

Thermal Destruction of Metal-Containing Nanocomposites Based on Isotactic Polypropylene

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Abstract: Created new thermoplastic elastomers based on isotactic polypropylene and ternary ethylene-propylene-diene elastomer using a metal-containing nanofillers. Studied the influence of nanofillers containing nanoparticles of different metals oxides on the physico-mechanical and thermal properties, as well as the structure of the uncured and dynamically vulcanized blends using differential scanning calorimetry (DSC), differential thermal analysis (DTA) and scanning electron microscope (SEM). Shown the emergence in the polymer containing metal nanoparticles, a fine spherulitic structure, promoting the improvement of properties of obtained nanocomposites.

Key words: Thermoplastic elastomers, isotactic polypropylene, triple ethylene-propylene-diene elastomer, the metal-containing nanofillers, DTA - DSC analysis

1. Preface

One of the most promising directions of development of modern science is nanotechnology – the production and use of materials consisting of nanoparticles.

Considerable attention paid to the nanomaterials has been caused by at least two reasons. First, the reduction in size is a traditional way to improve such material properties as catalytic activity and activity in solid-phase reactions. Second, the unique physical properties of nanomaterials has been determined, primarily magnetic and electrophysical [1-3].

The development of nanotechnology opened up the possibility of conducting research in the area of composite nanomaterials, and currently is allowed for the development and use of advanced polymer materials for sensors, catalysis, nano-electronics etc. [4-6].

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It is known that for improving of performance of plastics applied fillers in the amount of 30-50 wt.%. Filled plastics are used mainly as structural material [7].

In the world today different types of polymer nanofiller-based composites are actively replacing traditional materials [8]. Polymer nanocomposites can be obtained in situ, i.e., by the polymerization of monomer in presence of pre-dispersed in the reaction medium of the nanofiller [9]. The method of introduction of nanofillers in molten polymers is more preferred. This method is most suitable for use in modern industry. It allows to obtain nanocomposite polymers to a wide range of manufacturers, which makes this method promising and cost effective [10].

Modification of polypropylene by creating a variety of composite materials allows to significantly expand the scope of its application. Filled polypropylene is one of the first places among the filled thermoplastics. At present, more attention is paid to the development of composites with nanosized fillers. Such composite materials have higher parameters than the composite materials with micro - and macrofillers. Introduction into the polypropylene even of a small amount of nanoscale filler could significantly change the physical properties, improve barrier performance, enhance thermal stability, electrical conductivity, etc [11, 12].

The use of metal nanoparticles of variable valency (copper, cobalt, nickel, etc.) in polymers allows to obtain fundamentally new materials that find wide application in radio - and optoelectronics as magnetic, electro-conductive and optical media [5, 12].

Intensive development of the global petrochemical industry involves a constant search for a new materials with high application properties, environmental safety and ease of processing. Such materials are not without reason are thermoplastic elastomers (TPE). The creation of a TPE – is a priority direction of work in the field of polymer materials science. Distinguishing feature of TPE is a combination of properties of vulcanized rubbers during operation and thermoplastics during processing. [13-15].

The most promising approach to obtaining new types of TPE is mixing of elastomers with plastics with simultaneous vulcanization of the elastomer. This leads to a high degree of dispersion of the rubber phase in the obtained thermoplastic vulcanizers. Obtained by this method, the TPE has received the name of dynamic thermoplastic elastomers (TPV). Due to the complex of high physical-mechanical properties, a wide temperature range of performance, lower cost of end products, TPV are considered one of the most promising classes of polymer composite materials [16, 17].

There are works on obtaining of TPE and TPV with use of isotactic polypropylene(PP) as a thermoplast, and of triple ethylene-propylene-diene elastomer (EPDM) or butadiene-nitrile rubber (NBR) as elastomers

using a variety of fillers or compatibilizers to improve the compatibility as well as physico-mechanical and technological properties of the compositions [18-20].

Previously, we studied the effect of small additions of nanofillers (NF), containing nanoparticles (NPs) of oxides of copper, nickel and iron, stabilized in polymer matrix, on the features of properties of thermoplastic elastomer mixed (TPE) and dynamically vulcanized (TPV) based on isotactic polypropylene (PP) and ethylene-propylene-diene elastomer (EPDM). It is shown that a small addition of NF in the amount of 1 weight part has virtually no effect on the crystallinity and dielectric permittivity of the TPE and TPV, but reduces their elastic modulus. The obtained data of the electrical properties of TPE match those of conventional dielectrics [21-22].

The work purpose - analysis of influence of additives for metal-containing nanofillers on the specifics of thermophysical and thermal properties, as well as structure of mixed TPE and dynamically vulcanized TPV based on isotactic PP and EPDM.

2. Materials and Research Methods

In the work has been used: isotactic polypropylene (PP) grade 21030-16 (Russia) with $M_p=7.7 \times 10^4$ and $M_w=3.4 \times 10^5$; density $\rho=0.907 \text{ g/cm}^3$; the degree of crystallinity of 55%; melting temperature $T_M=165^\circ\text{C}$; MFI=2.3 g/10 min at $T=190^\circ\text{C}$ and load 2.16 kg; brand EPDM Dutral TER 4044 (EPDM) with the number of propylene units of 35%, a Mooney viscosity of 44 (at 100°C); In the composition of the EPDM diene component was 5-ethyliden-2-norbornene in the amount of 4-5%.

As nanofillers (NF) used nanoparticles (NPs) of metal oxides, stabilized in polymer matrix: (NF-1) – NPs of copper oxide I (Cu_2O) and (NF-2) - nickel oxide (NiO) was stabilized in the matrix of the polyethylene obtained with the use of titanium-phenolate catalytic system in the amount of 1 wt.% on the polymer mixture. The content of nanoparticles in the polymer matrix: NPs of copper oxide - 3.9%, NPs of nickel oxide - 18%, NPS size 11-15 nm, the degree of crystallinity of the NPs 25-45%[23].

