



Thermal stability of polypropylene–montmorillonite clay nanocomposites: Limitation of the thermogravimetric analysis



Lays B. Fitaroni ^a, Juliana A. de Lima ^a, Sandra A. Cruz ^{a,*}, Walter R. Waldman ^b

^a Universidade Federal do ABC, Centro de Engenharia, Modelagem e Ciências Sociais Aplicada, Avenida dos Estados, 5001, Bairro Bangu, CEP: 09210-580, Santo André, SP, Brazil

^b Universidade Federal de São Carlos, Campus Sorocaba, Departamento de Física, Química e Matemática, Rodovia João Leme dos Santos, Km 110, SP-264, Bairro do Itinga, CEP: 18.052-780, Sorocaba, SP, Brazil

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ABSTRACT

The development of nanocomposite materials with polymeric matrices, especially those using layered silicates, provides an alternative to composites with conventional fillers. One of the controversial aspects in the scientific literature about polypropylene–montmorillonite nanocomposites (PP/OMMT) regards its thermal stability compared to the PP matrix. The aim of this work is to evaluate the influence of the presence of montmorillonite clay in the degradation of composites, showing the limitations of thermogravimetric analysis (TGA) and emphasizing the importance of complementary analyzes such as differential scanning calorimetry (DSC) and oxidation induction time (OIT). The TGA results showed that the higher the organoclay content, the higher the temperature at which the release of volatiles takes place. However, the OIT results indicated a lower temperature for the onset of exothermic reactions for these materials and consequently the stability of the material is reduced. The use of DSC method simulating conditions of TGA, called oxidation induction temperature or dynamic OIT, was used to evaluate the stability of the composites explaining the divergence between the TGA and OIT results. The thermal analysis results were correlated to organoclay morphology, as evaluated by WAXS. It was concluded that the clay contributed to the beginning of exothermic oxidation reactions and to the kinetics decrease of volatile release and its formation.

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1. Introduction

The development of nanocomposite materials with polymeric matrices, especially those using layered silicates, provides an alternative to composites with conventional fillers. Organically modified montmorillonite clay (OMMT) has been widely used in polymeric matrices such as polypropylene (PP) due to its high aspect ratio and its capacity to produce materials with good final properties, such as mechanic, high gas barrier and solvent resistance [1].

Despite many papers and its discrepancies on PP/montmorillonite clay nanocomposites [2–4], very little is known about the influence of the filler on the PP stability. Many studies have reported increased thermal stability of nanocomposites in relation to the pristine PP in the presence of an organoclay [5–9]. However, other authors have described that the polymeric matrix degradation is accelerated due to the presence of the same clay [4,10–12].

Santos et al. [5] studied PP/OMMT nanocomposites and verified that the incorporation of the filler induces an increase in thermal stability as well as the ability to promote flame retardancy even in small quantities. According to them, during the combustion process a charred layer is formed reducing the heat and mass transfer, decreasing the polymeric matrix degradation processes. In another work, Golebiewski and Galeski [6] analyzed the thermal and thermo-oxidative stability of nanocomposites PP/OMMT. They used two thermal analysis techniques, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), and transmission electronic microscopy (TEM) and oxygen permeability testing. The results showed a significant inhibition of the thermal degradation of the polymeric matrix in the nanocomposites. The degradation temperature in an inert atmosphere was of around 420 °C for the nanocomposites instead of 300 °C for pristine PP. The authors also verified that nanocomposites could be less sensitive to thermal oxidation. This was attributed to the presence of the lamellae clay increasing the diffusion path of oxygen or volatile products.

However, the work of Gutiérrez et al. [11] demonstrated that the montmorillonite clay in the nanocomposite of the PP provides a

* Corresponding author. Tel.: +55 11 4996 0147.

E-mail address: sandra.cruz@ufabc.edu.br (S.A. Cruz).

catalytic effect leading to a necessary time reduction for the material thermal oxidation. The authors reported that the higher the montmorillonite content, the higher the product oxidation concentration in the material.

Studies evaluated the stability of organoclay [13] in nanocomposites made with polyesters [14], polyamides [15] or polyesters and polyolefins blends [16,17]. Scaffaro et al. [13] verified that the organic modifier present on the clay suffers degradation. It was observed an increase in the degradation rate in the presence of oxygen, producing carboxyl compounds. The degradation of the modifiers initially leads to an increase in the basal spacing, but after the decomposition products had migrated to the surface the structure collapses. Some studies show that the polyesters [14] and polyamides [15] nanocomposites present modifiers degradation in the processing temperature. Scaffaro [16] evaluated the effect of various quaternary alkyl ammonium organoclays on Nylon 6 with different molar mass. The results prove that the degradation level depends on the Nylon type as well the surfactant chemistry in the clay. Another study concerning polyamides/polyolefins blends with Cloisite 15A shows the interactions between the organic modifier degradation products (carbonyl groups) and the oxazoline compatibilization promoter [15]. The authors proved the need of stabilization of this system.

