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### Mechanical, Thermal and Morphological Characterization of High-Density Polyethylene and Vermiculate Composites

Iara Thais D. Oliveira<sup>a</sup>; Leila L. Y. Visconte<sup>a</sup>; Ana Lucia A. Vendramini<sup>a</sup>

<sup>a</sup> Instituto de Macromoléculas Professora Eloisa Mano, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil

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## Mechanical, Thermal and Morphological Characterization of High-Density Polyethylene and Vermiculite Composites

Iara Thais D. Oliveira, Leila L. Y. Visconte, and Ana Lucia A. Vendramini

Instituto de Macromoléculas Professora Eloisa Mano, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil

*High-density polyethylene composites containing 7, 10, 15 and 20% w/w vermiculite (VMT) were prepared by extrusion in a twin-screw extruder at various shear rates. The thermal and mechanical properties and morphological characteristics of the composites were evaluated and compared with pure high-density polyethylene. The blend morphologies were determined by scanning electron microscopy (SEM). The thermal properties of the composites were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The TGA results reveal that the use of VMT particles to fill polyethylene increased the thermal stability of the composite. The results obtained indicate that a shear speed of 400 rpm and vermiculite content of 7% showed the best properties of impact resistance. These observations were confirmed by morphology analysis.*

**Keywords:** blends, polyethylene, vermiculite

### INTRODUCTION

To fulfill the requirements for new engineering materials and because pure polymers do not present the necessary properties for specific applications, the search for new materials has been stimulated [1].

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Address correspondence to Iara Thais D. Oliveira, Instituto de Macromoléculas Professora Eloisa Mano, Universidade Federal do Rio de Janeiro, P.O. Box 68525, 21945-970 Rio de Janeiro, Brazil. E-mail: iara@ima.ufrj.br

Sometimes, instead of developing a synthetic route for attainment of a new polymeric material, research efforts are directed to the study of physical mixtures involving polymers or polymers and a filler, which can be of mineral nature. Composites combining inorganic clay and polymer material at a very fine structural level are some of the most interesting prospectives for polyethylene [2–6]. Raw materials such as vermiculite are being used as an inorganic filler in polymer composites with the objective to reduce costs and/or to modify properties such as modulus, hardness, thermal stability, opacity and brightness. Brazil is the third biggest vermiculite producer, with reserves in Piauí, Goiás, Paraíba and Bahia states. Vermiculite has low density and is formed by plaques (lamellae), it presents several applications in construction, agriculture and horticulture. It is extensively used in concrete and in sound insulation, in panels and fireproof walls, fertilizers, pesticides, oil, greases and heavy metals absorbers [7]. Brazilian minerals do not contain asbestos, and this gives vermiculite concentrates a higher added value.

When submitted to heating at high temperatures, vermiculite volume increases up to 20 times, becoming highly porous and light [8,9]. It expands perpendicularly and secreted water violently.

Based on its good processability, low cost and excellent balance of physical properties, such as good heat resistance, moderate mechanical properties and outstanding chemical resistance, high-density polyethylene (HDPE) was chosen as the polymeric matrix [10,11]. HDPE is one of the most versatile polymers, with great applications in the packaging industry mainly for the packing of milk, coffee, and juices, and as flexible films for food.

In this work the preparation of high-density polyethylene composites with Brazilian vermiculite in different ratios was investigated by using a twin-screw extruder under different rotation rates. An evaluation of these composites was carried out to determine their morphological and thermal characteristics and impact resistance.

## EXPERIMENTAL

### Materials

The high-density polyethylene (HDPE) GF 4950 (density of 0.956 g/cm<sup>3</sup> and melt flow index 0.34 g/10 min) used was supplied by Ipiranga Petroquímica. The vermiculite (melting point 1300°C and 1–6% moisture content) was purchased from Brasil Minérios Industria e Comércio, Brazil.

## Vermiculite Treatment

Vermiculite was milled to 100 mesh particle size, then dried in an air-circulating oven for 24 h at 80°C immediately before processing.

## Preparation of HDPE/VMT Blends

The composites have been prepared in a co-rotating twin-screw extruder (TECK TRIL, model DCT 20). Before obtaining the composites, a master batch was prepared by mixing the HDPE and VMT (50:50) in order to attain better homogenization between the mixture components. This master batch was then added in adequate amounts to HDPE to obtain compositions with 7, 10, 15 and 20% vermiculite. These composites were obtained at two screw rates, 200 and 400 rpm.

