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**Thermal stability of nanoclay polypropylene composites by simultaneous DSC and TGA**

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## Abstract

The thermooxidative and thermal stability of polypropylene nanocomposite with fully exfoliated MMT was studied by simultaneous measurements by DSC and TGA methods in a wide range of temperature. By comparing both the mass loss from TGA and enthalpy changes from DSC in a temperature range from room temperature to 500°C it was possible to identify precisely the specific mechanisms of polymer degradation. In oxygen-free atmosphere the thermal degradation of polypropylene in nanocomposites is strongly inhibited up to the temperature of 420°C in contrast to pristine polypropylene degradation beginning with 300°C. Simultaneous TGA and DSC made possible to show that exfoliated clay platelets modified with alkylammonium salt exhibit a strong stabilizing effect on polypropylene macromolecules in oxygen-free atmosphere. It was further shown that the lower sensibility to thermal oxidation of nanocomposites was correlated with lower oxygen permeability resulting from an increased diffusion path for oxygen as well as for volatile decomposition products.

Keywords: polypropylene, TGA, DSC, nanocomposite, montmorillonite, stability, degradation, oxidation

## 1. Introduction

Recently, polymer nanocomposites became a subject of many studies and applications, whose aim is, among the others, to determine the effect of a nanofiller, polymeric materials and processing conditions on such nanocomposite properties as strength, ultimate elongation, elasticity of elongation, impact strength, gas and water vapor permeability, thermal properties, flammability, resistance to thermal degradation and thermooxidation, and melt strength. Among many nanocomposites studied and applied in industry very important are polymer nanocomposites with platelet nanofillers, most frequently with montmorillonite

(MMT) [1]. However, MMT is hydrophilic and when used to fill non-polar polymers, its surface properties must be modified [1-3]. One of the modification methods is the exchange of alkali metal ions present between MMT platelets into alkylammonium ions [e.g. 4,5]. However, the use of this modifier is limited in two ways: because of health concerns the allowable concentration of alkylammonium compounds should not exceed 5 ppm, and additionally, these compounds are characterized by low thermal stability and most of them are thermally degraded at the temperature not higher than 220 to 250°C, which reduces their applicability to certain polymeric materials only [1].

Melt intercalation of polypropylene was studied in the past by many researchers, first in Toyota Research Center [6-8] and latter by others [9- 16]. In several of those papers [11- 16] the achievement of partial or full exfoliation of MMT platelets was claimed.

The susceptibility of organo-modifiers and polymers toward thermal and thermooxidative degradation and the role of  $Al^{+3}$  ions on MMT platelets are the important concerns and recently they have been a subject of several studies [17-34]. Some of the aspects were reviewed recently in [35].

Usually the elucidation of degradation is based solely on thermogravimetric analysis(TGA) [see for example 36-42]. In other papers the DSC measurements are used only within narrow ranges of temperature in order to record the phase transitions such as melting and not observing the thermal effects of degradation at a high temperature [e.g. 29-34, 43,44]. In TGA a loss of mass is measured, whereas the degradation of polymeric materials begins frequently with enthalpy changes. This is especially true for thermooxidation. Enthalpy changes cannot be detected in TGA and are obtainable by DSC measurements. Also, in most of those studies the exfoliation of MMT was not adequate and/or not optimized. Therefore, we suggest that it is essential to analyze both the thermogravimetric and calorimetric data collected over a large temperature range at similar heating rates and under similar other

conditions. The aim of this communication is to study the thermooxidative and thermal stability of polypropylene nanocomposite with highly exfoliated MMT by simultaneous measurements by DSC and TGA methods in a wide temperature range. In this way thermal effects are observed separately but in parallel with the mass loss in a wide range of temperature and can be ascribed precisely to specific mechanisms of degradation. Before starting the research on thermal stability of polypropylene nanocomposite we made an effort to optimize the exfoliation of MMT in polypropylene nanocomposite by varying a brand of maleinated compatibilizer, compounding conditions and twin screw extruder configuration. A route to obtain highly exfoliated MMT in polypropylene is illustrated.

