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**STUDY OF POLYPROPYLENE (PP)/ETHYLENE-PROPYLENE-DIENE
MONOMER (EPDM) BLENDS REINFORCED WITH SISAL FIBERS**

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ABSTRACT

Thermoplastics reinforced with natural fibers have attracted much attention from researchers due to their advantages, especially regarding environmental aspects. However, poor impact strength, particularly at low temperatures, limits the application of some thermoplastics, such as polypropylene (PP). In order to minimize this drawback, impact modifiers have been used, including the terpolymer of ethylene-propylene-diene (EPDM). In this work, PP/EPDM/sisal composites of distinct compositions were investigated focusing on the effect of the alkali (NaOH) treatment of the vegetable fiber on the composites properties regarding physical, mechanical, thermal and morphological behavior. The results indicated that flow rate decreases at higher fiber content due to flow hindering by the presence of the fibers. The addition of the fiber, in general, increased Young's modulus and strength (tensile and flexural), whereas impact strength increased for higher EPDM content. The alkali treatment was considered generally efficient in terms of mechanical properties, even though this was not found in the dynamic mechanical analysis.

Keywords: Green composites; PP/EPDM blends; natural fiber; alkali treatment.

INTRODUCTION

Polypropylene is a versatile thermoplastic material with interesting characteristics which make it a highly consumed polymer [1], including high melting temperature and chemical strength [2], low density, easy processing and low cost. However, due to its relatively high glass transition temperature (T_g), it shows poor impact behavior at low temperatures. To overcome this drawback, different polymers have been studied for blending with PP, such as polystyrene [3] and high density polyethylene [4].

Polymer blends is a highly interesting class of material, featured by the intimate combination of two or more polymers, which can be completely miscible, partially miscible or fully immiscible blends [5]. The study of thermoplastic elastomers (TPE) such as those based on polypropylene (PP) and ethylene-propylene-diene terpolymers (EPDM) blends increased in the last years based on a wide range of manufacturing techniques and properties, which may combine the elastic behavior of elastomers and the thermal reversibility and good processability of thermoplastics [6]. The similarity in chemical structure combined with their distinct physical properties yields a material with an interesting set of properties, and crystallization, morphology, mechanical behavior and rheological characteristics of these blends must be known [2].

Reports on PP/EPDM with a wide composition range are scarce and mainly focus on the blending effect on crystallization and mechanical properties [1]. Aiming to improve mechanical or thermal properties of this blend, the inclusion of a third component, e.g. short fibers [7], have been proposed. The fibers used to produce these thermoplastic composites can be of synthetic or natural origin. Natural fibers (e.g. sisal, curaua, jute, banana and flax) show some advantages when compared to synthetic fibers such as low density, low cost, easy processing and recyclability.

Biagiotti et al. [8] carried out mechanical and morphological analysis of PP/EPDM/flax and reported that the fibers were effective in reinforcing this system, improving tensile, flexural and impact strength. But, the combination of sisal with PP/EPDM is scarcely seen, even though there are some reports focusing on sisal/PP composites, as in Fung et al. [9].

When considering vegetable fibers for polymer composites, it is important to bear in mind the hydrophilic character and poor fiber/matrix adhesion displayed by these fibers [10]. Seeking to minimize these drawbacks, surface chemical treatments are vastly suggested, being the most common that with sodium hydroxide (NaOH), mainly due to its availability, efficiency and low cost [11]. Sgriccia et al. [12] treated various natural fibers with NaOH and reported the removal of lignin and hemicellulose from the surface of the fibers, yielding composites with higher flexural modulus.

On this context, the aim of this paper was to study PP/EPDM/sisal composites of distinct compositions focusing on the effect of the alkali treatment (NaOH) of the vegetable fiber on the composites properties regarding physical, rheological, mechanical, thermal dynamic-mechanical and morphological behavior.

EXPERIMENTAL

Materials and Sample preparation

The raw materials used in this study were: polypropylene homopolymer (PP) (MFI: 7.0 g.10min⁻¹ at 230 °C, density: 0.89 g.cm⁻³) supplied by Ipiranga Petroquímica (PH 0950); ethylene-propylene-diene terpolymer (EPDM) BUNA EP G 6850 and commercial regular sisal fiber ropes. Sodium hydroxide (Nuclear pa. 98%) and acetic acid (Nuclear pa. 99.7%) were used as received.