## Morphological, Thermal and Mechanical Characterization of HDPE/VMT Blends

The extruded materials were injection-molded into specimens for the impact resistance test, according to ASTM D 256. The Izod test was performed at 24°C and 2.70 J hammer. From the energy value given by the equipment and the thickness of each specimen, the property was evaluated. For each composite 6 specimens were tested.

The specimens prepared for the morphological study were soaked in liquid nitrogen for a few minutes and broken manually, then covered with a fine gold layer and observed on a JEOL JSL 5300 microscope, using electron beam acceleration voltage of 10 kV, in order to study the morphology.

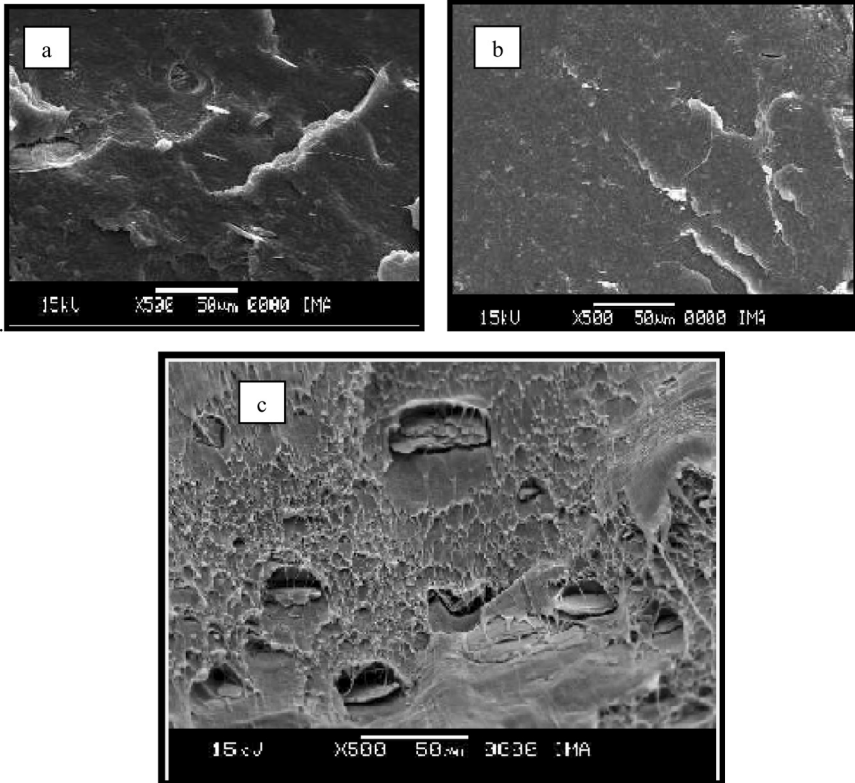
The crystallinity ( $X_c$ ) and melting temperature ( $T_m$ ) of HDPE in the blends were studied through differential scanning calorimetry (DSC) using a Perkin-Elmer thermal analyzer. The samples were scanned at heating and cooling rates of 10°C min<sup>-1</sup> in a nitrogen atmosphere. The melting and crystallization temperatures were analyzed from the second heating and the second cooling curves, respectively. The crystallinity of HDPE was determined from the ratio of the fusion heat of the blend to that of 100% crystalline HDPE ( $\Delta H^\circ = 182 \text{ J/g}$ ) [12].

Thermogravimetry analysis (TGA) was carried out in nitrogen with a Q500 TA Instrument heating from 10 to 600°C at 10°C/min. A thermal gravimetric analyzer was used to evaluate the thermal stability of the HDPE composites.

## RESULTS AND DISCUSSION

The dispersion of clay particles in the HDPE matrix was evaluated by scanning electron microscopy after nitrogen fracture. Figure 1 presents SEM photomicrographs at  $500\times$  enlargement, of the HDPE-vermiculite composites with different filler contents prepared at two shear rates. It can be clearly seen in the Figure 1(a and c) small voids which probably are the result of bubbles forming during the molding process, or the result of a poor adhesion polymer-vermiculite. Comparing these two photomicrographs, there seems to exist a higher agglomeration of the filler particles in the sample with 20% vermiculite.

With regard to Figure 1(b), it can be said that, apparently, a better adhesion of the matrix to the filler was achieved, when compared



**FIGURE 1** SEM micrographs for samples of pure PEAD and the composites with 7% and 20% of vermiculite: (a) HDPE/7% filler  $-200$  rpm; (b) HDPE/7% filler  $-400$  rpm; and (c) HDPE/20% filler  $-200$  rpm.