The thermal stability of materials, such as the polymeric composites studied in this work, can be evaluated using thermal analysis, such as TGA, DSC and oxidation induction time (OIT). The autocatalytic cycle of polymer degradation consists of radical reactions involving oxygen, generating exothermic reactions [18]. The heat release in these exothermic reactions is the basis of analytical techniques such as OIT. Cruz and Zanin [19], for example, demonstrated that these variations of heat flow depend on the oxidized species content in the polymeric material.

On the other hand, DSC is based on endo and exothermic events in an inert environment with a closed sample holder [20]. The TGA analysis detects mass changes as a function of temperature in a controlled atmosphere, inert and oxidative. In the case of polymeric materials, the mass loss occurs from the low molar mass volatile fragments formation after several autocatalytic degradation cycles [20,21]. Therefore, release of volatiles and mass change always occur after the exothermic reactions have started. Thus, TGA results indicate processes that occur subsequently to those measurements by OIT. Erroneous conclusions about the matrix stability can be avoided using TGA and DSC in a complementary manner [16], correlating the heat and mass release with two distinct techniques under the same conditions.

The aim of the present study is to evaluate the influence of organically modified clay in PP nanocomposite degradation and to propose the use of TGA and DSC as complementary techniques in order to assist in the controversies found in the literature. Nanocomposites samples were produced with different montmorillonite clay content to analyze the effects of organoclay on the thermal degradation.

2. Experimental

2.1. Materials

The materials used were polypropylene H105 (Braskem S.A., Brazil), with a melt flow index (MFI) of 40 g/10 min (ASTM 1238, 230 °C, 2.16 kg), and Cloisite® 20A montmorillonite organoclay (Southern Clay Products), modified with bis(hydrogenated tallow alkyl)dimethyl quaternary ammonium salt, with a cation exchange capacity of 95 meq/100 g clay and a real density of 1.77 g/cm³ [22]. The samples were termed as PP (pristine polypropylene), PP:1 (polypropylene with 1wt% montmorillonite clay); PP:3

(polypropylene with 3wt% montmorillonite clay) and PP:5 (polypropylene with 5wt% montmorillonite clay).

2.2. Processing

Pure PP and additives were mixed manually and then extruded in a twin screw extruder (Haake Rheomex model) at 170 °C in all zones with a screw speed of 120 rpm and L/D 20. After extrusion, the nanocomposites were injection molded according to ASTM D-638 (type 1) in an injection molding machine (Demag Ergotech Pro 35-115), at a temperature between 220 and 230 °C in the cylinder, and 60 °C in the mold. Thermal analyzes were performed on injected specimens.

2.3. Wide angle X-ray scattering

WAXS experiments were performed at the D11A-SAXS1 beamline with a two-dimensional imaging plate detector (2D-SAXS) at the Brazilian Synchrotron Light Source (LNLS), using a position sensitive detector for the small angle region. The wavelength used was $\lambda = 1.608 \text{ \AA}$ and the sample-to-detector distance used was 477.5 mm. The data were collected with a two dimensional imaging plate and the scattering profiles were obtained from radial integration of the images. The measurements were taken at 25 °C and the scattering profiles were corrected for sample absorption and detector response.

2.4. Thermogravimetric analysis

The thermogravimetric characterization of the nanocomposites and the organoclay were performed on a TA instrument model Q500-1153. The samples have an average mass of $6.0 \pm 0.7 \text{ mg}$ and were subjected to heating up to 600 °C (pure polymer and nanocomposites) and 900 °C (organoclay) at a heating rate of 10 °C/min under oxygen atmosphere (50 mL/min). All measurements were made in duplicate.

2.5. Differential scanning calorimetry

The DSC analysis, DSC Q2000 – TA Instruments, was performed using two different methods. The first method is the usual DSC, where the samples were characterized in relation to the heat of melting and crystallization. The samples were subjected to a heating/cooling cycle from 25 to 200 °C, then cooled to –20 °C and heated again to 200 °C in an atmosphere of nitrogen (50 mL/min) at a heating rate of 20 °C/min in a closed sample holder. Melting temperature (T_m), melting enthalpy (ΔH_m) and degree of crystallinity ($\%_{\text{cryst}}$) were obtained. The first heating curve was evaluated to assist in the interpretation of the TGA results, since the samples used in TGA did not have their thermal history deleted. The degree of crystallinity ($\%_{\text{cryst}}$) of the samples was calculated from the melting enthalpy results (ΔH_m) of each sample using Equation (1), where χ_{PP} is the mass fraction of the PP in the samples, ΔH_m is the experimental melting enthalpy and ΔH_m^0 is the melting enthalpy for 100% crystalline PP, 207.1 J/g [23].

