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Thermal properties of new composites based on nanoclay, polyethylene and polypropylene

Ewa Olewnik · Krzysztof Garman ·
Wojciech Czerwiński

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Abstract The results presented by a number of researchers indicate that the introduction of montmorillonite into polymer matrix results in an increase of thermal stability of polymer nanocomposites. The main purpose of this study was to evaluate the effect of the organoclay on the thermal degradation of polyolefins (polyethylene and polypropylene). Polyolefin-clay nanocomposites were prepared by melt compounding of polyolefins and montmorillonite clay organically modified with 4,4′-methylenebisaniline (MBA) (from 1.5 to 5 wt%). Changes in the surface of montmorillonite and the dispersion of organoclay in the polymer matrix were evaluated using X-ray diffraction (XRD) and elemental analysis. The thermal stability of the clay and nanocomposites were analysed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TG). The XRD results show that almost complete exfoliation of the silicate layers took place and nanocomposite structure was obtained for all new materials. The thermal stability of the PE and PP/clay nanocomposites can be improved in the case of loading above 5 wt%.

Keywords Thermal degradation · Nanocomposites · Nanofillers · Montmorillonite · Polyolefins

Introduction

Montmorillonite is one of the most common smectites, which is widely used in a range of applications because of its high cation exchange capacity, swelling capacity, high surface areas, and resulting strong adsorption [1]. There are two natural varieties of montmorillonite: sodium montmorillonite having a high swelling capacity in water and calcium montmorillonite with slight swelling capacity. The ability to cation exchange in the interlayer space determines the most interesting property of this material which can be used as a filler for nanocomposites showing unique mechanical properties [2].

Key point, during the formation of nanomaterials, is the dispersion of the clay particles in the polymer matrix. The most desired situation occurs when the individual clay platelets disperse uniformly into the polymer (exfoliation or delamination) which results in desired beneficial properties [3]. The properties of the composites are determined by such factors as shape and volume fraction of the filler as well as the morphology of the system and the nature of the interphase that sometimes develops at the interface of the two components [4].

Organoclay-based nanocomposites exhibit a remarkable improvement in properties when compared with an untreated polymer or conventional micro- and macrocomposites. These improvements include increased thermal stability of polymer/clay nanocomposites, strength and heat resistance, decreased gas permeability and increased biodegradability of biodegradable polymers [5]. To date, polymer/clay nanocomposites have been successfully used in several kinds of polar polymers. However, for polymers with low polarity, such as polyolefins, the current results are not satisfactory due to the low compatibility between the clay and the polyolefins [4].

In this article, we describe the synthesis of polyolefins/modified montmorillonite nanocomposites with 1.5–5 wt% clay modified with MBA. The MBA has been chosen because, according to the Iwasa's mechanism of exfoliation,

E. Olewnik (✉) · K. Garman · W. Czerwiński
Faculty of Chemistry, Chair of Physical Chemistry
and Physicochemistry of Polymers, Nicolaus Copernicus
University, 7 Gagarin Street, 87100 Torun, Poland
e-mail: olewnik@uni.torun.pl

it is possible that a molecule with two amine functionalities can be an exfoliating agent [6]. The modified montmorillonite (MMT–MBA) was expected to be useful as a filler of polymers in the process of nanocomposite production ((PE/MMT–MBA) and (PP/MMT–MBA)). This article focuses on the structure and thermal properties of new nanocomposites. The potential property improvements usually depend on the degree of delamination and dispersion, which depends on a combination of the proper chemical treatment and optimized processing.

Experimental part

Materials

The natural clay mineral—montmorillonite, used in this study was provided by the Riedel–de Haen. The surfactant used for the modification was MBA and was supplied by Sigma–Aldrich (melting point: 361–366 K, boiling point: 671–672 K). The modification was carried out using hydrochloric acid and ethanol (POCH, Poland). Polyolefins were delivered by Basell–ORLEN Polyolefins (Plock, Poland). PE was LDPE, Malen E FABS 23D022, MFR 2 g 10 min^{-1}, d 0.92 g cm^{-3}. PP was Malen P F-401, MFR 2.8 g 10 min^{-1}.