**TABLE 1** Thermal Properties of HDPE and HDPE/VMT Blends Prepared at 200 rpm

Samples 200 rpm	$T_m$ (°C)	$\Delta H_f^a$ (J/g)	$X_c$ (%)
HDPE	134	193	66
HDPE + 7%VMT	136	163	56
HDPE + 10%VMT	134	159	54
HDPE + 15%VMT	134	158	53
HDPE + 20%VMT	133	127.7	46

with Figure 1(a), which can be confirmed by the results of impact resistance.

Changes in the thermal transitions of the blends were investigated by DSC. Tables 1 and 2 show the crystallinity degree and melting and crystallization temperatures for HDPE and HDPE/VMT blends prepared at 200 and 400 rpm, respectively.

The DSC results reveal that the addition of clay to the HDPE matrix does not lead to significant changes in the crystallization of the polymer matrix. The crystallinity degree ( $X_c$ ) values of the blends decreased with an increase in clay content, and were lower than that of the neat HDPE. The presence of 20 wt% VMT may inhibit the crystallization of HDPE. The melting temperatures were around 134°C for all blends.

Tables 3 and 4 show the TGA results for pure HDPE and HDPE/VMT blends obtained at 200 and 400 rpm, respectively. The maximum weight loss temperature ( $T_{max}$ ) and real VMT content (wt%) content are listed in Tables 3 and 4. These tables reveal that the HDPE/VMT blends show an increase in  $T_{max}$ . The incorporation of VMT into HDPE improved the  $T_{max}$ . The presence of metal oxides, such as silicon dioxide, aluminum, iron and magnesium oxides in the VMT was attributed to this improvement [13].

**TABLE 2** Thermal Properties of HDPE and HDPE/VMT Blends Prepared at 400 rpm

Samples 400 rpm	$T_m$ (°C)	$\Delta H_f^a$ (J/g)	$X_c$ (%)
HDPE	134	193	66
HDPE + 7%VMT	135	162	55
HDPE + 10%VMT	135	160	54
HDPE + 15%VMT	134	158	52
HDPE + 20%VMT	134	122	41

**TABLE 3** Thermal Properties of HDPE and HDPE/VMT Blends Obtained at 200 rpm

Samples 200 rpm	T <sub>max</sub> (°C)	VMT nominal content (%wt)	VMT real content (%wt)
HDPE	401	–	–
HDPE + 7%VMT	406	7	5.3
HDPE + 10%VMT	410	10	7.2
HDPE + 15%VMT	409	15	8.2
HDPE + 20%VMT	436	20	12.6

The residual mass of the TGA analysis was checked and it was observed that the real amount of VMT present in the mixtures was less than the planned amount (Tables 3 and 4).

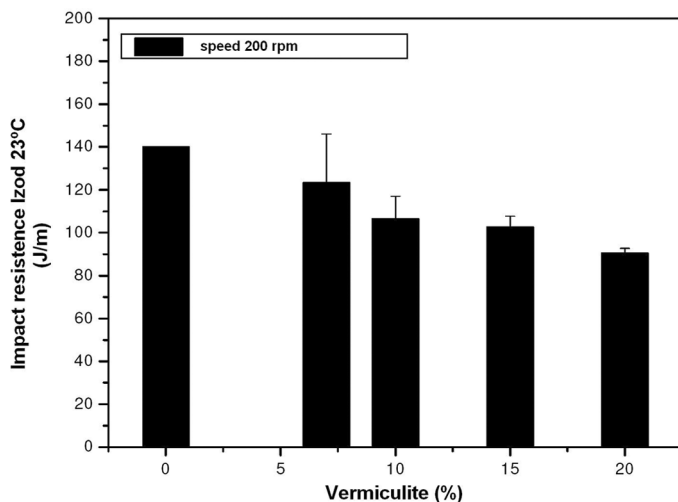
In order to evaluate the reinforcing effect of VMT in the HDPE matrix, mechanical properties were measured. Figures 2–4 show the results of impact resistance for the samples of pure HDPE and the composites prepared under different rotation rates for the various vermiculite contents.

The effect of the vermiculite content on the impact resistance was studied for the composites with 7, 10, 15 and 20% w/w of vermiculite. From the results it is possible to observe that, with the addition of the filler, a decrease in the property was found, in relation to pure HDPE, followed by a continuous reduction as vermiculite concentration increased, independent of the rotation speed. An increase in filler load inhibits the cohesion mechanisms of the material, making it more fragile.