$$\%_{\text{cryst}} = \frac{\Delta H_m}{\chi_{\text{PP}} \cdot \Delta H_m^0} \times 100 \quad (1)$$

In the second method, called oxidation induction temperature or dynamic OIT [24], the samples were characterized with respect to the energy released during the oxidation reactions. The samples were subjected to heating from 25 to 300 °C in an oxygen atmosphere (50 mL/min) at a heating rate of 10 °C/min with the sample holder open (to simulate the thermogravimetric analysis

conditions). The samples have an average mass of 6.0 ± 0.7 mg and the measurements were done in duplicate.

2.6. Oxidation induction time

The equipment DSC Q2000 (TA Instruments) was used to measure the OIT. Samples of 5.2 ± 0.3 mg were heated at $20^\circ\text{C}/\text{min}$ in a nitrogen atmosphere until 200°C (according to ASTM D3895-07 [25]). After 5 min of isotherm, the nitrogen atmosphere was replaced by oxygen (50 mL/min), and then a 35 min isotherm was performed. All samples were measured in duplicate.

3. Results and discussion

3.1. Wide angle X-ray scattering

In order to characterize the microstructure of the organoclay layers in PP nanocomposites, WAXS technique was used. The curves, in Fig. 1, are shifted from each other to enhance the visualization of each curve.

In the wide-angle region ($q > 1 \text{ nm}^{-1}$), the peaks in the curves indicate that the scattering vector (q) at maximum $I(q)$ corresponding to the d-spacings of the different PP/OMMT nanocomposites. The original OMMT d-spacing is 2.42 nm (q), as described in the literature [26].

The peak in the curve for PP:3 nanocomposite indicates that the scattering vector (q) at maximum $I(q)$ is slightly shifted to lower values of q in relation to pure OMMT, despite the slight intensity of this peak, showing that the clay interlayer spacing increased during the extrusion process. This shows that PP chains intercalated within the organoclay galleries. Thus, the WAXS results suggest that the PP:3 nanocomposites have an intercalated morphology. On the other hand, for other nanocomposites compositions there is no peak in this region. Paiva and cols [27] and Morelli and Ruvolo Filho [23] also observed the peak scattering disappearance referring to clay nanocomposites PP/OMMT. The authors attributed this disappearance to probable exfoliation of clay in the nanocomposites.

Fig. 1 shows that the PP peaks (region between 4 and 5 nm^{-1}), have not shifted. However, the intensities were decreased as a function of organoclay addition. This behavior can be attributed to reduction of the crystalline PP in nanocomposites. The presence of organoclay may hinder the polymer chains segments movement and hence retard the growth of crystals [28]. This result agrees with the crystallinity degree obtained by DSC technique.

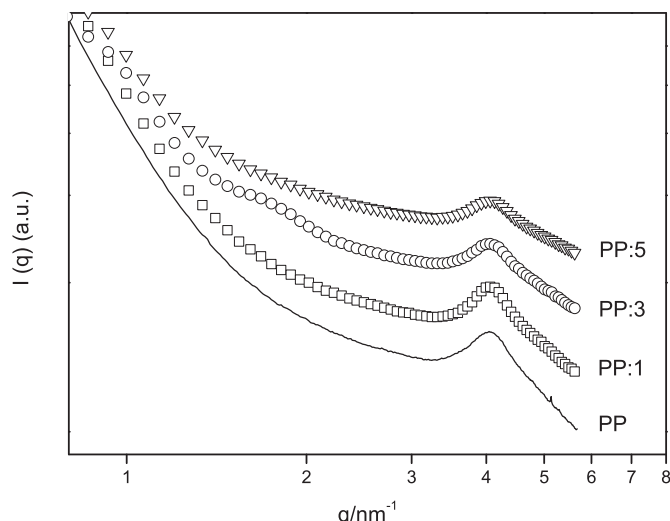


Fig. 1. WAXS profiles for PP and nanocomposites with different organoclay content.

Table 1

Values of melting enthalpy and crystalline percentage for the first ('') and the second (') heating and melting temperature (T_m), obtained from the DSC curves for nanocomposites PP/OMMT with different organoclay content and for the PP sample. All the data was corrected to real polymer content in each sample.

