

Thermal characterization of polypropylene/vermiculite composites

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Abstract Vermiculite clay (VMT) was organically modified with a quaternary organic salt and added to polypropylene (PP). The compounds were prepared by melt intercalation using a twin extruder. The morphology of the composites was investigated through wide-angle X-ray diffraction (WAXD). The WAXD results suggested that exfoliation phenomena were found for the composites with modified clay. The thermal properties of the obtained composites were studied by means differential scanning calorimetry (DSC) and thermogravimetry (TG) measurements. A variation in the crystallinity of PP was found. A significant increase of the thermal stability of PP was achieved in the presence of the modified VMT.

Keywords Polypropylene · Organo-vermiculite · Composites · Vermiculite

Introduction

Nowadays, composite materials play an important role in the engineering field. These materials usually comprise effective polymeric matrix in which fibers and (or) small filler particles are thoroughly dispersed in composite system. The filler may be well dispersed in the matrix to avoid zones of weaker cohesion where flaws and other defects will be initiated upon stressing [1–6]. Polypropylene

(PP) based composite material is one of the many composite systems that are successfully utilized in engineering applications. PP has been known for its good mechanical properties and processability, which allow it to accept numerous types of natural and synthetic fillers. Its versatility has also led to the possibility of producing particulate-filled composites [7–10]. The main objectives of producing these polymer composites are the reduction of industrial costs and also in improvements in properties like mechanical strength, thermal stability, permeability and flammability [11–13]. Layered silicates, and in particular clay minerals, have been used for their excellent intercalation abilities. Natural clays, containing inorganic cations in interlays, are hydrophilic, while on exchanging an inorganic cation, for a large organic cation, the clay properties are altered and material becomes hydrophobic which make them more compatible with the polymer matrix. [14–16]. Vermiculite (VMT), like the well-known montmorillonite (MMT), belongs to the general family of 2:1 layered silicates which consist of two tetrahedral sheets and one octahedral sheet [17]. This clay contains either Al^{3+} or Mg^{2+} and Fe^{2+} as normal octahedral ions, and a tetrahedral sheet in which Al^{3+} occurs as a substituted ion in place of some of the Si^{4+} [18]. VMT is an abundant and much cheaper silicate as compared with MMT, hectorite or saponite. It is used as packaging material to provide anti-shock protection [19, 20].

In previous work [21] it was related the direct melt intercalation of PP and vermiculite *in natura*. The aim of this work is to analyze the mixtures of polypropylene (PP) and different organo-vermiculite (org-VMT) content. The influence of the addition of anhydride graft polypropylene (PP-g-MAH) to the blends was studied. DSC, TGA and WAXD analysis were carried out in order to evaluate the thermal and morphological properties.

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Experimental

Materials

Polypropylene (PP) used was supplied by Suzano Petroquímica, Brazil, with a melt flow index and density of 3.5 g/10 min (230 °C/2.16 kg) and 0.905 g/cm³, respectively. The vermiculite was purchased from Brasil Minérios Indústria e Comércio, Brazil. The clay sample was ground and sieved (40 mesh) before use. The quaternary ammonium salt (cetyltrimethyl ammonium chloride) was purchased from Pharmaspecial Especialidades Químicas e Farmacêuticas, Brazil.

Preparation of organo-vermiculite

The inorganic cations presents in the crystals of the VMT clay were first ion exchanged with sodium ions. This reaction was refluxed for 72 h under vigorous stirring and the temperature was controlled in the range of 50–60 °C. The precipitate obtained was washed in a centrifuge with distilled water until no Cl⁻ was detected, which was performed using 0.1 mol/L AgNO₃. The Na-exchanged VMT (VMT-Na) was dried at 80 °C for 48 h, it was kept in a dryer before use. The VMT-Na was added to a solution containing the quaternary ammonium salt in and deionized water. The mixture of VMT and alkyl ammonium salt (org-VMT) was stirred for 3 days at 70 °C. The resulting org-VMT was washed in a centrifuge with distilled water until no precipitate was observed using 0.1 mol/L AgNO₃. The final org-VMT was dried at 80 °C for 48 h, it was kept in a dryer for further use.

