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## THE STUDY OF THE PROCESS OF MODIFICATION OF RECYCLED POLYETHYLENE WITH HEXAMETHYLENETETRAMINE

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**Abstract.** Pyrolysis mass-spectrometry (PMS) has been employed to investigate the process of thermal destruction of the secondary polyethylene (SPE), which was modified using hexamethylenetetramine (HMTA). The introduction of powdered HMTA in the polymer matrix on the basis of SPE, with a view to its mechano-chemical modification, leads to structural changes in the polymer matrix, to the formation of cross chemical bonds between macromolecules in SPE with the participation of the ionic fragments of the collapse of HMTA, and to high content of gel-fraction of compositions with increasing of HMTA content in them.

**Keywords:** secondary polyethylene, hexamethylenetetramine, modification, composites, pyrolysis mass spectrometry.

### 1. Introduction

The problem of environmental pollution by industrial and household polymeric wastes calls for the development of scientific researches on the creation of composite materials based on them.

Polyolefins, in particular PE, dominate in the total mass of polymer wastes. The influence of various external factors leads to the significant structural and chemical changes in PE, which complicate its recycling and reduce its physical-mechanical characteristics. The analysis of trends in fundamental and applied research in the field of polymer materials and polymer materials with valuable physical and mechanical and chemical properties shows that the most promising way of using of polymeric wastes is the creation of new modified materials on their basis [1-6]. In this regard, the research to develop ways and methods of secondary modification of thermoplastics, in particular, SPE, which allow to improve its technological and operational characteristics of composite materials based on it, is topical. One of the promising directions of

SPE modification is the introduction of compatibilizers, polymer additives with functional groups, *etc.* Our previous studies [7, 8] have demonstrated the possibility of obtaining composites on the basis of SPE with superior physical and mechanical properties, through the use of modifying additives of HMTA. However, the mechanism of the modifying action of HMTA on the structure of the SPE has not been fully determined.

Based on the above, the aim of this work was to investigate the PMS method and to analyze structural changes which occur in SPE during its mechano-chemical modification using HMTA, to obtain information about the chemical structure of a modified SPE on the composition of the products of its thermal degradation, specific intensity and qualitative composition of volatile products of pyrolysis. This will make it possible to explain the mechanism of the process of SPE modification and is important and relevant at search of new approaches to the development of modified polymeric materials based on polymer waste using existing chemical products.

### 2. Experimental

The objects of investigation were samples of compositions on the basis of SPE, which were mechano-chemically modified with reactive compounds of hexamethylenetetramine (HMTA) –  $C_6H_{12}N_4$  (Khimlaborreactiv, Ltd, Ukraine). Secondary (from agricultural film) low density polyethylene (SPE) in the form of granules (according to the technical standards of Ukraine), which have been previously crushed to a particle size of less than 2 mm, was used for preparation of compositions. Content of modifying additives in the compositions was changed in the range from 0.1 to 30 wt %. Pre-cooked sample of SPE pellets and powder GMTA were mixed in appropriate proportions and intensively stirred. Mechanical mixture of SPE-GMTA was filed in screw laboratory extruder (a screw diameter is

25 mm and a screw ratio of length to diameter ( $L:D$ ) is 15), that has a download area with forced cooling and three areas with adjustable heat mode. The temperatures in the heating zones were: zone I – 408 K, zone II – 428 K, and zone III – 438 K. Compositions were subjected to doubling formation and effect of thermal and shear deformations. The resulting extrudate was ground and the samples for research were formed from it by the method of direct pressing.

The study of the composition of volatile products and the intensity of their allocation during the pyrolysis of samples was performed by the method of pyrolysis mass-spectrometry (PMS) using MX-1321 mass-spectrometer. This method gives the opportunity to assess the chemical transformations of organic matter on the composition of the products of pyrolysis [9, 10], provides a definition of the components of gas mixtures in the range of mass numbers 1–4000, that is programmed in the temperature range of 298–673 K. Before research samples were vacuumized ( $1.33 \cdot 10^{-4}$  Pa) for 30 min at 298 K directly in the cell of the mass-spectrometer. This pressure was maintained during the experiment. The heating rate was  $(6 \pm 1)^\circ/\text{min}$ . Accuracy sample temperature was  $\pm 1$  K. Analysis of mass-spectra of volatile products of thermal destruction was carried out by a specially developed computer program, values of the intensity of selection for each volatile component were calculated as the integrated area under the curve of relevant peaks mass-spectra.