The ratio of the initial components (mass.p.): PP/EPDM/NF = 50/50/1, Polymer composites are obtained by mixing in a high-speed mixer of a closed type Brabender at $T=190^\circ\text{C}$ and rotor speed of 100 rpm for 10 min, and vulcanized – by the method of dynamic vulcanization at the same conditions with the use of sulfur-containing curing system comprising the following ingredients (in wt.p. on 100 wt. p. of rubber): elemental sulfur 1.00, 2.50 zinc oxide, 1.00 stearic acid, di(2-benzothiazolyl)disulfide 0.25, the tetramethylthiuramdisulfide 0.73 [24]. Samples for testing were obtained by hot pressing in the form of plates with a thickness of 0.35 mm at 190°C and a pressure of 10 MPa for 10 min followed by cooling to room temperature at a speed of 20 deg /min.

For the study of mechanical characteristics of polymer mixtures from hotpressed plates were cut samples in the form of blades with dimensions of 35.00x5.00x0.35 mm. Uniaxial tension of the specimens was performed on test machine "Instron-1122" at room temperature and a constant rate of displacement of the upper crosshead of 50 mm/min. From the diagrams of deformation by the initial part of the curve was determined the modulus of elasticity E , ultimate strength σ_p and elongation at fracture E_p . The results were averaged by 10-14 samples. The error of measurement of elastic modulus and of ultimate strength did not exceed 10%, and elongation at fracture -20%. The melt flow index (MFI) was determined on capillary microviscosimeter IIRT-5 (Russia) at the temperature of 190°C and load of 2.16, 5.00, and 10.6 kg. The measurements of composition thermal properties are carried out on the instrument LINSEIS STA PT-1600 (Germany) at a heating rate of 20 ° C in an atmosphere of air.

SEM - analysis of the compositions performed on the ZEISS instrument.

3. Results and discussion

Obtained and studied physical-mechanical properties of mixed and dynamically vulcanized nanocomposites based on PP/EPDM containing fillers with nanoparticles of oxides of various metals. Mechanical properties and melt flow index (MFI) of the systems studied are presented in table.1

Table1. Physico-mechanical properties of the obtained nanocomposites

Composition	E, MPa	σ_p , MPa	ε_p , %	MFI, g/10min, T=190°C		
				2.16kg	5.00kg	10.6kg
TPE						
PP/ EPDM	395	11	167	0.9	3.7	14.8
PP/ EPDM / NF -1	260	9.3	153	1.1	4.3	18.0
PP/ EPDM / NF -2	263	8.7	110	1.1	4.4	16.8
TPV						
PP/ EPDM	215	13.2	373	-	-	-
PP/ EPDM / NF -1	165	14.0	390	-	-	0.15
PP/ EPDM / NF -2	114	12.8	340	-	-	-

E - the modulus of elasticity, σ_p - limit of tensile strength, ε_p - elongation at break, MFI- melt flow index.

As can be seen from the table in the mixed TPE application of NF contributes to enhancing of the MFI index under load 10.6 kg 1.22 times, however, it leads to some reduction of the modulus of elasticity at a certain preservation of the strength characteristics of the system. The application of NF in vulcanized compositions - TPV results in reducing of modulus of elasticity E in 1.3 times, while maintaining the tensile strength at break and specific elongation. The system does not flow under loads of 2.16

and 5.0 kg, and the load increase to 10.6 kg leads to a flow of a mixture (in the case of NF -1), which is very vital for the processing of the system.

The reduction of modulus of elasticity of the composite, probably due to aggregation of NP, leading to the formation of microdefects in the bulk of the polymer matrix. The emergence of the flow of the composite appears to be related to increased mobility of polymer segments in the nanoscale interaction of NP with the matrix.

It is shown that the obtained PP/EPDM based nanocomposite TPE with the application of NF, containing NP of oxides of copper and nickel, have improved melt flow index, with preservation of tensile strength and specific elongation, with some decrease of elastic modulus. The application of NP in vulcanized compositions –TPV leads to a flow of the mixture (only in the case of NF-1).

Studied thermophysical and thermal properties of obtained nanocomposites using combined thermal analysis including DSC and TGA techniques (Fig.1-6). It should be noted that all of the thermograms of DSC – TGA / T had the same character for all test conditions and all the samples of thermoplastic elastomers.

Analysis of the DSC curves in the thermograms of DTA - DSC showed that for all examined samples of thermoplastic elastomers (TPE and TPV) melting temperature (T_m) is the same and totals 140°C.

In the case of TPE (Fig.1) with increasing temperature the DSC curve gradually rises to 140°C, followed by a sharp endothermic peak (absorption of heat) corresponding T_m of TPE, then a smooth rise up to 300°C - exothermic process related to oxidation of the polymer chain. After 320°C starts weight loss (5%), then the curve slowly goes down to 350°C (10%), then a sharp endothermic peak - the process of sublimation or evaporation of degradation products, reaching a maximum at 388.5°C (mass loss of 40%). Along with this the rate of the mass loss on the TGA thermogram is also maximum at 465°C, the mass loss corresponds to 95.5%. About the middle of the process of thermooxidative degradation at 394°C there is a sharp transition from heat absorption to its release up to 420°C and then to 600°C – competition of endo-ecso process and then a sharp endothermic peak with a gradual process fading up to a full release of degradation products from experimental cell. Thus there is a reduction of mass to 0.5 mg.

In the case of TPE with NF (Fig.2,3) also with increasing temperature the DSC curve gradually rises to 140°C, followed by a sharp endothermic peak (absorption of heat), the corresponding T_M of TPV, then rise up to 350°C - exothermic processes related to the oxidation of the polymer chain. After 360°C starts weight loss (4-5%), then a sharp endothermic peak - sublimation process of degradation products reaching a maximum at 410°C (mass loss 20-23%). Along with this the rate of the mass loss on the TGA thermogram, is also maximum at 485°C, the mass loss corresponds to the 90%. About the middle of the process of

thermooxidative degradation at 400°C there is a sharp transition from heat absorption to its release to 420°C and then to 600°C – competition of endo-ecso-process and then a sharp endothermic peak with a gradual fading of the process up to a full release of degradation products from experimental cell. Thus there is a decrease in the mass of 0.5 mg.

