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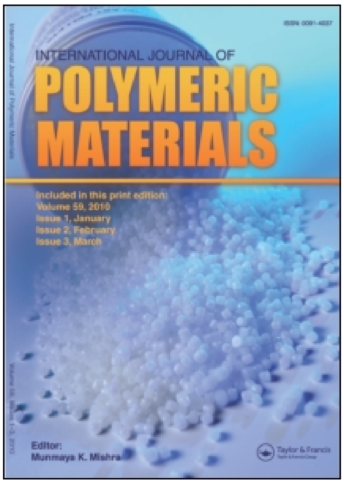

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Morphological, Thermal and Mechanical Properties of Polypropylene and Vermiculite Blends

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Morphological, Thermal and Mechanical Properties of Polypropylene and Vermiculite Blends

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Morphological, thermal and mechanical properties of blends prepared from polypropylene (PP) and 1, 3 and 5 wt% of vermiculite (VMT) were studied. The samples were prepared in a twin-screw extruder. The addition of maleic anhydride-functionalized polypropylene (PP-g-MAH) was also investigated. The blend morphologies were determined by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The thermal properties of the composites were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The DSC results showed that PP crystallizes on cooling at higher temperatures as VMT content increases. The increase in crystallization temperature was most evident for blends with 5 wt% VMT. The TGA results showed that the use of VMT particles to fill polypropylene increased the thermal stability of the composite. The mechanical properties, tensile modulus and tensile strength at yield point of the PP improved by the presence of VMT.

Keywords: blends, polypropylene, vermiculite

INTRODUCTION

Polypropylene (PP) is a versatile thermoplastic material, compatible with many processing techniques and used in many different commercial applications. Of the thermoplastics, the worldwide use of the polymer

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PP has grown the fastest in recent decades [1,2]. It is widely used in flexible packaging and containers. The automotive industry, for instance, uses PP both in unfilled and filled states for battery and bumper applications, among others [3]. This is not only because of its attractive properties for various applications and a favorable price/performance ratio, but also the possibility to modify its properties within a very wide range [4,5].

The development of composites combining inorganic clay and polymer material characteristics at a very fine structural level is one of the most interesting perspectives for polypropylene [6–10]. These materials usually comprise an effective polymeric matrix in which small filler particles are thoroughly dispersed in a composite system [9,10]. Composite material based on polypropylene is one of the many systems that are successfully utilized in engineering applications [11].

PP accepts numerous types of natural and synthetic fillers. Its versatility has also led to the possibility of producing certain late-filled composites [11,12]. The incorporation of fillers such as talc [9], calcium carbonate ($CaCO_3$) [10] and clay [11] into thermoplastics is a common practice in the plastics industry, used to reduce the production costs of molded products [11]. Fillers, such as $CaCO_3$ and talc are also used to improve the working properties of thermoplastic, such as the strength, rigidity, durability and hardness [13,14]. Layered silicates, in particular clay minerals, have been used for their excellent intercalation abilities [15].

Nanocomposites of polypropylene with vermiculite have been described in the literature [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]. Each layer consists of octahedrally coordinated cations (typically Mg, Al and Fe) sandwiched by tetrahedrally coordinated cations (typically Si and Al). The isomorphous substitution of Si^{4+} by Al^{3+} leads to a net negative surface charge that is compensated by an interlayer of exchangeable hydrated cations (Ca^{2+}, Mg^{2+}, Cu^{2+}, Na^{+} and H^{+}). Adjoining layers are held together by a combination of electrostatic and Van der Waals forces [18]. VMT is an abundant and much cheaper silicate than MMT, hetorite or saponite. It is used as packaging material to provide anti-shock protection [19,20].

The purpose of this study is to analyze the mixtures of polypropylene (PP) and different Brazilian vermiculite content. The influence of the addition of PP-*g*-MAH to the blends will be evaluated through their mechanical, morphological and thermal properties.

EXPERIMENTAL

Materials

The 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/cm^3, respectively. The vermiculite was purchased from Brasil Minérios Indústria e Comércio, Brazil. The clay sample was ground and sieved (40 mesh) before use. Maleic anhydride-functionalized polypropylene, PP-*g*-MAH (melt flow index: 10 g/10 min (230°C/2.16 kg), 0.6 mol of maleic anhydride), was supplied by Honeywell, USA.

