper-

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ties, it is necessary to know more about melting processes and thermodestruction of polymer (PE) which enters the CM. The upper level of performance of these materials depends on the above described processes as well, besides a thermal regimen of CM processing into articles.

Up to date, clear-cut regularities of changing melting and thermodestruction characteristics affected by fillers in polymeric CM have not been established [4–6], therefore the use of a not enough studied nanocrystalline nickel in composition requires setting up of new studies relative to the influence of this component and processes of its structure formation on the above mentioned processes in polymeric composite systems (PCS).

The purpose of the study is to determine the influence of the content of nanocrystalline Ni on melting processes and polymer thermodestruction in CM in the model system poly(ethylene)-nanocrystalline Ni.

The data obtained are interpreted from the viewpoint of the conception elaborated by us earlier [7] which is based on a cluster approach and usage of percolation effects for formation of polymer composition systems, principles of similarity and self-similarity of clusters, on ideas upon formation of structures of PCS fractals. The conception allows to establish a relation between parameters of CM properties for a definite content of a filler and macrostructural characteristics of PCS.

Experimental procedures

To prepare CM we used powders of high density PE and nanocrystalline nickel powders (a particle size 0.1–0.5 micron, a surface area 1.6 $m^2 g^{-1}$, a middle size of nanocrystallites 10–12 nm). The latter was prepared by means of a chemical reduction of nickel chloride with sodium hypophosphite (NaH_2PO_2) in the presence of triethanolamine in alkaline medium as described in [3]. The powders of composition mixes were prepared by a special technology that included a stage of a concurrent dispergation of finely divided PE and Ni particles using the ultrasound apparatus UZDN-A [3]. The content of Ni in the composition was altered from 0 to 1 volume part (0 to 100 mass%). The composition powders that have been produced in this way, have a high degree of uniformity and are not stratified while compacting in spite of the fact that PE and Ni densities are differing nine times.

CM samples having a thickness of 0.5–0.7 mm were prepared from these composition powders pressing them on heating (up to 170°C).

The mean size of nickel particles and its clusters were estimated by optical and electron microscopy, a middle size of nickel crystallite particles was estimated on the basis of X-graphy data studying its powders by means of X-ray diffractometer DRON-UM-1 [3]. The method of differential thermal analysis and thermogravimetry was employed to study processes of melting and thermodestruction in CM based on PE and Ni. Curves of DTA, TG, and DTG were recorded with derivatograph of Q-1500 D type (MOM company, Budapest). A rate of heating was 5°C min^{-1} in the temperature range of 20–1000°C. Al_2O_3 was used as a standard. For the calculation of average values of melting and thermodestruction characteristics we used the data of 3–5 DTA curves of CM specimens of each concentration, and of seven curves for nanocrystalline Ni.

The melting temperature T_m, thermal effect of melting ΔQ were determined by the procedure described in [6, 8]. The method of area restrictions on curves suggested in [9] was used. To calculate true melting heats ΔH_m (change of enthalpy in PE going from the crystalline condition into the liquid one) of PE and CM samples, a DTA curve of benzoic acid purified by sublimation method was recorded; its melting heat is known (33.9 cal g^{-1}) [8]. The true melting heats for samples of unfilled PE and CM have been established by using a thermal effect of melting of benzoic acid as standard for calibration. To calculate a degree of crystallinity (χ) one assumed that ΔH_m^* of a fully crystallized PE amounted to 64.6 cal g^{-1} [8]. A value of χ, % was estimated by the expression:

$$\chi=\frac{\Delta H_m}{\Delta H_m^*}100$$

Coefficients of variation (v) for calculation of T_m and χ were 0.4 and 1.4%, respectively. v was calculated similarly to the described in [10].

To evaluate processes of oxidation and thermodestruction in unfilled and filled PE one used such parameters: T_0 – the temperature that characterizes beginning of PE oxidation (the temperature at which a sharp elevation of DTA branch takes place after ending melting processes); T_1 corresponds to the first exothermal maximum in the DTA curve; T_2, $T_3^{'}$, T_3 are responsible for major deep endothermal minima in the DTA curve; T_4 – for a start of mass loss; T_5 – for a loss of 10% mass of CM samples (a curve of TG); T_6 – for a maximum rate of mass loss (a curve of DTG).

