



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



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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].

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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

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 $\lambda = 1.608$ Å 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 ± 0.7 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

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