## 2. Experimental

1. Preparation of nanocomposites. The experimental materials were polypropylene nanocomposites with montmorillonite and a compatibilizer. The composites were based on polypropylene Malen P, F401; MFR (2.16 kg; 230°C, g/10 min) = 2.4-3.2, tensile yield point = 30 MPa, stress at fracture = 20 MPa, (manufacturer Basell-Orlen), modified montmorillonite Cloisite 15A; ( $d_{001} = 3.15$  nm, CEC = 125 meq/100g, density = 1.66 Mg/m<sup>3</sup>), modified with quaternary ammonium salts of fatty acids (manufacturer Southern Clay Products) and a compatibilizer, Polybond 3150; MFR (2.16 kg; 230°C, g/10 min) = 50, polypropylene grafted by maleic anhydride, content of maleic groups: 0.5% vol., (manufacturer Uniroyal Chemical Products). To optimize MMT exfoliation, the content of MMT and the compatibilizer was varied and mixing was carried out according to different protocols. Also the configuration of twin screws was changed. For further studies the following samples were selected:

- Nano1; twin-screw corrotating extruder, simultaneous charge of all premixed components, screw configuration with two degassing zones, described in details in [45] rotational speed of

the screws 250 1/min, temperature profile of a plasticizing system 185, 195, 195, 195°C, head temperature 195°C,

- Nano2; twin-screw corrotating extrusion, i.e. Nano1 nanocomposite obtained in these conditions was extruded again in the same conditions.

- Nano3; twin-screw corrotating extruder, two-step extrusion, i.e. extrusion of the compatibilizer with montmorillonite, and then extrusion of the concentrate prepared in this way with polypropylene. For all three nanocomposites the weight ratio of components of the nanocomposite, i.e. montmorillonite : compatibilizer : polypropylene was 1:4:15. Other processing conditions – as for Nano1.

Polypropylene alone for comparison:

- PP1; plain polypropylene extruded in the same way as nanocomposite Nano1.

2. Thermogravimetry (TGA) and differential scanning calorimetry (DSC); STA 625 thermogravimetric analyzer (Polymer Labs). Investigations were made while heating the samples from 20 to 600°C at the rate of 20°C/min in the air or in nitrogen. Mass of the samples was about 10 mg. Simultaneous recording of thermogravimetric and DSC signals.

3. Exfoliation of MMT platelets in the PP matrix was tested by the WAXS method in transmission within the angle  $2\Theta$  from 1 to 9°. A computer-controlled x-ray diffractometer connected to a Cu  $K_{\alpha}$  x-ray generator operating at 50 kV and 30 mA, was used. The line of wavelength  $\lambda = 0.1541$  nm was filtered by a Ni filter  $\lambda$  and electronically. Diffractograms  $2\Theta$  were obtained at the aperture opening 0.05°. To avoid the effect of orientation of MMT platelets in nanocomposite formed during mixing-shearing extrusion, powdered samples were produced. To do this pellets of nanocomposites were ground in a knife mill at liquid nitrogen temperature. Platelets 1 mm thick were formed from the loose ground material between two layers of Capton foil. Powdered samples did not reveal any privileged orientations of MMT platelets, opposite to molded film or injected nanocomposite bars.

4. Transmission electron microscopy; from 4 mm × 4 mm × 10 mm nanocomposite sections pressed at 210°C, ultra-thin sections were made at room temperature by a Tesla ultramicrotome using freshly prepared glass knives. The cuts were collected on the surface of 10% aqueous acetone solution and placed on a standard microscopic copper grid. Ultra thin sections were tested in a Tesla BS 500 transmission electron microscope at the accelerating voltage 90 kV.

5. Oxygen permeability. Tests were made according to the ASTM D 1434-1988 method V (volumetric), using a CS 135C apparatus (Custom Scientific Instruments). Experimental conditions: capillary 0.5 mm in diameter, temperature 21°C, pressure difference 100 – 95 psi.