Preparation of PP/VMT Blends

Composites were obtained by first preparing of a master batch by mixing the PP and VMT (25 wt% clay – 40 mesh) with and without PP-*g*-MAH (10 wt%) in a co-rotating twin-screw extruder (TECK TRIL, model DCT 20) at 300 rpm screw speed, with a 120 to 200°C temperature profile. The clay was added through a side feeder. Subsequently, the amount of pure PP and the master batch required to obtain 1, 3 and 5 wt% of VMT were mixed in the twin-screw extruder at the same temperature and rotation speed used in the master batch processing.

Morphological, Thermal and Mechanical Characterization of PP/VMT Blends

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

The morphology of the specimens was determined by XRD measurements to evaluate the intercalation of the silicate layers in the PP matrix. XRD analysis was obtained using Rigaku (model miniflex) with Cu-Ka ($\lambda = 1.5418\,\text{Å}$) radiation, operated at 40 kV and 40 mA; the data were collected from 2 to 35°. The data were recorded using a scanning speed and increments of 5°/min and 0.05°, respectively.

The specimens prepared for the tensile test and fractured in liquid nitrogen were examined by scanning electron microscopy (SEM). This analysis was performed with a JEOL - JSL 5300 scanning electron microscope.

The crystallinity (X_c), melting temperature (T_m) and crystallization temperature on cooling (T_{cc}) of PP 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^{-1} in nitrogen atmosphere. The melting and crystallization temperatures were analyzed from the second heating and the second cooling curves, respectively. The crystallinity of PP was determined from the ratio of the fusion heat of the blend to that of 100% crystalline PP ($\Delta H^\circ = 138\,J/g$) [21].

Thermogravimetry analysis (TGA) was carried out in nitrogen with a Q500 TA Instrument heating from 25 to 700°C at 10°C/min to evaluate the thermal stability of the PP composites.

Tensile tests were performed according to ASTM D 882, using an Instron testing machine (model 4204) for computerized data acquisition.

RESULTS AND DISCUSSION

The morphological structures of blends were studied by the use of XRD and SEM. The X-ray diffraction results of the composites with and without PP-*g*-MAH and with and without the clay used for their preparation are shown in Figures 1 and 2.

Direct dispersion of a phyllosilicate in the molten polymer with an extruder allows the preparation of intercalated or exfoliated lamellar

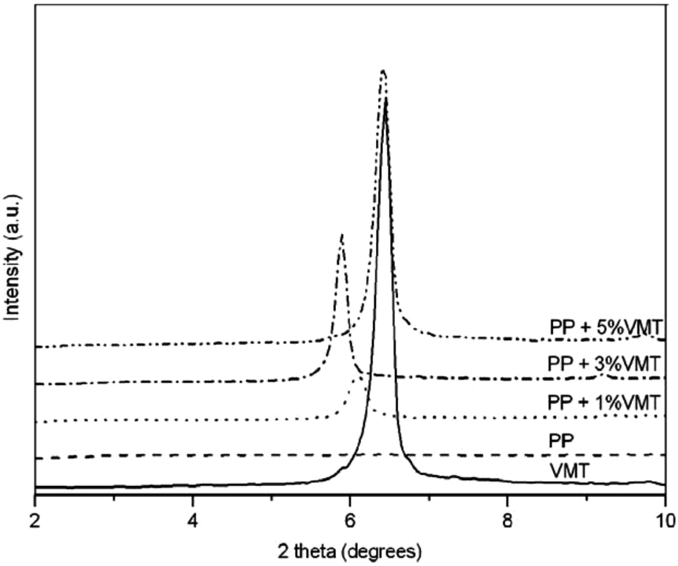

FIGURE 1 XRD patterns of VMT and PP/VMT composites without PP-*g*-MAH.