The degree of crosslinking SPE was assessed by determination of the content of gel-fraction. For this an accurately weighed sample was wrapped in filter paper (5 parallel measurements per 1 sample) and extracted in *o*-xylene at the boiling point for 16 h. Extracted samples were dried in air during the day and then in vacuum at 343–373 K to constant weight. The content of gel-fraction was estimated by the method [7].

### 3. Results and Discussion

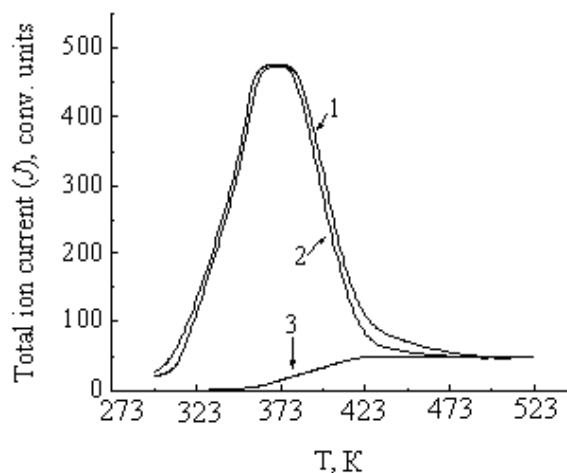
The choice of HMTA for modification of SPE is due to its extensive use as a modifying agent and curing accelerator processes in the production of elastomeric materials (donor of methylene groups that participate in the reactions of polycondensation and the formation of new functional groups), its availability and the low cost. The idea of its use as modifying additives to SPE consisted in possibility of obtaining structurally crosslinked materials with improved physical and mechanical properties due to the formation of active compounds (ion fragments) with HMTA in the process of thermo-mechano-chemical activation with SPE, which can enter into reaction with functional groups, which are

present on the surface of SPE and in the macromolecules of the polymer by a simple and relatively cheap economically justified technology.

Samples of compositions (SPE+1 wt % HMTA) and samples of the original HMTA and HMTA heated with ethyl alcohol and heated in an oven at the temperature of 433 K for 30 min were studied using PMS method. This method allows to estimate the structural characteristics of thermal decomposition of samples on the composition of the products of their thermal degradation. The temperature dependence of the emission rate of volatile products of thermal destruction of the samples (total ion current,  $J$ ) and the composition of the ion fragments, which were formed during pyrolysis, were studied. The release intensity,  $I$ , of certain volatile products (ion fragments) is expressed in conventional units.