Sample	$\Delta H'_m$ (J/g) \pm SD	$\Delta H''_m$ (J/g) \pm SD	$\%_{\text{cryst}}'$ \pm SD	$\%_{\text{cryst}}''$ \pm SD	$T_m \pm$ SD
PP	102 ± 1^a	120 ± 3^a	49.3 ± 1.0^a	57.9 ± 2.0^a	172 ± 1^a
PP:1	101 ± 1^a	118 ± 3^a	49.3 ± 1.0^a	57.5 ± 2.0^a	172 ± 1^a
PP:3	92 ± 6^b	109 ± 5^b	$45.8 \pm 5.0^{a,b}$	$54.3 \pm 4.0^{a,b}$	172 ± 3^a
PP:5	87 ± 5^b	103 ± 3^b	44.2 ± 4.0^b	52.3 ± 3.0^b	174 ± 2^a

^{a, b} Means followed by the same letters in the column do not differ statistically from each other.

Obtained from first heating cycle.

3.2. Characterization – differential scanning calorimeter

Table 1 presents the results for the melting enthalpy and the crystalline percentages of the first and second heating cycle ($\Delta H'_m, \Delta H''_m, \%_{\text{cryst}}', \%_{\text{cryst}}''$, respectively) and the crystalline melting temperature (T_m – obtained in the first heating cycle) of pure PP and nanocomposites with different organoclay contents.

The results of the two heating cycles show that the nanocomposites crystallinity and ΔH_m have a decreasing tendency as a function of higher clay content nanocomposites (Table 1). This behavior can be attributed to the presence of the lamellae organoclay, which causes difficulty for the polymer chains segments to move [3]. Furthermore, it can be noted that the crystalline melting temperature of the samples did not change with the addition of organoclay.

3.3. Degradation – thermogravimetric analysis

The initial mass loss temperature (T_i), in this work, considered as the temperature when the sample loses 4% of its mass [29]; maximum speed mass loss temperature (T_{max}), determined by the maximum value of the first derivative; the difference between T_{max} and T_i (ΔT), and the inorganic residue fraction at 500°C were obtained from the thermograms. From the values of ΔT , it is possible to obtain information on the mass loss kinetics. Therefore, the larger the ΔT value the slower the release or generation of volatiles during the degradation processes after the start of mass loss.

Table 2 shows the parameter values obtained from the TGA curves for the PP and the nanocomposites with different organoclay content.

T_i values for the nanocomposites do not exhibit significant variation as a function of the organoclay content (Table 2). However, the T_i value for pure polypropylene presents a shift in the mass loss to a slightly lower temperature when compared to the nanocomposites. This is probably due to the degradation of the

Table 2

Average values of the parameters obtained from the TGA curves for PP and nanocomposites with different organoclay content.

Sample	T_i ($^\circ\text{C}$) \pm SD	T_{max} ($^\circ\text{C}$) \pm SD	ΔT ($^\circ\text{C}$) \pm SD	Residue at 500°C (%) \pm SD
PP	225 ± 2^a	258 ± 1^a	33 ± 3^a	0.2 ± 0.1
PP:1	229 ± 1^b	337 ± 3^b	108 ± 1^b	0.7 ± 0.3
PP:3	232 ± 3^b	391 ± 10^c	159 ± 4^c	2.5 ± 0.2
PP:5	231 ± 2^b	435 ± 8^d	204 ± 3^d	4.1 ± 0.2
Organoclay	237 ± 1^c	265 ± 1^e	28 ± 1^e	71.5 ± 0.1

^{a, b, c, d, e} Means followed by the same letters in the column do not differ statistically from each other.

Initial temperature of mass loss, with loss of 4%.

Maximum temperature of the first derivative of the mass percentage by temperature.

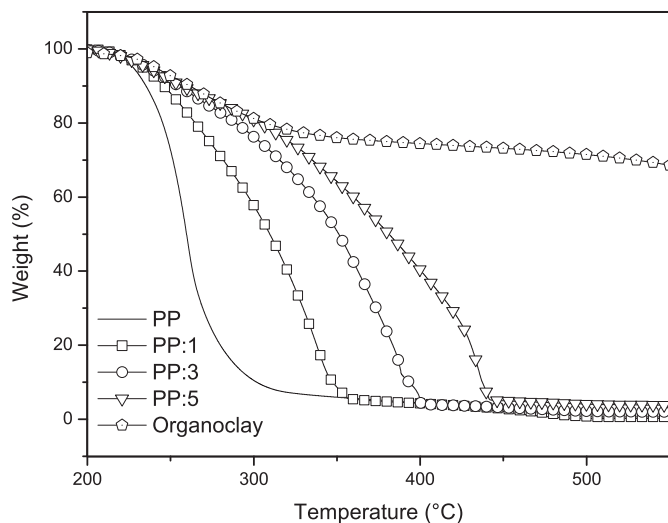


Fig. 2. Average of thermogravimetric curves for PP, organoclay and nanocomposites with different organoclay content.

montmorillonite's organic modifier which degrades at temperatures greater than 180 °C [30–32]. The degradation of quaternary ammonium salt used as organic modifier can influence the degradation of polymeric matrix degradation [33].