### **3. Results**

#### **3.1. The degree of MMT exfoliation**

The degree of intercalation and exfoliation was estimated by the analysis of  $2\theta$  x-ray diffractograms of powdered nanocomposite samples. Curves shown in Fig. 2 reveal very small bulges on an increasing slope of the curve at a  $2\theta$  angle near to  $\approx 2.4$ - $2.7^\circ$ . This range of x-ray diffraction angles is characteristic of non-exfoliated MMT. An exception is the curve for Nano3 sample for which the bulge is very small. This confirms a very high degree of MMT exfoliation in all three samples of the nanocomposites. It is worth noting that nanocomposites Nano1 and Nano2 reveal a high degree of MMT exfoliation, while Nano3 sample shows the highest exfoliation degree despite the same composition; it differs only in the preparation procedure. These pictures confirm that the high degree of delamination of the clay platelets was achieved in both cases with a somewhat better dispersion of the nano-sized particles within the matrix in the case of sample Nano 3.

Bulges on the slopes of diffraction curves almost do not change their position in relation to relevant peak for plain MMT (Closite 15A) showing only a slight penetration of the



compatibilizer and/or PP into MMT galleries in these nanocomposites. On the other hand, exfoliation takes place without any distinct stage of intercalation. The exfoliation of clay apparently relies on the mechanism proposed by Iwasa et al. [46]. In Iwasa et al. mechanism the top sheet of MMT is removed from the stack starting from the edge. The exfoliation proceeds by removal of MMT platelets sheet by sheet. The attachment of the functionalized compatibilizer to the platelet edges provide a good leverage for its detachment from the stack. The results indicate that the strongest MMT exfoliation occurred in the Nano3 sample, which can be attributed to the two-step preparation procedure yielding more possibilities for action of Iwasa et al. mechanism: mixing of the compatibilizer with montmorillonite, and then compounding the concentrate with polypropylene.

The above observation is confirmed by the results of TEM studies of ultra thin sections of nanocomposite Nano3. Figure 3 shows a micrograph of mostly exfoliated MMT platelets. Each platelet in the microphotograph is isolated from other ones, and their mutual position reminds of the construction of a house of cards, the longitudinal dimensions of platelets ranges from 0.5 to 2  $\mu\text{m}$  and there are nearly no stacks of platelets visible. Micrographs of larger nanocomposite areas taken at lower magnification reveal full exfoliation and uniform dispersion of all MMT platelets within PP volume, besides there are occasional stacks of non-exfoliated MMT. The number of non-exfoliated MMT, estimated on the basis of counting visible MMT stacks in ultra thin sections, is around 0.5-1% of a total number of MMT particles introduced to the composite.

Additionally, the studies of other properties showed that the Nano3 sample had the lowest melt flow rate and superior mechanical properties in comparison with plain PP and the two other composites. Nano3 sample has the highest tensile strength, highest impact strength and the highest heat deflection temperature among the samples studied (77°C vs. 68°C for

plain PP) [see Ref.47 for the detailed characterization of those properties for the range of nanocomposites studied]. These properties, along with the highest elongation at break, can indicate very good MMT exfoliation of most particles.

### 3.2 Oxygen permeability

Results of studies on oxygen permeability at room temperature for plain polypropylene and nanocomposites are given in Table 1.

The reduced oxygen permeability of Nano3 sample as compared to the two other nanocomposites and polypropylene alone indicated also superior exfoliation of clay platelets over Nano1 and Nano2 composites.