Preparation of surfactant-modified montmorillonite and nanocomposites

The organophilic montmorillonite was prepared in the ion-exchange reaction. 4,4′-methylenebisaniline was dissolved in water/ethanol mixture and protonated in situ with HCl to obtain cations. The temperature of the mixture was increased from room temperature to about 343 K. Then montmorillonite powder was slowly added and dispersed in a solution of pre-dissolved amount of surfactant. The reaction was continued for 3 h. The precipitate was collected by filtration and washed several times with water until no chloride ions were detected by $AgNO_3$ solution. Organoclay was being dried for 24 h at 353 K. The initial ratios of amine/clay and HCl/MBA were 2 mmol g^{-1} and 2 M ratio, respectively.

The nanocomposites of polyolefins (LDPE and PP) with modified montmorillonite (from 1.5 to 5 wt%) were prepared by melt intercalation process, using a single-screw extruder with temperature setup in range 403–433 K for LDPE and 423–473 K for PP, from loading section to dye, respectively.

Characterization techniques

Differential scanning calorimetry (DSC) was performed on a Polymer Laboratories, Epson, GB differential scanning calorimeter under N_2 screening with flow rate about 15 ml min^{-1}. Various conditions were used for different kinds of nanocomposites depending on polymer matrix. In the first step PE and its nanocomposites were cooled from room temperature to 123 K at a cooling rate of 10 K min^{-1}, then this temperature was maintained for 10 min. In the next step samples were heated to 473 K with a heating rate of 10 K min^{-1}. Thermal behaviour of PP and PP/clay nanocomposites was examined in the similar conditions to PE with one difference: in the first step samples were cooled to 223 K. The melting and crystallization characteristics were evaluated without elimination of thermal and mechanical prehistory.

Powder X-ray diffraction (XRD) patterns between angles 1° and 12° were obtained with an X'Pert Philips diffractometer using CuK_α filtered radiation ($\lambda = 1.5418$ Å) at 40 kV, 40 mA. Divergence slit size was 0.125°; scan step time 25 s. The basal spacing of the montmorillonite layer was calculated using the Bragg's equation.

Thermal analyses of surfactant-modified montmorillonite and nanocomposites were performed on TA Instruments, SPT 2960 Simultaneous DSC-TGA. All measurements were carried out at a heating rate of 10 K min^{-1} under the flow of air and nitrogen from room temperature to 873 K.

Elemental analysis of the modified montmorillonite for the determination of C and N was carried out with Vario MACRO CHN Elementary Analyzer (Analysensysteme, Germany).

Results and discussion

Elemental analysis

This method was used for determining the quantity of the modifying agent absorbed by montmorillonite during modification process. In order to achieve this the content of C and N was checked in a few samples of MMT–MBA and neat MMT. Results of this analysis and calculation are presented in Table 1. Value '% consumption of MBA' represents the effective quantity of MBA consumed in the modification process in relation to the initial quantity introduced in the reaction.

In view of the above-mentioned results the quantity of the modifier absorbed by 1 g of montmorillonite and percentage consumption of MBA were determined. It can be deduced that the values of used MBA (Fig. 1a) depend strongly on the geometry of this molecule and changes in its conformation during modification process. It arises from the fact that tetrahedral atom of carbon presences in MBA molecule it is a specific centre of rotation (Fig. 1b). Rotation around the methyl group in this particular case results in a perpendicular position of the two rings of the molecule (Fig. 1c).

Table 1 Results of elementary analysis of MMT and MMT modified with MBA

Parameter	Sample	
	MMT	MMT–MBA
Mass of sample/mg	132.110	144.410
%C in sample/%	0.822	3.498
%N in sample/%	0.036	0.585
Mass of MBA in sample/mg	–	4.907
Mass MBA per 1 g MMT/mg g^{-1}	–	35.175
Quality of MBA per 1 g MMT/mmol g^{-1}	–	0.177
% consumption MBA/%	–	8.870

XRD analysis

The XRD technique is often applied to identify structures through Bragg's relation. Figure 2 displays XRD patterns of modified (MMT–MBA) and unmodified (MMT) montmorillonite clay. Pristine MMT shows a characteristic diffraction peak at 6.20° which corresponds to a d-spacing of 1.38 nm. Organo-modified MMT shows the 001 diffraction peak at 6.00°, indicating increased d-spacing of MMT–MBA (1.47 nm) which confirms the presence of the salt molecule intercalation between montmorillonite clay layers [7]. Similar values of basal spacing were found for e.g. montmorillonite organophilised by phenylalanine (1.49 nm) and tyrosine (1.46 nm) [8].