The results of inorganic residues at 500 °C are associated with the amount of organoclay used in the nanocomposites production. Therefore, there is an increase in the residue content which is proportional to the increase in the clay content in the nanocomposites. This result is in agreement with the experimentally obtained results in other studies in the literature [23].

Fig. 2 shows the thermogravimetric curves obtained for polypropylene (PP), nanocomposites with 1, 3 and 5% of organoclay (PP:1, PP:3 and PP:5, respectively) and the organoclay.

Although T_i values did not change expressively, in Table 2 different values of T_{max} and ΔT (Table 2) were observed for the nanocomposites. Therefore, ΔT values show that the mass loss evolution is slower due to the presence of organoclay [21]. This behavior may be explained by different mechanisms. First, the effect of thermal insulation which has the organoclay, influencing the increasing of the thermal gradient between the temperature inside the sample and the furnace [34]. Secondly, the higher the organoclay content, the slower the gases diffusion (volatiles output and oxygen input) through the polymeric mass due to the barrier effect [6,20]. This behavior decreases the thermo-oxidative degradation kinetics [35], by increasing the mean free path of the gas in the polymer mass (Fig. 3) [6,28]. The WAXS results previously presented (Fig. 1) confirms that the organoclay was intercalated/exfoliated, providing an increasing of mean free path for gases diffusion.

Analyzing the first derivative of percentage mass loss (Fig. 4a), it is observed that with the increasing organoclay content the mass loss profile is closer to the mass loss profile of organoclay. Fig. 4b–d shows this effect more clearly. Thus, it can be seen that the mass

loss onset process for the nanocomposites studied is a process driven by the presence of organoclay.

As described earlier, the T_i values do not change significantly with the organoclay addition. However a significant difference in ΔT and T_{max} values has been observed. In order to explain these results, one must notice that the oxidative reactions occur as a function of oxygen presence. On the surface it may be expected: 1) a lower organoclay influence on the input of oxygen and 2) the output of volatiles formed when compared to the polymer bulk due to the lower mean free path [23]. These two assumptions indicate a lower degradation on the surface resulting in low difference among T_i value. Throughout the thermogravimetric analysis the effects of the thermal insulating barrier become more pronounced and the differences caused by the increased clay concentration become more important, generating the ΔT values obtained. These results were according to those obtained by WAXS that shows a clay intercalation/exfoliation, directly responsible for the increase on mean free path.

3.4. Degradation – oxidation induction time

After the TGA results that indicate the increasing stability of the nanocomposites, it was decided to analyze the samples by OIT in order to determine whether oxidative degradation reactions followed the same stabilization effect obtained earlier.

Fig. 5 shows the curves expanded for OIT, in duplicate, obtained for samples of pure PP and the nanocomposites. The full curves can be found in the Supplementary Material.

Table 3 presents the mean results for OIT obtained for pure PP and its nanocomposites with different organoclay content.

According to the results in Table 3, the PP was more stable when compared to the nanocomposites. Although the induction time is the same for the nanocomposites (Table 2), a differentiated aspect in Fig. 5 can be identified. It can be seen that heat release is inversely proportional to the concentration of organoclay. Complementary to the question of the self-catalytic degradation cycle, as described earlier, with the increasing clay concentration, there was a reduction of the oxygen diffusion through the polymer. This behavior results in a lower variation in the heat flow for the samples with higher organoclay content. Similar results were also found in the literature. Cruz and Zanin [19] also observed differences in the heat flow between reprocessed and recovered polyethylene materials. The authors describe that, even with the same onset temperature of the exothermic reactions, the reprocessed material, immediately after the beginning of the oxidative process, presented a greater heat flow variation when compared to the recovered material, and it was considered that in the reprocessed material more species are prone to oxidize when compared to the material that has not been reprocessed.

3.5. Degradation – oxidation induction temperature

The TGA and OIT results present different conclusions in relation to the matrix thermal stability. This is mainly because these techniques are employed in different analysis conditions. In TGA the oxygen diffusion occurs initially in a solid state sample, however in



Fig. 3. Schematic representation of the effect of the physical barrier provided by the lamellae organoclay in a polymeric matrix.