The general temperature characteristics of Ni oxidation are as follows: $T_0^{'}$ – the temperature that characterizes beginning of the intense oxidation of Ni (the arbitrary temperature at which a sharp elevation on TG curve of the Ni sample occurs); $T_1^{'}$ is responsible for a main exothermal maximum of Ni oxidation on DTA curve.

The methods of determination of electric characteristics of CM were used to explain the obtained results and to evaluate formation processes for a macrostructure of components. The specific volume electric resistance of CM electro-conductive samples (ρ_{CM}) was measured by the four-probe method under a direct current (GOST 20214-74). Electric resistance of non-conducting CM specimens ($0\leq\theta<0.1$ volume part of Ni) was calculated by GOST 6433.2-71.

Results and discussion

Figures 1 and 2 and Tables 1 and 2 give the DTA and thermogravimetry data relative to melting and thermodestruction processes for samples of unfilled PE, CM having a different content of the nanocrystalline Ni and the nanocrystalline Ni (without polymer) as well. Figure 3 presents the dependence of a logarithm of the specific volume electric resistance ($\lg\rho_{CM}$) of CM samples on a volume content of the nanocrystalline Ni. The ρ_{CM} values (dots - •) were measured for electro-conductive CM samples at 20°C by the four-probe method. The ρ_{CM} values (dots - o) were determined for non-conductive CM samples by standard method (GOST 6433.2-71). Figure 4 represents microphotograph of CM based on PE and the nanocrystalline Ni that has been obtained with the aid of a scanning electron microscope. The content of the nanocrystalline Ni in CM is 0.37 volume part.

As seen from Fig. 1, clear endothermal peaks are observed in DTA curves for unfilled PE and CM with a different Ni content, that are responsible for PE melting processes. For the unfilled PE (T_m=130°C), the temperature interval of melting is 62°C, the crystallinity degree is 65.7% that is consistent with literature data [7]. In Ni DTA, TG and DTG curves in the temperature interval of PE melting (T<160°C), thermal effects are absent.

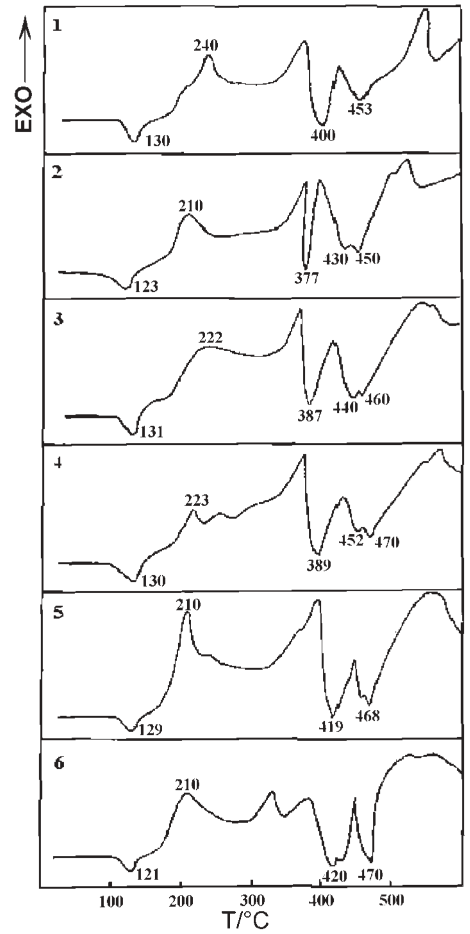

Fig. 1 DTA curves of samples of the unfilled PE (1) as well as CM with a varying content of nanocrystalline Ni, vol. part: 2 – 0.01; 3 – 0.033; 4 – 0.1; 5 – 0.24; 6 – 0.37

Table 1 Effect of the content of nanocrystalline nickel on characteristics of PE melting

Ni content/ vol. part	Temperature of melting/°C	Melting interval/°C	True melting heat ΔH_m/cal g^{-1}	Degree of crystallinity/%
0	130	88–150 (62)	42.4	65.7
0.004	130	87–149 (62)	42.3	65.6
0.01	123	87–145 (58)	37.1	57.4
0.03	132	87–150 (63)	43.7	67.6
0.10	130	87–155 (68)	39.2	60.6
0.24	129	95–148 (51)	38.0	58.8
0.37	121	95–145 (50)	37.8	58.6