Three distinct variables were used in this study: fiber content (15 and 30 phr), fiber preparation (washing with distilled water and 2% NaOH treatment) and EPDM content (16 and 24 phr, in relation to the PP weight, without considering the fiber inclusion).

The fibers were grinded in a knife mill (granulometry range used: 350-750 μm) and washed with distilled water. A chemical treatment was used in part of the fibers, which included fiber immersion in 2% sodium hydroxide solution for 1 h and after that in an acetic acid solution (1%) for neutralization. Then the fibers were thoroughly washed in distilled water and dried in an oven with air circulation for 2 h at 105 °C.

Prior to the mixture, the fibers were dried at 65 °C for 30 min in an air-circulation oven. The samples were prepared in a MH-100 mixer, firstly the polymer was melt and then the fibers were added. The mixture process occurs during approximately 15 s, aiming to minimize fiber degradation. The obtained material was grinded in a knife mill (MF300 – Mecanofar) and injection molded in a HIMACO (LHS-130-400) equipment using the following temperature profile: 170, 175 and 180 °C. Table 1 shows the nomenclature used for the studied samples.

<< Table 1 >>

Characterization

Density of the samples was evaluated using a 25 ml pycnometer with n-butyl acetate. Rheometry analysis was carried out using Galaxy III model 9052 equipment at 190 °C, from 100 to 1000 s^{-1} shear rate. The melt flow rate (at 230 °C and using 2.16 kg) was obtained using Ceast equipment, based on ASTM D1238. Water absorption of the samples was evaluated by immersion in deionized water at 25 °C using water for a period of up to 1008 h.

Thermogravimetric analysis was performed using TA instrument (2050model) under N₂ atmosphere, from 25 to 1000 °C at heating rate of 20 °C.min⁻¹. Dynamic mechanical analysis (DMA) was performed in TA instruments (2980 model) at a frequency of 1 Hz and from -100 to 100 °C, at a heating rate of 3 °C.min⁻¹ under N₂ atmosphere.

Tensile testing was realized at room temperature in an EMIC DL10000 testing machine according to ASTM D638 at a crosshead speed of 5 mm.min⁻¹ and load cell of 500 kgf. A minimum of five samples were tested and the average values are reported. Flexural testing (ASTM D790) was performed in a Universal EMIC DL 10.000 testing machine at a crosshead speed of 5.3 mm.min⁻¹ and 100 kgf load cell in a minimum of five samples. The Izod impact strength was obtained using a minimum of seven V-notched specimens (ASTM D256), in a CEAST model 6545 impact tester. Shore D hardness was obtained using a Shore GSD – 702 Teclock Politest Durometer.

Micrographs were obtained using a Jeol model JSN 6060 after cryogenic fracture of the samples in the following conditions: 10 keV at 100× and 850× magnification. Chemical etching for 3 min was carried out prior to the analysis aiming to remove the EPDM fraction.

RESULTS AND DISCUSSION

Physical and rheological properties

The specific gravity of the composites is shown in Table 2 and a slight increase in the values with fiber incorporation can be noted for the treated fibers. This table also shows lower flow index for higher EPDM incorporation, which is expected since the high viscosity of the elastomer inhibits material flow. As earlier mentioned, the fibers hinder the flow of the blend and this justifies the difficulties in obtaining the results for the samples containing 30% fiber content. It was also observed that the treatment increased flow index. During chemical treatment, the fibers lose mass (so more particles are needed to achieve the same fiber volume

fraction), decrease in diameter and increase in roughness [11, 13] and a combination of these factors, together with the difference in density between washed fiber, treated fiber and polymer itself, alter the weight of the polymer melt that left the die of the melt-flow equipment.

<< Table 2 >>

Viscosity variation as a function of the shear rate is depicted in Figs.1a-b. It can be noted that, for all samples, viscosity decreases when increasing shear rate. Also, fiber incorporation increases viscosity of the blends and the EPDM presence slight increases the PP viscosity which becomes more evident with fiber incorporation. These results corroborate those obtained with MFI.