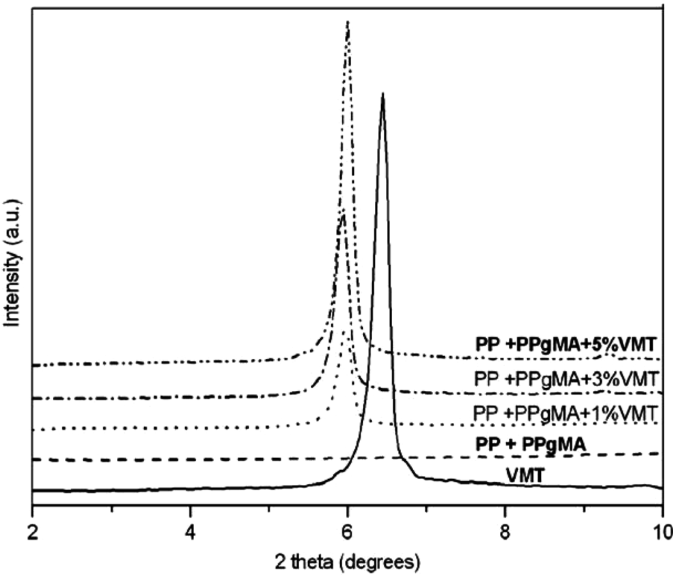

FIGURE 2 XRD patterns of VMT and PP/VMT composites in the presence of PP-*g*-MAH.

nanocomposites and the evidence of intercalation can be provided by the XRD patterns of the hybrids obtained [22,23].

The results show that there was a slight shift of the main peak (Table 1) towards lower angles, indicating that the distance between clay platelets had become greater. They also show that the basal-plane spacing (*d-spacing*) of the mineral increases from 13.68 to 15.21 Å in the blend processed with 3 wt% of clay. However, this slight displacement does not confirm the occurrence of VMT intercalation or exfoliation by the polymer.

The dispersion of clay particles in the PP matrix was evaluated by scanning electron microscopy after liquid nitrogen fracture. Figures 3 and 4 show the SEM photomicrographs of the fractured surface for the samples with 1 and 5 wt% of VMT with and without of PP-*g*-MAH, respectively.

The SEM micrographs of the blends with 1 and 5 wt% VMT (Figures 3A and 4A) are very similar. However, some differences were observed in the morphologies of the mixtures with PP-*g*-MAH. The particles of the mixture with 1 wt% VMT (Figure 3B) and 5 wt% VMT (Figure 4B) with PP-*g*-MAH seem to be less compact and visible than the mixtures without PP-*g*-MAH.

TABLE 1 *d-spacing* of Mean Peak of VMT and PP/VMT Blends with and without PP-*g*-MAH

Samples	2 theta (degrees)	*d-spacing* (Å)
VMT, *natural*	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
PP + PP-*g*-MAH + 1% VMT	5,96	14,68
PP + PP-*g*-MAH + 3% VMT	5,91	14,95
PP + PP-*g*-MAH + 5% VMT	5,91	14,95

Changes in the thermal transitions of the blends were investigated by DSC. Tables 2 and 3 show the crystallinity degree and melting and crystallization temperatures for PP, PP/VMT blends without and with PP-*g*-MAH, respectively.

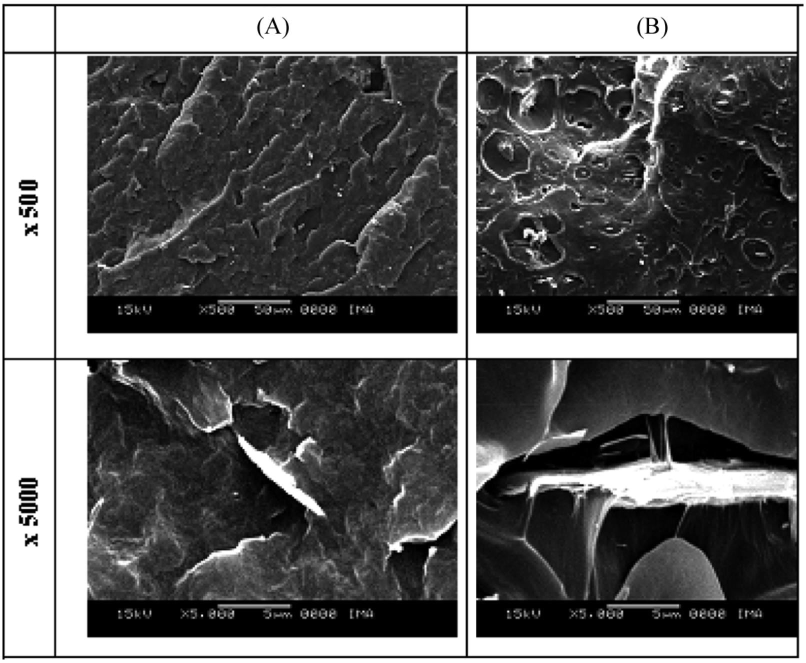

FIGURE 3 SEM photomicrographs of fractured surfaces of PP and VMT blends at magnifications of 500× and 5000× : (A) PP/VMT (1 wt%) without PP-*g*-MAH (B) PP/VMT (1 wt%) with PP-*g*-MAH.