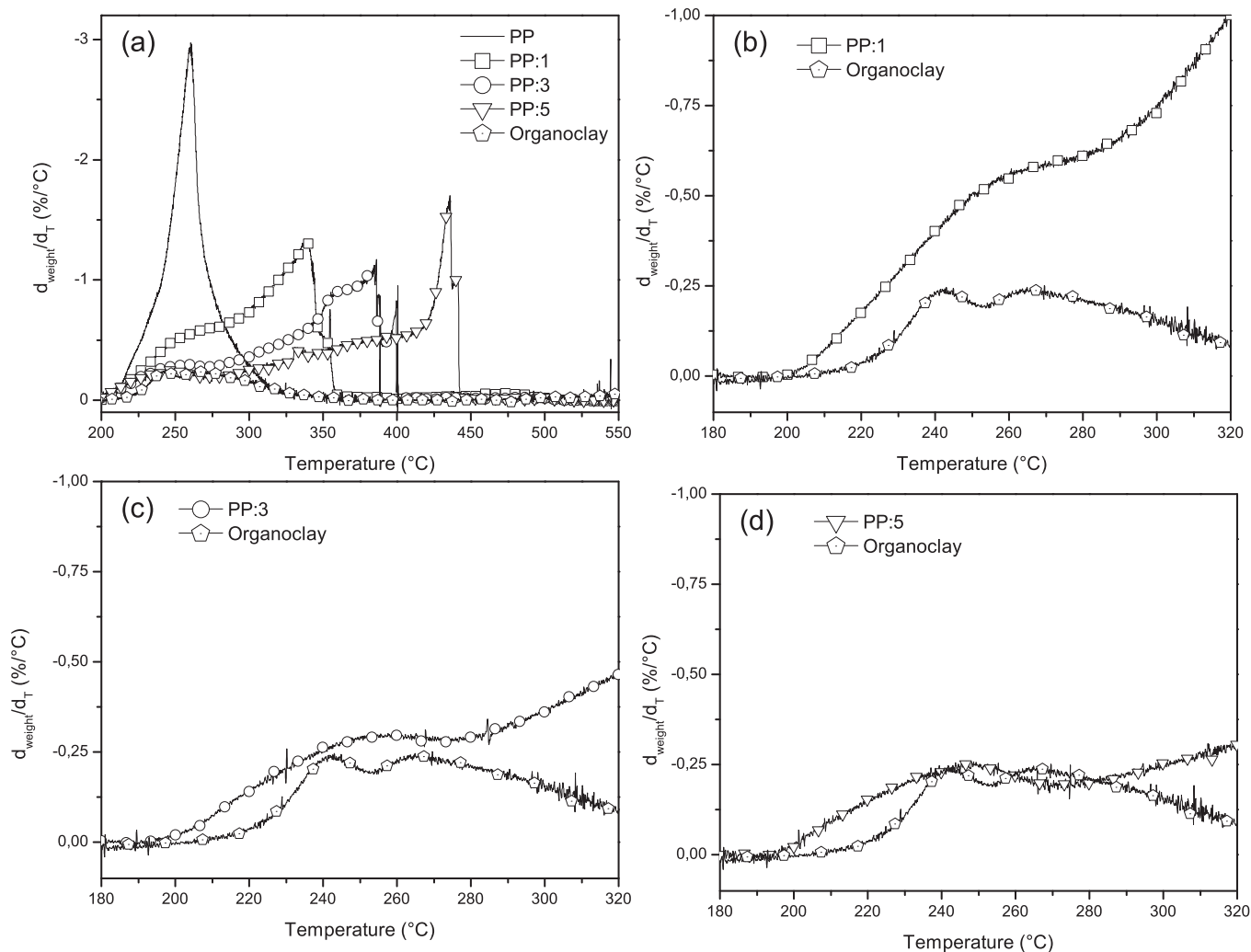


Fig. 4. Average of first derivative curves of the percent mass loss versus temperature for PP (a) and nanocomposites with different organoclay content (b–d).

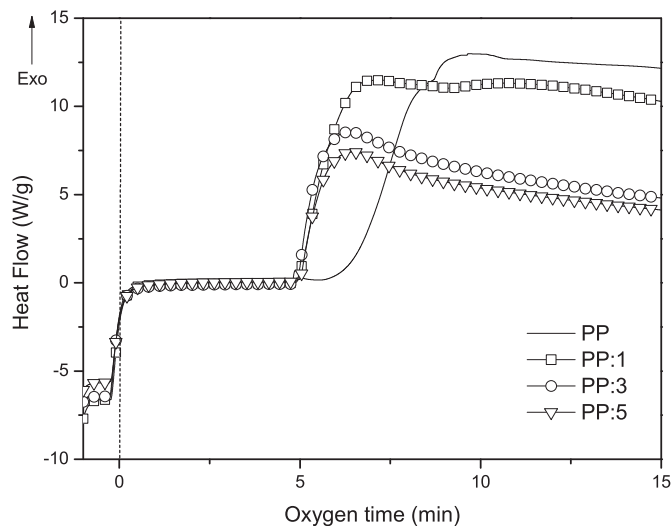


Fig. 5. Average of OIT curves for PP and nanocomposites with different organoclay content.