Reinforced polymeric systems tend to show higher viscosity than the respective neat matrix. However, according to the results shown in Fig. 1a, this behavior was not observed for the B16-S15 samples. In addition, the alkaline treatment of the fibers did not significantly alter viscosity, even though it appears, for some samples that the treated fibers lead to slightly higher viscosity.

<< Figure 1 >>

Figs. 2a-b shows water sorption as a function of time for the studied samples. Sorption increased with fiber addition, but it was mostly independent on the matrix (blend) composition. The overall water sorption can be treated as Fickian, even though two other non-Fickian mechanisms play a role. For all samples, the composite absorbs water quickly at first,

slowing down after some time, outlining a sigmoid curve, approaching the equilibrium state, known as quasi-equilibrium.

<< **Figure 2** >>

All components of the formulation can suffer environmental aging, and the sorbed water is able to degrade matrix and fibers, at different velocities, and also cause debonding at the interface. Water absorption is highly expected for natural fibers due to its highly hydrophilic character, which promotes water transport especially at the fiber-matrix interface. This characteristic tends to be diminished after surface treatment, but this was not noticed in this work with the simple alkaline treatment used. In addition, for both B16 and B24 samples, doubling the fiber content showed a more prominent influence on water absorption than the surface treatment itself. Furthermore, the samples containing higher fiber content showed a more prominent 2nd order polynomial fitting curve whereas, for the other samples, the quasi-equilibrium state approaches faster.

Thermal properties

The TGA results indicate that the degradation process initiates at c.a. 350 °C for both B16 (Fig. 3a) and B24 blends (Fig. 3b), with an associated weight loss up to 500 °C, being this a one-stage process, which lead to a residual mass of c.a. 0.5% for both samples. The incorporation of the fiber yielded an increase in weight loss, but the treatment did not show a clearly identifiable trend.

Similar behavior was observed comparing the results of thermal degradation for the B16 and B24 blends. For B16 samples, for instance, degradation of the samples containing

15% and 30% of fiber initiates at approximately 250 °C and 150 °C, respectively, therefore ratifying the limitations of the vegetable fibers regarding high temperatures.

Figs. 4a-b show the DTG for the blends. Higher peaks are observed for the B16 and B24 samples in around 450 °C, corresponding to the degradation of the polymers. Comparing the blends with the reinforced blends, it can be noted a change in intensity of the peaks and the appearance of a lower peak in the 350-380 °C range, related to fiber degradation. The weight loss stages are especially visible for those samples with higher fiber content.

<< **Figure 3** >>

<< **Figure 4** >>

Mechanical properties

Table 3 shows the tensile, flexural and impact properties obtained for the composites studied. It was noted an increase in modulus with the fiber content, showing that the incorporation of the sisal fibers was uniform and lead to an effective stress transferring within the composites. Also, a slight increase in tensile modulus was noted for the treated fibers, suggesting a better fiber/matrix interfacial bonding [14].

<< **Table 3** >>

It can be noted a decrease in tensile strength for higher EPDM content, whereas the presence of the fiber did not show a significant trend for all samples, with exception of the 30% treated fibers, which shows an inferior behavior. This was not expected and it only occurred due to processing difficulties during injection molding at high fiber content,

affecting the quality of the samples. According to Biagiotti et al. [8], at higher EPDM content (30%), the fibers act as reinforcing agent increasing tensile strength. On the other hand, for lower EPDM content (more rigid), the fibers can act as defects, promoting the appearance of microcracks due to poor fiber-matrix adhesion with associated loss in strength.

The flexural modulus showed similar behavior in comparison with the tensile modulus, i.e., there is a gradual decrease by increasing the EPDM content on the blend. However, rigidity of the material varied considerably with fiber content, corroborating the study reported by Costa et al. [15]. It can also be observed in Table 3 that the fiber increased flexural strength. According to Ruksakulpiwat et al. [16], flexural strength of a thermoplastic matrix composite is more dependent on matrix composition than fiber content, and a decrease in this property is expected for higher EPDM content. In addition, the fiber alkaline treatment did not show any trend in comparison with the washed fibers regarding flexural modulus or strength.