In an attempt to evaluate whether the nanocomposite structure was formed or not, filled samples were analysed by XRD. The XRD profiles of PP and PP nanocomposites containing 1.5–5 wt% clay are shown in Fig. 3. XRD studies of PP/MMT–MBA samples indicate that the d-spacing of the clay in the composite is almost equal to the one for the modified clay mineral. This can indicate the formation of an ordinary composite, not a nanocomposite [7]. But simultaneously we observed the substantial reduction in the intensity of the diffraction peak derived from the interlayer spacing of the clay and this can be the indication of the fact that almost complete exfoliation of the silicate layers took place and nanocomposite structure was obtained [9].

Similar trends were also observed in the final PE/clay materials (Fig. 4). According to the calculation the value of d001 for new materials is 1.53 nm and evidently is close to the distance of the modified clay, which allows for conclusion that the increase of the basal spacing did not occur. The reason is that the polarity of PE is probably too low to gain any interaction with the organoclay and insufficient to form an intercalated nanocomposite. It is possible that for non-polar polyethylene, the hydroxyl groups at the edge of clay layers can impair the formation of nanocomposites and only conventional microcomposites can be obtained

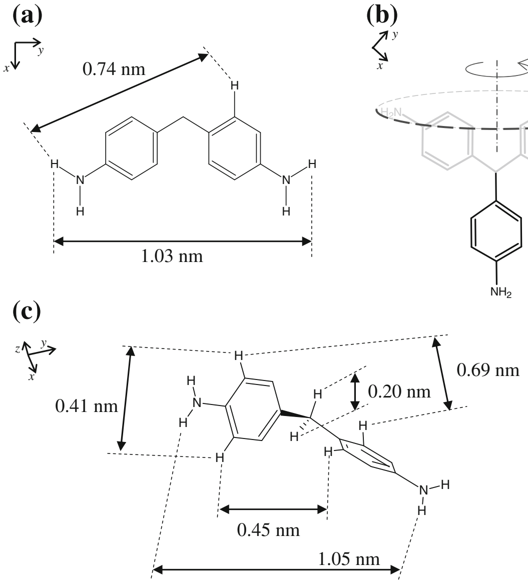

Fig. 1 Geometry of molecule MBA

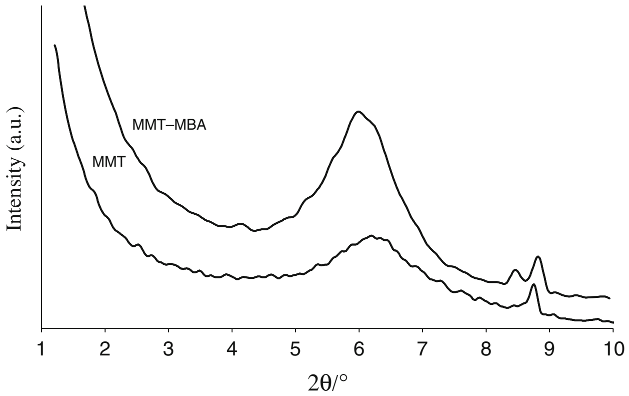

Fig. 2 X-ray diffraction patterns of modified (MMT–MBA) and unmodified (MMT) montmorillonite