In the case of TPV (Fig.4), the DSC curve has a similar appearance, as for TPE (Fig1), however indicators of temperature change.

In the case of TPV with NF (Fig. 5,6) the DSC curve has a similar appearance, as for TPE with NF (Fig.2,3), however indicators of temperature change.

Analysis of DTA curves in the thermograms of DTA - DSC for the examined nanocomposites showed that in the beginning of the experiment under the effect of air oxygen the oxidative processes are occurring and the masses of the samples increase to 0.658 mg(4.5%).

Analysis of thermograms of DTA - DSC of obtained mixed nanocomposites showed that all the samples of examined TPE are thermally stable in air atmosphere up to 300°C. The initial TPE loses 5% of mass at 320°C, at the time, as TPE with NF, containing NP of metals are stable up to 350°C. At 360°C the initial TPE loses 10% of weight, and TPE with NN - 3÷5%. When 388.5°C initial TPE loses 40% of its mass, and TPE with NF - 18÷20%, i.e. in 2 times less, at 465°C the mass loss corresponds to 95.5%.

Analysis of thermograms of DTA - DSC of the obtained vulcanized nanocomposites (TPV) showed that they are thermally stable in air up to 350°C, while TPV with NF containing NP of metals, are stable up to 400°C. Source TPV after 350°C loses 5% of its mass, and TPV with NP - 2÷3%; At 410°C TPV loses 25% of its mass, and TPV with NP - 18÷20% at 485°C the mass loss corresponds to the 90%.

All the samples of examined TPE are thermally stable in the air atmosphere up to 300°C, at the time, as TPE with NP, containing NP of metals are stable up to 350°C. The source TPV is stable up to 350°C, and TPV with NP, containing NP of metals, are stable up to 400°C. The temperature of the beginning of thermo-oxidative degradation increases for TPE and TPV at 50 °C, indicating high thermal stability of obtained nanocomposites.

The activation energy of thermooxidative degradation (E_a) was calculated in the temperature range 320÷420°C according to the method of the double logarithms [25]. It is shown that the E_a for TPE amounts to 190.5 kJ/mol, and for TPE with NP- 205.9÷215.2 kJ/mol. Introduction of NP increases the activation energy of thermooxidative degradation for TPE to 15÷25 kJ/mol.

E_a for TPV is 205.3 kJ/mol, and for TPV with NP - 208.5÷210.7 kJ/mol, which is 3÷5 kJ/mol more. The introduction of NP has little effect on the the mass loss and activation energy of thermooxidative degradation for TPV.

Conducted the SEM analysis of the obtained nanocomposites (Fig.7-10). The Fig.7 shows the micrograph of the initial mixture PP/EPDM. It is seen that the composite structure is crumbly, shapeless. Introduction into the mixture composition of the nanofiller NN-1 promotes the formation of spherulitic structure, which leads to an increase of fluidity of the nanocomposite (Fig.8). The vulcanization of the initial mixture using sulfur-containing vulcanizing system leads to the formation of compact spherulitic structure (Fig.9). However, the composite does not flow, which complicates its processing. Introduction into the composition of a vulcanizate of the nanofiller NN-1 promotes the formation of more fine spherulitic structure, which causes a tenuous flow of the nanocomposite (Fig.10).

It is shown that small amounts of nanofiller (1.0 mass%) introduced into the polymer, obviously, play the role of builders - artificial germs of crystallization, which contributes to the emerging of a fine spherulitic structure in polymer, characterized by the improved melt flow rate and high thermal properties of the obtained nanocomposites.

4. Conclusion

Obtained new nanocomposites based on PP/EPDM through the use of metal-containing (Si, Ni) nanofillers, stabilized in the matrix of the polyethylene obtained with using of titanium-phenolate catalytic system, with improved melt flow index.

Conducted thermal and thermophysical analysis of obtained mixed and vulcanized nanocomposites through the use of a combined DTA-DSC-method. It is shown that for all examined samples of thermoplastic elastomers (TPE and TPV) melting temperature (T_M) is identical and equal to 140°C. All the samples of initial TPE are thermally stable in the air atmosphere up to 300°C and TPE with NF, containing NP of metals are stable to 350°C. Source TPV is thermally stable up to 350°C, and TPV with NP- up to 400°C. The temperature of the beginning of thermo-oxidative degradation increases for TPE and TPV with NP at 50 °C, indicating high thermal stability of obtained nanocomposites.

Conducted the SEM analysis of the obtained nanocomposites. Shown the appearance in the polymer containing NPs of metals of a fine spherulitic structure, promoting the enhancement of properties of resulting nanocomposites.