OIT the sample is initially heated in an inert atmosphere and afterwards the melted sample is exposed to oxidative atmosphere. These controversial results led us to the analysis method called dynamic OIT [24]. The differences between the usual OIT and dynamic OIT are that in the second there is no isotherm and the diffusion of oxygen through the sample also occurs during heating and before melting. This enables to correlate the heat released from oxidative reactions, measured by DSC, with the onset of mass loss, measured by TGA. The overlapped curves, obtained by dynamic OIT and TGA, allow observing the difference between the beginning of the volatiles release and the initial exothermic oxidation reactions (T_{re}). According to Araújo, Waldman and De Paoli [35], there should

Table 3

Average results of the oxidation induction time, performed for PP and nanocomposites with different organoclay content.

Sample	Oxidation Induction time (min) \pm SD
PP	7.3 ± 0.1^a
PP:1	5.4 ± 0.1^b
PP:3	5.4 ± 0.1^b
PP:5	5.3 ± 0.1^b

^{a, b} Means followed by the same letters in the column do not differ statistically from each other.

Table 4

Initial temperature of mass loss obtained from TGA (T_i) and initial temperature of exothermic reactions obtained from the dynamic OIT (T_{re}^*) for samples of PP and nanocomposites with different organoclay content.

Sample	T_{re}^* (°C) \pm SD from DSC	T_i (°C) \pm SD from TGA	Difference between T_i and T_{re}^* (°C) \pm SD
PP	193 \pm 1 ^a	225 \pm 2 ^a	32 \pm 1 ^a
PP:1	184 \pm 2 ^b	229 \pm 1 ^b	45 \pm 1 ^b
PP:3	188 \pm 1 ^c	232 \pm 3 ^b	44 \pm 2 ^b
PP:5	185 \pm 3 ^{b,c}	231 \pm 2 ^b	46 \pm 2 ^b

a, b, c Means followed by the same letters in the column do not differ statistically from each other.

be differences in temperature between the beginning of exothermic reactions and the initial mass loss since the oxidation reactions must occur prior to the release of volatiles.

Table 4 shows the average results of the initial temperature of mass loss obtained by TGA and the initial temperature of the exothermic reactions obtained from dynamic OIT. Dynamic OIT for PP and the nanocomposites are shown in Fig. 6, and allow to better visualize the difference between the onset of oxidative reactions for PP and its nanocomposites.

Fig. 6 and Table 4 show that the beginning of the oxidative reactions for nanocomposites occurs at lower temperatures than for pure PP, indicating that the nanocomposites exhibit lower

thermal stability. This result is different from that obtained from TGA, where T_i values for the nanocomposites are slightly higher than for pure PP. From the expanded curves in Fig. 6b–d it is observed that all nanocomposites begin the exothermic reactions before pure PP.

The difference between the initial mass loss temperature and initial temperature of exothermic reactions for the nanocomposites is around 10 °C higher than for the pure PP (Table 4). This difference can be the basis for questioning the use of only thermogravimetric analysis in determining thermal stability for multicomponent polymeric materials. As the TGA determines the products volatilized from the oxidative degradation reactions, its detection begins at higher temperatures. Multicomponent systems and different materials have different kinetics. Therefore the oxidative degradation reactions must also take into account the factors influencing the volatiles diffusion or the permeation of oxygen.

According to Fig. 6a different heat profiles were observed for each nanocomposite above 210 °C. This behavior could be attributed to the influence of the oxygen diffusion on the polymeric bulk, since exothermic reactions occur less once there is a lower concentration of the oxygen reactant.

Thus, it can be concluded that the evaluation of the nanocomposites degradation has greater precision when using the combination of TGA and dynamic OIT.