Analysing Table 1 it is seen that values of the melting temperature T_m, the melting interval ΔT_i, ΔH_m and crystallinity degree are changed non-linearly with increasing the content of nanocrystalline Ni. Most efficiently, these characteristics are affected by low additives of Ni. Thus, when a content of Ni is small (0.01 volume part) T_m decreases by 7°C, ΔT_i – by 4°C, a crystallinity degree – by 8% in comparison to the unfilled PE. CM with a content of 0.03 vol. part of Ni have the highest T_m and the crystallinity degree (χ=67.6 %). A further increase in the Ni content (from 0.1 to 0.37 volume part) leads to a decrease in T_m. In the concentration range of Ni 0.24–0.37 vol. part ΔT_i=50–51°C, χ is in limits of 58.6–58.8%.

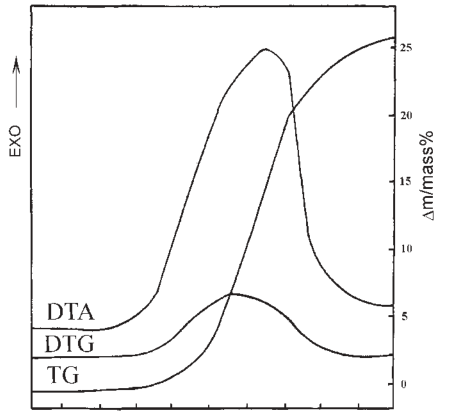

Fig. 2 DTA, TG and DTG curves of a nanocrystalline nickel

It is known [4, 5], that various factors influence processes of melting and crystallization of polymers: the chemical nature of a polymer and filler, a characteristic of its surface, a size and shape of particles, structurizing properties of a filler, processing conditions of CM production and other factors. However, in the concrete polymer-filler system, cooperative processes of cluster formation of components play an important role under the certain technological regime of CM production [6]. Thus, formation of the continuous branched cluster of a thermoexfoliated graphite in the composition of polypropylene – thermoexfoliated graphite systems results in amorphization of polypropylene [6]. A sensitive method for studying processes of formation of intercontact links between conducting particles of a filler, and formation of its continuous structures is the method for definition of the electric conductance.

As seen from Fig. 3, the $\rho_{CM}(\theta)$ dependence has a jump-like character. The critical concentration of Ni, a percolation threshold (θ=0.1 vol. part), divides a dependence $\rho_{CM}(\theta)$ into conductive and non-conductive regions. We have shown in [3] that in the concentration range of Ni $0<\theta<\theta_c$, the structure of CM samples represents a matrix of PE that includes isolated clusters of Ni particles (inclusions). Clusters of Ni aggregate when approaching to the critical concentration. Provided that $\theta=\theta_c$=0.1 vol. part, a continuous chain-like structure (a continuous endless cluster (CEC)) is formed that passes through the whole sample causing its conductance. Above a percolation threshold $\theta_c<\theta<1$, CEC of Ni particles influences crystallization processes in the PE cluster while forming it from the melt.

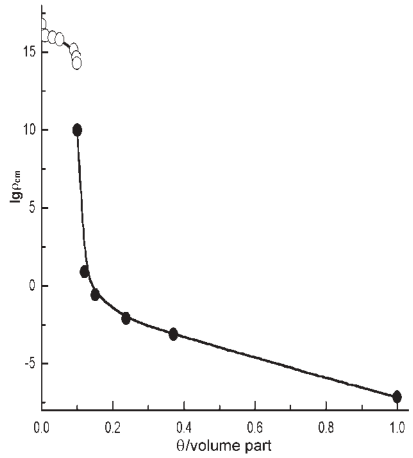

Fig. 3 The dependence of a logarithm of the specific volume electric resistance of CM samples (lg ρ_{CM}) on the volume content of a nanocrystalline Ni. The ρ_{CM} values were mearured for CM samples: o – in accordance with GOST 6433.2-71, • – by GOST 20214-74

The investigation using a scanning electron microscope has shown that a spherolytic structure is typical of the filled PE and PE at low degrees of filling (θ= 0.01 vol. part) of Ni. It was assumed that individual particles of the nanocrystalline Ni or energetically active patches of its small clusters could be nuclei of structure formation.