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Captions

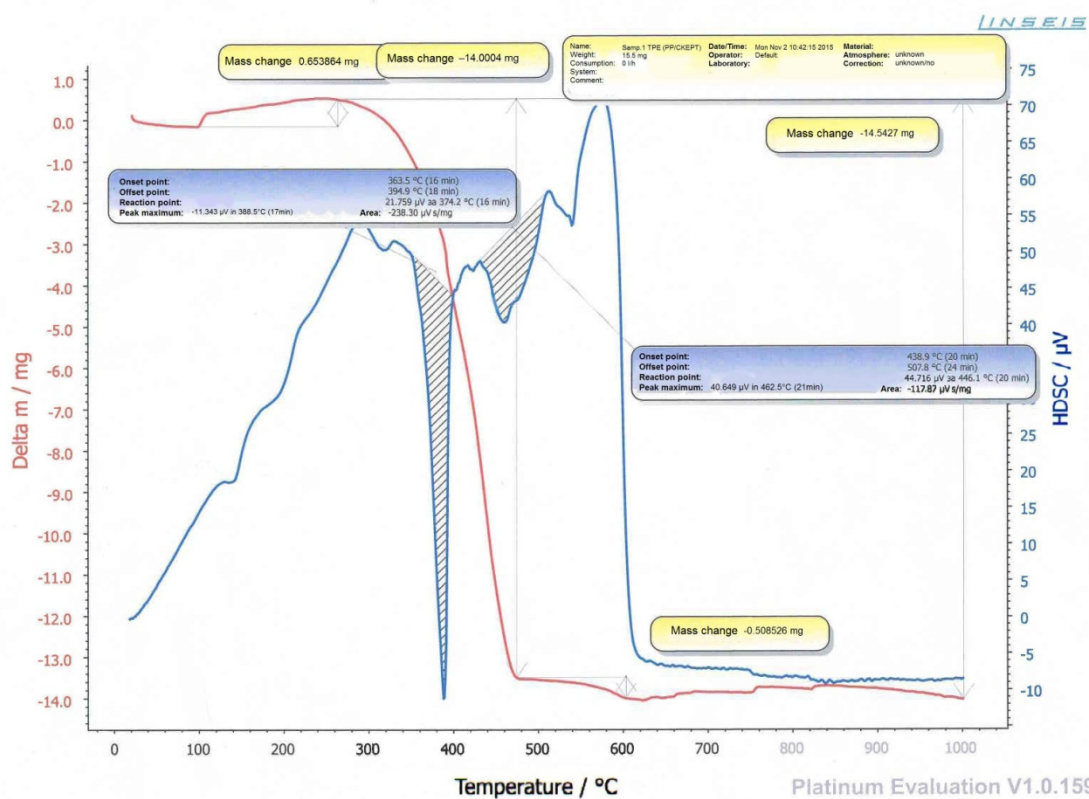


Fig.1. Thermogram of the initial TPE

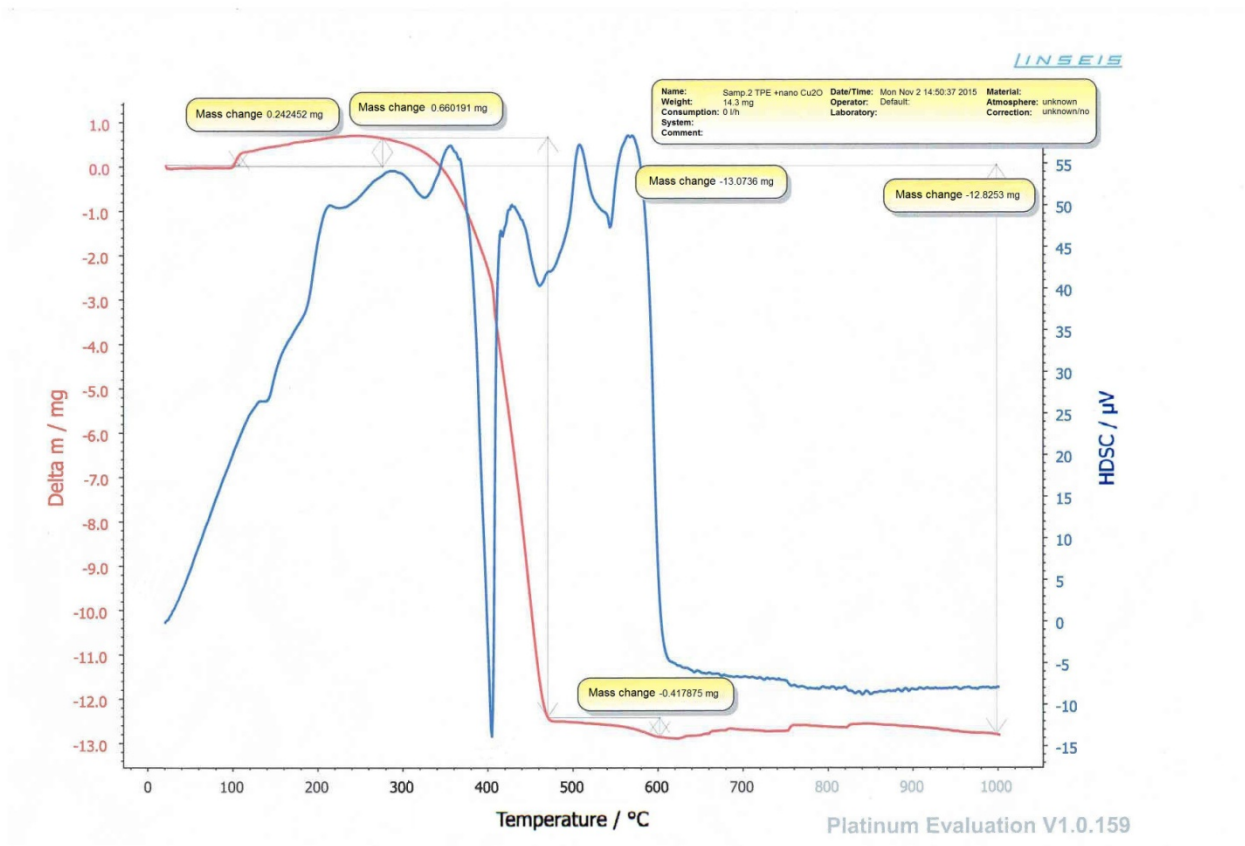