Composites preparation

Two masterbatches containing 25 wt% VMT *in natura* and org-VMT in PP were initially prepared using the co-rotating twin screw extruder (TECK TRIL, model DCT 20) at 300 rpm screw speed, with a 120–200 °C temperature profile. The clay was added through a side feeder. The masterbatch was then added to PP in appropriate amounts to obtain nominal contents of 1, 3 and 5 wt% of VMT in the composites. These were compounded in the twin screw extruder at the same temperature and rotation speed used in the master batch processing.

After blending the samples were molded by compression in a Carver press at 240 °C. The thickness of the samples was 0.55 mm.

Characterization methods

Wide-angle X-ray diffraction (WAXD)

The morphology of the specimens was determined by WAXD measurements. The WAXD of filler, polymer and composites were conducted in a Rigaku (model miniflex) with Cu-K α ($\lambda = 1.5418 \text{ \AA}$), radiation operated at 40 kV and 40 mA; corresponding data were collected from 2 to 35°. The data were recorded using a scanning speed and increments of 5°/min and 0.05°, respectively.

Differential scanning calorimetry (DSC)

The DSC measurements were performed using Perkin-Elmer thermal analyzer. The samples were first heated from -20 to 280 °C at 10 °C min⁻¹ under nitrogen atmosphere. After the samples were cooled to -20 °C at 10 °C min⁻¹ and then reheated to 280 °C at 10 °C min⁻¹. The melting temperature was analyzed from the second heating curve. The crystallinity of PP was determined from the ratio of the fusion heat of the blend to that of 100% crystalline PP ($\Delta H^{\circ} = 138 \text{ J/g}$) [22].

Thermogravimetry (TG)

The samples were analyzed by TG using a Q500 TA Instrument under nitrogen flow from 25 to 700 °C at 10 °C/min. The thermal gravimetric analysis was used to evaluate the thermal stability of the PP composites. This technique also was used to determine the real VMT content that was incorporated as much in masterbatches as in the composites through the amount of final residue.

Results and discussion

Characterization of org-VMT

WAXD analysis

Figure 1 shows WAXD patterns for VMT, VMT-Na and org-VMT. The analysis by WAXD of VMT-Na (curve B) showed that the basal-plane spacing (*d-spacing*) of the mineral decreases from 13.68 to 11.74 Å on exchanging its Mg²⁺ by Na⁺. The org-VMT, trace C of Fig. 1, gave three distinct peaks at $2\theta = 3.02^{\circ}$, 5.83° and 6.68° , corresponding to the *d-spacing* of 29.25, 15.16 and 13.23 Å, respectively. These three peaks had evidenced that probably there are three expansions with three different orientations of molecules, there was the intercalation of cation quaternary of ammonium. It should be noted from the

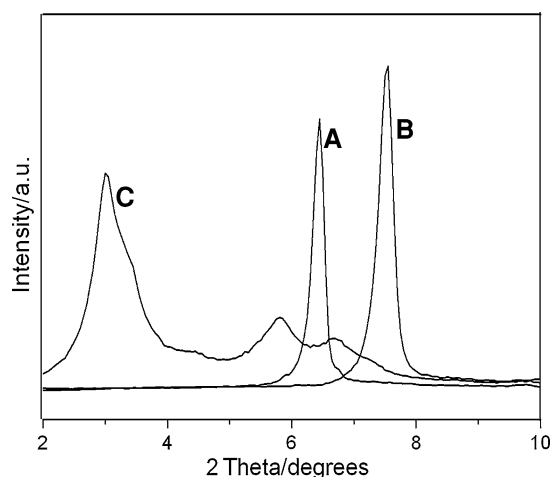


Fig. 1 WAXD patterns for (A) VMT, (B) VMT-Na and (C) org-VMT

WAXD pattern of org-VMT that the d -spacing of 29.25 Å was significantly larger than that of the unmodified VMT-Na, which had a d -spacing of 15.16 Å. The larger gallery spacing indicated the intercalation of alkyl ammonium in between the silicate layers.