### 3.3. Simultaneous TGA and DSC

Figures 3 and 4 illustrate results of thermogravimetric examination performed in the air and nitrogen, respectively. Tests made in the air showed that degradation of the PP1 sample started at 295 °C while of Nano3 at 365°C. The onset temperatures of degradation of these samples in nitrogen are 370-380 and 420°C, respectively. A significant difference in the temperature of degradation initiated in the air, 70°C, indicates that oxygen diffusion in the nanocomposite Nano3 is seriously impeded as compared to plain polymer (PP1). In nitrogen, thermal degradation is mainly expected with a slight or no thermooxidation due to the presence of a residual amount of absorbed oxygen. Therefore, in polypropylene and nanocomposites, the degradation in nitrogen should proceed in a similar manner and actually differences in the temperatures of the degradation onset are much smaller (34°C).

Figures 3 and 4 show also DSC thermograms for air and nitrogen, respectively, plotted against thermogravimetric runs. The DSC thermogram for plain polypropylene PP1 in the air in Fig. 3 shows a strong exothermic effect after exceeding the temperature of 215°C which is related to thermooxidative degradation, but still does not involve mass loss. This behavior is

typical of thermooxidative degradation of weakly stabilized polypropylene (time to start the oxidation ca. 3.1 min, according to EN 728/1999). At a higher temperature, above 245°C, the exothermic signal of degradation is now correlated with the mass loss of this sample due to thermooxidation, as recorded in TGA. This exothermic signal in DSC is associated with a decrease of heat capacity of the sample due to mass loss.

In nanocomposites Nano1 and Nano2 the first exothermic effect on DSC curves near 215°C related to polypropylene degradation is similar to the analogous effect in plain polypropylene. It is supposed that the first of these steps corresponds to the degradation of neat PP on the sample surface; during this first stage, PP macromolecules are degraded into volatile oligomers by the well-known fragmentation process [48,49]. Some propylene monomer units take part in peroxidation in positions opposing methyl groups which finally leads to double bonds between adjacent carbons in the main chain. This reaction is responsible for the brown color of oxidized PP [50].

A simple model to explain the second weight loss step involves the degradation of the residue formed during the first step. The oxidation of the sample surface determines the accumulation of MMT on the surface, with formation of a thermally stable phase, similar to the one previously observed on neat MMT heating. This ceramic superficial layer probably acts as a physical barrier, limiting the gas transport at the interface, thus influencing the kinetics of the degradation reactions. The proposed mechanism for such a barrier is based on two main steps: reducing oxygen diffusion towards the bulk and hindering the exit of the volatile degradation gases from the sample. The third factor is limiting the heat flux to the sample, however, as it follows from heat conductivity consideration, for a thin surface layer of MMT its insulation action is very sparse [48,49].

Above 245°C the exothermic effect is much reduced as compared to plain polypropylene PP1, and in nanocomposite Nano3 it appears only at the temperature around 380°C. This reduction

of exothermic effect is evidently connected with the two factors: 1. depressed oxygen diffusion in nanocomposites, and 2. reduced release of gas products of degradation. As follows clearly from the DSC curves, polymer degradation proceeds, but gas products are liberated in much smaller amount than in the case of plain PP1, as can be observed on the TGA curves.

A minor amount of charred residue is formed (ca. 4%) due to limited transformation to a thermally stable charred material of reactive degrading species during decomposition similarly as it was observed by Camino et al. [51].

This conclusion is confirmed by DSC runs in the nitrogen shown in Fig. 4, which does not reveal any exothermic effects. Instead, for plain PP1 the endothermic effects initiated at the temperature around 300°C appear, while mass loss starts at the temperature 370-380°C in the case of plain polypropylene (PP1) and at 420°C in the case of nanocomposites. Obviously, thermal degradation of polypropylene PP1 in the absence of oxygen (in nitrogen) is related to the endothermic effect (see the DSC curve for PP1 in Fig.4). In the case of nanocomposites Nano1, Nano2 and Nano3 the presence of exfoliated clay induces a stabilizing effect and prevents anaerobic polypropylene degradation up to the temperature 420°C

because on the DSC curves there is no other effect of enthalpy changes but the natural change of heat capacity with the temperature. . In the past some authors [e.g. Ref. 52] attributed the much better thermal stability to hindered out-diffusion of the volatile decomposition products (mainly cyclic silicates), as a direct result of the decrease in permeability, usually observed in exfoliated nanocomposites. Other authors [53] proposed other possible origins for the observed thermal stability improvement (which was also reported, in the same study, for silica-based nanocomposites) such as some inactivation of the centers active in the main chain decomposition by interaction with the filler or by prevention of the unzipping degradation from occurring through physical and chemical cross-linking points built up between polymer

chains and filler particles. Some of other older explanations are described in a review paper by Dubois et al. [54].