Fig.2. Thermogram of TPE containing NF-1

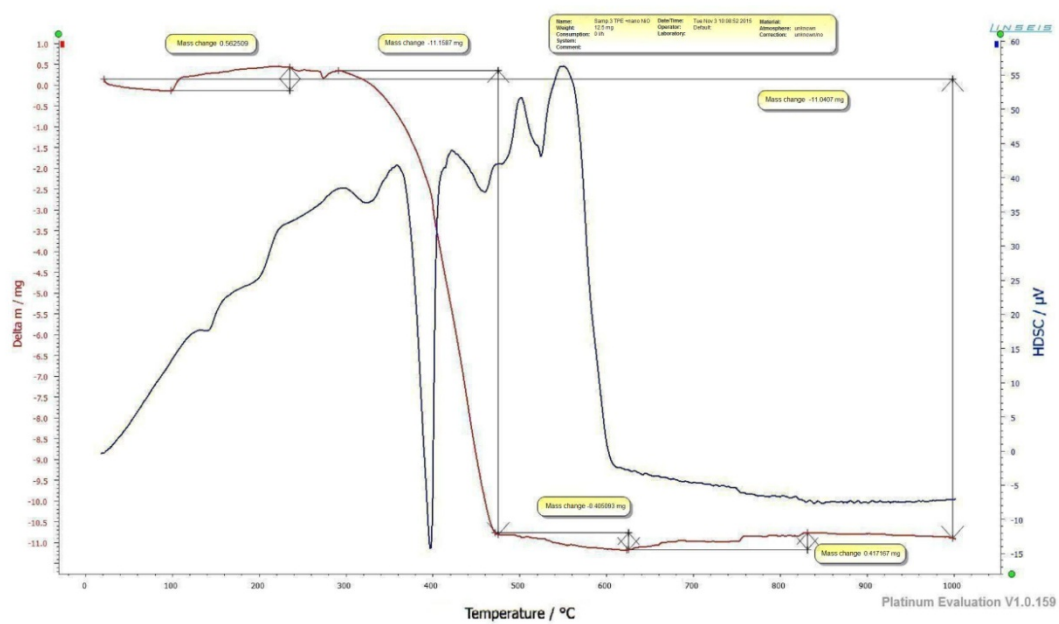


Fig.3. Thermogram of TPE containing NF-2

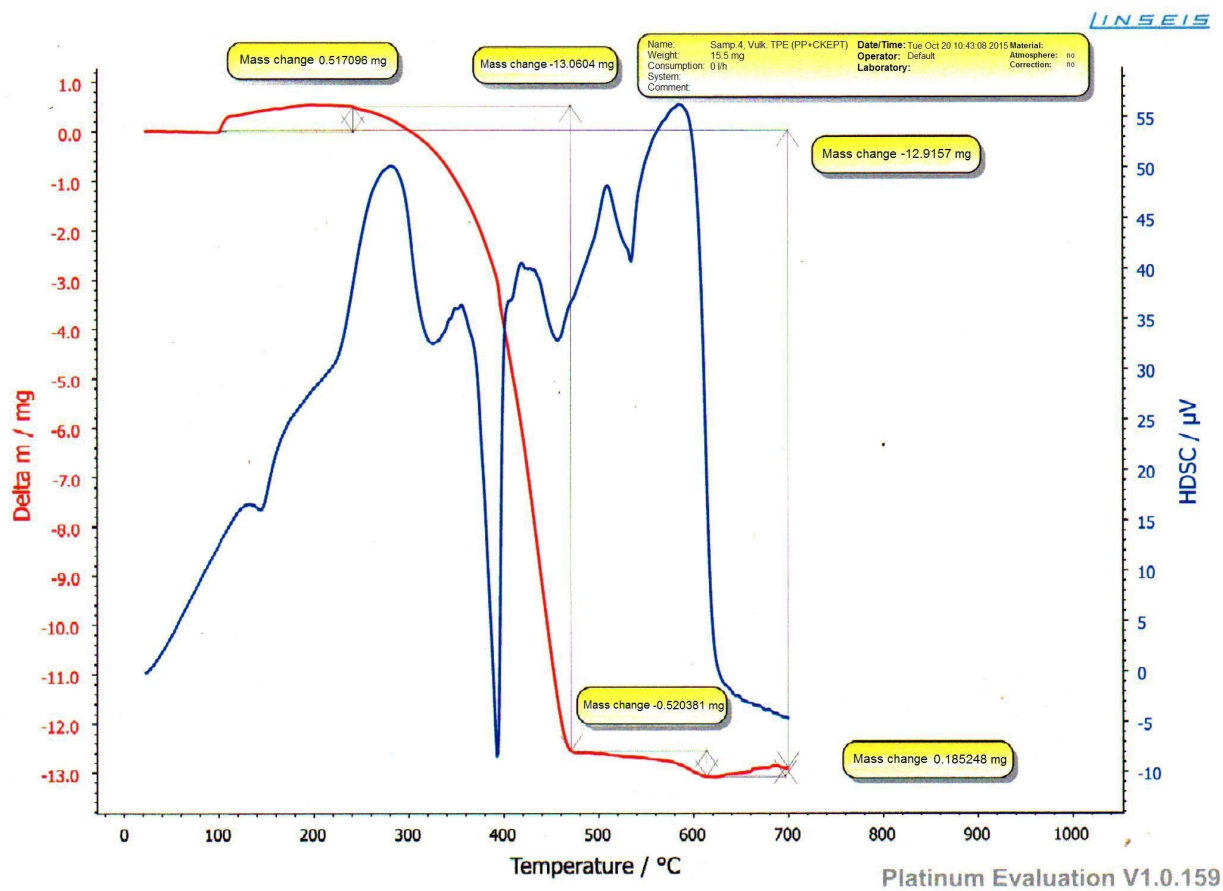