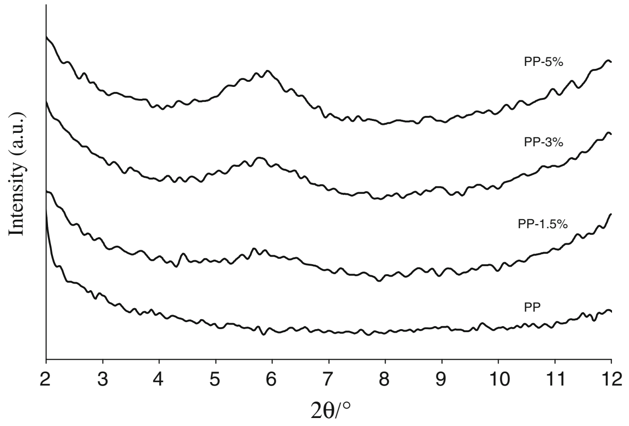

Fig. 3 X-ray diffraction curves of PP and PP/MMT–MBA nanocomposites

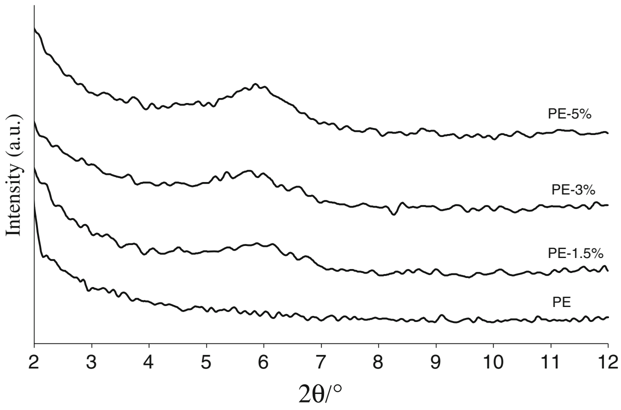

Fig. 4 X-ray diffraction profiles of PE and PE/MMT–MBA nanocomposites

[10]. But in our case we observed the reduction in the intensity of the diffraction peak as in the case of PP/MMT–MBA materials. In view of these results, we suggest that the product is an exfoliated nanocomposite.

Differential scanning calorimetry

Differential Scanning Calorimetry (DSC) analysis is generally one of the most convenient methods for analysing first order transitions like melting and crystallization. The nanocomposite samples with varying concentration of clay were subjected to DSC analysis and the results are presented in Table 2. The properties studied were the melting temperature taken at the melting peak T_m, glass transition temperature T_g, the heat of fusion H_m due to the PE and PP melting, measured by the melting peak and the degree of crystallinity X_c, where enthalpy of melting of pure crystalline PE and PP are, respectively, 279 and 207.1 J g^{-1} [11, 12]. No meaningful difference was observed in the melting temperatures of the PE matrix for the different samples studied, but DSC showed an 18 K decrease in the glass transition temperature of the nanocomposite prepared by melt intercalation process with 5 wt% of nanofiller when compared to pure polyethylene. This decrease in T_g is related to the nanocomposite morphology—partially exfoliated nanocomposite [13]. We did not observe glass transition temperature for PP and its nanocomposites.

Table 2 Heat of melting H_m, degree of crystallinity X_c, melting and glass temperature T_m,T_g of nanocomposites as a function of MMT–MBA content

Sample	T_g/K	T_m/K	H_m/J g^{-1}	X_c/%
PE	195.5	385.9	69.9	25.1
PE-1.5%	183.0	385.3	90.4	32.4
PE-3%	183.7	385.7	88.9	31.9
PE-5%	178.9	385.5	75.4	27.0
PP	–	445.5	66.1	31.9
PP-1.5%	–	441.3	86.2	41.6
PP-3%	–	440.1	85.8	41.4
PP-5%	–	439.6	83.3	40.2

It was found that the heat of fusion for PE-based samples increases considerably, especially at a lower, 1.5 wt% concentration of loading (90.4 J g^{-1}) and decreases very slightly with further increase in clay concentration until 75.4 J g^{-1}. The same results can be observed for nanocomposites of PP where the DSC results clearly show that the addition of a small amount of modified montmorillonite into the PP matrix causes an increase of heat enthalpy.

There are two possible reasons why the H_m does not increase in relation to the addition of clay but even decreases slightly. On the one hand, this phenomenon may be caused by the slowing down of kinetics of crystallization. The second reason may be the blockage of crystalline growth front caused by the clay platelets, dispersed in an irregular array in the nanocomposite, as it is evident in view of hot-stage microscopy studies [14].

In the case of nanocomposites the decrease in T_m is usually attributed to the fact that clay platelets act as nucleating centres and favour crystallization by providing a higher level of nucleation density [15]. We can speculate that this effect takes place in the case of PP/MMT–MBA nanocomposites where the increasing amount of modified MMT causes the melting peak temperature to decrease to the point of 439.6 K for 5 wt% of organoclay. We did not observe this effect for PE nanocomposites where the addition of nanofiller had a minimal effect on the melt temperature of the new materials. We also managed to confirm that the presence of the organoclay had a nucleating effect, because the degree of crystallinity was more significant than for pure polymers [15].

Therefore, this study on the thermal stability, besides using DSC, must be complemented by other kinds of analysis techniques such as TG.

Thermogravimetric analysis

Another highly interesting property exhibited by polymer-modified montmorillonite nanocomposites concerns not only their thermal stability but also their unique ability to promote flame retardancy at low filling level through the formation of insulating and incombustible char. Char may act as a physical barrier between the polymer medium and the superficial zone where flame combustion occurs. The first indication of thermal stability improvement in nanocomposites appears in the context of study of the thermal stability of PMMA intercalated within montmorillonite [16].

The role of clay in the nanocomposite structure may be the main reason for the difference in TG results of these systems when compared to neat polyolefins. The clay acts as a heat barrier and assists in the formation of char after thermal decomposition [17].