Optimal thermal stabilization is obtained at a filler content of ca. 2.5-5 wt.%. Below this value no thermal stabilization was observed while increasing too much the amount of nanofiller also decreases the thermal stability. At low filler content, exfoliation dominates but the amount of exfoliated particles is not high enough to promote the thermal stability through char formation. When increasing the filler content, relatively more exfoliated particles are formed, char forms more easily and increases the thermal stability of the nanocomposite until 2.5- 5 wt.% of nanofiller is reached. This explanation, likely valid for PP nanocomposites may not be applicable to other polymer matrices as demonstrated in a study on poly(etherimide) nanocomposites [55] where intercalated nanolayers were found to be better thermal stabilizers than the exfoliated ones.

However, the lack of mass loss in the nanocomposites alone does not provide an evidence that there is no thermal degradation of a polymer. On the other hand, the lack of endo- or exo-thermic effects on the DSC curves at high temperatures provides this evidence. In this case, this is not the mechanism of prolonged diffusion of oxygen and gas products of degradation, but a direct stabilizing action of clay platelets on polypropylene macromolecules that is observed. Most probably this is the stabilizing effect of the presence of MMT organo-modified with alkylammonium salts. Compounds that contain ammonium groups in organic compounds are known for their stabilizing properties.

As it is seen from Fig.4 the TGA curve for plain PP1 crosses the respective curves for nanocomposites at around 460°C which indicates that PP alone is more stable than nanocomposites at higher temperature. However, the lower stability of nanocomposites results from lower stability of the polymeric component in nanocomposite, which is a blend of polypropylene and maleinated polypropylene, and not plain polypropylene.

This communication on a stabilizing action of MMT platelets on both the enthalpy change and the release of volatile product in anaerobic degradation of polypropylene was made possible because of a simultaneous recording of TGA and DSC signals in the oxygen and oxygen-free atmosphere.

Contrary to the observation presented above, Filho et al. [11] described and explained an enhanced polypropylene degradation in the presence of intercalated organo-modified bentonite by its catalytic activity, specially due to the presence of  $Al^{3+}$  ions on the surface of clay platelets. However, those studies were carried out mainly in oxygen atmosphere (air) and bentonite was neither organo-modified nor exfoliated.

#### 4. Conclusions

Correlated DSC and TGA measurements allowed exothermic effects related to polypropylene thermooxidation to be separated from exothermic effects induced by a decrease of heat capacity of a material and related to the release of gas products of degradation. It has become evident that the improved resistance of a nanocomposite to degradation determined by the TGA method, is affected by the real reduced oxygen diffusion and apparent increase of resistance connected with depressed release of gas products of degradation.

Simultaneous DSC and TGA measurements showed explicitly a stabilizing effect of modified MMT platelets on thermal degradation of polypropylene in the oxygen-free atmosphere. Thermal degradation of plain polypropylene is related to the endothermic effect and occurs before the mass loss starts. In nanocomposites the endothermic effect is totally reduced and thermal degradation is shifted towards higher temperatures and correlated with mass loss.

Studies showed that lower susceptibility of nanocomposites to thermooxidation is strongly correlated with reduced oxygen permeability resulting from an elongated diffusion

path. This effect has been known for many years and can be emphasized specially in the case of platelet orientation in the foil plane. In the oxygen-free atmosphere, thermal degradation of polypropylene in the tested nanocomposites is reduced up to the temperature 420°C. There is a new mechanism that consists in a stabilizing effect which the surface of exfoliated MMT platelets or their alkylammonium modification has on polypropylene macromolecules that are in contact with them in the oxygen-free atmosphere.