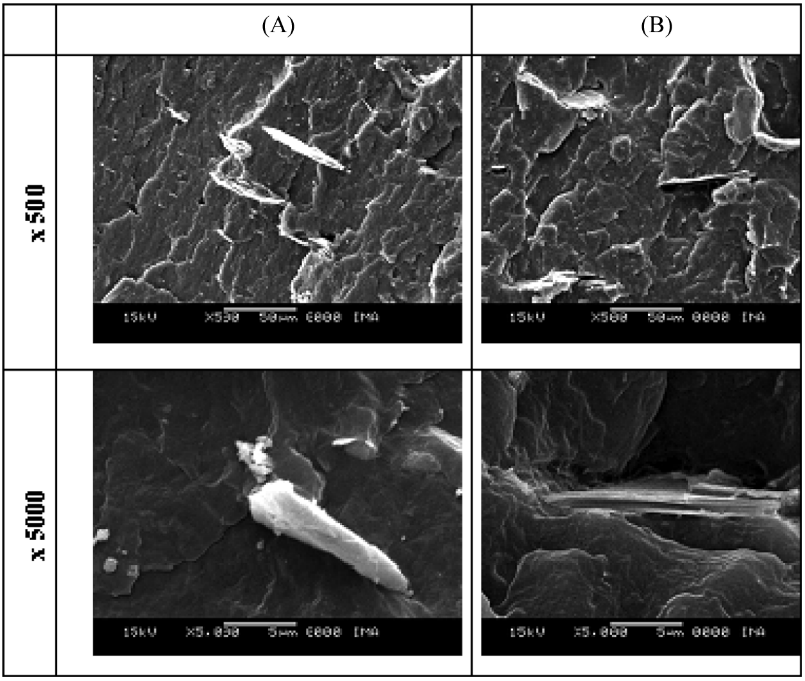

FIGURE 4 SEM photomicrographs of fractured surfaces of PP and VMT blends at magnifications of 500× and 5000×: (A) PP/VMT (5 wt%) without PP-*g*-MAH (B) PP/VMT (5 wt%) with PP-*g*-MAH.

The DSC results show that the addition of clay to the PP matrix does not lead to significant changes in the crystallization of the polymer matrix. The T_{cc} values of the blends increased with increased clay content, and were higher than that of the PP matrix. The melting temperatures were around 160°C for all blends.

The crystallinity degree of the mixtures without PP-*g*-MA was the same as that for the pure polymer (Table 2), but a decrease in the

TABLE 2 Thermal Properties of PP and PP/VMT Blends

Samples	T_m (°C)	T_{cc} (°C)	X_c (%)
PP	157	115	72
PP + 1%VMT	160	118	72
PP + 3%VMT	158	120	74
PP + 5%VMT	161	121	68

TABLE 3 Thermal Properties of PP and PP/PP-*g*-MAH/VMT Blends

Samples	T_m (°C)	T_{cc} (°C)	X_c (%)
PP/PP-*g*-MAH	156	113	72
PP + PP-*g*-MAH + 1%VMT	161	123	71
PP + PP-*g*-MAH + 3%VMT	159	122	78
PP + PP-*g*-MAH + 5%VMT	161	122	60

PP/VMT (5 wt%) without PP-*g*-MAH was observed. The crystallinity of the system in the presence of the grafted polymer was greater for the composite containing 3 wt% VMT (Table 3). At higher clay contents (5 wt%), the X_c was 60%. This result indicates that the formation of crystallites was affected by the quantity of VMT in the blend. The presence of PP-g-MAH led to a significant increase in the T_{cc} values of the blends (about 10°C) in relative to PP.

The presence of 5 wt% VMT may inhibit the crystallization of PP. The amount of 3 wt% VMT with PP-g-MAH was the optimum in terms of crystallinity degree in this study.