The thermal degradation of a material is usually determined by a thermogravimetric analysis. The important parameters are the onset temperature of the degradation, which is measured as the point in which 10% of the sample is lost, the mid-point of the degradation, and the last measurement of thermal degradation is the fraction of material which is non-volatile at 873 K, known as char [17].

Figure 5 shows the TG curves for unmodified (MMT) and modified montmorillonite (MMT–MBA). It is apparent from this study that the initial degradation temperatures are similar fort both samples. For the natural and modified clay the initial mass loss between 293 and 473 K is observed due to residual water, but in the case of MMT–MBA the quantity of water is significantly lower. There was also a decomposition between 673 and 873 K which can be connected with dehydroxylation of the aluminosilicate [9].

Figure 6a shows the TG results for pure PE and for nanocomposites containing 1.5, 3 and 5 wt% of the organo-montmorillonite tested in air atmosphere. First of all we can note that in both cases 1.5 and 3 wt% the organo-montmorillonite caused faster thermal degradation of the matrix, it can be observed that the decomposition temperatures at 10% mass loss of these materials were lower than the pure PE (Table 3). It is not a novelty and we have to bear in mind that the alkylammonium cations in the organoclay could suffer decomposition following the Hofmann elimination reaction, and what is interesting its product simultaneously with the clay itself would catalyse the degradation of polymer matrixes [11].

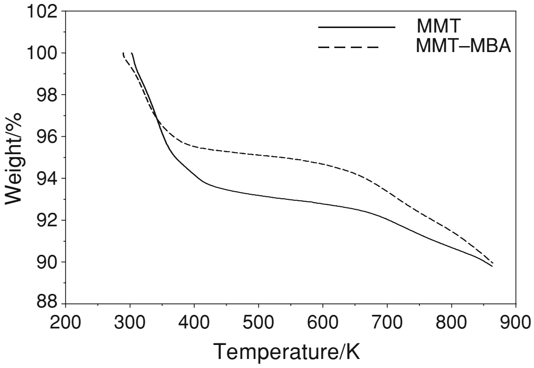

Fig. 5 TG curves for unmodified (MMT) and modified montmorillonite (MMT–MBA)

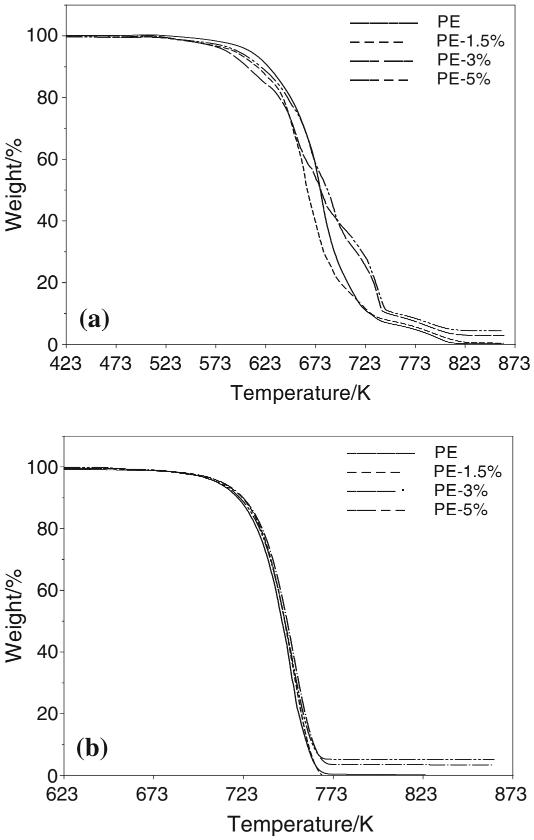

Fig. 6 TG analysis for PE and PE/MMT–MBA nanocomposites under air (**a**) and nitrogen (**b**) flow

The thermal degradation of PE and PE/clay nanocomposites tested by TG in nitrogen atmosphere are shown in Fig. 6b. In contrast to above-discussed results, the temperature for the onset of thermal decomposition decreased slightly with the increase in the clay content. The reason is that under nitrogen flow we do not observe the catalysis effect towards the degradation of the polymer matrix.