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ACCEPTED MANUSCRIPT

Table 1. Oxygen permeabilities of nanocomposites Nano1, Nano2 and Nano3 and plain polypropylene PP1

Sample	Mean sample thickness [mm]	Mean oxygen permeability [ $\text{cm}^3 \text{mm}/\text{m}^2 \text{24h atm}$ ]
PP1	0.47	27.6
Nano1	0.48	24.6
Nano2	0.49	22.2
Nano3	0.46	16.1

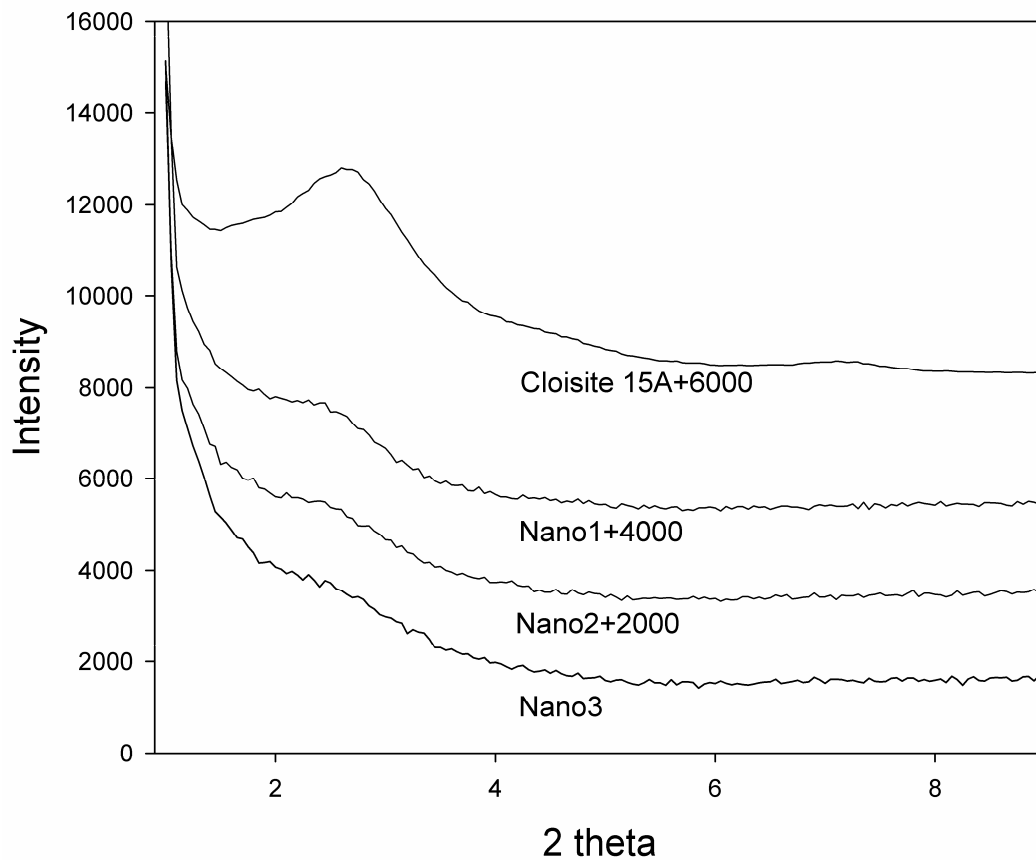


Fig. 1.  $2\theta$  x-ray diffraction curves of powdered nanocomposites Nano1, Nano2 and Nano3. Curves are shifted in the vertical direction by the value indicated at the sample description.