Table 2 Effect of the content of nanocrystalline Ni on characteristics of thermodestruction of PE and compositions on its basis

Ni content/ vol part	Temperature of beginning of PE oxidation T_0/°C	Temperature of exothermic maximum T_1/°C	Temperature of endothermic minima, DTA/°C		Temperature of mass loss T_4/°C	Temperature of 10% mass T_5/°C	Max. rate of mass loss T_6/°C
			T_2	$(T_3^{'})T_3$			
0	170	240	400	453	240	387	465
0.01	167	210	377	(430) 450	220	383	450
0.03	172	222	387	(440) 460	245	390	460
0.10	170	223	389	(452) 470	240	378	470
0.24	169	210	419	468	230	340	452
0.37	165	210	420	470	215	277	445

However, the existence of a great number of ultradisperse particles in the nanocrystalline Ni leads to the enlargement of defectness of a crystalline PE structure that causes a decrease in T_m, ΔH_m, and crystallinity degree. Increasing the Ni content to 0.03 vol. part in the filled PE favored aggregation of fraction of ultradisperse particles of the filler, as well as formation of less defect spherolites. As a result, T_m, ΔH_m and χ increase. Together with it, a further increase in the Ni content up to 0.1 vol. part in CM and the formation of Ni CEC is favorable for a rise of its high surface area and increasing in a number of defects in the PE crystalline structure. In addition, the formation of continuous extended multifractal clusters from Ni particles can considerably decrease a mobility of patches of polymer chains near the surface of Ni cluster owing to adsorption interaction with a filler surface. As a result of the above mentioned processes, a size of PE crystallites (a height of lamellae folds) diminishes and the values of T_m, ΔH_m and χ diminish, too. The results obtained are consistent with data of studies [4–6]. It is known [4, 5] that T_m diminishes when sizes of polymer crystallites decrease. It is shown in [5] that an increase in the contribution of excessive free energy on end faces of a crystallite as its height decreases leads to diminishing melting enthalpy. So, lowering the values of ΔH_m and T_m in the $0.1<\theta\leq 0.37$ range while increasing the volume content of Ni may be associated with this factor. Thus, processes of cluster formation of particles of nanocrystalline Ni essentially influence the melting characteristics of the filled PE.

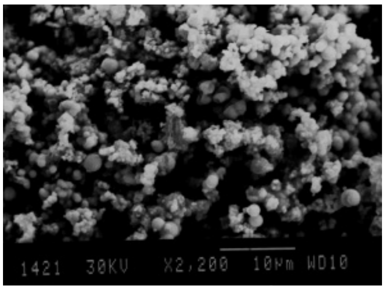

Fig. 4 Microphotograph of the composite material based on polyethylene and nanocrystalline Ni at its content θ=0.37 volume part. Ni particles on the microphotograph have a white color and form a continuous branched percolation cluster

After the melting processes at temperatures of 165–170°C in unfilled and filled PE are completed, an abrupt rise of a branch in a DTA curve is observed that is responsible for the beginning of PE oxidation. Under conditions of higher temperatures, on the DTA curves of the above-mentioned materials there appear a series of exothermal maxima and endothermic minima alternating with each other. The first exothermal maximum in the unfilled PE is located near 240°C and coincides by value with the temperature beginning of loss of a sample mass (T_4). The 10% mass loss of the PE sample occurs at temperature T_5=387°C. Above this temperature two deep minima are observed: T_2 and T_3.

It is known [8] that the emergence of the endothermic minimum for T_2=400°C is due to processes of disruption of weak bonds in PE macromolecules, and processes of

PE depolymerization take place in the temperature range of a T_3 minimum. As seen in [11], primary products of PE oxidation are hydroperoxides which disintegrate afterwards forming oxygen-containing compounds. Oxidation of PE is described by a radical-chain scheme [11]. Reactions with participation of hydroperoxide groups and radicals lead to the rupture of molecular chains, i.e., to the destruction of the polymer.

It was shown in [11] that a surface of dispersed metals even in the presence of protective substances, contains their adsorbed and chemisorbed molecules as well as M–OH, M–H, M–O groups (where M is metal). These groups are formed when the surface is in contact with the atmospheric air. The great majority of these surface groups and combination may play an active role while contacting with polymer molecules and, at a certain extent, influence their thermal stability. Moreover, the most of these compounds are characterized insufficiently high thermostability and a tendency towards various transformations on the metal surfaces at higher temperatures takes place.