Fig.4. Thermogram of the initial TPV

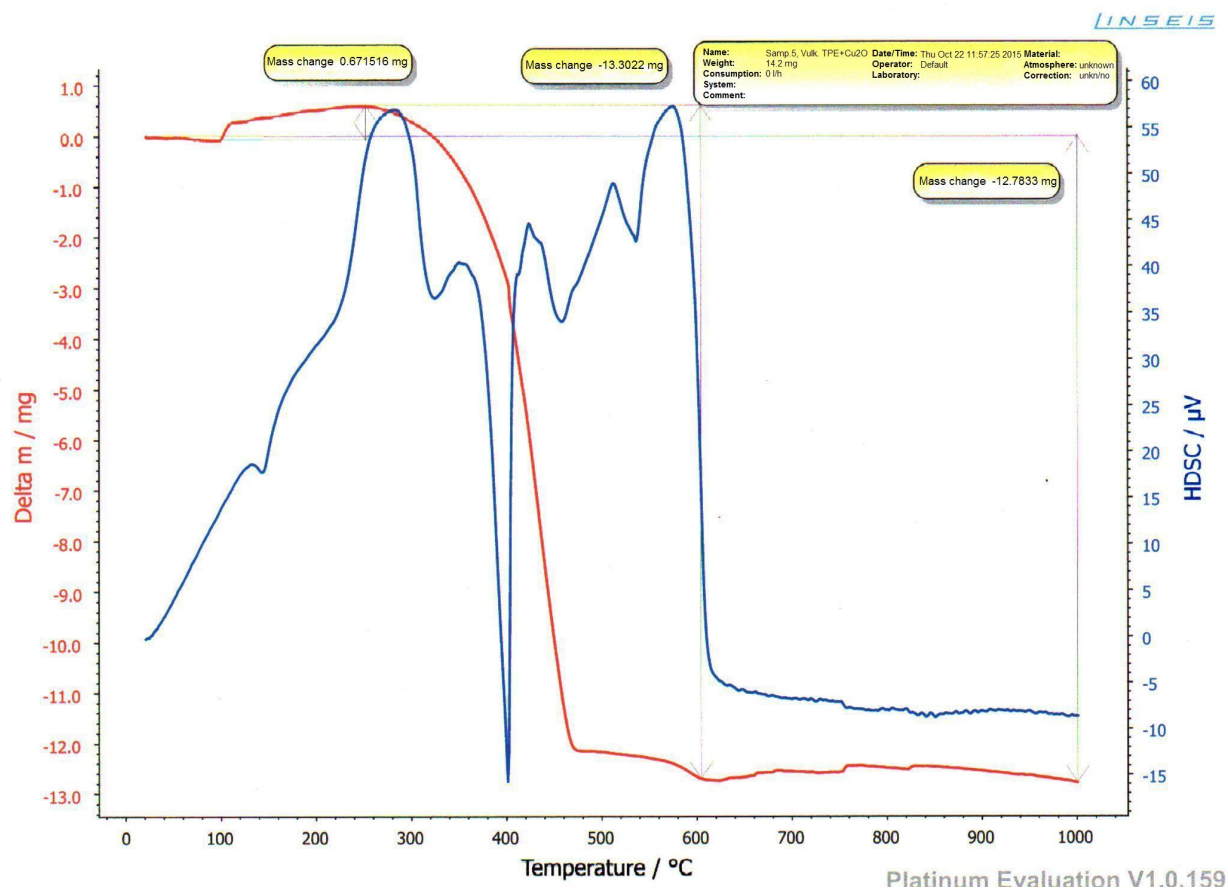


Fig.5. Thermogram of the TPV containing NF-1

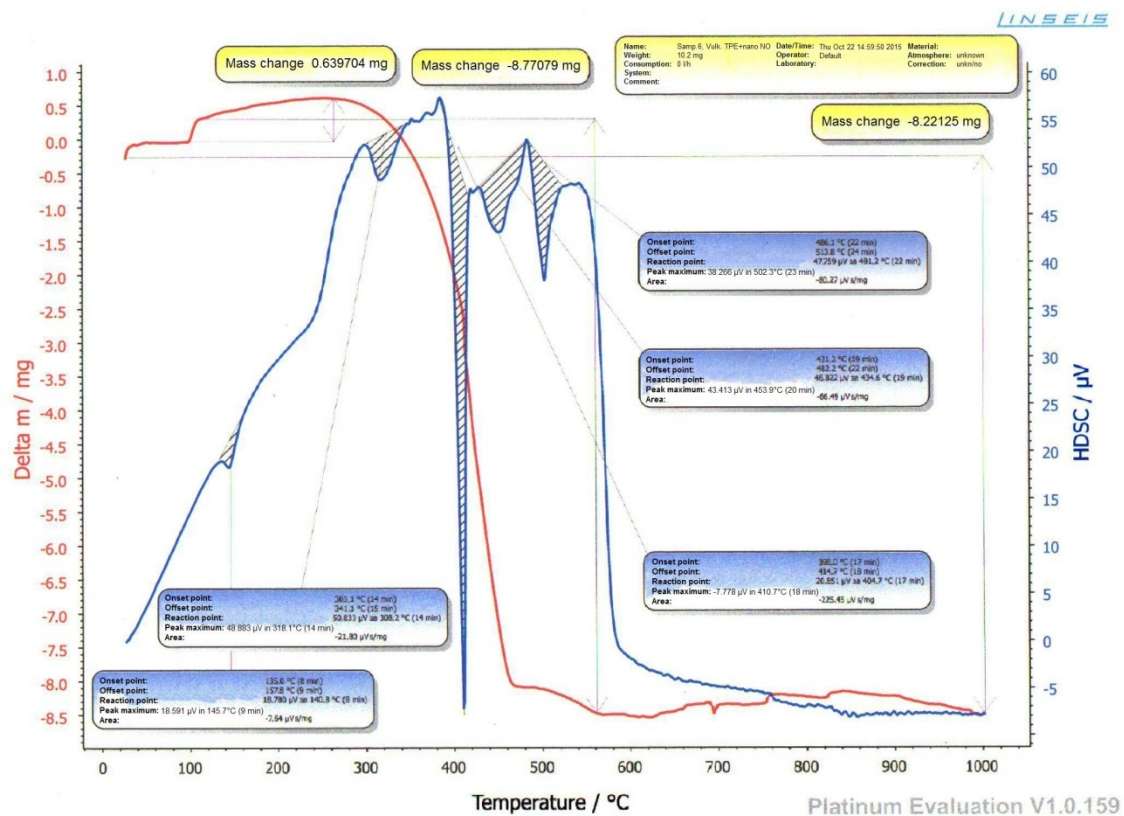


Fig.6. Thermogram of the TPV, containing NF-2