Table 3 also shows the impact strength results obtained for all samples. Impact strength evaluates the ability of a material to resist fracture under an applied stress at high speed. The energy dissipation mechanisms operating during impact loading are mainly matrix and fiber fracture, fiber/matrix debonding and fiber pull out [14]. It can be noted that by increasing the EPDM content there was an increase in tenacity (energy absorption), and the B24 sample achieved the highest value ($\approx 19 \text{ kJ.m}^{-2}$), similar to what was found by Silva et al. [17]. It can be noted that reinforcement incorporation and fiber treatment did not significantly change impact strength of the B16 matrix. However, for the B24 matrix, there was a decreasing in impact strength with fiber addition, this may have occurred because, at higher fiber loading, the friction between fibers directly contributes to fracture [18], resulting in lower energy dissipation and hence lower impact strength.

Ruksakulpiwat et al. [16] found that the impact strength of the composites does not change when the EPDM content in the matrix is high enough ($>15\%$). However, the fibers can reduce the strength by acting as stress concentrators, mainly in poorly adhered areas or in regions with fiber-to-fiber contact. In the case of this work, it can be noted for the B24-S30-w and B24-S30-t samples that there is a more attenuated decrease in impact strength, due to higher fiber content. Finally, the Shore D hardness results did not show any variation, and an average value of 63 was obtained for all samples, suggesting similar hardness of all constituents of the samples and the absence of surface flaws.

Dynamic mechanical analysis

- Storage modulus

The modulus of a semi-crystalline polymer is directly proportional to the degree of crystallinity and does not affect the modulus below T_g . As the temperature increases, the crystallites anchoring points that are thermally labile, disintegrate as the material approaches melting, and the material undergoes a progressive structural change until beyond T_m , when becomes molten. For composite materials, the incorporation of fillers and/or reinforcement can promote significantly changes in the storage modulus [19] mainly for temperatures beyond T_g .

Figs.5a-b show the storage modulus obtained for the composites containing 16 and 24% of EPDM, respectively. The storage modulus may be used to evaluate rigidity of the system and the results showed lower modulus for the samples containing more EPDM, as can be seen when comparing the results obtained for the B16 and B24 samples in the whole studied temperature range. This can be attributed to the elastomeric characteristic of EPDM that decreases rigidity of the material by promoting molecular mobility of the chain segments.

In addition, higher modulus values were obtained for higher fiber incorporation. On the other hand, the influence of the chemical treatment on storage modulus was inconclusive. Perhaps the fiber treatment was severe enough to reduce the mechanical properties of the fiber [20]. The removal of the hemicellulose that involves the cellulose microfibrils and also of some extractive compounds may have exposed the hydroxyls groups of the cellulose, which becomes more hydrophilic, which in turn may reduce adhesion.

<< Figure 5 >>

- Loss modulus

The transitions and relaxation processes are attributed to molecular motions that reflect on the size or concentration of open spaces within the polymers. Since the molecular motion requires a swept-out volume in the matrix, the cooperative motion of large molecule segments requires higher energy than limited local rotation-like or crankshaft motions of small parts of the molecules [21]. Also, as explained by Cowie [22], when molecular motion increases to a sufficiently high level, all the chains turn from strong to weak springs, i.e., there is more cooperativity among the polymeric chains which facilitates their motion. For stronger interactions in the molecules, higher thermal energy is required to start the relaxation processes. Similarly, smaller free volume holes bring more difficulty to the energy diffusion among chain segments, hindering the relaxation processes.

According to Figs.6a-b, two distinct peaks are noted for the composites due to relaxation transitions corresponding to the EPDM and PP phases, respectively, as opposed to a single peak for the PP sample (not shown here). It can also be noted that, for the same fiber volume fraction, higher loss modulus values were obtained for the treated fibers. This can be

due to a decrease in fiber/matrix adhesion (as mentioned earlier) which leads to higher energy dissipation at the fiber interface, since the reinforcing effect may not have been significant.