Figure 7a shows TG results for PP-based nanocomposites filled with increasing filler content in air atmosphere. It can be observed that for PP-based nanocomposites, a small amount of clay (1–3 wt%) also slightly decreases initial thermal stability of PP/MMT–MBA (Table 3). But we have to bear in mind that it has been indicated that at low clay loading (1–3 wt%), exfoliation dominates but the amount of exfoliated nanoclay is not enough to enhance the thermal stability through char formation. The situation changes with increase of the clay concentration (5 wt%), where as result much more exfoliated clay is formed, char forms more easily, which effectively and consequently promotes the thermal stability of the nanocomposites [18]. In view of the above-mentioned facts our results confirm that the PP/MMT–MBA nanocomposite with 5 wt% modified MMT shows a higher thermal stability than pure PP. Figure 7b shows the TG curves, in a nitrogen

Table 3 TG data for PE, PP and their nanocomposites under air and nitrogen flow

Sample	Temperature/K at mass loss under air flow		Residue at 873 K/%
	10%	50%	
PE	625.5	677.3	0.39
PE-1.5%	614.2	664.4	0.41
PE-3%	604.2	677.9	2.89
PE-5%	617.9	684.8	4.34
PP	540.0	581.9	0.32
PP-1.5%	535.0	574.8	1.73
PP-3%	535.1	582.5	0.69
PP-5%	548.4	610.6	2.69

Sample	Temperature/K at mass loss under nitrogen flow		Residue at 873 K/%
	10%	50%	
PE	719.6	744.2	0.37
PE-1.5%	721.9	746.4	0.82
PE-3%	722.6	747.0	3.40
PE-5%	720.8	745.8	5.16
PP	703.9	727.0	0.38
PP-1.5%	707.5	729.0	1.09
PP-3%	705.4	726.6	2.13
PP-5%	706.6	725.2	3.48

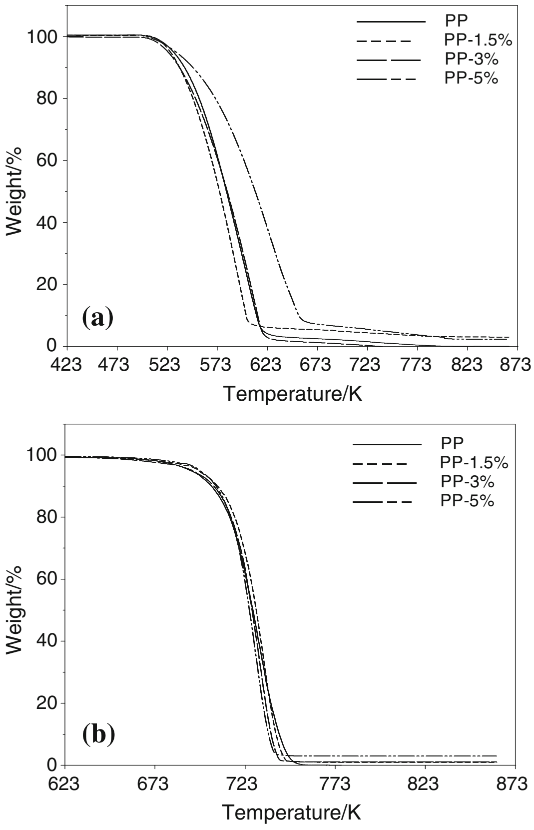

Fig. 7 TG analysis for PP and PP/MMT–MBA nanocomposites under air (**a**) and nitrogen (**b**) flow

atmosphere, of PP and its nanocomposites. In this case we can observe an opposite effect where the introduction of the nanoclay does not impair the thermal stability of polypropylene, but even very slightly improves (Table 3). It can be assumed that the Hofmann elimination reaction does not occur in nitrogen atmosphere, but it does take place under air flow.

Conclusions

- The substantial reduction in the intensity of the diffraction peak derived from the interlayer spacing of the clay can be the evidence that almost complete exfoliation of the silicate layers took place and that nanocomposite structure was obtained for all new materials.
- Due to the characteristic structure of layers in polymer matrix, their shape and dimensions close to molecular level, several effects have been observed that can explain the changes in thermal properties.
- Organoclay has two opposed functions in the thermal stability of the PE and PP/clay nanocomposites, one is being the barrier effect improving the thermal stability, and another is being catalyst, leading to the decrease of thermal stability. The obtained results for the PE and PP/clay nanocomposites warrant a conclusion that thermal stability of this kind of material will be greatly

improved due to the formation of the clay-enriched protective char during the combustion but apparent only in the case of loading above 5 wt%.

– The DSC results show that the heat of melting of nanocomposites was increased in comparison with the neat polyolefins. All nanocomposites based on PE display a lower T_g than the virgin PE.

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