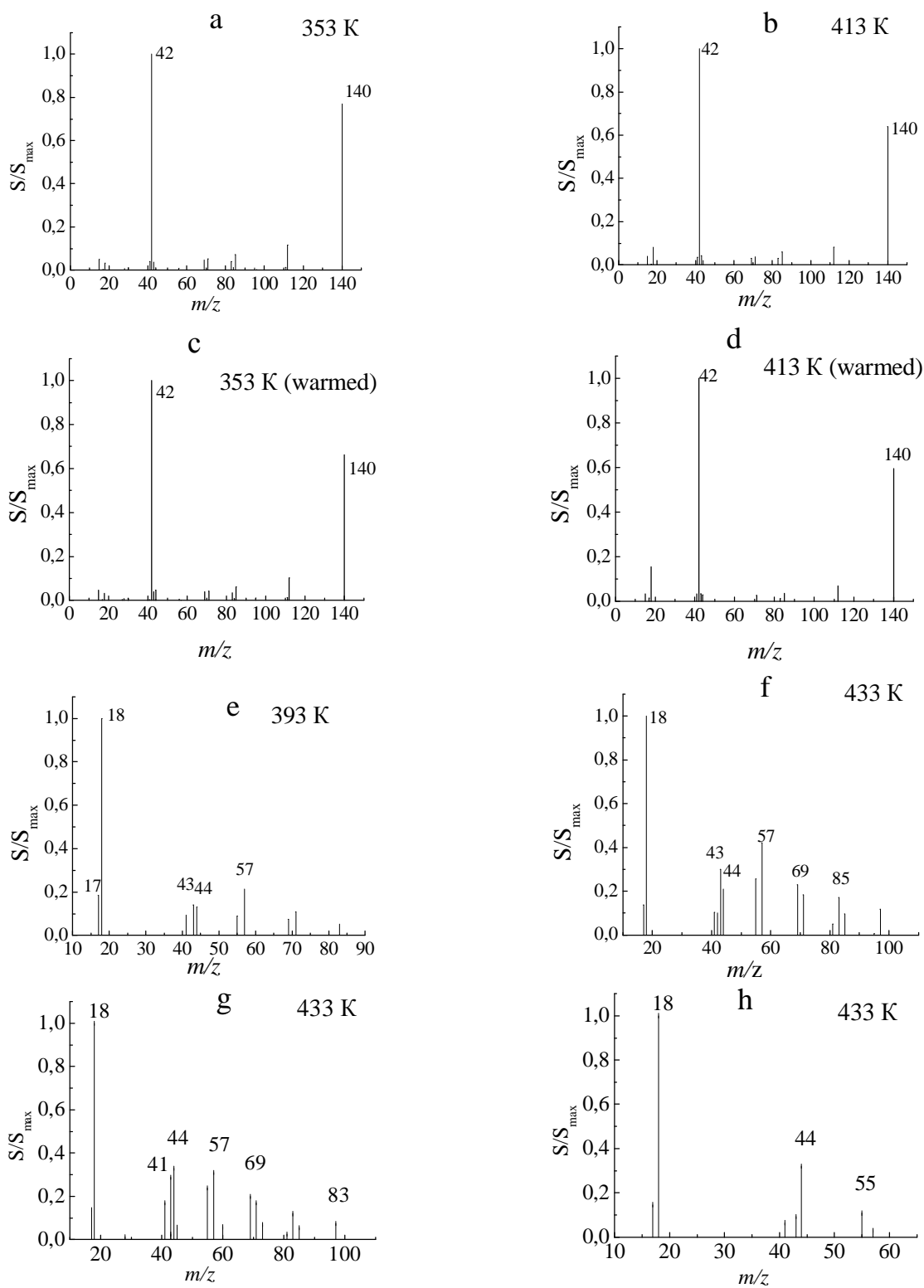
The thermograms of the investigated samples are shown in Fig. 1. As we can see, the original of HMTA (*curve 1*) and heated HMTA (*curve 2*) decompose in the same temperature range (313–443 K) with a maximum emission of volatile compounds in the range of 358–388 K and the maximum total ion current is 474 conv. units.

The thermal degradation of the sample SPE which was modified using 1 wt % HMTA (*curve 3*) begins approximately at the temperature of 373 K and slowly rises to 423 K. Total ion current is 50 conv. units in the temperature range of 423–523 K.



**Fig. 1.** Temperature dependence of total ion current emission of volatile products of thermal destruction: HMTA original (1); HMTA heated (2) and SPE+1 wt % HMTA (3).

Mass-spectra of volatile products which formed during thermal degradation of the samples of HMTA, SPE and its compositions with HMTA are shown in Fig. 2.



**Fig. 2.** Mass-spectra of volatile products of thermal degradation of samples: HMTA original (a, b); HMTA heated (c, d); SPE+1 wt % HMTA (e, f); SPE+3 wt % HMTA (g) and SPE (h) at different temperatures

Table 1

Probable composition of ion fragments and relative intensity of separation (*I*) in the mass-spectra in the pyrolysis original HMTA, HMTA (heated), and SPE modified with 1 wt % HMTA