Characterization of composites

WAXD analysis

The resulting morphologies were monitored by mean WAXD. Figure 2 present the WAXD patterns of PP/VMT and PP/org-VMT composites, respectively. In the blends with VMT *in natura* there was a slight shift of the main peak ((001) peak) towards lower angles (Fig. 2a). They also showed that the d -spacing of the clay increase from 13.68 to 15.21 Å in the composite processed with 3 wt% of VMT (Table 1). However, this slight displacement does not confirm the occurrence of VMT intercalation or exfoliation in the polymer galleries.

In the X-ray diffraction of the composites with org-VMT (Fig. 2b) was not observed the main peak around

Table 1 d -spacing (d_{001}) of main peak of VMT and PP/VMT composites

Samples	2θ /degrees	$d_{001}/\text{Å}$
VMT <i>in natura</i>	6.46	13.68
PP/1% VMT	6.10	14.48
PP/3% VMT	5.81	15.21
PP/5% VMT	6.39	13.83

$2\theta = 3.02^\circ$ characteristic of the modified clay. The absence of the (001) peak in the WAXD pattern suggests that the clay has a nearly exfoliated dispersion in the polymer matrix or the amount of clay was too low to be detected in WAXD analysis. In this case, the use of transmission electron microscopy is necessary to clarify the structure [23].

DSC investigations

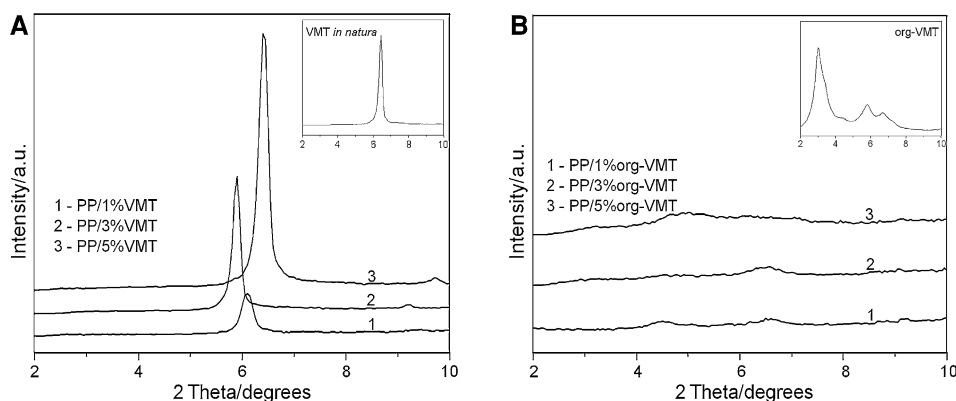
In Table 2 the melting temperature (T_m) and crystallinity values of the different composites are collected. They indicate not have a significant variation of these parameters for the composites PP/VMT (Table 2).

The crystallinity degree of the composites PP/VMT had practically remained unchanged in relation to pure polymer (Table 2). The composite PP/3%VMT presented greater crystallinity degree when compared with the other

Table 2 DSC parameters for PP/VMT and PP/org-VMT composites

Samples	$T_m/^\circ\text{C}$	$X_c/\%$
PP	157	72
PP/1%VMT	160	72
PP/3%VMT	158	74
PP/5%VMT	161	68
PP/1%org-VMT	159	85
PP/3%org-VMT	159	77
PP/5%org-VMT	160	70

Fig. 2 WAXD patterns of VMT and PP/VMT composites (a) and org-VMT and PP/org-VMT (b)