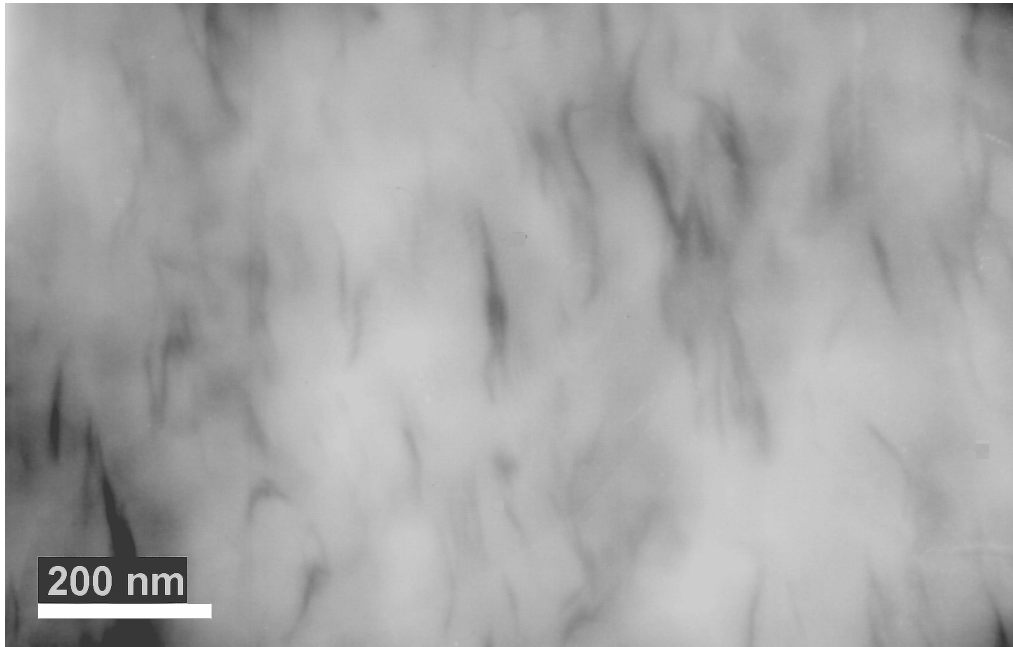


Fig. 2. Transmission electron micrograph of ultra thin section of a nanocomposite Nano3 sample.