Peak <i>m/z</i>	Ion fragment	<i>I</i> 10 <sup>4</sup> , cond. units					
		HMTA		HMTA (heated)		SPE+1%HMTA	
		353 K 24 peaks	413 K 14 peaks	353 K 24 peaks	413 K 12 peaks	393 K 10 peaks	433 K 15 peaks
15	CH <sub>3</sub>	0.39	0.09	0.35	0.06	–	–
17	NH <sub>3</sub> , OH	0.02	0.01	0.02	0.02	0.11	0.06
18	NH <sub>4</sub> , H <sub>2</sub> O	0.25	0.08	0.21	0.27	0.58	0.43
28	C <sub>2</sub> H <sub>4</sub> , CO, NCH <sub>2</sub>	0.07	–	0.06	–	–	–
30	CH <sub>2</sub> NH <sub>2</sub> , HCHO	0.08	–	0.06	–	–	–
41	C <sub>3</sub> H <sub>5</sub> , C <sub>2</sub> H <sub>2</sub> NH	0.31	0.09	0.25	0.06	0.05	0.04
42	C <sub>3</sub> H <sub>6</sub> , CNO, CH <sub>2</sub> NCH <sub>2</sub>	7.9	2.4	7.3	1.7	–	0.04
43	C <sub>3</sub> H <sub>7</sub> , CH <sub>2</sub> NHCH <sub>2</sub> , CH <sub>2</sub> CHO, CONH	0.3	0.10	0.29	0.06	0.08	0.13
44	CH <sub>2</sub> CHOH, CO <sub>2</sub> , CH <sub>3</sub> CHO, (CH <sub>3</sub> ) <sub>2</sub> NH	0.03	0.05	0.016	0.05	0.08	0.09
57	C <sub>4</sub> H <sub>9</sub> , C <sub>3</sub> H <sub>5</sub> O, C <sub>3</sub> H <sub>5</sub> NH <sub>2</sub>	–	–	0.005	–	0.12	0.12
69	C <sub>5</sub> H <sub>9</sub> , CH <sub>2</sub> C(CH <sub>3</sub> )CO	0.36	0.07	0.28	–	0.04	0.1
71	HOCCHCHO	0.41	0.09	0.3	0.05	0.06	0.08
84	N <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub>	0.1	0.15	0.06	–	–	–
85	C <sub>3</sub> H <sub>6</sub> O, C <sub>6</sub> H <sub>13</sub>	0.57	0.15	0.46	0.06	–	0.04
95	C <sub>7</sub> H <sub>11</sub>	–	–	–	–	–	0.03
112	N <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub>	0.92	0.2	0.75	0.12	–	–
140	N <sub>4</sub> (CH <sub>2</sub> ) <sub>6</sub> , C <sub>6</sub> H <sub>12</sub> N <sub>4</sub>	6.06	1.56	4.8	1.01	–	–

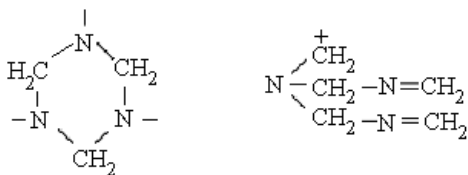
Table 2

Influence of HMTA modifying additives on the content of gel-fraction compositions on the basis of SPE

Serial number	The compositions SPE/HMTA, wt %	Gel-fraction content, %
1	100/0	1.93
2	99.8/0.2	14.49
3	99.5/0.5	30.47
4	99/1	36.28
5	90/10	37.60

This ion has a maximum intensity in the spectra of HMTA (at the temperature of 298 K its content is 40.1 %, and at 413 K – 46.8 %). Azomethines group (CH<sub>2</sub>=N–CH<sub>2</sub>) is thermostable.

There is also the formation of ion fragments with molecular masses of 28, which correspond to the compounds with the structure type metilenimin –N=CH<sub>2</sub>, as well as 84 and 112:



From the mass-spectra of the modified SPE 1 wt % HMTA (Fig. 2 e, f) we can see that there are fragments with *m/z* = 17 with the combination of atoms of NH<sub>3</sub>, OH.

The most intense ion fragment, which has been gotten at the temperature of 393 and 433 K, is a molecular ion with *m/z* = 18, NH<sub>4</sub> and H<sub>2</sub>O, respectively. During pyrolysis of the sample it was found that the main fragments present in the volatile products are molecular ions with *m/z* = 41–44, 57, 69, 71, 85. It gives the possibility to identify molecules of carbon dioxide, propylene, butane, pentene, heptane, and their ionic fragments. This is due to the thermo-mechano-chemical destruction of SPE. During pyrolysis of the modified SPE a maximum (peak) *m/z* = 42 is present in the mass-spectra. This maximum can be attributed both to C<sub>3</sub>H<sub>6</sub> fragment ion and fragment ion CH<sub>2</sub>NCH<sub>2</sub>, which formed during the pyrolysis of HMTA. Fragmental ion with *m/z* = 140 are not detected in the mass-spectrum. This may indicate that HMTA under the action of temperature field and the shear strain is destroyed to reactive ionic fragments, which react in the

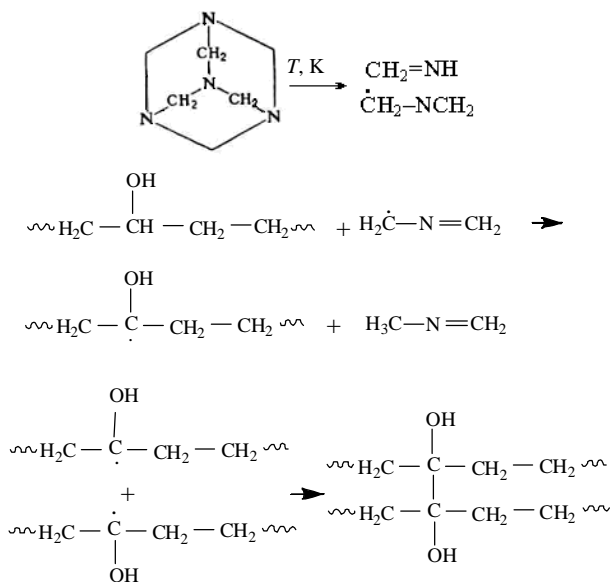
process of mechano-chemical modification with reactive groups present in SPE.