Analysis of DTA, TG and DTG curves (Fig. 2) testifies that there are no peaks of thermal effects in the interval of temperatures of 20–360°C. Indeed, we know from literature sources [10] that Ni loses its ferromagnetic properties at the temperature – T=359°C (at Curie point). But this transition is of second order and is not accompanied by jumping variation of the enthalpy (ΔH=0); it is only an abnormal change of heat capacity which happens [9, 10]. In the area of ferromagnetic transition (320–360°C) we observe a change of DTA curve slope (Fig. 2). However, in this particular case ferromagnetic transition cannot be observed in pure form due to Ni oxidization. Thus, increase of the Ni sample mass is observed in the interval of temperatures of 360–385°C (Δm, mass%, Fig. 2, TG curve), that is accompanied by a rise of exothermic processes in DTA curve. A maximum on DTA and DTG curves corresponds to 658°C, and its occurrence is due to oxidation of Ni. Thus, a calculation showed that in the case of reaction

$$2Ni+O_2=2NiO$$

the sample mass after oxidation up to T=1000°C is responsible for the formation of 95% NiO.

The existence of a considerable exothermal effect for samples of a nanocrystalline Ni influences somewhat the appearance of CM DTA curves for its content of θ>0.1 vol. part. Also, a slight growth of the sample mass due to PE oxidation is observed, if θ=0.24 and θ=0.37 vol. part in TG curves for T=190°C and T=182°C.

Low additions of Ni influence most efficiently. Thus, introducing 0.01 vol. part Ni into the composition (Table 2) results in a reduction of respective temperatures that characterize thermodestruction processes as compared to the unfilled PE: T_1 – by 30°C, T_2 – by 23°C, T_3 – by 3°C, T_4 – by 20°C, and T_6 – by 15°C.

An increase of Ni content from 0.01 to 0.37 vol. part causes an increase of T_2, T_3 and a non-linear change of T_4, T_5, T_6 in this concentration range. Maximum values of T_4 and T_5 are observed for CM that has 0.03 vol. part Ni. It should be noted that samples of this composition themselves have the highest values of melting temperature (T_m=132°C) and degree of crystallinity (χ=67.6%) in the CM concentration range of Ni from 0 to 0.37 vol. part. It is known [8, 11] that amorphous samples of polymers are subject to destruction to a greater extent than crystalline ones. So, a rise of T_4, T_5 for the above mentioned sample could be due to an increase in the crystallinity degree. However, processes of CM thermodestruction depend on many factors, especially on condition of formation and technologic process parameters [11, 12]. In our opinion, for a present system, such factors influence thermodestruction processes significantly: a Ni content, a catalytic process of PE oxidation in the presence of Ni, a degree of PE crystallinity in CM, a degree of Ni oxidation, an effect of structure formation of its particles, temperature. As our studies have shown, the catalytic process of PE oxidation occurs most intensely under conditions $170<T<350$°C. It is evidenced by decreasing T_1 values of CM samples (in the Ni concentration range studied) as compared to the unfilled PE, decreasing T_2 in the Ni content range from 0.01 to 0.1 vol. part as well as increasing the sample mass of CM at T=180–190°C and Ni content within the ranges 0.24–0.37 vol. part. Under temperatures of $T>360$°C, an intense oxidation of Ni itself occurs (Fig. 2). It is favorable for slowing processes of PE depolymerization, increasing T_2 and T_3 in CM in the range of increased Ni content (0.24–0.37 vol. part) as compared to the unfilled PE.

Along with processes of the catalytic PE oxidation in the presence of Ni, the general characteristics of thermodestruction of CM based on Ni are influenced by effects of formation of proper Ni structures (Table 2). Under conditions of a low Ni content (θ=0.01 vol. part) its particles (inclusions) are uniformly distributed in a PE matrix. Although dendritic paths with supply of oxygen are absent for this concentration, but all general characteristics of thermodestruction of CM samples diminish as compared to the unfilled PE. This is explained by both a catalytic effect of Ni on PE oxidation and a decrease in a crystallinity degree of PE.