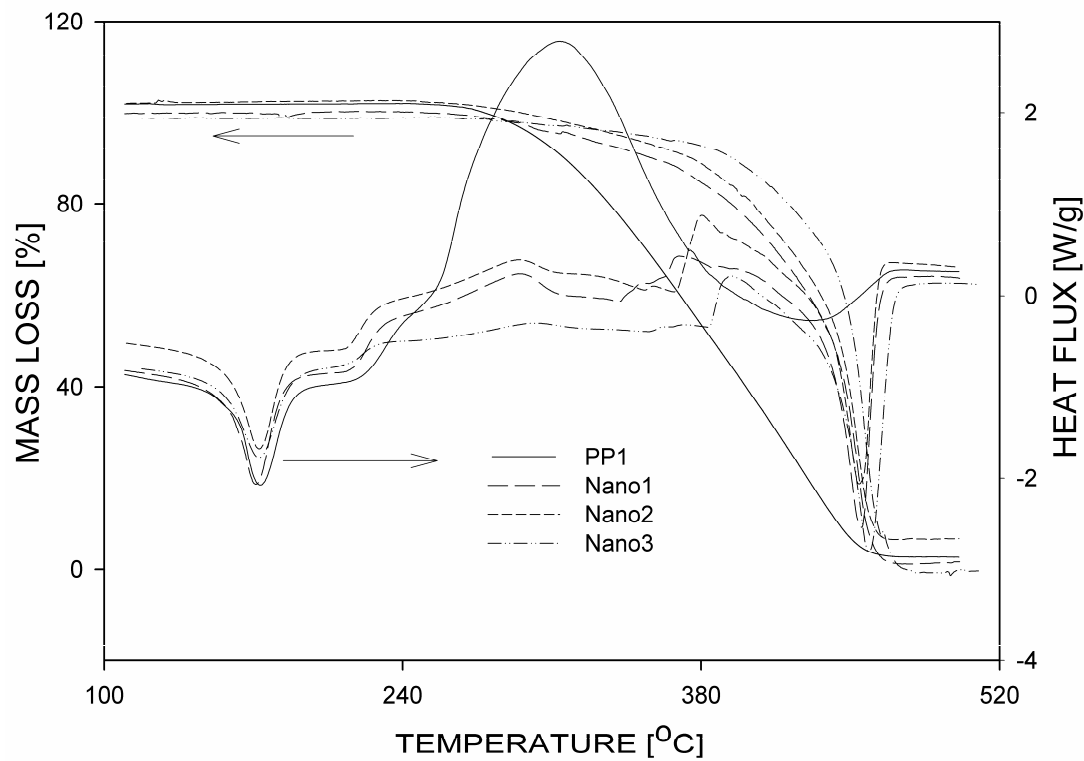


Fig. 3. TGA and DSC curves for nanocomposites PP1, Nano1, Nano2 and Nano3 under air flow. TGA and DSC curves were slightly shifted vertically for better visualization.

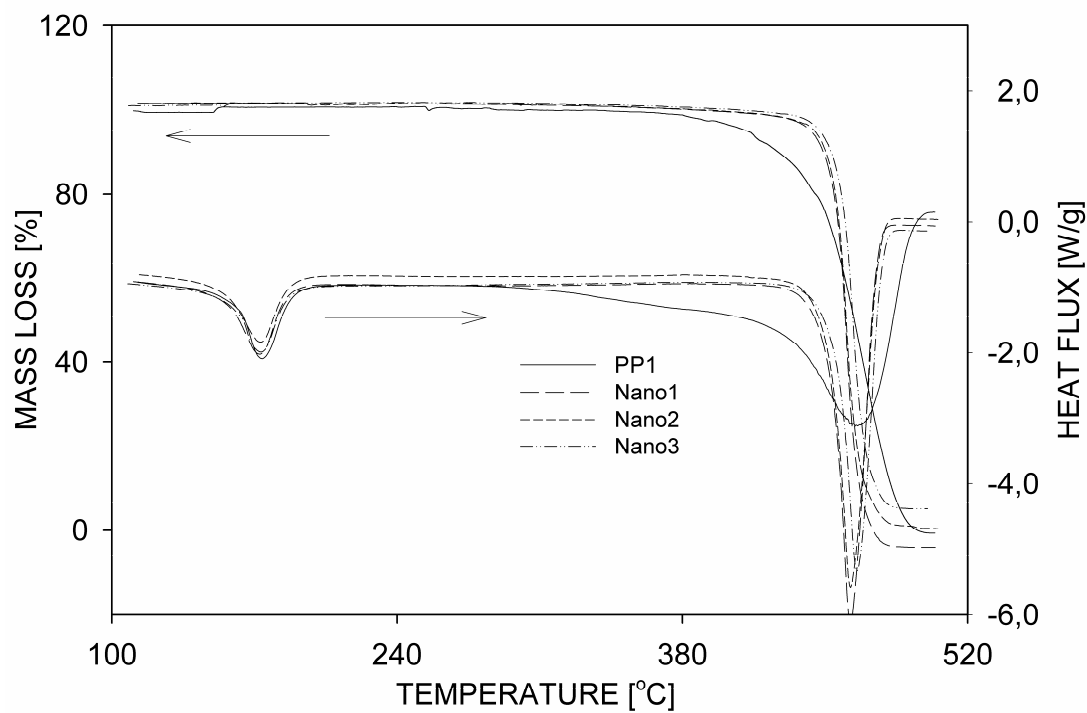


Fig. 4. TGA and DSC curves for nanocomposites PP1, Nano1, Nano2 and Nano3 under nitrogen flow. TGA and DSC curves were lightly shifted vertically for better visualization.