Tables 4 and 5 show theTGA results for pure PP and PP/VMT blends, without and with PP-*g*-MAH, respectively. The maximum weight loss temperature (T_{max}), real VMT content (wt%) and PP-*g*-MAH (wt%) content are listed in Tables 4 and 5. These tables reveal that the PP/VMT blends show an increase in T_{max}. The incorporation of VMT into PP 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 [11]. In the future, studies on the influence of organophilic VMT addition to PP could be investigated. An interesting result was observed with the master batch with PP-*g*-MAH, with a T_{max} of 460°C.

From the residual mass of the TGA analysis, it was observed that the real amount of VMT present in the mixtures was less that the planned amount (Tables 4 and 5).

TABLE 4 Thermal Properties of PP and PP/VMT Blends

Samples	T_{max} (°C)	VMT nominal content (%wt)	VMT real content (%wt)
PP	411	–	–
Masterbach	434	25	36
PP + 1%VMT	414	1	0.6
PP + 3%VMT	422	3	1.6
PP + 5%VMT	424	5	3.0

TABLE 5 Thermal Properties of PP/PP-*g*-MAH and PP/PP-*g*-MAH/VMT Blends

Samples	T_{max} (°C)	VMT nominal content (%wt)	VMT real content (%wt)	PP-*g*-MAH estimated content (%wt)
PP + PP-*g*-MAH	415	–	–	–
Masterbach	460	25	34	13.7
PP + PP-*g*-MAH + 1%VMT	417	1	0.7	0.3
PP + PP-*g*-MAH + 3%VMT	419	3	1.5	0.6
PP + PP-*g*-MAH + 5%VMT	415	5	2.1	0.8

In order to evaluate the reinforcing effect of VMT in the PP matrix, mechanical properties were measured. The mechanical properties of the PP/VMT and PP/PP-*g*-MAH/VMT blends are shown in Figures 5–7.Thetensile modulus as a function of the VMT content prepared with and without PP-*g*-MAH is shown in Figure 5.

The tensile modulus of the PP/VMT and PP/PP-*g*-MAH/VMT blends increased with clay content for the blends with 3 and 5 wt% of VMT compared with pure PP. However, the addition of PP-*g*-MAH was only effective for the blend with 1 wt% of VMT. Premalal

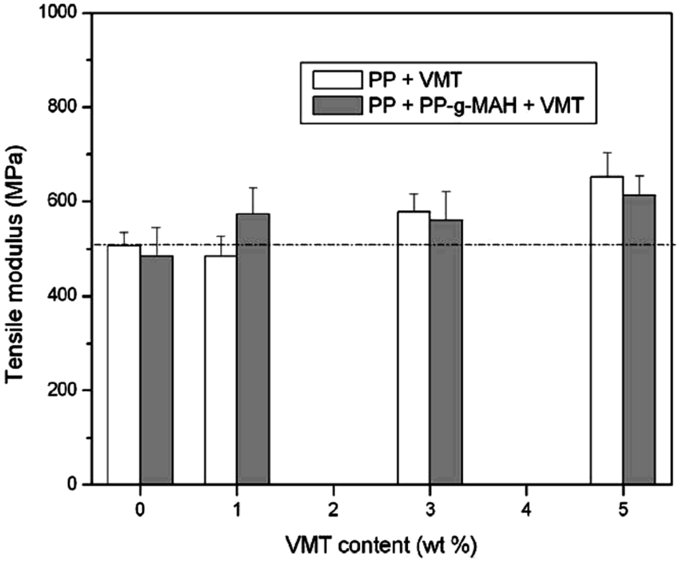

FIGURE 5 Tensile modulus of PP/VMT and PP/PP-*g*-MAH/VMT blends.