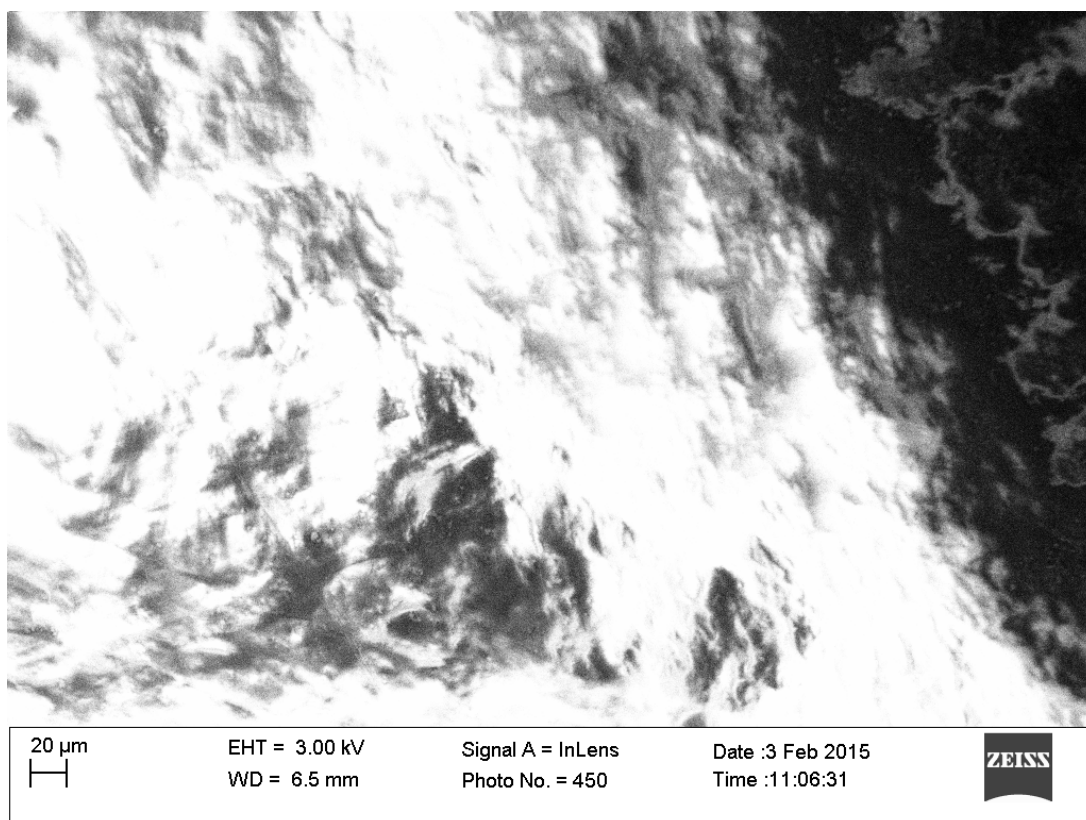


Fig.7. Photomicrographs of the initial TPE

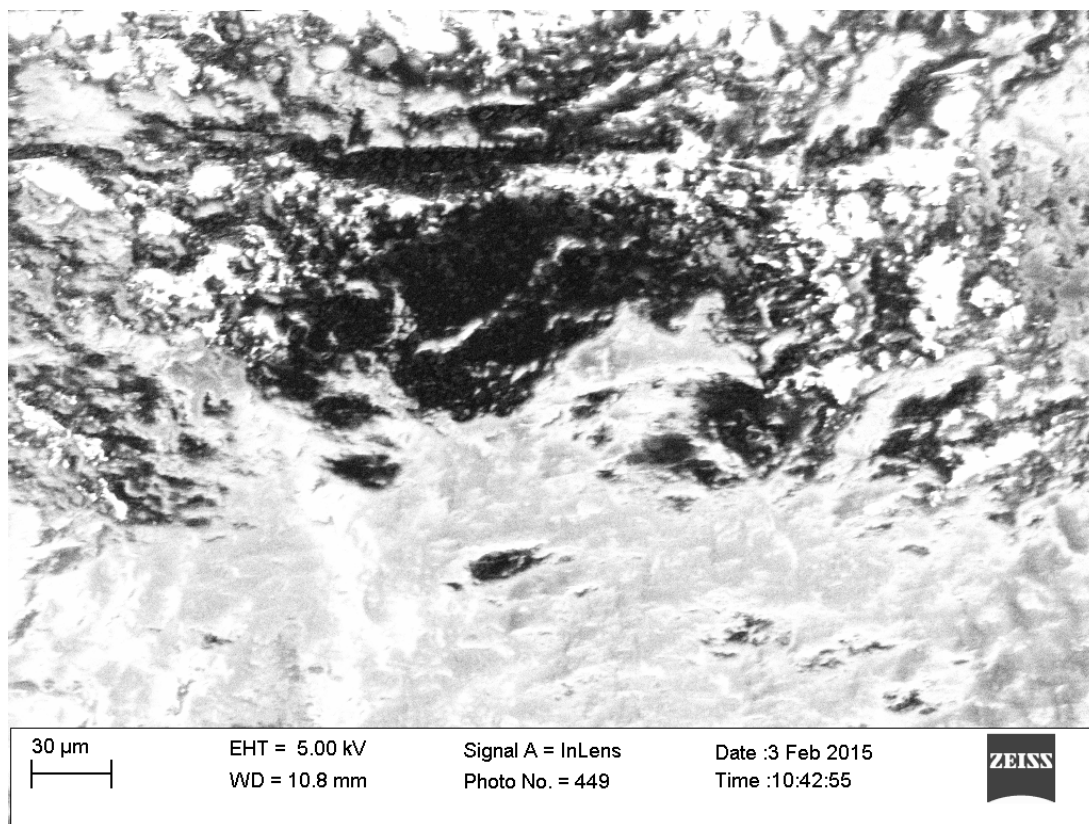


Fig.8. Photomicrographs of TPE containing NF-1