Probable composition of ion fragments and relative intensity of separation (*I*) in the mass-spectra during the pyrolysis of the samples are shown in Table 1.

In the literature there are no works devoted to the mechanism of SPE modification using HMTA. Analysis of the results of IR-spectroscopy, which were described in [7, 11], literature data [12], and the results of mass-spectrometry shows that cross-linking of polyethylene by reactive ion fragments, which were formed during the destruction of HMTA, can take place with formation of carbon-carbon cross-linking between polyethylene macrochain. One of the possible mechanisms of the modifying actions of HMTA on SPE can be represented by the following scheme:

1) Under the action of temperature fields and shear deformations, HMTA breaks up with the formation of a number of ion-fragments, in particular azomethines. Azomethines, that are formed, are extremely reactive and can react with the polyethylene matrix, according to the scheme below, and with the functional groups on the surface of the SPE, with the formation of different composition of structural fragments (Table 1);

2) Interaction of ion-fragments HMTA with macrochain SPE is accompanied by the formation of free radicals. Migration of radicals on the SPE polymer chain and the emergence of new radicals lead to the formation of pairs of radicals in close proximity next to each other, which leads to their recombination with the formation of carbon-carbon cross-linking between macrochain polyethylene:



3) The presence of a significant amount of ion-fragments of HMTA in the polyethylene composition and

the presence of unsaturated groups also increase the number of crosslinking sites, which are unsaturated groups that are capable of interacting with ion-fragments and can participate in further transformations.

As the result of such processes crosslinked structures are formed in the phase of the modified polymer. The presence of reactive groups (carboxyl, carbonyl, ester and aldehyde) on the surface of the SPE and the decay products of HMTA intensify the process of gelation significantly [12]. The results of measurements of the content of gel-fraction in composites on the basis of SPE with HMTA confirm the increase of cross-linked structures in them (Table 2).

As can be seen from Table 2, the content of gel-fraction in the polymer intensively increases with the content of modifying additives HMTA from 0 to 1.0 wt %. A further increase in the content of HMTA to 10 wt % and above does not lead to a significant increase of content of gel-fraction, which indicates that the optimal concentration of modifying HMTA additives is in the range of 0.5–1 wt %.

## 4. Conclusions

Thus, on the basis of the results obtained by PMS and by measuring the content of gel-fraction of compositions on the basis of HMTA modified SPE it was found that mechano-chemical modification of SPE using chemically-active component HMTA in the studied range of concentrations is accompanied by its decay into chemically active ion-fragments. These ion-fragments are extremely reactive and can react both with polyethylene matrix as well as with functional groups on the surface of the SPE with the formation of structural fragments of different composition. As a result of such processes the crosslinked structures are formed in the phase of the modified polymer, which affect the thermal and physico-mechanical properties of the compositions. The obtained results can serve as a basis of technological process of obtaining composite material using secondary polyethylene as polymer matrix.

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### ДОСЛІДЖЕННЯ ПРОЦЕСУ МОДИФІКАЦІЇ ВТОРИННОГО ПОЛІЕТИЛЕНУ ГЕКСАМЕТИЛЕНТЕТРАМІНОМ

**Анотація.** *Методом піролітичної мас-спектрометрії (ПМС) досліджено процеси термодеструкції вторинного поліетилену (ВПЕ), модифікованого гексаметилентетраміном (ГМТА). Введення порошкоподібного ГМТА в полімерну матрицю на основі ВПЕ з метою його механо-хімічної модифікації призводить до структурних змін полімеру-матриці, утворення поперечних хімічних зв'язків між макромолекулами ВПЕ за участю йонних фрагментів розкладу ГМТА, збільшення вмісту гель-фракції композицій, при підвищенні в них вмісту ГМТА.*

**Ключові слова:** *вторинний поліетилен, гексаметилентетрамін, модифікація, композити, піролітична мас-спектрометрія.*