The studied rotation speeds were 400 and 200 rpm. Generally speaking, the best results were found at 400 rpm, mainly when low amounts of vermiculite were used. Such behavior indicates that the homogeneity of the mixture exerts strong influence on impact resistance since under high shear a more homogeneous mixture results.

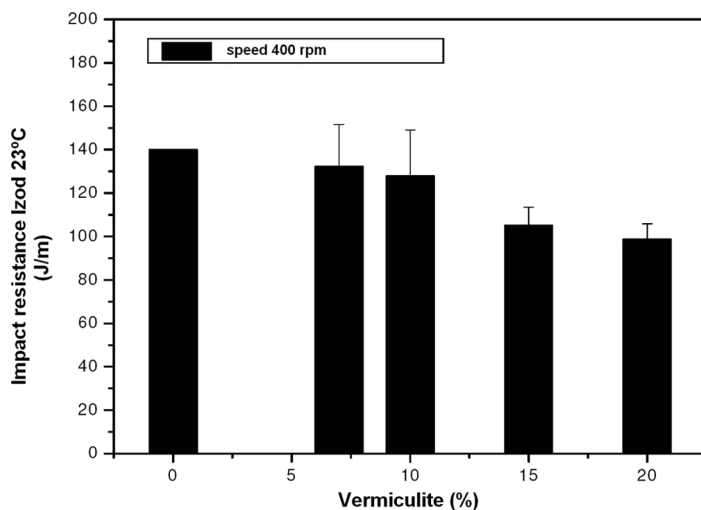
**TABLE 4** Thermal Properties of HDPE and HDPE/VMT Blends Obtained at 400 rpm

Samples 400 rpm	T <sub>max</sub> (°C)	VMT nominal content (%wt)	VMT real content (%wt)
HDPE	401	–	–
HDPE + 7%VMT	417	7	4.1
HDPE + 10%VMT	441	10	6.2
HDPE + 15%VMT	429	15	9.6
HDPE + 20%VMT	412	20	12.2



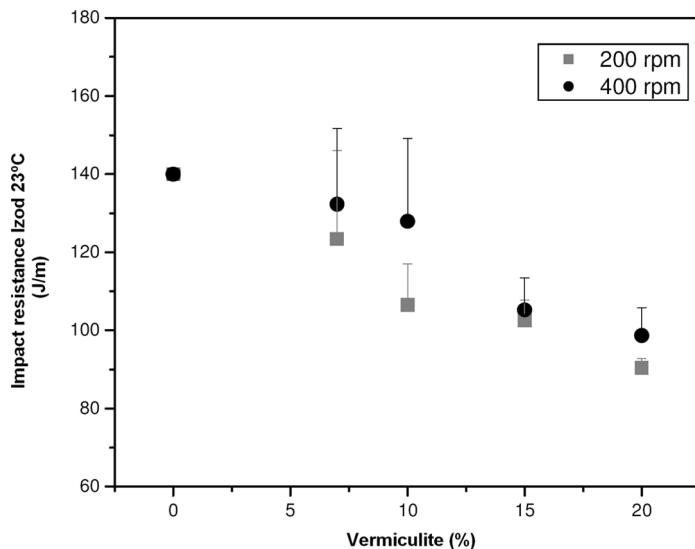
**FIGURE 2** Impact resistance of mixtures of PEAD/vermiculite prepared at 200 rpm.

Slightly higher values of the property are found when rotation speed is increased from 200 to 400 rpm. This improvement is more significant for the sample with 10% vermiculite. This shows that at lower



**FIGURE 3** Impact resistance of mixtures of PEAD/vermiculite prepared at 400 rpm.





**FIGURE 4** Impact resistance as a function of filler concentration and rotation.

levels of filler, a more vigorous shear is needed in order to achieve good dispersion, thus resulting in better properties.

As the filler amount increases, the occurrence of failure due to spots where filler agglomerates occur becomes easier. Since vermiculite has a lamellar structure, one can suppose that the fracture happens when this structure is destroyed.

## CONCLUSIONS

From the results obtained it can be concluded that the use of a twin-screw extruder to prepare high-density polyethylene and vermiculite composites was efficient. The thermal performance of the composites was superior to that for the pure polyethylene. The best processing conditions to generate composites with better properties were found to be 400 rpm shear rate and 7% vermiculite. From the DSC thermograms obtained in this study, it was observed that the crystallinity degree ( $X_c$ ) values of the blends decreased with an increase in clay content. Moreover, the TGA results indicate that the thermal stability of HDPE-VMT blends is improved.

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