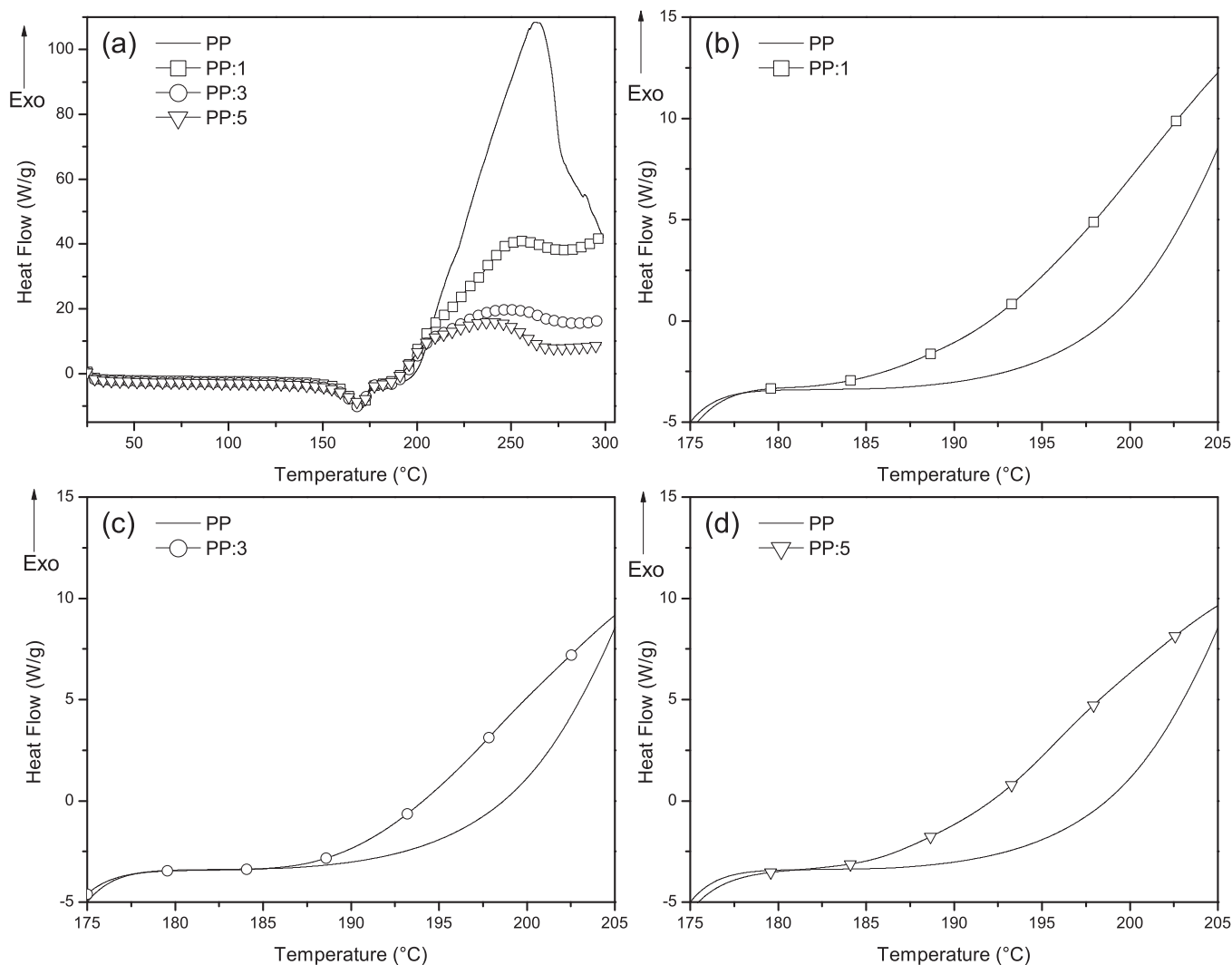


Fig. 6. Average of dynamic OIT curves for PP (a) and for samples of PP/OMMT with different organoclay content (b–d).

4. Conclusions

It can be concluded that the evaluation of the stability for nanocomposites is more accurate when the set of thermogravimetric analysis and dynamic OIT is used in a complementary manner. With the analysis of the TGA results, it was concluded that the nanocomposites are more stable than pure PP. Considering the thermal data obtained from usual and dynamic OIT we can broaden this discussion by showing that the presence of organoclay has a negative influence on the stability of the initial steps, but acts by slowing down the degradation reactions in the subsequent steps.

From heat released data, it was observed that the main process regarding diffusion/permeation of gases was the delayed permeation of oxygen gas in order to participate in the oxidative reactions. From the complete data, it can be concluded that an isolated analysis of the results for TGA may indicate a false positive in materials with lamellar fillers. Organoclay acts as a degrading influence on initial steps before reaching 210 °C and as a stabilizer agent after this temperature. Using TGA and dynamic OIT in a complementary manner can avoid misleading conclusions about the stability of multicomponent polymeric materials.

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Appendix A. Supplementary data

Supplementary data related to this article can be found online at <http://dx.doi.org/10.1016/j.polymdegradstab.2014.10.016>.

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