<< Figure 6 >>

- Tan delta (δ)

Figs.7a-b show the tan delta curves as a function of the temperature for the reinforced blends. All systems showed two distinct peaks corresponding to its constituents, evidencing their immiscibility. The lower peak, in the -50 to -40 °C temperature range, can be attributed to the glass transition temperature of the elastomeric phase, whereas the higher peak, in the 10 to 30 °C range, is related to the relaxation of amorphous regions of PP.

It is known that transition and relaxation processes for this type of material (PP) depends on the conditions of the specimens, but the results must agree with those from other techniques, such as nuclear magnetic resonance and dilatometry, for example [21]. It can be seen that the temperature dependence below the glass transition temperature is different from that above T_g because of the increase in size of the open spaces brought by the cooperative motion of large molecule segments. Below T_g , only limited local crankshaft or rotation-like motions of small parts of molecules are possible. Furthermore, the free volumes collapse at low temperatures and molecular mobility decreases up to the point that the time required for molecular rearrangement is longer than the time-scale of the experiment [23].

The early figures suggest that fiber treatment is more important in affecting the tan δ dissipation than the fiber volume fraction. And since the composites containing treated fibers showed higher dissipation, this alkaline treatment may even be leading to poorer adhesion than the simpler washing of the fibers.

<< Figure 7 >>

Morphological analysis

Some micrographs of the fracture surface of the studied blends are displayed in Fig.8. It was observed that in the PP/EPDM blends (B16 and B24), the elastomer can be found as small dispersed particles in “drop” shape throughout the PP matrix. Some of the observed voids correspond to the EPDM that was detached from the PP surface whereas other voids correspond to the EPDM removed by chemical attack. The B24 sample showed a more homogeneous mixture than B16 (Figs.8b and 8a, respectively), with more particles of smaller size due to the breakage and dispersion of EPDM during the mixing process.

The fracture surfaces of some of the studied composites are displayed in Fig.9. In this case, voids at the surface correspond to fibers that were detached (pull-out) during the impact event. This is an indicative that the washed fibers (Fig.9a) show poor fiber adhesion to the hydrophobic polymeric matrix. Fig.9b suggests a more adequate interface, with higher affinity and watability between the matrix and the treated fibers, perhaps due to a better fiber encapsulation by the matrix, hindering the fiber/matrix distinction.

<< Figure 8 >>

<< Figure 9 >>

CONCLUSIONS

In this work, rheological, thermal, mechanical, dynamic-mechanical and morphological properties of PP/EPDM blends reinforced by short sisal fibers were studied. For higher EPDM content, melting flow index decreased. About the rheological behavior, a

decrease in viscosity with shear rate was noted, and viscosity increased with fiber incorporation for both thermoplastic composites studied (B16 and B24). Higher fiber content lead to an increase in weight loss due to the lignocellulosic components of the natural fiber. In the DTG curves, the most evident peaks were associated with PP and EPDM degradation and the smaller peaks referred to the lignocellulosic components of the sisal fiber.

Higher content of fibers increased water absorption due to their hydrophilic character and the fiber alkali treatment was not able to reduce that. About the mechanical properties, the reinforcement incorporation increased tensile and flexural modulus, and flexural strength, but with less influence on tensile strength. Additionally, the alkali treatment improve all mechanical properties, showing a better fiber/matrix adhesion, providing a stronger interface compared to washed fibers. Higher content of EPDM do not show higher tensile and flexural properties, as opposed to tenacity (impact strength), that increase with higher concentrations of EPDM, behavior typically of elastomers, and due to this, the blend B24 shows a higher impact strength among the composites studied.

The viscoelastic properties showed an increase in storage modulus with sisal incorporation on the blends, besides the alkali treatment improved this modulus, suggesting better fiber/matrix adhesion, corroborating the findings of the morphological and mechanical analysis, which showed fewer voids at the surface related to pull-out of the fibers. For the loss modulus and, it is noted peaks referent to amorphous region relaxation of the PP and other peak referred to glass transition temperature. On the other hand, analysis of the $\tan \delta$ curves was contradictory, since the composites containing treated fibers showed higher dissipation, which suggests poorer adhesion than that obtained by the simpler washing of the fibers.

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