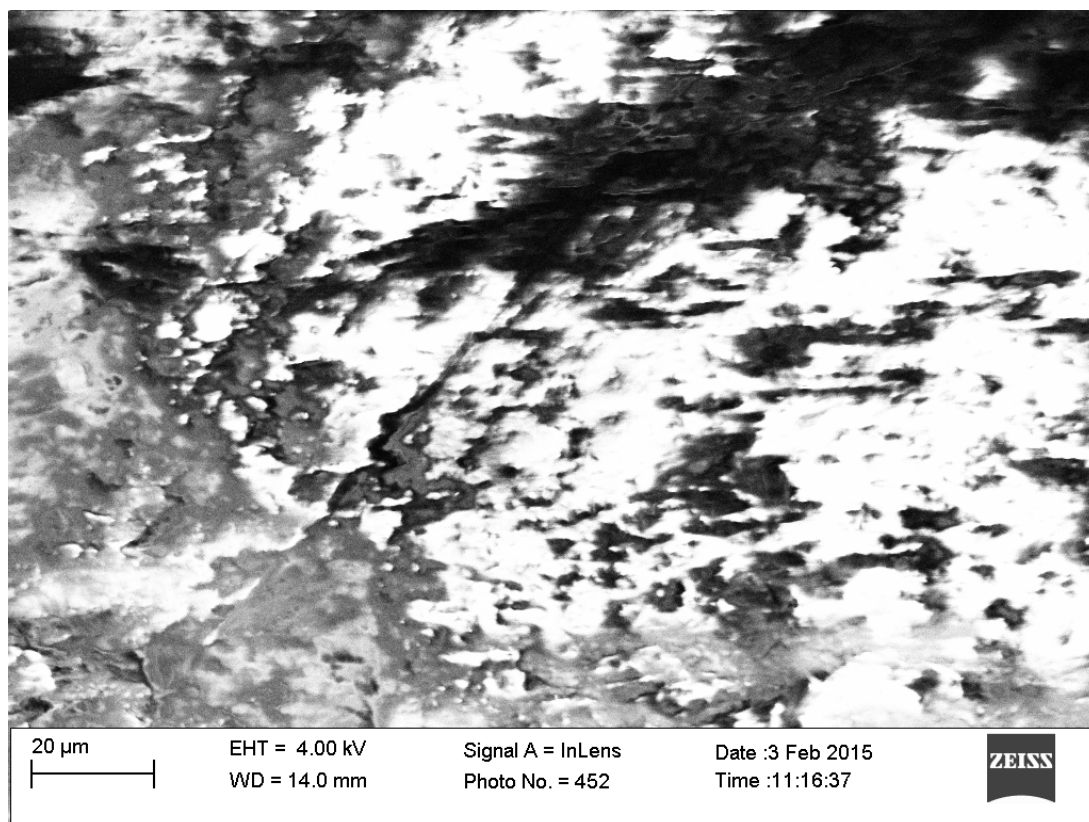


Fig.9. Photomicrographs of the initial TPV

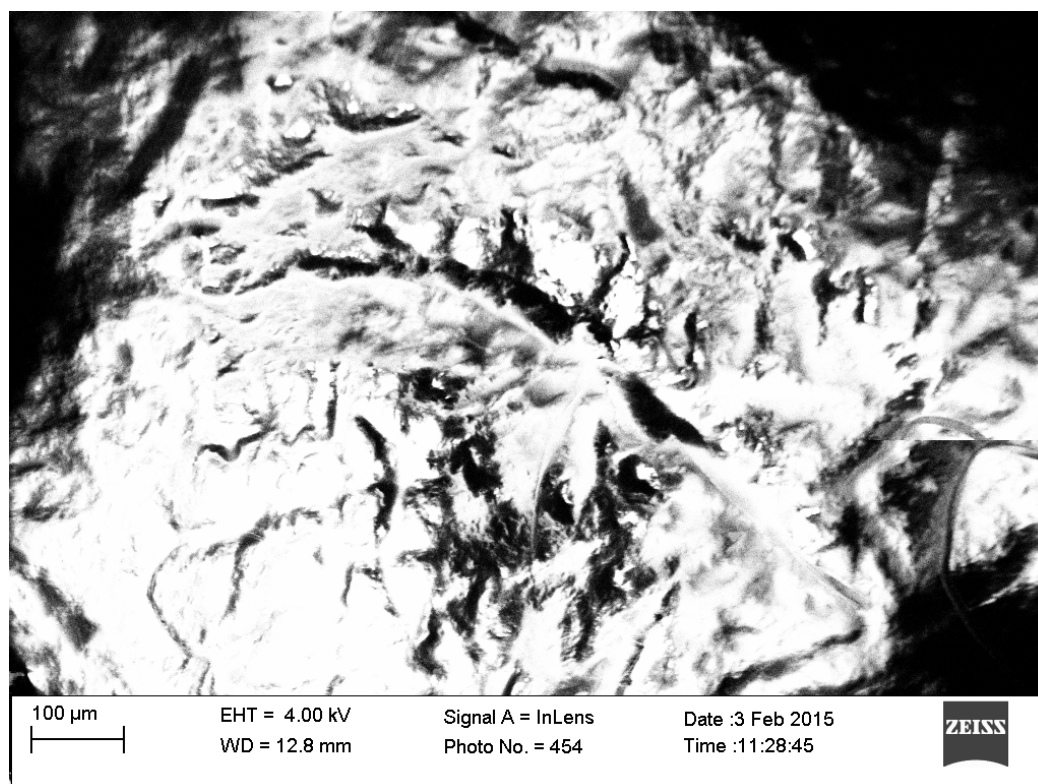


Fig.10. Photomicrographs of TPV containing NF-1