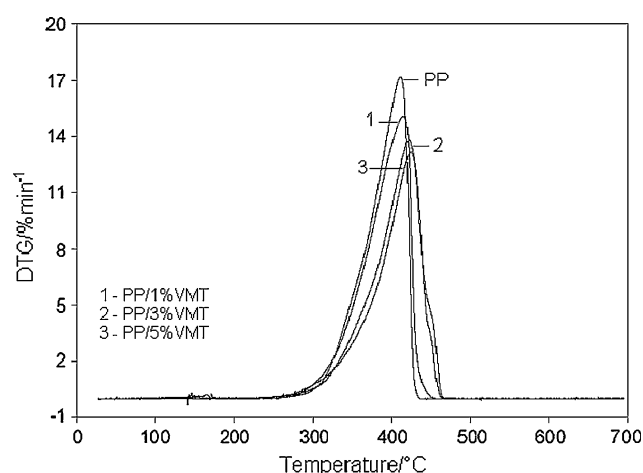


Fig. 3 DTG curves of PP/VMT composites

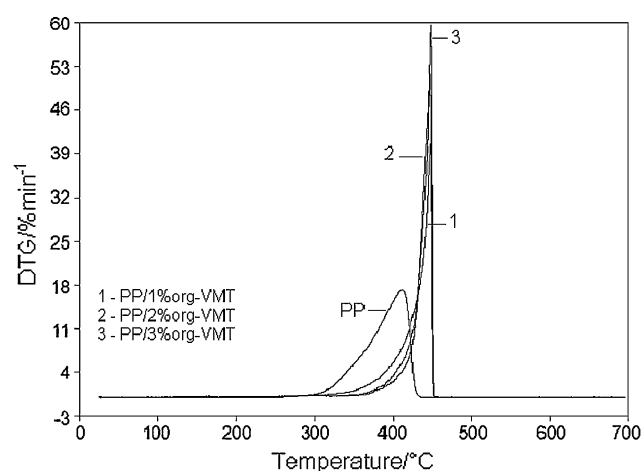


Fig. 4 DTG curves of PP/PP-g-MAH/org-VMT composites

mixtures (1 and 5 wt%). The DSC results for the composites using org-VMT are showed in Table 2. This results revealed that the addition of clay organophilic to the PP matrix promoted an increase in the crystallinity degree of the composites with low content of org-VMT (1 and 3 wt%). These results suggest that the crystallinity of PP was affected by the treatment of the clay and the amount of the same one in the composites. The melting temperatures were around 160 °C for all blends.

TGA analysis

The thermal stability of the composites was investigated by TG analysis. The DTG curves of PP and composites with VMT *in natura* and org-VMT are presented in Figs. 3 and 4, respectively. The obtained results showed that the presence of clay had a clear effect on the thermal stability of samples. The thermal curves of composites with VMT *in natura* and org-VMT showed an increase in maximum weight loss temperature (T_{max}).

Table 3 Thermal properties of PP and PP/VMT and PP/org-VMT composites

Samples	$T_{max}/^{\circ}\text{C}$	VMT nominal content/%wt	VMT real content/%wt
PP	411	–	–
Masterbach (PP/VMT)	434	25	36
PP/1%VMT	414	1	0.6
PP/3%VMT	422	3	1.6
PP/5%VMT	424	5	3.0
Masterbach (PP/org-VMT)	437	25	32
PP/1%org-VMT	447	1	0.4
PP/3% org-VMT	446	3	0.8
PP/5% org-VMT	448	5	1.5

The T_{max} and real VMT content (%wt) are listed in Table 3. The clay addition to the PP improved the T_{max} being this sharper effect in the composites with the modified VMT. These results can be attributed to the slowing down of the oxygen diffusion, since the presence of the intercalated or exfoliated nanofillers determines an increase of the path length of the gas molecules through the polymer matrix [24].

Conclusions

Vermiculite can be intercalated by quaternary ammonium salt to yield org-VMT. After the treatment with the surfactant, the clay exhibited an increase of its basal spacing value, indicating a strong interaction between the two components. The morphology of the PP composites was investigated through WAXD. These results suggested that the exfoliation phenomena were found for the composites prepared in presence of org-VMT. The thermal properties of the obtained composites were studied by means of DSC and TG measurements. The crystallinity degree of the composites with low content of org-VMT (1 and 3 wt%) increased compared with the pure polymer suggesting that it had modification in the crystallinity of the PP. A significant increase of the thermal stability of composites was achieved. No variation of T_m was found in the presence of clays (VMT *in natura* or org-VMT).

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