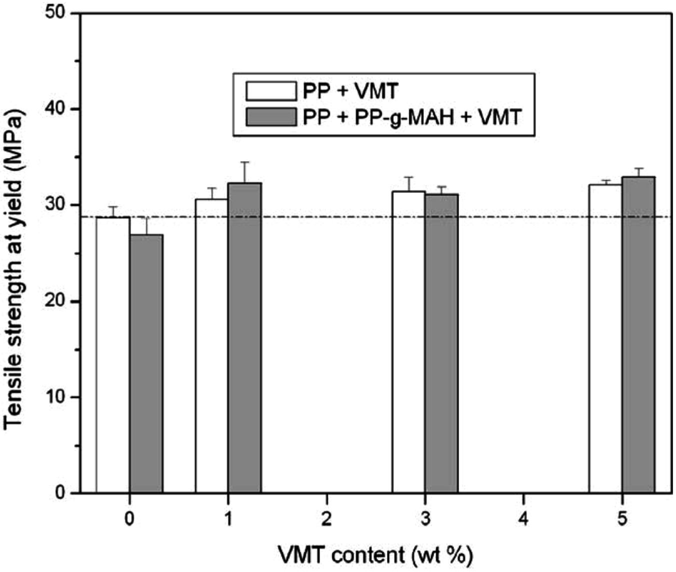

FIGURE 6 Tensile strength at yield of PP/VMT and PP/PP-*g*-MAH/VMT blends.

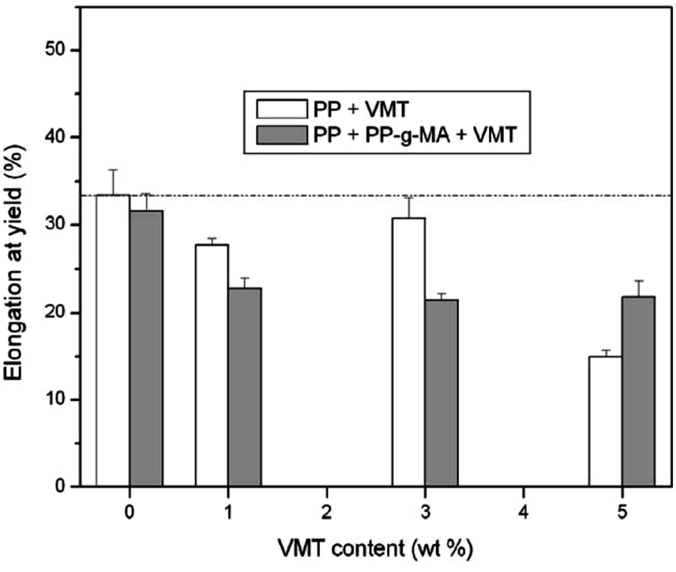

FIGURE 7 Elongation at yield of PP/VMT and PP/PP-*g*-MAH/VMT blends.

et al. [9] also reported an increase in the tensile modulus with an increase in the talc content of the PP matrix.

Figures 6 and 7 show the tensile strength and elongation at yield of the PP/VMT and PP/PP-*g*-MAH/VMT blends as a function of VMT content, respectively. In the presence of VMT, tensile strength at yield increased with increasing clay content. For both blends, the elongation at yield was lower than for the virgin polymer. This result is to be expected, because the presence of filling, for example clay, generally decreases the elongation at yield point [24].

CONCLUSIONS

In this study, polypropylene-clay blends were prepared by direct melt intercalation. The composite structures were determined by XRD, showing that there was a slight shift of the main peak of VMT, but this slight displacement does not confirm the occurrence of intercalation or exfoliation. Morphological assessments provided by the SEM micrographs reveal that the amount and the presence of VMT seem to influence the crystallization process of the PP. The thermal properties were studied by DSC and TGA analyses. From the DSC thermograms, it was observed that the crystallization temperatures on cooling of composites increase with the addition of VMT as compared to PP pure. Moreover, the TGA results indicate that the thermal stability of PP-clay blends without and with PP-*g*-MAH is improved. The expected increase in the tensile modulus is shown to be greater with an increase in clay content (3 and 5 wt%) in the blends. In the mixture with 5 wt% VMT, the increase in modulus was around 30%. The tensile strength at yield of the composites increased in the presence of filler in the PP, but the increase is not proportional to the VMT amount in the blend. The elongation at yield of the materials is lower than that of the polymer matrix. The use of PP-*g*-MAH in the PP and VMT mixtures did not lead to an improvement in the mechanical properties, except for blends with 1 wt% of VMT. Generally, the nanometric dispersion of silicate layers in a polymeric matrix leads to improved tensile modulus and strength, due to the stiffness of the silicate layers or possibly even to the layer or molecular orientation. Since clay is not compatible with most polymers because it is hydrophilic, it needs to be chemically modified to render its surface more hydrophobic [24]. To achieve a nanoscale dispersion of silicates in polypropylene, the silicates are generally pretreated with alkyl ammonium ions that exchange with the inorganic cations of the clays [25]. Therefore, in future work, organophilic VMT should be used and the properties of the blends obtained compared.

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