Aggregation of clusters near a percolation threshold θ_c leads to a rise of temperatures that characterize CM thermodestruction processes in connection with the increase in χ of these samples compared to respective characteristics of the previous CM sample (θ=0.01). Formation of the branched CEC for $\theta>\theta_c$ favours to a fall in T_0, T_1, T_4, T_5, T_6. This is explained by the formation of continuous paths for transportation of oxygen into a sample in the composition containing Ni, θ=0.24–0.37 vol. part. It should be noted that only temperatures T_2 (which corresponds to a rupture of weak bonds in PE macromolecules) and T_3 (of depolymerization) increase with increasing Ni content in CM from 0.01 to 0.37 vol. part. Such a rise, most probably, is due to the fact that a partial oxidation of Ni in CM occurs at $T>360$°C (owing to formation of dendrite paths by which an oxygen in PE is transported). Ni clusters take oxygen from CM that favors to a rise of T_2 and T_3. In turn, for contents of $\theta>0.1$ vol. part, a marked growth of Ni mass at the expense of oxidation (Fig. 2, curve of TG) is observed after completion of processes of PE thermodestruction ($T>500$°C). Namely, PE at $T<500$°C prevents a Ni oxidation.

Conclusions

With the use of DTA and thermogravimetry techniques it has been shown that T_m, ΔH_m, χ values and characteristics of thermodestruction varied non-linearly with the increase of content of nanocrystalline Ni. This was explained by a complex influence of different factors on these characteristics. The most efficient effect of nanocrystalline Ni on melting parameters (T_m, ΔH_m, χ) as well as on general temperature characteristics of thermodestruction were observed when its content is low (0.01 vol. part). It was suggested that the catalytic process of PE oxidation with participation of Ni ran most intensely at low Ni concentrations and temperatures, $170<T<350$°C. An intense oxidation of Ni itself at $T>360$°C favored to slowing down endothermic processes of PE depolymerization, increasing T_2 and T_3 values of CM samples with a content of 0.24–0.37 vol. part Ni as compared to unfilled PE. It was found that processes of cluster formation had a considerable influence on melting and thermodestruction characteristics of the filled poly(ethylene). It was shown that the formation of the branched multifractal cluster of nickel above a percolation threshold was favorable for decreasing T_m, of the filled PE as well as for the characteristics of thermodestruction: T_0, T_1, T_4, T_5 and T_6.

The data obtained might be used to prognosticate melting processes and thermodestruction of the above mentioned CM for production of functional materials.

References

1 A. D. Pomogailo, A. S. Rosenberg and I. E. Uflend, Nanoparticles of Metals in Polymers, Khimiya, Moscow 2000, p. 672.
2 H.-G. Busmann, B. Gunther and U. Meyer, Fourth International Conf. on Nanostructured Materials, Nano’98, Stockholm, Sweden, 1998, p. 296.
3 L. S. Semko, V. M. Ogenko, S. L. Revo, V. M. Mischenko, M. P. Semenko, O. I. Oranska and K. O. Ivanenko, Dopovidi NAN Ukraine, N6 (2001) 86.
4 V.P. Solomko, Filled crystallized polymers, Naukova Dumka, Kiev 1980, p. 264.
5 V. F. Babich, M. T. Bryk and R. A. Veselovsky, Physical chemistry of multicomponent polymer systems: In two vol./ Edited by Yu.S. Lipatov, Vol.1. Filled polymers, 1986, p. 376.
6 L. S. Semko, L. S. Dzyubenko, I. G. Chernysh and V. L. Kocherov, Polimery (Poland), T. 42 (1997) 380.
7 L. S. Semko, Khimichna Promyslovist’ Ukrainy, N4 (1997) 46.
8 B. Ke, Newer Methods of Polymer Characterization, New York, London, Sydney 1964.
9 L. G. Berg, Tutorial of Thermography, Nauka, Moscow 1969, p. 395.
10 J. Šesták, Theory of Thermal Analysis. Physico-thermal properties of solid inorganic matters: Translation from English – Moscow, Mir 1987, p. 455.
11 M. T. Brick, Destruction of filled polymers, Khimiya, Moscow 1989.
12 L. S. Semko, L. S. Dzyubenko and V. L. Kocherov, J. Therm. Anal. Cal., 62 (2000) 485.